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Zhang, JC
Wang, X
Marriott, G
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Publication Date

2019-06-01

DOI

10.1016/j.pmatsci.2019.02.001

Peer reviewed

Contents lists available at ScienceDirect

Progress in Materials Science

journal homepage: www.elsevier.com/locate/pmatsci

Trap-controlled mechanoluminescent materials

Jun-Cheng Zhang^{a,*}, Xusheng Wang^d, Gerard Marriott^{c,f,*}, Chao-Nan Xu^{b,e,*}^a College of Physics, Qingdao University, Qingdao 266071, PR China^b National Institute of Advanced Industrial Science and Technology (AIST), Saga 841-0052, Japan^c TBSI, University of California, Berkeley, CA 94720, United States^d Functional Materials Research Laboratory, Tongji University, Shanghai 200092, PR China^e Department of Molecular and Material Science, Kyushu University, Fukuoka 816-8580, Japan^f Department of Bioengineering, University of California, Berkeley, CA 94720, United States

ARTICLE INFO

Keywords:

Mechanoluminescence
Crystal structure
Doping
Carrier trap
Stress imaging

ABSTRACT

Mechanoluminescence (ML) is generated during exposures of certain materials to mechanical stimuli. Many solid materials produce ML during their fracturing, however, the irreversibility of fracture-induced ML limits the practical applications of these materials. In 1999, Chao-Nan Xu discovered an intense and reproducible ML from trap-controlled materials, including ZnS:Mn^{2+} and $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$, and introduced the principles and applications of hybrid inorganic/organic mechanoluminescent (ML) composites, and related sensors to visualize stress/strain in target structures. This discovery has triggered intense research interest in trap-controlled ML materials and composites over the past 2 decades. Notable achievements of this research include the development of trap-controlled materials that exhibit bright ML emission from the ultraviolet to the near infra-red, and multiscale mechano-optical sensitivities. This research has also increased our understanding of the mechanisms of ML phenomena, enabling the rational design of trap-controlled ML materials. Practical applications of ML are also being driven by the discovery that ML composites can serve as “mechano-optical sensitive skin” for structural health diagnosis, stress sensors for biomechanics, and mechanically-activated light sources. This review focuses on the design, synthesis, characterization, optimization and application of trap-controlled ML materials, and concludes with discussions on future directions of ML research and specific challenges to improve ML materials for real-world applications.

1. Introduction

1.1. Brief history of ML

Many types of material emit light during exposures to mechanical stimuli [1,2]. In 1978, B. P. Chandra proposed the general term of “*mechanoluminescence*” (ML) to describe all types of luminescence that result from the transfer of mechanical action to a material [3,4]. ML has been observed from materials during exposures to friction, impact, compression, stretching, bending, twisting, loading, shaking, rubbing, scratching, grinding, crushing, cutting and cleaving. ML phenomena are classified according to the nature of the mechanical stimulus on the material, and fall into three broad categories, namely, deformation luminescence, fractoluminescence

* Corresponding authors at: College of Physics, Qingdao University, Qingdao 266071, PR China (J.-C. Zhang). TBSI, University of California, Berkeley, CA 94720, United States (G. Marriott). National Institute of Advanced Industrial Science and Technology (AIST), Saga 841-0052, Japan (C.-N. Xu).

E-mail addresses: jc-zhang@qdu.edu.cn (J.-C. Zhang), gmlab@berkeley.edu (G. Marriott), cn-xu@aist.go.jp (C.-N. Xu).

<https://doi.org/10.1016/j.pmatsci.2019.02.001>

Received 11 January 2018; Accepted 4 February 2019

Available online 05 February 2019

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Nomenclature

AFM	atomic force microscopy
AgNW	Ag nanowire
CCD	charge coupled device
CMOD	crack mouth opening displacement
Compress-L	compression excited mechanoluminescence
EL	electroluminescence, electroluminescent
FEM	finite element method
FITC	fluorescein isothiocyanate isomer-I
H_{rms}	root-mean-square magnetic field
Impact-L	impact excited mechanoluminescence
IoT	Internet of Things
Ln^{3+}	trivalent lanthanide dopants
M^{2+}	divalent host ions
ML	mechanoluminescence, mechanoluminescent
NIR	near infrared
PC	poly(bisphenol A carbonate)
PDMS	polydimethylsiloxane
PersL	persistent luminescence

PL	photoluminescence, photoluminescent
PMMA	poly(methyl methacrylate)
PMT	photomultiplier tube
PS	polystyrene
RE	rare earth ions
ROS	reactive oxygen species
rpm	round min^{-1}
SAO	SrAl_2O_4
SAOE	$\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$
SEM	scanning electron microscope
SHI	swift heavy ion
ThL	thermoluminescence, thermoluminescent
TPU	thermoplastic polyurethane
Tribo-L	friction excited mechanoluminescence
Ultrasonic-L	ultrasonic vibration excited mechanoluminescence
UCL	up-conversion luminescence
UV	ultraviolet
XRD	X-ray diffraction

(left of dash line in Fig. 1), and triboluminescence (right of dash line in Fig. 1) [4–8].

In his celebrated work on “Of the Proficiency and Advancement of Learning, Divine and Human” [9–11], Francis Bacon described mechanically-induced light emission during the scraping or breaking of hard sugar “*sugar shineth only while in scraping*”, and in putrefied and old fir and pine “*yet in the sudden breaking they will sparkle like hard sugar*”. This type of mechanically-induced light emission is classified as fractoluminescence, and it is generated within the destructive range of the material (Fig. 1; Section 1.2). Interestingly, Jeffery Zink showed almost 4 centuries later, that the fractoluminescence emitted on crushing hardened sugar is composed of multiple emission bands from 300 to 410 nm [12]. It is entirely possible therefore, that the shining light observed by Francis Bacon was violet-blue in color.

Almost 60 years after Bacon’s report, Robert Boyle wrote to Sir Robert Moray relaying results of studies he had performed on a diamond he borrowed from the Reverend John Clayton. In one of these letters, Boyle described how rubbing the surface of the diamond with his own flesh produced a whitish light [13] – this category of ML is now called triboluminescence (Fig. 1; Section 1). Boyle described other luminescent phenomena using the Clayton diamond, including mechanoluminescence which he observed on pressing the diamond with a finger or steel needle (a bodkin), thermoluminescence which he observed on warming the diamond with the heat of his flesh, and photo-induced delayed luminescence, inferred from his observation of the long afterglow of sunlight-induced emission [13]. Bacon’s and Boyle’s observations on fractoluminescence and triboluminescence dominated the direction of research on ML for almost four centuries. The reader is directed to the following reviews for detailed accounts of the background and

Fig. 1. Schematic diagram of mechanoluminescence [7,8].

history of ML phenomena [2,4,5,12,14].

In 1999, Chao-Nan Xu and coworkers (the Xu group) showed trap-controlled materials, including ZnS:Mn^{2+} and $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$ that emitted robust and recoverable ML – as we shall see, these discoveries are driving renewed interest in ML research, and creating opportunities to develop ML materials to solve real-world problems [15–19]. For example, enhanced ML properties of composite materials are being used for remote monitoring of the structural health of buildings and social infrastructure, including load-bearing on bridges, and for dynamic monitoring of components of industrial machines and artificial bone [7,20–35].

1.2. Classification of ML

Deformation luminescence and fractoluminescence: A solid material may experience an elastic deformation when exposed to a mechanical stimulus – higher energies of the mechanical stimulus may lead to plastic deformation, and ultimately fracturing of the material.

A characteristic of deformation luminescence is that the material is not fractured or damaged during the ML process, and consequently these materials may generate a reproducible ML signal over multiple cycles of an applied mechanical stimulus. Deformation luminescence includes the sub-categories of elasticoluminescence and plasticoluminescence, each being triggered by elastic deformation and plastic deformation of the material, respectively. The ML intensity of elasticoluminescence of the material is linear with the amplitude of the applied stress, i.e., within the range of the elastic deformation (Fig. 1). This property is highly valued for stress-sensing, and it is driving the discovery and development of new elasticoluminescent materials for real-time detection and imaging of stress distributions in target structures [7,8]. Examples of elasticoluminescent materials include luminescent ions doped piezoelectric materials [7]. Examples of plasticoluminescent materials include colored alkali halides [36–38], II-VI semiconductors [39], and rubbers [40,41].

Fractoluminescence is generated during the breaking of atomic and chemical bonds in a material, and is usually accompanied by plasma discharge. Roughly 50% of all inorganic solids and 30% of organic crystals emit light on fracturing, including quartz, sugar, alkali halide, II-VI semiconductors, metals, phosphors, minerals, silica glass, piezoelectric complexes, and polymer crystals [2,4–7,42]. Unlike elasticoluminescence and plasticoluminescence, fractoluminescence is associated with irreversible physical damage to the material, and so these materials do not show reproducible ML (Fig. 1) [2]. Correspondingly, applications of fractoluminescent materials are limited to real-time sensing of structural damage in the target structure [43–56]. Fractoluminescence is not discussed in any detail in this review and the reader is directed to the following articles and reviews for further information [57–63].

Relationships between the ML emission of elasticoluminescent, plasticoluminescent and fractoluminescent materials are schematized in Fig. 2. Elasticoluminescent materials may exhibit both plasticoluminescence and fractoluminescence. Specifically, an elasticoluminescent material exhibits elasticoluminescence when the amplitude of a mechanical stimulus is within the limit of elastic deformation. At higher energies, mechanical perturbations to the same material may lead to plastic deformation and plasticoluminescence. Finally, the same material may undergo irreversible fracturing and fractoluminescence in the case of mechanical insults in the destructive limit (Fig. 1). Accordingly, plasticoluminescent materials may exhibit fractoluminescence during fracturing.

Triboluminescence: The third category of ML is triboluminescence, which is generated on contacting or separating two specific types of material. Triboluminescence can be further sub-classified as being triboelectrically-induced, tribochemically-induced or tribothermally-induced (Fig. 1) [4–6]. Triboluminescence, unlike deformation luminescence and fractoluminescence, depends on the nature of material used to apply the mechanical stimulus. For example, one can generate elasticoluminescence and fractoluminescence on scraping a $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$ composite film with a rod composed of any material – the triboluminescence of a $\text{ZnAl}_2\text{O}_4\text{:Mn}^{2+}$ composite disk however, depends on the composition of the rod material. Specifically, the triboluminescence depends on the contact potential between $\text{ZnAl}_2\text{O}_4\text{:Mn}^{2+}$ and the rod material. This topic is discussed further in Section 5.2.

Fig. 2. Relationships among fractoluminescent (Fracto-L), plasticoluminescent (Plastico-L) and elasticoluminescent (Elastico-L) materials [8].

1.3. Trap-controlled ML

The mechanisms that underlie the transfer of mechanical energy to light emission in ML materials are complex and may differ in each category of ML. Moreover, ML may arise from multiple mechanical effects in the material, each of which contributes to the observed ML response. To this end, we have found it useful to simplify the classification of ML materials to those that exhibit reproducible ML and non-reproducible ML. Reproducible ML occurs in trap-controlled materials, including inorganic materials doped with luminescent lanthanide or transition metal ions. A characteristic feature of these materials is that they emit ML in response to repeated cycles of mechanical stimuli within their non-destructive limits. Reproducible ML in trap-controlled ML materials arises from two processes: first by the trapping of carriers (electrons and/or holes) in long-lived trap levels, and second, by mechanically-induced de-trapping of carriers, which is coincident with light emission (Section 5).

Trap-controlled ML materials may be further categorized according to the mechanism of trap-formation. The first category includes high-energy irradiated alkali halide crystals, alkaline earth oxides and salts, such as X- or γ -irradiated NaCl, NaCl:Dy³⁺, CaF₂:Er³⁺, Al₂O₃:Tb³⁺, CaSO₄:Sm³⁺/Mn²⁺, Li₂BaP₂O₇:Eu³⁺ and Li₃PO₄:Ce³⁺/Eu³⁺ [5,64–77]. The trap levels associated with ML in this category do not exist in the original material, rather they are introduced during exposures of the original material to high-energy irradiation. The ML properties of irradiation-generated trap centers depend strongly on the composition of the material, and the dose of the high-energy radiation. Given these complications, this category of ML material is not discussed in this review, and the reader is directed to the following articles for further information [36,37,65,78–81].

In the case of the second category of ML material, the trap centers associated with ML are generated during the synthesis of the material. The concentration and depth of these traps can be controlled by adjusting the composition of reagents, modifying the method of material synthesis, and by using ion-doping techniques. This category of trap-controlled ML material include lanthanide ions doped dielectrics, for example SrAl₂O₄:Eu²⁺, CaAl₂Si₂O₈:Eu²⁺, (Ba,Ca)TiO₃:Pr³⁺ and Sr₃Sn₂O₇:Sm³⁺, and metal ions doped II-VI semiconductors, such as ZnS:Mn²⁺/Mn²⁺, Te²⁺/Cu,Mn²⁺/Al³⁺, Cu/Al³⁺, Cu,Mn²⁺ and CaZnOS:Mn²⁺/Cu/Er³⁺/Sm³⁺ [82–114]. Specific properties of the traps in these materials may be fine-tuned during their synthesis, and by co-doping with specific lanthanide or transition metal ions. This category of ML material is well-suited for ML-based sensing of stress distributions in target structures. Indeed, since the discovery of ZnS:Mn²⁺ and SrAl₂O₄:Eu²⁺ by the Xu group 20 years ago [15,16], this category of trap-controlled ML materials has dominated research in the field of ML. Moreover, studies on lanthanide ions doped dielectrics and metal ions doped semiconductors have increased our understanding of the mechanisms that underlie ML phenomenon. One could argue that the rapid growth of new and high performing trap-controlled ML materials has resulted from a better understanding of the mechanisms of ML in these materials. The objective of this review is to survey remarkable progress that has been made over the past 2-decades on the design, synthesis, characterization, mechanism of ML responses, and applications of trap-controlled ML materials. Our review covers all aspects of trap-controlled ML phenomena, and we hope that it will serve as a valuable resource for new and established researchers. The review focuses primarily on trap-controlled materials that exhibit reproducible ML, and includes frequent references to SrAl₂O₄:Eu²⁺, the first, and still one of the best understood ML materials.

Key milestones in the history and development of trap-controlled ML are schematized in Fig. 3. The earliest reports on trap-controlled ML can be traced to studies on the piezoluminescence and triboluminescence of ZnS:Mn²⁺/Cu bulk of single crystals during exposures to compression and friction [2,4–6] – research on the mechanism of ML in II-VI compounds continued throughout the twentieth century [115–119]. While significant from a historical perspective, the ML emission of these materials in their non-destructive limit is very weak, and so they are unsuitable for most stress-sensing applications [14].

Fig. 3. Milestones in the development of trap-controlled ML.

The discovery by the Xu group of an intense and repeatable ML in luminescent ions doped inorganic materials, including ZnS:Mn^{2+} [15] and $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ [16], marked a turning point in the 4-century history of ML. It should be noted here, that the ML of $\text{Sr}_3\text{Al}_2\text{O}_6:\text{Eu}^{2+}, \text{Dy}^{3+}$, $\text{Sr}_3\text{Al}_2\text{O}_6:\text{Eu}^{2+}$, and $\text{SrMgAl}_6\text{O}_{11}:\text{Eu}^{2+}$ [120–123] was originally found in $\alpha\text{-SrAl}_2\text{O}_4$, i.e., monoclinic $P2_1$ SrAl_2O_4 [83]. The robust, repeatable and visible ML of this material led Xu and her coworkers to embark on the development of optical-based sensors of stress distributions of target structures, which triggered an intense effort to discover new and improved trap-controlled ML materials for applications in stress-sensing. In this regard, the Xu lab also introduced ML composite materials, including ZnS:Mn^{2+} and $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ microparticles embedded in elastic polymers and thin films. For example, adhesive ML elastic coatings and ML films were introduced by the Xu group as a new class of stress sensors for remote ML image-based monitoring of the structural health of load-bearing structures in buildings and bridges [7,15,16,21,22,24,25]. This research has led to the discovery of dozens of useful trap-controlled ML materials, the majority of which are based on luminescent ions doped inorganic materials containing aluminate, sulfide, silicate, titanate and phosphate, with a smaller number containing gallate, oxide, nitroxide, stannate, oxysulfide, and germanium silicate. The colors of the ML of these materials cover the entire visible range as highlighted in following list (in accordance with the reported order): ZnS:Mn (orange) [15], $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ (green) [16], $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Ce}^{3+}$ (blue) [82], $\text{ZnGa}_2\text{O}_4:\text{Mn}^{2+}$ (green) [84], $\text{MgGa}_2\text{O}_4:\text{Mn}^{2+}$ (green) [84], $\text{ZnAl}_2\text{O}_4:\text{Mn}^{2+}$ (green) [85], $\text{ZrO}_2:\text{Ti}^{4+}$ (green) [86], $\text{ZnS:Mn}^{2+}, \text{Te}^{2+}$ (red) [87,88], $(\text{Ba,Ca})\text{TiO}_3:\text{Pr}^{3+}$ (red) [89], $\text{SrCaMgSi}_2\text{O}_7:\text{Eu}^{2+}$ (bluish-green) [90], $\text{SrAl}_2\text{O}_4:\text{Ce}^{3+}$ (ultraviolet, UV) [91], $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ (green) [92], $\text{CaYAl}_3\text{O}_7:\text{Eu}^{2+}$ (blue) [93], $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ (blue) [94], $\text{SrBaMgSi}_2\text{O}_7:\text{Eu}^{2+}$ (deep blue) [95], $\text{BaSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ (bluish-green) [96–98], $\text{CaYAl}_3\text{O}_7:\text{Ce}^{3+}$ (deep blue) [99], $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Er}^{3+}$ (near infrared, NIR) [20], $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Nd}^{3+}$ (NIR) [124], $\text{SrMg}_2(\text{PO}_4)_2:\text{Eu}^{2+}$ (purple) [100], $\text{Sr}_3\text{Sn}_2\text{O}_7:\text{Sm}^{3+}$ and $\text{Sr}_2\text{SnO}_4:\text{Sm}^{3+}$ (reddish-orange) [101], CaZnOS:Mn^{2+} (red) [102], $\text{CaZr}(\text{PO}_4)_2:\text{Eu}^{2+}$ (cyan) [103], ZnS:Cu (green) and ZnS:Cu,Mn^{2+} (orange) [104], $\text{ZnS:Al}^{3+}, \text{Cu}$ (green) and $\text{ZnS:Al}^{3+}, \text{Cu,Mn}^{2+}$ (cool white) [105], $\text{Zn}_2(\text{Ge}_{0.9}\text{Si}_{0.1})\text{O}_4:\text{Mn}^{2+}$ (green) [106], CaZnOS:Cu (cyan) [107], CaZnOS:Er^{3+} (green) [108], BaZnOS:Mn^{2+} (orange, red) [109,110], CaZnOS:Sm^{3+} (red) [111], $\text{mCaO-Nb}_2\text{O}_5:\text{Pr}^{3+}$ ($m = 1, 2$ and 3) (red) [112], $\text{LiNbO}_3:\text{Pr}^{3+}$ (red) [113], $\text{Ca}_3\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$ (red) [114], CaZnOS:Nd^{3+} (NIR) [125], $(\text{Ca,Sr})_2\text{Nb}_2\text{O}_7:\text{Pr}^{3+}$ (red) [126,127], $\text{Ba}_2\text{Zr}_2\text{Si}_3\text{O}_{12}:\text{Eu}^{2+}, \text{Dy}^{3+}$ (cyan) [128], $\text{NaNbO}_3:\text{Pr}^{3+}$ (red) [129,130], and $\text{CaZnOS:Tb}^{3+}/\text{Eu}^{3+}/\text{Pr}^{3+}/\text{Sm}^{3+}/\text{Er}^{3+}/\text{Dy}^{3+}/\text{Ho}^{3+}/\text{Nd}^{3+}/\text{Tm}^{3+}/\text{Yb}^{3+}$ (from violet to NIR) [131].

A summary of physical, structural, chemical and ML properties of the best-studied trap-controlled ML materials is presented in Table 1. To function as an effective probe for stress-sensing, the ML material should exhibit the following properties: (1) the ML emission should be robust and reproducible (or recoverable); (2) the ML intensity should scale quantitatively with the amplitude of the stress in the target object; (3) the brightness of ML should be high, and allow for sensitive and high-contrast ML-imaging of stress distributions in the target structure. In the following paragraphs, we summarize studies on the development of thin sheets or films of ML composite materials. These ML composite materials are designed to function as a mechano-optical skin and have great potential as low-cost stress sensors for remote and real-time detection of faults and defects in critical components of social infrastructure, and in components of dynamic machines used in the automotive, aeronautic and astronautic industries [7,15,16]. Our survey also identifies new applications of trap-controlled ML composite materials in biomedicine, including dynamic imaging of stress distributions and fractures in artificial joints and limbs.

To perform effectively as a mechano-optical skin, the ML composite material must bond tightly to the target structure [7,8,15,16]. To this end, the Xu group has developed ML composite thin films and adhesive polymer coatings that can be applied directly to the surface of any arbitrarily-shaped target structure [7,8]. Once bonded, these ML composites simultaneously “feel” (sense) and “see” (image) changes in stress distribution at the contact between the structure and the ML sensor. Another requirement is that the intensity of the ML signal in the surface-attached ML composite material scales quantitatively with the amplitude and distribution of load/stress/strain in the target structure [7,15,16,82–114,124–133]. Once demonstrated, the effectiveness of a mechano-optical skin can be further enhanced by integrating multiple types of ML particles within the polymer coating, each of which may emit a unique color corresponding to a particular energy range, or type of defect. Analysis of images of an optimized mechano-optical skin can be used to quantify real-time changes in the distribution of stress in a target structure in response to mechanical insults over a broad-amplitude of applied energy [15,16,82,84–114]. Aside from applications related to stress-sensing, ML composite films have also been fabricated to function as mechanically-driven light sources, and as force-triggered optical displays [8,104,134–136].

This review is organized according to the schematic shown in Fig. 4. First, we summarize state-of-the-art methods used in the design, synthesis and characterization of trap-controlled ML materials and ML composite coatings. Second, we present an overview of the literature to help understand mechanisms of ML of trap-controlled ML materials. Third, we present a comprehensive discussion on the practical, industrial and biomedical applications of ML and ML materials. Finally, we discuss challenges and solutions to realize the full potential of ML materials as stress sensors, including those related to dynamic monitoring of the structural health of buildings and social infrastructure and medical implants.

2. Material synthesis and coating preparation

2.1. Synthesis of ML particle materials

Single- or poly-crystalline ML particles with mean diameters from 10 nm to 100 μm have been synthesized using solid state reactions, sol–gel method and ultrasonic pyrolysis. The actual method employed for the preparation of an ML material will depend on the intended application, and include considerations of the diameter of the ML particles, and the spatial resolution of the stress measurement. In the following sections, we describe synthetic methods to prepare various forms of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, the first and best-studied of all trap-controlled ML materials.

Table 1
Type, crystal structure, centrosymmetry, persistent luminescence and ML characteristics of the best-studied trap-controlled ML materials.*

Structure	Host	Type [®]	Space group	Symmetry [□]	Dopants	PersL [°]	λ_{ML} (nm), color	Multi-mechano-sensitivity	Linearity	Reproducibility	Dynamic response	Refs.
Tridymite	SrAl ₂ O ₄	Dielec.	<i>P2₁</i>	–	Eu ²⁺	✓	520 (green)	✓	✓	✓	✓	[7,16,83,137–140,15–6–160,173–175,180–1–87,262]
Melilite	Zn ₂ (Ge _{0.5} Si _{0.5})O ₄	Dielec.	<i>R3</i>	–	Ce ³⁺	–	375 (UV)	✓	✓	✓	✓	[91]
					Eu ²⁺ , Er ³⁺	–	1530 (NIR)	✓	✓	✓	✓	[20]
					Eu ²⁺ , Nd ³⁺	–	883 (NIR)	✓	✓	✓	✓	[124]
					Mn ²⁺	✓	535 (green)	–	✓	✓	✓	[106]
					Ce ³⁺	✓	402 (blue)	–	✓	✓	✓	[82,191,192]
					Eu ²⁺	✓	464 (blue)	–	✓	✓	✓	[95,153,195]
Anorthite	SrBaMgSi ₂ O ₇	Dielec.	<i>P4₂/m</i>	–	Eu ²⁺	✓	440 (blue)	–	✓	✓	✓	[95,153,196]
					Eu ²⁺	✓	499 (bluish-green)	–	✓	✓	✓	[90,95,153,195,196]
					Eu ²⁺	✓	530 (green)	–	✓	✓	✓	[92,153,197]
					Ce ³⁺	✓	440 (blue)	–	✓	✓	✓	[93,190]
Ilmenite	LiNbO ₃	Dielec.	<i>R3c</i>	–	Pr ³⁺	✓	619 (red)	✓	✓	✓	✓	[113]
					Pr ³⁺	✓	613 (red)	–	✓	✓	✓	[89,143–145]
					Sm ³⁺	✓	570,582,610,624–,665 (reddish-orange)	–	✓	✓	✓	[101,200–203,241,242]
					Pr ³⁺	×	613 (red)	–	✓	✓	✓	[112]
Perovskite	(Ba,Ca)TiO ₃	Dielec.	<i>P4mm</i>	–	Pr ³⁺	✓	613 (red)	✓	✓	✓	✓	[112]
					Sm ³⁺	✓	613 (red)	✓	✓	✓	✓	[126]
					Pr ³⁺	✓	613 (red)	✓	✓	✓	✓	[127]
					Pr ³⁺	×	613 (red)	–	✓	✓	✓	[112]
					Pr ³⁺	✓	613 (red)	✓	✓	✓	✓	[129,130]
					Pr ³⁺	✓	615 (red)	✓	✓	✓	✓	[114]
MSi ₂ O ₂ N ₂ (M = Ba, Sr)	BaSi ₂ O ₂ N ₂	Dielec.	<i>Cmc2₁</i>	–	Eu ²⁺	✓	493 (bluish-green)	✓	✓	✓	✓	[96–98,198]
					Eu ²⁺	✓	–	–	–	–	–	[97,198]
					Ti ⁴⁺	✓	478 (green)	–	✓	✓	✓	[86,188,189]
					Eu ²⁺	✓	474 (cyan)	–	✓	✓	✓	[103,204,205]

(continued on next page)

Table 1 (continued)

Structure	Host	Type [®]	Space group	Symmetry [□]	Dopants	PersL [◊]	λ_{ML} (nm), color	Multi-mechano-sensitivity	Linearity	Reproducibility	Dynamic response	Refs.
Wurtzite	ZnS	Semic.	$P6_{3mm}$	–	Mn ²⁺	✓	585 (yellow)	✓	✓	✓	✓	[15–17,42,176,177,20–6]
					Mn ²⁺ , Te ²⁺	✓	648 (red)	✓	✓	✓	✓	[87,88,207–209]
					Cu ⁸	✓	456,505,520,586 (blue, green, orange)	✓	✓	✓	✓	[104,134,154,178,210]
	CaZnOS	Semic.	$P6_3mc$	–	Al ³⁺ , Cu ⁸	–	516 (green)	✓	✓	✓	✓	[105]
					Mn ²⁺	✓	610 (red)	✓	✓	✓	✓	[102,149,211–215,274]
					Cu ⁸	✓	498 (cyan)	✓	✓	–	✓	[107]
					Er ³⁺	–	530,560 (green)	✓	✓	–	✓	[108]
					Sm ³⁺	–	566,602,610,620–,649,670 (red)	–	✓	–	✓	[111]
					Nd ³⁺	–	908,1094,1390 (NIR)	–	✓	–	✓	[125]
					Tb ³⁺	–	485,545,580, 619 (green)	–	✓	–	✓	[131]
					Mn ²⁺	✓	584,610 (orange, red) [§]	✓	✓	✓	✓	[109,110]
Spinel	ZnGa ₂ O ₄	Semic.	$Fd\bar{3}m$	+	Mn ²⁺	✓	505 (green)	–	✓	✓	✓	[84,216–218]
	MgGa ₂ O ₄	Semic.	$Fd\bar{3}m$	+	Mn ²⁺	✓	506 (green)	–	✓	✓	✓	[84,154,216,219,220]
	ZnAl ₂ O ₄	Semic.	$Fd\bar{3}m$	+	Mn ²⁺	✓	512 (green)	–	✓	✓	✓	[85,221,222]

[®]: Properties at room temperature.

Type[®]: Semic. = Semiconductor; Dielec. = Dielectric.

Symmetry[□]: + = centrosymmetric; – = non-centrosymmetric.

PersL[◊]: PersL = persistent luminescence.

–: No related report.

Cu⁸: The valence state of Cu has not been marked due to the controversial valences (Cu⁺ or/and Cu²⁺) involved in luminescent process. (orange, red)[§]: The orange and red emissions are observed during the application of friction and compression, respectively.

Fig. 4. Schematic illustration of the organization of this review.

2.1.1. Solid state reactions

The simplest and most efficient approach to prepare ML particles is based on a solid-phase high-temperature reaction of component oxides or salts – many of the ML materials listed in Table 1 have been prepared using this method. For example, $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ was synthesized in a reaction comprised of designed non-stoichiometric amounts of high purity ($> 99.9\%$) and ultrafine powders ($< 0.2\ \mu\text{m}$) of SrCO_3 , $\alpha\text{-Al}_2\text{O}_3$, Eu [as either Eu_2O_3 , $\text{EuCl}_3 \cdot 5.9\text{H}_2\text{O}$, or $\text{Eu}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$], and a small quantity of flux (H_3BO_3) [7,16]. Following this reaction, the mixture was ground using a dry- or wet-mixing process, pressed into pellets and calcinated at $900\ ^\circ\text{C}$ for 1 h. After exposing the mixture to $1300\ ^\circ\text{C}$ in a reducing atmosphere ($5\%\text{H}_2\text{-N}_2$) for 4 h and further grinding, the final product was isolated by filtering through a $20\ \mu\text{m}$ sieve. The final product was in the form of polycrystalline $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ particles with a mean diameter of $5\text{--}10\ \mu\text{m}$.

2.1.2. Sol-gel method

The sol-gel method has been used to prepare ML particles with a mean diameter of a few microns [137]. The Xu group prepared $0.4\ \text{mol}$ of $\text{Sr}_{0.99}\text{Eu}_{0.01}\text{Al}_2\text{O}_4$ nanoparticles by dissolving $163.40\ \text{g}$ $\text{Al}(\text{O-i-C}_3\text{H}_7)_3$, $84.64\ \text{g}$ $\text{Sr}(\text{NO}_3)_3$ and $1.56\ \text{g}$ $\text{Eu}(\text{NO}_3)_3 \cdot 2.9\text{H}_2\text{O}$ in $400\ \text{mL}$ of $0.5\ \text{mol L}^{-1}$ ammonia water. After condensation and dispersion of the mixture in $200\ \text{mL}$ $\text{N,N-dimethylformamide}$ (DMF), the sol particles was dried at $200\ ^\circ\text{C}$ and calcinated at $700\ ^\circ\text{C}$ in an atmosphere of air. ML particles were generated from the sol particles following their exposure to $750\text{--}1400\ ^\circ\text{C}$ for 2 h in a reducing atmosphere ($5\%\text{H}_2\text{-Ar}$).

2.1.3. Ultrasonic pyrolysis technique

The ultrasonic pyrolysis technique has been used to prepare $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ nanoparticles [138,139]. The ultrasonic spray pyrolysis system comprises an ultrasonic atomizer with a $2.4\ \text{MHz}$ transducer, a horizontal reaction furnace, and an electrostatic precipitator. In this reaction, stoichiometric amounts of strontium acetylacetonate, aluminum acetylacetonate and europium acetylacetonate were mixed in deionized water. The atomized reaction mixture was subsequently passed into a $1300\ ^\circ\text{C}$ tube furnace using a $5\%\ \text{H}_2\text{-Ar}$ carrier gas ($2\ \text{L m}^{-1}$). The $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ nanoparticles produced by this method have diameters on the order of 10 to 30 nm with a single crystal structure. $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ nanoparticles have also been prepared from a polymer-coated precursor [140], and by CO_2 laser vaporization [141].

2.2. Trap formation

As we discussed in Section 1.3, trap-controlled ML materials harbor carrier traps that store the energy associated with ML emission. Several lines of evidence suggest that the ML of trap-controlled materials originates from point defects in the host material – these defects can be created during the synthesis by luminescent ion doping, or by element deficiency (Fig. 5) [8,82–114,142].

The luminescent ion doping approach can be sub-classified as non-equivalent substitution and equivalent substitution. Non-equivalent substitution involves substituting the mono- and divalent host metal ions with luminescent trivalent lanthanide dopants (Ln^{3+}). Taking the substitution of divalent host ions (M^{2+}) as an example, charge compensation will generate two types of defects, expressed as $2\text{Ln}^{3+} + 3\text{M}^{2+} \rightarrow 2[\text{Ln}^{3+}]_{\text{M}}^+ + [\text{V}_{\text{M}}]^{2-}$. The $[\text{Ln}^{3+}]_{\text{M}}^+$ defect will carry one positive charge, and the M^{2+} vacancy $[\text{V}_{\text{M}}]^{2-}$ will carry two negative charges – these defects act as the electron and hole traps, respectively. It is generally agreed that the energy levels of the luminescent ion-associated defects of $[\text{Ln}^{3+}]_{\text{M}}^+$ account for the trap levels associated with the emission of Ln^{3+} in the ML process. Examples of ML materials that are formed by non-equivalent substitution include $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Ce}^{3+}$ [82], $(\text{Ba,Ca})\text{TiO}_3:\text{Pr}^{3+}$ [143–145], $\text{SrAl}_2\text{O}_4:\text{Ce}^{3+}$ [91], $\text{CaYAl}_3\text{O}_7:\text{Ce}^{3+}$ [99], $\text{Sr}_3\text{Sn}_2\text{O}_7:\text{Sm}^{3+}$ [101], $\text{CaZnOS}:\text{Er}^{3+}$ [108], $\text{CaZnOS}:\text{Sm}^{3+}$ [111], $\text{mCaO-Nb}_2\text{O}_5:\text{Pr}^{3+}$ ($m = 1, 2$ and 3) [112], $\text{LiNbO}_3:\text{Pr}^{3+}$ [113], $\text{Ca}_3\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$ [114], $(\text{Ca,Sr})_2\text{Nb}_2\text{O}_7:\text{Pr}^{3+}$ (red) [126,127], and $\text{NaNbO}_3:\text{Pr}^{3+}$ (red) [129,130]. Equivalent substitution creates isoelectronic trap states that result from the discrepancies of host ions and dopant ions in terms of their electronegativity and covalent radius [146]. Equivalent substitutions occurs in certain semiconductors, for example where Mn^{2+} substitutes for Zn^{2+} in $\text{ZnS}:\text{Mn}^{2+}$, $\text{CaZnOS}:\text{Mn}^{2+}$ and $\text{BaZnOS}:\text{Mn}^{2+}$ [109,110,147–149]. Since the

Fig. 5. Schematic illustration on the generation of carrier traps associated with ML.

electronegativity of Mn is lower than that of Zn (1.55–1.65), Zn ions attract electrons as hole traps, and Mn ions combine with holes to function as electron traps.

Element deficiency can be controlled through the judicious choice of component materials, and the condition used to volatilize the element. Sr vacancies in $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ are created using a Sr non-stoichiometric approach [16] and, relatedly, in $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Ce}^{3+}$ by manipulating the compositions of Ca and Si [150]. Several studies have shown that the conditions of volatilization and reaction of elements during the heat-treatment process generate materials with a higher ML intensity, including those harboring oxygen vacancies, sulfide vacancies, zinc vacancies and calcium vacancies [84,85,100,102,151].

The nature of the carrier traps associated with the ML process is poorly understood, in part because these traps cannot be detected directly. Indeed, even studies on an identical ML material have generated different conclusions on the nature of component carrier traps [15,16,83–86,89–94,97–114]. In the following discussion, we analyze key aspects of two opposing models to explain the ML of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, in which hole and electron traps serve as the main carrier traps participating in ML process, respectively (Fig. 6). First, since Sr vacancies have a large effect on the intensity of ML in $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ [16], they could serve as the hole traps in the ML process (Fig. 6a). In the first model, optical excitation of Eu^{2+} allows a hole to escape to the valence band – this generates Eu^+ while the hole is trapped by a Sr vacancy. Subsequent exposure of the optically-excited material to a mechanical stimulus releases the hole, which recombines with Eu^+ to form an excited Eu^{2+} that decays rapidly emitting a green photon [16]. In the second model, oxygen vacancies are viewed as the primary traps, while electrons serve as carriers (Fig. 6b). Here, UV-irradiation of the material promotes a Eu^{2+} electron to the conduction band, where it is captured by an oxygen vacancy, with the excited Eu^{2+} oxidizing to Eu^{3+} . During an exposure of the optically-excited material to a mechanical stimulus, the trapped electron is released and subsequently recombines with Eu^{3+} to form an excited Eu^{2+} and emits a green photon [152].

Uncertainties about the nature of carrier traps in trap-controlled materials have also hindered efforts to understand the mechanism of long-lived emission in persistent phosphors – aspects of this controversy are discussed in the following reviews [153–155].

2.3. ML coating preparation

2.3.1. ML composite coating

The Xu group developed the first class of ML stress sensors composed of adherent thin films and elastic polymers embedded with ML particles (ML coatings). These thin films and coating materials are designed to bond tightly to target structures where they

Fig. 6. Schematic diagrams of proposed carrier traps and carrier pathways involved in ML of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$. (a) Hole traps serving as the main carrier traps. Reproduced with permission from Ref. [16], Copyright 1999, American Institute of Physics. (b) Electron traps serving as the main carrier traps. VB: valence band; CB: conduction band. Reproduced with permission from Ref. [152], Copyright 2007, The Electrochemical Society.

transduce mechanical energy in the structure to ML – analysis of ML images of these films allows one to generate dynamic maps of the distribution of stress in the target structure [7,16]. ML coatings are prepared by mixing pre-synthesized ML particles with a binding material. For example, ML coatings composed of organic polymer, glass or rubber have been prepared with a thickness from nanometers to millimeters using screen-printing, dip-coating, spin-coating and spray-coating techniques [156–159]. An illustrative example of a multi-mechano-sensitive ML composite coating is shown schematically in Fig. 7. Typically, ML composite materials of this class are composed of a transparent elastic polymer that is embedded prior to polymerization with a uniform distribution of ML particles. Scanning electron microscope (SEM) cross-sectional images of patterned composite coatings composed of diverse transparent polymer matrices embedded with different spherical ML particles, including $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ and $\text{ZnS}:\text{Cu}$, are shown in Fig. 8a–c and d, respectively. Of course, to couple the transfer of mechanical energy from the target structure to the ML coating, it is essential to bond the ML coating or film tightly and uniformly to the surface of the target object.

In our view, the ML particles in the ML-coating material mimic sensory mechanosensitive neurons of human skin, in that they respond spatio-temporally to external mechanical stimuli. The most effective mechano-optical skins are based on elastic polymers, which include poly(methyl methacrylate) (PMMA), polystyrene (PS), poly(bisphenol A carbonate) (PC), and polydimethylsiloxane (PDMS). These polymers can be further engineered to improve the transmission of external mechanical forces from the target object to the embedded ML particles. In this way, the polymer material mimics the extracellular matrix of vascular tissue. Furthering this analogy, while the distribution of mechanical forces in natural skin is interpreted by the brain, the mechanically-triggered photon signals generated in ML-coating materials are recorded on a charge-coupled-device (CCD) camera or photomultiplier tube (PMT) detector, analyzed using algorithms on a computer and finally relayed to the user via a display or alerting device (Fig. 7). Several types of adhesive ML coating materials have been shown to function as mechano-optical skins [7,8,21,22,24,148,149,160]. Importantly, the ML intensity of the embedded ML particles in these ML composite materials depends quantitatively on the amplitude of the applied load/stress/strain in the target structure (Section 4.4.1). Mechano-optical skins can respond to diverse types of mechanical stimuli, including compression, bending, stretching, loading, ultrasonic vibration and gas-flow driving (Section 4.3).

The ML intensity of ML particles embedded in a composite material is sensitive to the amplitude of the mechanical stimulus, and to specific mechanical and optical properties of the polymer matrix [156]. For example, the transmission of mechanical energy is sensitive to differences in the elastic modulus of the polymer and the inorganic ML particles, and differences in the size, shape and dispersion of ML particles in the polymer. Other factors include the degree of mechanical coupling between the ML particles and the polymer matrix, and between the ML coating and the surface of target structure. The performance of the ML coating may be further affected by “optical factors”, for example light scattering in opaque polymers. The ML intensity of a composite material is also reduced in cases where there is a mismatch of the refractive indices of the polymer and the ML particle. These factors, while problematic, can be mitigated through careful design of high-performance ML coatings. In summary, one can engineer ML coatings to function as a sensitive optical-mechanical skin that generate real-time, high-resolution maps of the amplitudes of the load/stress/strain in a target structure.

2.3.2. ML thin films

Several methods have been developed to grow ML thin film coatings directly on the surface of a target object, including physical vapour deposition of ion-plating, and radio-frequency magnetron sputtering techniques [15,17–19,105,152,161–171]. ML thin films offer advantages over powder/polymer composite coatings to image stress distributions in target structures, including thinner films (less than 10 μm), good thermal stability, and a preferred orientation of crystallinity – these features may help to overcome some of the optical and mechanical transmission problems discussed above for composite films (Section 2.3.1). However, the bonding of ML thin films to target structures is not always strong, while the high temperatures required to grow ML thin films could damage the

Fig. 7. Schematic representation of multi-mechano-sensitive ML composite coating. Adapted with permission from Ref. [102], Copyright 2013, Optical Society of America.

Fig. 8. Cross-sectional SEM images of the composite coatings: (a) PMMA/SrAl₂O₄:Eu²⁺ (SAOE); (b) PS/SAOE; (c) PC/SAOE. Reproduced with permission from Ref. [156], Copyright 2007, Elsevier B.V. (d) PDMS/ZnS:Cu. Reproduced with permission from Ref. [104], Copyright 2013, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

target structure. Moreover, the methods employed to apply thin films to target structures are complex and more expensive compared to adhesive ML polymer coatings.

The SEM image of a ZnS:Mn²⁺ film grown on a glass substrate shown in Fig. 9a reveals details of bonds between the thin film and the substrate. This sample was prepared by pre-treating the source material (ZnS:Mn²⁺) at 1050 °C for 3 h in a vacuum-sealed quartz tube [15], followed by exposing the glass substrate to a vapor of ZnS:Mn²⁺ vapor at 160 °C at a rate of 2 nm s⁻¹. Finally, the thin film was heated to 700 °C in a vacuum for one hour to improve the crystallinity of the ZnS:Mn²⁺ and to reduce defects and stress in the film. The SEM image in Fig. 9b shows the locations of the homo-buffer layer (grown on a glass substrate) and the SrAl₂O₄:Eu²⁺ film, which was prepared in this case using the radio frequency magnetron sputtering technique followed by heat-treatment. The buffer layer was integrated into the design of the film to reduce adverse effects of structural and thermal mismatches between the ML film and the substrate [162,165].

Fig. 9. (a) SEM image of ZnS:Mn²⁺ film grown on a glass substrate. Adapted with permission from Ref. [15], Copyright 1999, The American Institute of Physics. (b) SEM image of SrAl₂O₄:Eu²⁺ based multilayer films grown on a glass substrate. Adapted with permission from Ref. [165], Copyright 2008, Elsevier B.V.

3. Characterization of ML sensors and systems

New ML materials and their composite coatings should be characterized using a broad spectrum of quantitative measurement techniques including structural analyses, mechano-optical responses and luminescent properties. A selection of instruments and devices that have been used to characterize ML properties of new materials are shown in Fig. 10. In the following section, we describe techniques and devices developed by the Xu group to characterize ML properties of materials [7,172], including the compression test (Fig. 10a), the friction test (Fig. 10b) and the impact test (Fig. 10c). The ML response of materials to multiscale mechanical stimuli, including compression, bending, stretching, loading, ball impact, friction, twist, ultrasonic vibration and gas-flow blowing are recorded using CCD digital cameras and PMT detectors. In these studies, the ML particles are dispersed uniformly in a transparent polymer film, or in a circular polymer disk (25 mm in diameter and 15 mm in thickness). The circular disks are prepared by sequential mixing and polymerization of a suspension of ML particles in a transparent epoxy resin (at a weight ratio of 1:9). In practice, one can improve the mechano-optical response of an ML circular disk by layering the ML particles to 1 mm of the outer surface of the disk. ML polymer films with thicknesses from μm to mm have also been prepared by suspending the ML particles in an epoxy resin at a weight ratio of 1:1 followed by polymerization.

Defined mechanical loads can be applied to ML circular disks using a universal test machine, a power press machine with a force gauge, and vises (Fig. 10a) [7]. The ML response of the mounted circular disk is recorded during the application of a time-varying compressive load (from 0 to 1000 N) at a constant rate of deformation ($1\text{--}10\text{ mm min}^{-1}$) (Fig. 10a). Moreover, one can characterize ML responses of circular disk and thin film samples to tensile and bending forces by exchanging the sample holder on a universal test machine (Fig. 10d) [160,173]. For example, the Xu group used a fatigue test machine to record the ML response of a metal plate coated with an ML film to a uniaxial tension test [160]. The ML response of thin films or disks to friction can be measured using different materials in the friction rod and by varying the applied load (Fig. 10b) [7]. Finally, one can record the response of an ML material to impact by imaging ML signals generated during the impact of free-falling ball with a surface (Fig. 10c) [7,172].

As we have previously indicated, the ML response of a material to a mechanical insult will depend on the nature and amplitude of the stimulus, and specific physical, mechano-optical and luminescent properties of the ML particles in the polymer coating. Given the number of variables involved, it is essential to define the experimental condition used to record the ML response, and to apply the same condition to a reference ML material.

Specialized techniques and instrumentation have been developed to characterize ML properties of individual ML particles, including the ultrasonic vibration test (Fig. 10e) [174] and atomic force microscopy (AFM) (Fig. 10f) [175]. In addition, Fontenot et al. described a simple low-cost drop-tower apparatus to measure the ML properties of powdered samples (Fig. 10g) [176,177]. ML responses have also been measured during mechanical perturbations associated with gas-flow and twisting – these specialized techniques are described further in Sections 7.1 and 7.6, respectively [134,178,179].

4. Properties of trap-controlled ML materials

The mechanisms responsible for the ML of trap-controlled ML materials are not well understood. Characterizing trap centers in

Fig. 10. Schematic diagram of ML characterization apparatus. (a) Compression test and (b) friction test. Reproduced with permission from Ref. [7], Copyright 2002, John Wiley and Sons, Inc. (c) Impact test. Reproduced with permission from Ref. [172], Copyright 2012, American Institute of Physics. (d) Tension test. Reproduced with permission from Ref. [160], Copyright 2010, Blackwell Publishing Ltd. (e) Ultrasonic vibration test. Reproduced with permission from Ref. [174], Copyright 2010, Elsevier B.V. (f) ML test of single particle. Reproduced with permission from Ref. [175], Copyright 2006, the Owner Societies. (g) Drop-tower test. Reproduced with permission from Ref. [176], Copyright 2012, Elsevier B.V.

ML materials and the pathways of energy transfer from mechanical stimuli to optical transitions via long-lived trapped states requires a concerted research effort that integrates theory and experimental studies. In our view, having a deeper understanding of ML processes would allow researchers to design high-performance ML materials rationally, and to fine tune their properties for real-world applications. In the following section, we summarize the findings of an extensive body of literature on important properties of trap-controlled ML materials, including information on their structures, centrosymmetry, optical properties and mechanically triggered luminescence. This summary is followed by discussions on the photophysical and photomechanical properties, reproducible ML, multi-mechano-sensitivity, dependence of ML intensity on dynamic load, and finally water resistance of trap-controlled ML materials.

4.1. Trap-controlled ML materials

The ML materials summarized in Table 1 can be divided into two groups according to the conductivity of the material. The first group is comprised of luminescent ion-doped dielectric materials. The second group contains semiconductor materials, including the metal ion-doped ZnS and CaZnOS series, BaZnOS:Mn²⁺, ZnGa₂O₄:Mn²⁺, MgGa₂O₄:Mn²⁺ and ZnAl₂O₄:Mn²⁺. Interestingly, most of the members of these groups of ML materials are piezoelectric, a consequence of their non-centrosymmetric crystal structures. In addition, most of these ML materials exhibit a persistent luminescence, i.e., they harbor long-lived trap levels. The correlation between piezoelectricity, trap levels and ML is discussed in more detail in Section 5.

4.2. Spectra and intensity of ML

4.2.1. ML spectra

Trap-controlled ML materials emit light over broad range of wavelengths, covering the UV to the NIR (Table 1). Light emitted by ML materials originates primarily from electronic transitions in the doped luminescent ions. According to the nature of electronic transitions, the doped luminescent ions can be classified into three categories, i.e., the transition metal ions Mn²⁺, Cu and Ti⁴⁺ (dⁿ transitions), the lanthanide ions Eu²⁺ and Ce³⁺ (5d-4f transitions), and the trivalent lanthanide ions Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺ and Yb³⁺ (4f-4f transitions). The first category of ML materials (Mn²⁺, Cu and Ti⁴⁺) emit broadband emission from dⁿ transitions – examples include ZnS:Mn²⁺ (yellow) [15], ZnS:Mn²⁺,Te²⁺ (red) [87,88], ZnS:Cu (blue, green, orange) [104,134,178,210], ZnS:Cu,Mn²⁺ (orange) [104,134,178,210], CaZnOS:Mn²⁺ (red) [102], BaZnOS:Mn²⁺ (orange, red) [109,110], CaZnOS:Cu (cyan) [107], ZnGa₂O₄:Mn²⁺ (green) [84], MgGa₂O₄:Mn²⁺ (green) [84], ZnAl₂O₄:Mn²⁺ (green) [85], Zn₂(Ge_{0.9}Si_{0.1})O₄:Mn²⁺ (green) [106], and ZrO₂:Ti⁴⁺ (green) [86]. We note that the valence state of Cu in ZnS and CaZnOS is not well-defined, as Cu⁺ or/and Cu²⁺ may be involved in the luminescent process. The second category of luminescent ions include doped lanthanide ions (Eu²⁺ and Ce³⁺) that emit broadband emission as a result of 5d-4f transitions – examples include SrAl₂O₄:Eu²⁺ (green) [16], SrCaMgSi₂O₇:Eu²⁺ (bluish-green) [90], Ca₂MgSi₂O₇:Eu²⁺ (green) [92], CaYAl₃O₇:Eu²⁺ (blue) [93], CaAl₂Si₂O₈:Eu²⁺ (blue) [94], SrBaMgSi₂O₇:Eu²⁺ (blue) [95], BaSi₂O₂N₂:Eu²⁺ (bluish-green) [96–98], SrMg₂(PO₄)₂:Eu²⁺ (purple) [100], Ca₂Al₂SiO₇:Ce³⁺ (blue) [82], SrAl₂O₄:Ce³⁺ (UV) [91], CaYAl₃O₇:Ce³⁺ (blue) [99], and CaZr(PO₄)₂:Eu²⁺ (cyan) [103]. The emission spectra of ML materials in the first two categories are strongly influenced by the crystal field strength [223], and so the ML spectra may differ for different host lattices, even if these hosts are doped with the same luminescent ion. The third category of luminescent ions includes the trivalent lanthanide ions (Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺ and Yb³⁺) that emit narrow emission peaks due to 4f-4f transitions – examples include (Ba,Ca)TiO₃:Pr³⁺ (red) [89], mCaO:Nb₂O₅:Pr³⁺ (m = 1, 2 and 3) (red) [112], LiNbO₃:Pr³⁺ (red) [113], NaNbO₃:Pr³⁺ (red) [129,130], Ca₃Ti₂O₇:Pr³⁺ (red) [114], Sr₃Sn₂O₇:Sm³⁺ and Sr₂SnO₄:Sm³⁺ (reddish-orange) [101], SrAl₂O₄:Eu²⁺,Er³⁺ (NIR) [20], SrAl₂O₄:Eu²⁺,Nd³⁺ (near infrared, NIR) [124], and CaZnOS:Pr³⁺/Nd³⁺/Sm³⁺/Eu³⁺/Tb³⁺/Dy³⁺/Ho³⁺/Er³⁺/Tm³⁺/Yb³⁺ (from violet to NIR) [108,111,125,131]. Because the internal 4f shell is shielded by the 5s² and 5p⁶ orbitals, the energy of the sharp emission bands associated with 4f-4f transition in this category of ML materials is not sensitive to the nature of the ligand [223].

The ML and PL spectra of most trap-controlled ML materials are identical. For example, the PL spectrum of CaZnOS:Mn²⁺ has a single broadband emission at 610 nm due to the ⁴T₁(⁴G) → ⁶A₁(⁶S) transition in the Mn²⁺ ion – the same transition has been recorded during exposures of this material to impact, friction and compression (Fig. 11a) [102]. Similarly, the PL and ML spectra of SrMg₂(PO₄)₂:Eu²⁺ exhibit a common broadband emission centered at 412 nm, corresponding to the 5d-4f transition in Eu²⁺ (Fig. 11b) [100]. The PL and ML spectra of Sr₃Sn₂O₇:Sm³⁺ are also coincident with five common peaks, centered at 570, 582, 610, 624 and 665 nm – these emission bands have been assigned to the ⁴G_{5/2} to ⁶H_j (j = 5/2, 7/2, 9/2) (4f-4f) transitions in Sm³⁺ (Fig. 11c) [101].

Non-identical PL and ML spectra have been reported for certain ML materials that arise from small spectral shifts and loss of specific emission bands [97,112,134,224]. For example, the ML spectrum of Pr³⁺-activated mCaO:Nb₂O₅ (m = 1, 2 and 3) is attenuated at specific wavelengths – this loss is believed to result from an alternate transition pathway between luminescent centers and traps (Section 5.1.2) [112]. Spectral shifts are common to ML materials doped with the aforementioned first and second categories of luminescent ions (such as Mn²⁺, Cu and Eu²⁺) whose emission is susceptible to the local crystal field [97,224]. Notably, we are not aware of any reports of spectral shifts in ML materials doped with the third category of trivalent lanthanide ions (4f-4f transitions), such as Pr³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Tb³⁺, Dy³⁺, Ho³⁺, Er³⁺, Tm³⁺ and Yb³⁺ – this may result from the shielding of the 4f shell by outer electron orbitals [20,89,101,125–131]. Botterman et al. have reported that the ML spectrum of BaSi₂O₂N₂:Eu²⁺ is red-shifted by ~4 nm compared to its PL spectrum (Fig. 12a) [97]. The authors excluded artifacts as possible causes for the difference in PL and ML spectra including instrument-dependent spectral responses and limited spectral resolution. Unfortunately, they did not investigate

Fig. 11. (a) ML spectra of CaZnOS:Mn²⁺ induced by different external excitations (UV light, friction, compression and impact, respectively). Reproduced with permission from Ref. [102], Copyright 2013, Optical Society of America. (b) Photoluminescent and elasticoluminescent spectra of SrMg₂(PO₄)₂:Eu²⁺. Reproduced with permission from Ref. [100], Copyright 2011, Elsevier B. V. (c) Spectra of photoluminescence (PL) and ML of Sr₃Sn₂O₇:Sm³⁺. Reproduced with permission from Ref. [101], Copyright 2012, American Institute of Physics.

Fig. 12. Spectral discrepancy in different excitation conditions. (a) PL (excited by 254 nm UV light) and ML (excited by compression) spectra of BaSi₂O₂N₂:Eu²⁺ composite pellet. Reproduced with permission from Ref. [97], Copyright 2012, Acta Materialia Inc. (b) ML spectral shift of ZnS:Cu composite films during stretching-releasing motion (100–500 cycles per minute); (c) ML spectral characteristics of ZnS:Cu composites during gas-flow driving (30–80 L min⁻¹). Reproduced with permission from Ref. [134], Copyright 2014, The Royal Society of Chemistry. (d) Band diagram of blue and green ML from ZnS:Cu induced by different stress rates. Reproduced with permission from Ref. [178], Copyright 2013, American Institute of Physics. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the origin or mechanism of this spectral shift [97]. We believe that this spectral red-shift results from a change in the crystal field strength during the mechanical stimulus and is associated with a deformation of the host lattice. Changes in the strength of the crystal field are more likely to affect emission from environmentally-sensitive luminescent centers, including those containing Eu^{2+} , Mn^{2+} and Cu. The same interpretation of spectral shifts could account for the finding by Fontenot et al. on a slight red-shift in the ML spectrum of ZnS:Mn^{2+} compared to its PL spectrum [224].

Interestingly, the ML spectra of transition metal ion-activated semiconductors are also dependent on the nature of, and the method used to apply, the mechanical stimulus. For example, Jeong et al. has shown that the ML spectrum of ZnS:Cu differentially shifts on exposures to different mechanical stimuli [134]. In this study, the authors triggered the ML of ZnS:Cu composite films using a stretching-releasing motion (a low stress-rate stimulus), or by gas-flow (a high stress-rate stimulus). They found that the ML emission of the ZnS:Cu composite film peaked at ~ 510 nm in response to low stress-rate cycles, whereas the spectrum blue-shifted by ~ 3 nm at higher stretching-releasing rates (Fig. 12b). Of equal interest, the authors identified a new blue emission centered at ~ 456 nm (with a concomitant decrease in the green emission) during exposures of the film to the high stress-rate stimulus (Fig. 12c). These authors argued that the loss of the blue emission band during low stress-rate stimuli was because this type of perturbation does not provide sufficient energy to activate recombination events between the trap levels and luminescent levels, whereas this condition is met in the high stress-rate stimulus (Fig. 12d). Separately, Peng et al. showed that the ML spectrum of BaZnOS:Mn^{2+} is also sensitive to the nature of the mechanical stimulus, with exposures to friction and compression triggering orange and red ML respectively. Unfortunately, the authors did not investigate the mechanism underlying this interesting ML behavior [110].

4.2.2. ML intensity

The intensity of ML emitted by trap-controlled materials is dependent on both the amplitude and the nature of the mechanical stimulus. For example, the ML emitted by scratching or pressing a $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ composite film with a fingernail is visible to the naked eye, even in daylight, and stronger ML signals are observed during exposures of the same material to higher energies of the same mechanical stimulus. On the other hand, the ML emitted on scratching $\text{CaYAl}_3\text{O}_7:\text{Eu}^{2+}/\text{Ce}^{3+}$ and $(\text{Sr,M})\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ ($\text{M} = \text{Ca, Sr, Ba}$) is weak, even at a high amplitude. In fact, the maximum ML of these materials is only visible to the naked eye in a darkened room. The unit of ML intensity can be defined in terms of cd m^{-2} – for comparison a value of 0.32 mcd m^{-2} is ~ 100 -times the sensitivity of the dark-adapted human eye [225], while 100 mcd m^{-2} is the standard used for road markings [226]. The ML intensities measured for trap-controlled ML materials (in units of cd m^{-2}) are as follows: $(\text{Ba,Ca})\text{TiO}_3:\text{Pr}^{3+}$ ($10\text{--}15 \text{ mcd m}^{-2}$) [102], $\text{CaZr}(\text{PO}_4)_2:\text{Eu}^{2+}$ ($\sim 15 \text{ mcd m}^{-2}$) [103], ZnS:Cu ($83.3\text{--}125.5 \text{ cd m}^{-2}$) [134], $\text{ZnS:Al}^{3+}, \text{Cu, Mn}^{2+}$ (21 cd m^{-2}) [105], CaZnOS:Mn^{2+} ($30\text{--}40 \text{ mcd m}^{-2}$) [102], and $\text{mCaO:Nb}_2\text{O}_5:\text{Pr}^{3+}$ ($\text{m} = 1, 2$ and 3) ($3\text{--}35 \text{ mcd m}^{-2}$) [112].

Unfortunately, measures of ML intensity for any particular material cannot be compared to ML responses of other ML materials because of differences in the mode of mechanical excitation and instruments used to detect the ML. For example, in the case of $(\text{Ba,Ca})\text{TiO}_3:\text{Pr}^{3+}$, $\text{CaZr}(\text{PO}_4)_2:\text{Eu}^{2+}$, CaZnOS:Mn^{2+} and $\text{mCaO:Nb}_2\text{O}_5:\text{Pr}^{3+}$ ($\text{m} = 1, 2$ and 3), the ML signals were recorded during dynamic compression [102,103,112], whereas in the case of ZnS:Cu [134,178] and $\text{ZnS:Al}^{3+}, \text{Cu, Mn}^{2+}$ [105], the ML signals were recorded during gas-flow driving and by stretch-release, respectively. Comparisons of ML intensities between different laboratories are further complicated by instrument-dependent factors, including those related to charging the ML material (intensity and duration of the excitation source), and in the application of the mechanical stimulus (the rate of deformation). Moreover, specific properties of the ML composite material can affect the ML intensity, including those related to the size and density of ML particles in the polymer, the optical and mechanical properties of the elastic matrix, the freshness of the preparation, and the mechano-optical properties, including the levels of stress required to initiate and to saturate the ML signal. Clearly, any sensible comparison of ML intensities between ML materials should employ identical experimental conditions. To this end, it would appear necessary for researchers to use standardized conditions that relate to the preparation of ML materials and composites, optical excitation of ML particles, the mechanical stimulus and the instrument or device used to record the ML. Currently, ML responses of new materials are compared to reference materials using qualitative measures of ML. In one classification system, a strong ML signal is one that is visible to the naked eye in a dark room. The strongest ML signals we have recorded during tests of ML materials in our portfolio belong to members of trap-controlled materials (Table 1), including $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, $\text{BaSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$, $(\text{Ca,Sr})\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$, $\text{Sr}_3\text{Sn}_2\text{O}_7:\text{Sm}^{3+}$, $\text{SrMg}_2(\text{PO}_4)_2:\text{Eu}^{2+}$, $\text{LiNbO}_3:\text{Pr}^{3+}$, $\text{NaNbO}_3:\text{Pr}^{3+}$, and metal ions doped ZnS and CaZnOS series. Materials that exhibit a strong ML are highly valued for applications in stress and fault monitoring of buildings and social infrastructure – this topic is discussed in greater detail in Section 7. Up to now, the trap-controlled $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ is the brightest commercial ML material on the market.

4.3. Multi-mechano-sensitivity

Materials that emit ML in response to multiple types of mechanical perturbation (namely, ML materials showing multi-mechano-sensitivity) are highly desired for real-world applications of ML. Examples of this class of ML material include $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, metal ions doped ZnS and CaZnOS series, $\text{BaSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$, BaZnOS:Mn^{2+} , $(\text{Ca,Sr})_2\text{Nb}_2\text{O}_7:\text{Pr}^{3+}$, $\text{LiNbO}_3:\text{Pr}^{3+}$, $\text{NaNbO}_3:\text{Pr}^{3+}$, and $\text{Ca}_3\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$ (Table 1). For example, $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ emits ML in response to impact [168,227,228], friction [168,229], compression [16], stretching [7,25,132,160], bending [173], twisting [7,179], vibration [23,25,174,230] and fracturing [231–233]. Images of the ML emitted by $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ in response to diverse mechanical stimuli, including impact by a free-falling ball, rod-mediated friction, three-point bending, compression, stretching, and ultrasonic vibration, are shown respectively in the sub-images of Fig. 13.

Time-resolved recordings of the ML of CaZnOS:Mn^{2+} during exposures to ultrasonic vibration (Ultrasonic-L), impact, friction and compression are shown in Fig. 14 [102]. The ML intensity of CaZnOS:Mn^{2+} embedded in a polymer coating increases rapidly during pulsed exposures of the material to ultrasonic vibration (20 MHz frequency and 2.94 mW output power) (Fig. 14a). The ML image of

Fig. 13. Multi-mechano-sensitive ML images of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ excited by different mechanical stimuli. (a) Impact. Reproduced with permission from Ref. [168], Copyright 2009, The Electrochemical Society. (b) Friction. Reproduced with permission from Ref. [229], Copyright 2009, The Japan Society of Applied Physics. (c) Three-point bending. Reproduced with permission from Ref. [173], Copyright 2000, American Institute of Physics. (d) Compression. (e) Stretching. Reproduced with permission from Ref. [132], Copyright 2008, The Visualization Society of Japan. (f) Ultrasonic vibration. Reproduced with permission from Ref. [174], Copyright 2010, Elsevier B.V.

Fig. 14. Multi-mechano-sensitive behaviors of $\text{CaZnOS}:\text{Mn}^{2+}$: (a) Ultrasonic-L response, (b) Impact-L response, (c) Tribo-L response, and (d) Compress-L response. The insets show the corresponding ML images. Reproduced with permission from Ref. [102], Copyright 2013, Optical Society of America.

this study (inset of Fig. 14a) shows that the ML signal is restricted to the diameter of the piezoelectric ceramic patch (~ 4 mm). A far stronger ML signal is generated during exposures of the same ML film to higher powers of ultrasound [102]. Incidentally, this study demonstrates the potential of using this material to generate ML in response to excitation by medical ultrasound devices within living tissue – for example this property could prove useful for ultrasound-triggered ML-mediated phototherapy and *in vivo* imaging – this topic is discussed in more detail in Sections 7.5.2 and 7.8. Next, we consider the generation of ML during the impact of a free-falling ball on CaZnOS:Mn^{2+} coatings. An ML image of this study (Fig. 14b) shows that the red ML is restricted to the site of impact on the film – in particular, the ML intensity reaches its peak at the instant of contact, and decays with a time constant of a few milliseconds. The CaZnOS:Mn^{2+} particles within the same composite material also emit red ML during the application of friction (i.e., shear stress). In this study, scratching the ML composite with a rod results in a strong red Tribo-L (inset of Fig. 14c) – time resolved analysis shows that the intensity of the ML signal rises to a peak coincident with the application of the mechanical stimulus, where after it undergoes periodic oscillations, and finally decreases to a lower level (Fig. 14c). These oscillations may result from a sample-instrument alignment issue [168]. In a final demonstration of multi-mechano-sensitivity of CaZnOS:Mn^{2+} composite materials, we show the ML behavior during cycles of compression (Fig. 14d). In this study, the ML intensity tracks the energy of the compression in each cycle, and decreases exponentially after releasing the compression. The intensity of the ML is at a maximum during the first compression cycle and lower for subsequent cycles – this behavior is due to the depletion of traps with increasing cycle number (Fig. 14d). However, on normalizing the ML peak-intensity for each cycle to that recorded during the first compression cycle, one can see that the ML intensity profiles for each cycle are identical (Fig. 14d; Sections 7.1 and 7.2).

4.4. Linear and nonlinear relations

4.4.1. Linearity

The linear dependence of ML intensity of trap-controlled materials on the amplitude of the mechanical stimulus has been verified in numerous studies [4,7,15,16,82–114,159,227–237]. For example, the ML intensity of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ exhibits a linear dependence on the amplitude of the applied strain, compressive stress, strain rate, torsion, tensile stress and ultrasonic power (Fig. 15). The ML intensity of CaZnOS:Mn^{2+} exhibits an identical relationship with applied energy in its responses to ultrasonic vibration, impact, frictional load and deformation (Fig. 16). Significantly, this linear dependence holds true for ML materials within composite materials

Fig. 15. Linear relationships between ML intensity of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ and different mechanical stimuli: (a) ML intensity of single particle vs. strain. Reproduced with permission from Ref. [234], Copyright 2013, Elsevier Inc. (b) ML intensity vs. compressive stress; (c) ML intensity vs. strain rate; (d) ML intensity vs. torsion. Reproduced with permission from Ref. [7], Copyright 2002, John Wiley and Sons, Inc. (e) ML intensity vs. tensile stress. Reproduced with permission from Ref. [132], Copyright 2008, The Visualization Society of Japan. (f) ML intensity vs. ultrasonic power. Reproduced with permission from Ref. [174], Copyright 2010, Elsevier B.V.

Fig. 16. Linear relations between ML intensity of CaZnOS:Mn²⁺ and different mechanical parameters: (a) Ultrasonic-L intensity vs. ultrasonic output power, (b) Impact-L intensity vs. impact energy, (c) Tribo-L intensity vs. load, and (d) Compress-L intensity vs. deformation rate. Reproduced with permission from Ref. [102], Copyright 2013, Optical Society of America.

and thin films. Examples of this dependence include studies on the ML intensity of ZnS:Mn²⁺-composite flexible films during stretching and release [178]; torque in a ZnS:Cu-based non-contacting torque sensor [179]; gas flow rate in a ZnS:Cu-based wind-driven ML device [134]; and the frequency of a magnetic field and H_{rms}^2 (H_{rms} is the root-mean-square magnetic field) in ZnS:Al³⁺, Cu and ZnS:Al³⁺, Cu, Mn²⁺-based magnetic-induced ML devices [136]. Thus, the linear dependence of ML intensity on the applied energy of a mechanical stimulus up to the non-destructive limit should be an inherent property of trap-controlled ML materials, i.e., the ML intensity depends proportionally on the level of deformation. This feature makes it possible to develop ML coatings that after bonding to the surface of a target structure function as mechano-optical skin – i.e., the ML intensity in the 2D coating can be used to map the distribution of stress within the target structure. Moreover, one can relate the intensity of ML to the actual amplitude of stress in the target structure by separately calibrating the ML intensity of the composite material to defined amplitudes of the mechanical stimulus. Along this line, we note that a database that relates the ML intensity of specific composite coatings to units of stress would facilitate real-time analysis of stress distributions in target materials [132,157,160]. In conclusion, dynamic imaging of the ML of a mechano-optical skin attached to target structures at remote sites allows one to monitor the structural health of remote structures. The practical applications in the detection of stress distribution are discussed further in Section 7.2.

4.4.2. Nonlinearity

While the linear relationship between ML and applied stress in trap-controlled ML materials is valid over a wide range of energy, there are certain conditions and situations where the ML response is nonlinear. Nonlinearity may arise from external and internal factors associated with the ML particles or the ML coating material. External factors include inefficient transfer of mechanical energy from the target structure to individual ML particles in a composite film, for example, poor mechanical-coupling between ML particles and the polymer backbone, or between the ML coating and the target structure. Nonlinearity can also arise during the manufacture of the ML particles and ML coating materials. These factors however, can be mitigated by analyzing the ML properties of free and polymer-embedded ML particles at each step of a synthetic scheme. For example, by measuring the size and shape of ML particles, by ensuring that ML particles are dispersed uniformly within the elastic matrix, by eliminating air bubbles within the polymer, and by ensuring that the contact between the target object and the ML coating is smooth and tight.

The nonlinear ML response may result from intrinsic factors, including ML materials that contain a low number of carriers that are

Fig. 17. Schematic illustration on the initial nonlinearity and saturated nonlinearity of ML response.

allowed to de-trap during the initial and final stages of the applied stress (Fig. 17). As we discussed earlier, light emission in some trap-controlled ML materials occurs during deformation of their host lattice – this change releases carriers from traps to recombine with luminescent centers in the same material. The linear dependence of ML may thereby be equated to the deformation/strain in unit time and to the rate of release of trapped carriers. Accordingly, one can assign the first phase of nonlinearity to the slow rate of carrier de-trapping at low strain energy. The second phase of nonlinearity occurs at much higher energy of deformation/strain, and originates from a saturation effect, which arises from the low number of trapped carriers remaining in material. In summary, many trap-controlled ML materials exhibit nonlinear ML phenomena at low and high strain energies [7,16,20,83,89,93,158,194,238–242]. Despite the importance of nonlinearity in practical applications of ML materials, the origin of this property has not been discussed in any detail. Clearly, more research is needed to understand this effect and to develop approaches to mitigate problems associated with the nonquantitative ML response for practical applications of ML sensors.

The trigger and saturation thresholds of an ML response will vary for different ML materials. This feature arises from differences in the crystal structures and properties of carrier traps. For example, the trigger threshold of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ is much lower than that recorded for other ML materials. Exposing $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ to a weak mechanical stress, such as gently scratching with a fingernail, produces a very strong ML that is visible to the naked eye under ambient light. Recently, the Xu group developed a nonstoichiometric ML material $\text{Li}_x\text{NbO}_3:\text{Pr}^{3+}$ that shows excellent strain sensitivity at the lowest strain level, with no threshold for stress sensing (Fig. 18) [113]. The superhigh stress-sensing performance of $\text{Li}_x\text{NbO}_3:\text{Pr}^{3+}$ makes it a promising candidate for stress or force sensors on the 10^3 Pa and piconewton scales. On the other hand, the ML of $\text{Sr}_3\text{Sn}_2\text{O}_7:\text{Sm}^{3+}$ and $\text{Sr}_2\text{SnO}_4:\text{Sm}^{3+}$ have relatively low saturation thresholds compared to other ML materials [101] – interestingly, one could include both types of material in a sensor that would generate distinct ML signals associated with low- and high-strain or stress in a target structure.

It should be emphasized here that linearity is not an absolute requirement for quantitative analysis of stress/strain in a target material – in fact, analysis of nonlinearity can also enable accurate and reliable analysis of stress [25]. What is more important here is to highlight the reproducibility of ML that enables accurate calibration of the ML-stress relationship for quantitative analyses of stress in target materials.

4.5. Reproducible ML

4.5.1. Reproducibility after light irradiation

Fig. 19 shows the ML response of a $\text{Ca}_2\text{Nb}_2\text{O}_7:\text{Pr}^{3+}$ composite coating during cycles of compression [112]. The ML intensity of this coating attenuates gradually after the first compression cycle (Fig. 19a), but recovers to the original value after the material is exposed to a pulse of UV light at the end of each cycle (Fig. 19b and c). Reproducible ML is shared by most trap-controlled ML materials, including $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}/\text{Eu}^{2+}, \text{Er}^{3+}/\text{Eu}^{2+}, \text{Nd}^{3+}$, $\text{ZrO}_2:\text{Ti}^{4+}$, $\text{CaYAl}_3\text{O}_7:\text{Eu}^{2+}$, $\text{CaYAl}_3\text{O}_7:\text{Ce}^{3+}$, $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Ce}^{3+}$, $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$, $(\text{Ca},\text{Sr})\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$, $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$, $\text{SrBaMgSi}_2\text{O}_7:\text{Eu}^{2+}$, $\text{SrCaMgSi}_2\text{O}_7:\text{Eu}^{2+}$, $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$, $(\text{Ba},\text{Ca})\text{-TiO}_3:\text{Pr}^{3+}$, $\text{BaSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$, $\text{SrSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$, $\text{SrMg}_2(\text{PO}_4)_2:\text{Eu}^{2+}$, $\text{Sr}_3\text{Sn}_2\text{O}_7:\text{Sm}^{3+}$, $\text{CaZr}(\text{PO}_4)_2:\text{Eu}^{2+}$, $\text{Zn}_2(\text{Ge}_{0.9}\text{Si}_{0.1})\text{O}_4:\text{Mn}^{2+}$, $\text{CaNb}_2\text{O}_6:\text{Pr}^{3+}$, $(\text{Ca},\text{Sr})_2\text{Nb}_2\text{O}_7:\text{Pr}^{3+}$, $\text{Ca}_3\text{Nb}_2\text{O}_8:\text{Pr}^{3+}$, $\text{LiNbO}_3:\text{Pr}^{3+}$, $\text{NaNbO}_3:\text{Pr}^{3+}$, and $\text{Ca}_3\text{Ti}_2\text{O}_7:\text{Pr}^{3+}$ (Table 1) [7,82,86,89,90,92–103,106,112–114,124–130]. Optically recharging trap-controlled materials allows one to generate a constant peak intensity for a given energy of a mechanical stimulus, and to do so over many cycles of the perturbation. Moreover, while recharging of ML materials usually requires UV light, a smaller number of materials can be recharged using visible light, including $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ and $\text{NaNbO}_3:\text{Pr}^{3+}$. This property should prove useful for the development of ML devices to monitor stress in remote structures where the optical recharging of component ML materials is limited to daylight or a visible LED. The constancy of the ML intensity profile over multiple cycles of the mechanical stimulus suggests that the ML material is not damaged by the mechanical perturbation, i.e., the energy results in a non-destructive deformation (Fig. 19b and c). In summary, trap-controlled ML materials belong to a defect-controlled type of luminescent material that harbor optically rechargeable carrier traps. The reproducible ML of these materials proceeds in the following sequence of events: excitation of luminescent centers, capture of carriers by traps,

Fig. 18. ML response of $\text{Li}_{1.00}\text{NbO}_3:\text{Pr}^{3+}$ during five repetitions of the tensile strain test. The inset shows the ML response of $\text{Li}_{1.00}\text{NbO}_3:\text{Pr}^{3+}$ in the strain range from 0 to 300 μst . Reproduced with permission from Ref. [113], Copyright 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Fig. 19. ML responses of $\text{Ca}_2\text{Nb}_2\text{O}_7:\text{Pr}^{3+}$ composite coating under the cyclic compression test and UV irradiation: (a) ML decay behavior; (b) ML recovery behavior; (c) ML reproducibility. Reproduced with permission from Ref. [112], Copyright 2016, American Chemical Society.

mechanically-induced de-trapping of carriers, recombination and luminescence. The transitions associated with the ML process are associated with specific states of defined energy and proceed with defined quantum yield. In other words, the de-trapping process triggered by mechanical stimuli accounts for dynamic ML (Section 4.6), whereas the recharging of traps by light irradiation accounts for reproducible ML [112].

Recently, the Xu group developed a high-performance and sustainable ML in $\text{Sr}_3\text{Sn}_2\text{O}_7:\text{Sm}^{3+}$ by a trap-pinning design (Fig. 20) [241,242]. The oxygen-free sintering atmospheres of N_2 and Ar were used to prepare $\text{Sr}_3\text{Sn}_2\text{O}_7:\text{Sm}^{3+}$ with high-density deep pinning traps (Trap-2 as shown in Fig. 20a). Since these deep pinning traps (such as 9.04 eV for N_2 atmosphere) can firmly capture the excited carriers, the ML intensity is relatively stable over a delay time from 3 h to 50 h (Fig. 20b). This finding will reduce adverse effects of pre-UV-irradiation process on ML detection and to improve the quantitative analyses of stress sensing (Fig. 20c).

4.5.2. Self-reproducibility without light irradiation

Interestingly, some ML materials exhibit self-reproducibility, i.e., the de-trapped carriers are charged without optical excitation. Self-reproducible ML has been demonstrated in metal ions doped ZnS series, namely $\text{ZnS}:\text{Mn}^{2+}/\text{Cu}/\text{Cu}, \text{Mn}^{2+}/\text{Al}^{3+}, \text{Cu}/\text{Al}^{3+}, \text{Cu}, \text{Mn}^{2+}$ [7,15,104,105,134,148,178,210]. The ML responses of $\text{ZnS}:\text{Mn}^{2+}$ and $\text{ZnS}:\text{Cu}$ during multiple cycles of a mechanical stimulus are shown in Fig. 21 (Fig. 21a, b, d for $\text{ZnS}:\text{Mn}^{2+}$ and Fig. 21c for $\text{ZnS}:\text{Cu}$). The ML intensity of a $\text{ZnS}:\text{Mn}^{2+}$ film exposed to a

Fig. 20. Sustainable ML in trap-pinned $\text{Sr}_3\text{Sn}_2\text{O}_7:\text{Sm}^{3+}$. (a) ThL curves of $\text{Sr}_3\text{Sn}_2\text{O}_7:\text{Sm}^{3+}$ sintered in N_2 after different delay times. (b) ML responses of $\text{Sr}_3\text{Sn}_2\text{O}_7:\text{Sm}^{3+}$ sintered in N_2 after different delay times. The inset shows dependence of ML intensity on delay time (5 min to 50 h). (c) Potential applications based on the sustainable ML. Reproduced with permission from Refs. [241,242], Copyright 2018, American Chemical Society.

Fig. 21. Self-reproducible ML responses of metal ions doped ZnS films. (a) and (b) Stable ML of $\text{ZnS}:\text{Mn}^{2+}$ film exposed to a repeating mechanical friction and a repeating compression test, respectively. Reproduced with permission from Ref. [15], Copyright 1999, The American Institute of Physics. (c) ML durability test of $\text{ZnS}:\text{Cu}$ composite film under the periodic stretching test. The inset shows a logarithmic x-axis scale. Reproduced with permission from Ref. [178], Copyright 2013, The American Institute of Physics. (d) ML stability test of $\text{ZnS}:\text{Mn}^{2+}$ composite film under the cyclic compression test. Reproduced with permission from Ref. [148], Copyright 2015, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

frictional force fluctuates around a plateau value without loss of signal, and decays to zero once the stimulus is removed (Fig. 21a). The ZnS:Mn²⁺ film also shows evidence of self-reproducible ML during multiple cycles of compression – in this case, the two ML peaks (I and I') correspond to the onset and release of stress, respectively. Notably, the ML intensity shows multiple spikes during a single compression cycle – remarkably, even without further optical excitation, subsequent cycles of compression elicit similar intensity profiles (II and II') (Fig. 21b). In a second example, the ML intensity of a ZnS:Cu composite film during multiple cycles of a stretching test is relatively constant until 30,000 cycles, where after it slowly decreases linearly to at least 100,000 cycles (Fig. 21c). The slow attenuation of the ML signal may result from a gradual weakening of bonds between the polymer and embedded ML particles [178]. Interestingly, Wang et al. reported ZnS:Mn²⁺ composite films emitted a stable ML intensity over 10,000 cycles of a cyclical compression test (Fig. 21d) [148]. Thus, ZnS:Mn²⁺ and ZnS:Cu represent a novel class of ML materials that exhibit self-reproducible, robust and repeatable ML over many thousands of cycles of a mechanical stimulus. We believe that self-reproducible ML materials hold great promise as stress sensors in devices designed for remote monitoring of mechanical stress in light-limited environments.

The mechanism that underlies self-reproducible ML is poorly understood [7,15,104,105,134,148,178,210], in part because this property only exists in a handful of ML materials. Chandra et al. have suggested that the self-reproducible ML of ZnS:Cu and ZnS:Mn²⁺ semiconductors arises from the contribution of drift current on the trap-recharging due to the higher conductivity of semiconductors compared to dielectric materials [243]. While this explanation is certainly plausible, we note that many semiconductors do not show self-reproducible ML, including the metal doped CaZnOS series, ZnGa₂O₄:Mn²⁺, MgGa₂O₄:Mn²⁺ and ZnAl₂O₄:Mn²⁺ [84,85,102,221]. More confusingly, SrAl₂O₄:Eu²⁺, a dielectric material, exhibits post-irradiation-mediated reproducible ML [7], and self-reproducible ML after annealing between 80 and 300 °C [157,244,245]. Clearly, more research is needed to understand the mechanism of self-reproducible ML – this challenge will require the discovery of a greater number of semiconductor and dielectric materials that exhibit self-reproducible ML, and comparative multiscale quantitative analyses of their structures, and spectroscopic and mechano-optical properties.

4.6. ML responses to dynamic mechanical stimuli

The ML intensity of a trap-controlled ML material correlates dynamically to a change in the amplitude of the mechanical stimulus [97,123,145,236]. The light stimulus condition is an exception to this rule – this topic will be discussed in Section 4.9.3. Here, we limit our discussion to the ubiquitous response of ML materials to a mechanical load. We begin our discussion by considering case studies for the following materials: SrAl₂O₄:Eu²⁺, Dy³⁺, BaSi₂O₂N₂:Eu²⁺ and (Ba,Ca)TiO₃:Pr³⁺ (Fig. 22). First, let's review the three stages of an ML response (Fig. 22a–c): first, once the applied stress on an ML material exceeds a characteristic energy threshold, it triggers ML response. Second, the ML intensity increases linearly with increasing dynamic load at a fixed rate of deformation (i.e., strain/stress) (Fig. 17). Third, the ML intensity attenuates rapidly while maintaining a static load on the material. In some cases, however, the ML signal increases on releasing the static load (Fig. 22a and b). This dynamic ML behavior is understood in terms of the conservation of energy. For example, for the above materials, the input of mechanical energy triggers the de-trapping of carriers from traps to generate light energy. Thus the static load does not lead to a displacement along the direction of force, then the energy input must be zero and so no ML is emitted. In other words, the ML response depends on the work done by the mechanical force, rather than by the force itself. The work associated with the mechanical force that gives rise to ML may be ML may be short-lived (ms or s), or long-lived (days or months). These properties can be exploited to develop stress sensors that respond to mechanical stimuli in the target structure over a broad range of strain/stress rates (Section 7).

Fig. 22. Typical ML responses during applying dynamic and static loads. (a) SrAl₂O₄:Eu²⁺, Dy³⁺. Reproduced with permission from Ref. [123], Copyright 2002, Elsevier Science B.V. (b) BaSi₂O₂N₂:Eu²⁺. Reproduced with permission from Ref. [97], Copyright 2012, Acta Materialia Inc. (c) (Ba,Ca)TiO₃:Pr³⁺. Reproduced with permission from Ref. [145], Copyright 2011, Elsevier Ltd and Techna Group S.r.l.

4.7. Persistent luminescence

4.7.1. Traps for persistent luminescence and ML

ML materials may emit light in the form of mechanically-induced luminescence and persistent luminescence (or called long-lasting afterglow) (Table 1) [15,16,82,84–114,126–129,153–155]. It is widely accepted that persistent luminescence and ML arise from transitions from trap-controlled carriers. However, the nature of carrier traps and the transitions that lead to persistent luminescence and ML from meta-stable trap states in these materials are poorly understood. The duration of persistent luminescence depends on the material, and can occur over a timescale of seconds to hours. Ultimately, the rate of decay depends on the rate of the thermally-driven liberation of trapped carriers. On the other hand, the liberation of trapped carriers in the ML process, i.e., during the application of applied stress, is significantly faster. The typical depth of the trap levels associated with persistent luminescence has been estimated at 0.6–1 eV [153,154,181]. Far fewer spontaneous transitions occur for carriers in deeper traps, since the associated energy levels of these transitions far exceed the thermal energy at room temperature. On the other hand, the release of carriers from deep-seated traps can be triggered by exposing the material to a mechanical stimulus with an energy appropriate for trap-release. Consequently, the trap levels of a high-performance ML material should be deeper than those that give rise to persistent luminescence (Fig. 23) – this feature can help to reduce contributions to the observed “ML” signal from persistent luminescence. The Xu group presented evidence to support this hypothesis in a case study using $\text{CaSrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ – here swift heavy ion (SHI) irradiation was used to destroy shallow trap levels associated with persistent luminescence, while creating a population of deeper trap levels associated with ML [172]. Consistent with the proposed model (Fig. 23), the authors showed that the irradiated material emitted low levels of persistent luminescence, whereas the ML intensity of the same material increased by an order of magnitude [172]. This study suggests that one can improve the performance of an ML material by eliminating the pathways responsible for the persistent luminescence, i.e., the ideal ML material would harbor deeper trap levels associated with ML transitions than those responsible for persistent luminescence.

4.7.2. Effects of persistent luminescence and loading rates

While a clear relationship exists between the number of deep trap levels and ML intensity, we must accept the fact that ML materials harbor multiple trap levels that cover a broad range of energy. Consequently, it is difficult to identify which de-trapped carriers will give rise to persistent luminescence versus ML. Moreover, charge carriers in shallower traps are likely to undergo both thermally-driven and mechanically-driven de-trapping, in which case the emission contains contributions from persistent luminescence and ML. Accordingly, several groups have suggested that persistent luminescence and ML arise from transitions from the same types of trap levels [84,90,92,93,97,99,100,112,126,127,129,172,235,247]. As we have already indicated, the co-existence of persistent luminescence and ML in the detected emission of an ML material complicates any analysis of the ML response, and so new methods are required to resolve the two types of emission pathways, and to isolate the true “ML” signal from the “noise background” of persistent luminescence.

Yun et al. have studied the effects of persistent luminescence on the strain-induced ML of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ [246]. In this study, the authors compared the ML intensity profiles of the material at different rates of strain (0.1, 0.2, 0.3 and 0.4 mm s^{-1}). They also recorded the corresponding stress-free persistent luminescence signal at different delay times ($t' = 1, 2, 3$ and 4 min) after the photoexcitation pulse (Fig. 24). Analysis of the decay of the relative ML intensity $I_{\text{peak}}/I_{(t'=0)}$ of this study showed that the persistent luminescence dominated the emission during the first 2 min after the photoexcitation pulse, making it difficult to isolate the ML signal at lower strain rates ($< 0.3 \text{ mm s}^{-1}$). The contribution of the ML signal to the total signal increased when they applied the mechanical perturbation at longer delay times ($\geq 3 \text{ min}$). On the other hand, they could resolve the ML signal from the persistent luminescence signal at higher strain rates ($\geq 0.3 \text{ mm s}^{-1}$), even for short decay times ($\leq 2 \text{ min}$). Thus, the authors recommended that recordings of the ML of materials that also show persistent luminescence should begin sometime after the photoexcitation pulse, as

Fig. 23. Schematic model of afterglow (AG) relevant to shallow trap level and ML relevant to deep trap level, assuming electrons as the majority charge carriers.

Fig. 24. Effects of persistent luminescence and strain rate on ML (LI, light intensity) of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$. Reproduced with permission from Ref. [246], Copyright 2013, Optical Society of America.

this should deplete trap states associated with the afterglow. This condition is easily realized by first exposing the ML material to the optical excitation source, and then leaving the ML material in the dark for a delay (normally 1–10 min) before applying the mechanical perturbation [100,152,248]. Yun et al. have also employed a stress-optics transduction model to predict the contribution of the ML signal to the total recorded emission of the material. Here the ML and persistent luminescence signals are separated into three parts, namely the net ML, the stress-free luminescence and the stress-induced persistent luminescence [249]. Adoption of this predictive model could make efforts to design high-performance ML composite films, and to quantify the ML component of materials that emit both persistent luminescence and ML.

Recently, Zhang et al. proposed a novel strategy of sacrificing trap density to resolve the problem that ML materials universally require long delay to fade the noise of persistent luminescence (Fig. 25) [126,127]. Considering the depth overlap and defect homology of persistent luminescence and ML traps, Zhang et al. employed Sr substitution to decrease the total trap density of $\text{Ca}_2\text{Nb}_2\text{O}_7:\text{Pr}^{3+}$ that is a typical ML material showing persistent luminescence (Fig. 25a). Despite such substitution weakens both the persistent luminescence and ML in the material, the decrease ratio of ML is much less than that of persistent luminescence due to much faster detrapping rate of electrons under the stress stimulus (Fig. 25c and d). These results therefore provide a possibility to obtain short-delay and high-contrast ML images in the material with an optimal substitution (Fig. 25b).

4.8. Water resistance

Applications of ML to biology and translational medicine are limited by the hydrolysis of ML materials in water. For example, $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, the gold standard material for practical applications of ML, dissolves soon after contacting water [94,185]. The Xu group has developed methods to render $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ nanoparticles water-resistant, for example by modifying the nanoparticle surface with pyrophosphoric acid [185]. They showed that depositing a layer aluminum phosphate layer on $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ nanoparticles protected against the effects of water and humidity for at least one month. In other studies, $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ microparticles were protected from water by a coat of apolar polymers, including epoxy resin and PDMS. In this case, the ML properties of polymer-embedded $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ survived exposures to hot water (60 °C) for up to 1 week [157]. In another study, the Xu group showed that ML particles embedded in

Fig. 25. Sacrificing trap density to achieve short-delay and high-contrast ML by Sr substitution in $(\text{Ca}_{1-x}\text{Sr}_x)_2\text{Nb}_2\text{O}_7:\text{Pr}^{3+}$. (a) Tl curves. Inset shows two Gaussian components assigned to trap A and trap B, respectively ($x = 0$). (b) Evolution of ML images with increasing delay time. (c) Dependence of relative PersL (persistent luminescence, left) and ML intensities (right) on delay time. (d) Dependence of contrast on delay time. Reproduced with permission from Ref. [126], Copyright 2018, Acta Materialia Inc. Published by Elsevier Ltd.

polymer coatings and applied to the surface of a weather-exposed concrete grinder of an in-service bridge functioned as stress sensors for up to 6 months, and even longer (2 years) when the same composite was attached to concrete walls within a building [157].

Another approach to confer water-resistance to ML materials is to utilize the water-resistant characteristic of the doped material matrix itself, such as aluminosilicate $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ [94], titanate $(\text{Ba,Ca})\text{TiO}_3:\text{Pr}^{3+}$ [145], and nitroxide $\text{BaSi}_2\text{O}_7:\text{Eu}^{2+}$ [96]. Typically, the XRD patterns and PL and ML intensities of $(\text{Ba,Ca})\text{TiO}_3:\text{Pr}^{3+}$ microparticles are identical before and after immersion in water for 30 days (Fig. 26) [145]. A similar level of protection against water would be anticipated for the following silicate-based ML materials, $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Ce}^{3+}$, $(\text{Sr,M})\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ ($\text{M} = \text{Ca, Sr, Ba}$), and $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$. We note that the properties of water

Fig. 26. Water resistance of $(\text{Ba,Ca})\text{TiO}_3:\text{Pr}^{3+}$ micro-particles with various immersion times: (a) XRD patterns; (b) relative PL and ML intensities. Reproduced with permission from Ref. [145], Copyright 2011, Elsevier Ltd and Techna Group S.r.l.

resistance of the materials discussed above depend on the size of the ML particle. For example, (Ba,Ca)TiO₃:Pr³⁺ particles with a diameter on the order of microns are water resistant but nanoparticles with a diameter of 100 nm are generally unstable in water.

4.9. Other special properties

4.9.1. Lifetime-based measurement of ML signals

As we discussed in Section 4.4.1, practical applications of ML materials, including quantitative analysis of stress distributions in target structures, are enabled by the quantitative relationship between the ML intensity and the amplitude of the mechanical stimulus. In most studies, the ML signal is represented in terms of a relative intensity (Section 7). However, the ML intensity depends on several factors, including the concentration of ML particles in the composite material, the wavelength of the ML emission, the excitation power and duration of the excitation pulse, and properties of the mechanical stimulus. Moreover, the instruments and protocols used to record ML signals are likely to differ between laboratories, limiting quantitative comparisons of the ML response of existing and newly discovered materials to mechanical stimuli. These complications led Someya et al. to propose a new time-resolved approach to analyze ML signals [250,251]. The time constant of the decay of ML is independent of the concentration of the emitting species, the mechanical excitation power, and exposures to ambient light [250]. For example, Someta et al. found that the intensity decay of the ML signal recorded during a triangular mechanical loading scheme (such as Fig. 14d and 19a) was best fit using two lifetime values (τ_{up} and τ_{down}), corresponding to the rise and decay times of the ML signal of the composite material. The authors showed that the two lifetimes correlated linearly with the applied load (Fig. 27a), and inversely with the loading rate (Fig. 27b). As expected, the values of the two lifetimes were unaffected by the concentration of the ML particle and the mechanical excitation power (Fig. 27c and d). The authors employed this novel ML lifetime-based approach to study the dynamics of stress and strain during cyclic elastic deformations of ML materials [251]. While lifetime-based measurements of ML signals may offer several advantages over other ML intensity based approaches to quantify ML responses of materials, more investigations are required to demonstrate the validity of the lifetime approach to quantitative analysis of stress/strain in 2D images of target structures.

Fig. 27. Comparisons of lifetime-based load measurement and intensity-based load measurement of mechanical load. (a) Relation between the ML peak intensity (I_{max}) and the maximum load (N_{max}), the rise and decay time of ML (τ_{up} and τ_{down}); (b) Effects of the loading rate (dN/dt) on N_{max} and I_{max} , τ_{up} and τ_{down} ; (c) I_{max} , τ_{up} , and τ_{down} at various SrAl₂O₄:Eu²⁺ concentrations; (d) I_{max} , τ_{up} , and τ_{down} at different excitation power values. Reproduced with permission from Ref. [250], Copyright 2013, Optical Society of America.

4.9.2. Harmonic and hysteresis behaviors

Sohn et al. reported that $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ exhibits novel harmonic and hysteresis ML behaviors during the application of cyclical loads [252]. This behavior is evident from a fast Fourier transform (FFT) analysis of the ML data during cyclic mechanical loading. The authors identified two lower order harmonic terms (ML1 and ML2) from the FFT analysis, whereas the intensities of the higher order components were insignificant. The frequency of the sinusoidal ML1 component correlated precisely with the applied load, and was exactly half the frequency of the ML2 component (Fig. 28a). The second harmonic component was integral to the ML process, as the authors had discounted contributions from potential artifacts. Further analysis of the data revealed phase-shifts between the ML1 and ML2 components with respect to the applied load, with the phase-lag of ML2 being greater than that of ML1 (Fig. 28a). The authors suggested that the harmonic behavior was a consequence of the phase-lag between the application of the stress stimulus and the luminescent response of the ML sensor. They further postulated that the phase-lag resulted in a hysteresis loop between the ML and the load during the loading-deloding cycles (Fig. 28b). Since ferroelectrics (including piezoelectrics) exhibit a similar hysteresis behavior, Sohn et al. speculated that the ML hysteresis behavior of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ originated from a piezoelectric effect. They further speculated the additional (slight) loop that emerged close to the point of maximum load (Fig. 28b) originated from the ML2 component.

4.9.3. ML behavior under continuous light-excitation

In the conventional ML measurement approach, the ML emitted from a material during the application of a cyclical mechanical stimulus is recorded some time after the photo-excitation event. As we discussed earlier, the ML signal recorded using this condition is sensitive to properties of the cyclic loading (Fig. 19), dynamic loading (Fig. 22), the rate of loading (Fig. 24), and hysteresis (Fig. 28).

Kim et al. introduced a new ML measurement condition in which the ML material is exposed to UV irradiation during the entire dynamic or static loading process [253]. The ML intensity of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ recorded using this condition differs significantly from that measured using the periodic irradiation condition. For example, in the periodic irradiation condition the ML intensity of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ attenuates rapidly with each new cycle of the mechanical stimulus (Fig. 28a). On the other hand, the ML signal recorded using Kim's method is constant over the entire period of the cyclical stimulus (Fig. 29a) and from cycle to cycle (Fig. 29b). Kim et al. showed that this ML behavior only occurs above a threshold level of the UV-power density (right, Fig. 29c). Below this threshold power density, the steepness of the ML-load relationship depends on the loading condition (left, Fig. 29c). The authors also suggested that their condition can identify ML loss and hysteresis in the ML-load relationship [253]. In summary, the Kim's group has established a linear relationship exists between the ML intensity and the load for a variety of loading conditions when ML materials are exposed to continuous UV-excitation above the threshold power density, regardless of the loading rate and frequency (right, Fig. 29c). Significantly, their condition does not lead to a loss of ML intensity or hysteresis. The ML responses recorded during constant excitation could result from an optically-driven saturation of the traps in the ML material at all stages of mechanical loading, i.e., even though the applied load leads to de-trapping and the depletion of traps, the intense excitation of the material recharges these states before the end of each cycle. Accordingly, one could speculate that the loss of ML and hysteresis observed using the periodic irradiation condition (Fig. 28c and d) is linked to the presence of unfilled traps in the ML material, i.e., the de-trapped carriers are re-trapped by the unfilled traps, rather than by transitioning to a state that decays with the emission of light. Kim's group has applied the continuous excitation condition to study ML systems including one that led to the development of a new class of ML torque sensor (Section 7.1) [179,254]. Notably, ML studies using the continuous excitation condition have been limited to $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ (Sections 4.9.2 and 4.9.3). Investigations of the ML behavior of other ML materials using Kim's condition are greatly anticipated, as they may uncover new ML phenomena and increase our understanding on trap-controlled ML. Additionally, we note that practical applications of this method will require boosting the low intensity and low signal-to-noise ratio of the ML (Fig. 29a and b).

Fig. 28. Harmonic and hysteresis behaviors of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$. (a) Phase shift of ML1 and ML2 deconvoluted components (1 Hz); (b) Hysteresis curves of ML under the loading-deloding cycles (1, 3, and 5 Hz). Reproduced with permission from Ref. [252], Copyright 2014, Optical Society of America.

Fig. 29. (a) and (b) ML behavior of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ under continuous high-energy UV irradiation: (a) during a cyclic loading (at a frequency of 1 Hz); (b) during a step loading (up to 750 N). (c) Schematic illustration of the characteristic ML behaviors below and above the threshold power density of UV irradiation. Reproduced with permission from Ref. [253], Copyright 2015, Optical Society of America.

5. Mechanisms of trap-controlled ML

As we discussed earlier, trap-controlled ML materials contain long-lived trap states. These captured carriers (electrons and/or holes) are de-trapped during exposures to mechanical stimuli, after which they may participate in the luminescent process. In the following sections, we focus our discussion on the mechanisms of carrier de-trapping in piezoelectric and non-piezoelectric ML materials.

5.1. Piezoelectricity-induced ML

Of the known 32 crystal classes, 20 exhibit direct piezoelectricity, a property of their non-centrosymmetric structures. Non-centrosymmetric point groups include 1; 2; m; 222; mm2; 4; $\bar{4}$; 422; 4 mm; $\bar{4}2m$; 3; 32; 3 m; 6; $\bar{6}$; 622; 6 mm; $\bar{6}2m$; 23; $\bar{4}3m$ – therefore most of the ML materials listed in Table 1 are piezoelectric. The stress-induced piezoelectric field associated with the piezoelectric effect is believed to de-trap carriers in the ML process. For example, investigations by the Xu group on Eu^{2+} -doped strontium aluminates, including pure-phase α - SrAl_2O_4 , β - SrAl_2O_4 , SrAl_4O_7 , $\text{SrAl}_{12}\text{O}_{19}$, $\text{Sr}_3\text{Al}_2\text{O}_6$ and $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$, as well as their mixed phases, showed that α - SrAl_2O_4 is the only material that emits ML, i.e., it is the only non-centrosymmetric structure. Consistent with this interpretation, the other non-ML materials in this study have centrosymmetric or high-symmetric structures [83,255]. In comparing the relationships between crystal structures and ML for 40 different materials, Chandra et al. concluded that most ML materials have a non-centrosymmetric structure [256]. Interestingly, ML does exist in some centrosymmetric structures, including $\text{ZrO}_2:\text{Ti}^{4+}$, $\text{Sr}_2\text{SnO}_4:\text{Sm}^{3+}$, $\text{CaNb}_2\text{O}_6:\text{Pr}^{3+}$, $\text{Ca}_3\text{Nb}_2\text{O}_8:\text{Pr}^{3+}$, and $\text{BaZnOS}:\text{Mn}^{2+}$ [86,101,110,112]. The ML of these materials may result from indirect piezoelectricity, which would arise from structural changes near defects, and impurities that are introduced during the synthesis or by ion-doping [101,112,256,257]. Next, we will consider two models to explain interactions between the piezoelectric field and trapped carriers, namely piezoelectricity-induced electroluminescence (EL), and piezoelectricity-induced carrier de-trapping.

5.1.1. Piezoelectricity-induced electroluminescence model

We begin our discussion on the mechanism of ML by considering physical properties that are induced by interactions within the mechano-electro-optical triangle, and their relationship to the piezoelectric effect, electroluminescence and mechanoluminescence

(Fig. 30). Intriguingly, certain ML materials exhibit all three properties highlighted in the triangle, and include the piezoelectric-type ML materials $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ [258], $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ [194], $\text{CaYAl}_3\text{O}_7:\text{Ce}^{3+}$ [99], $(\text{Ba,Ca})\text{TiO}_3:\text{Pr}^{3+}$ [89,259], $\text{BaSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ [96,97], $\text{SrMg}_2(\text{PO}_4)_2:\text{Eu}^{2+}$ [100], $\text{ZnS}:\text{Mn}^{2+}$ [15], $\text{ZnS}:\text{Cu}/\text{Cu},\text{Mn}^{2+}$ [104], and $\text{ZnS}:\text{Al}^{3+},\text{Cu}/\text{Al}^{3+},\text{Cu},\text{Mn}^{2+}$ [105]. Detailed analyses of the ML properties of these materials, especially with respect to piezoelectricity-induced EL, could lead to a better understanding of ML. To this end, we consider the ML material $(\text{Ba,Ca})\text{TiO}_3:\text{Pr}^{3+}$ as a proto-typical member of this class of material. In the following section, we summarize experimental studies on the ML of $(\text{Ba,Ca})\text{TiO}_3:\text{Pr}^{3+}$ with the view of gaining a better understanding of the mechanisms underlying the triangular relationships between the piezoelectric effect, EL and ML [143,145,259].

$\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3:\text{Pr}^{3+}$ is diphasic over the range of $0.25 < x < 0.90$, i.e., this material harbors a Ba-rich piezoelectric phase and a Ca-rich phosphor phase, while pure-phase solid solutions exist for $x \leq 0.23$ and $x > 0.90$ [143]. The EL intensity and the ML intensity of $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3:\text{Pr}^{3+}$ exhibit similar dependencies on the Ca composition (Fig. 31), which might indicate that the EL and ML properties of this material share a common origin. Moreover, strong ML and EL signals are only found close to the solubility limit and in the diphasic region. The ML and EL emission spectra of $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3:\text{Pr}^{3+}$ are essentially coincident, sharing a common emission peak that arises from the $^1\text{D}_2\text{-}^3\text{H}_4$ transition of Pr^{3+} in phosphor phase. The ML of $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3:\text{Pr}^{3+}$ may originate from a piezoelectric-field excited EL according to the compact piezoelectric/phosphor/piezoelectric sandwich structure of sub-micron diphasic grains [143]. To test this hypothesis, Wang et al. calculated the value of the piezoelectric field in $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3:\text{Pr}^{3+}$ at peak stress (where the applied force = 1000 N; the contact area = $0.59 \times 10^{-4} \text{ m}^2$; the piezoelectric constant of the piezoelectric = $2 \times 10^{-10} \text{ C N}^{-1}$ and the dielectric constant of the phosphor = 8.85). These authors calculated a piezoelectric field strength of $2 \times 10^4 \text{ V cm}^{-1}$, which is much higher than the experimentally determined EL thresholds, i.e., 1.64×10^4 , 1.50×10^4 , 1.36×10^4 and $1.20 \times 10^4 \text{ V cm}^{-1}$ for $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3:\text{Pr}^{3+}$ ($x = 0.3, 0.5, 0.6$ and 0.7), respectively. Thus, the applied stress on the material generates a piezoelectric field that is sufficiently large to induce EL. Moreover, this piezoelectricity-induced EL model may help to explain the ML mechanism of $(\text{Ba,Ca})\text{TiO}_3:\text{Pr}^{3+}$. In particular, the strong piezoelectric field induced by the external stress in the ML material leads to the de-trapping, and acceleration of electrons, which impact-excite luminescent centers to emit light [143]. We note here that the pure piezoelectric phase or phosphor phase emits low levels of ML, and so the strong ML of this material should arise from the piezoelectric/phosphor/piezoelectric sandwich structure in the diphasic region. If substantiated, the implementation of this mechanism could lead to the rational design of high-performance ML materials. Materials that exhibit both EL and ML share other similarities, including a similar dependence of luminescent intensity on Sr composition in the case of $(\text{Ca,Sr})\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ [194], and similar color shifts in $\text{ZnS}:\text{Mn}^{2+}$, i.e., in studies where one varies the stress rate and the frequency of the electric field [104,134]. Related mechanism-driven studies on $\text{ZnS}:\text{Mn}^{2+}$ [15], $(\text{Ca,Sr})\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ [94,194], $\text{CaYAl}_3\text{O}_7:\text{Ce}^{3+}$ [99], and $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ [258], suggest that their ML originates from a piezoelectric field-induced EL. Interestingly, all of the compounds listed above exist as single-phase materials, and so each particle in a single-phase material can act simultaneously as a piezoelectric and as a phosphor.

5.1.2. Piezoelectricity-induced carrier de-trapping model

The piezoelectricity-induced EL model however, cannot explain the emission of ML from materials during exposures to weak mechanical stress. A case in point here is the strong ML observed during gentle scratching or pressing of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ – the piezoelectric field induced by such a weak stress is insufficient to accelerate electrons to impact-excite luminescent centers. This observation led to the development of the piezoelectricity-induced carrier de-trapping model [7,16,143,152,126–129]. A schematic of a generic dynamic ML model for this system is shown Fig. 32 – this model does not consider specific types of carriers, traps and luminescent centers (Section 2.2). Exposing the material to excitation light produces charge carriers that are captured by traps in the material (Fig. 32a). Next, exposure of the optically-excited material to a low amplitude stress produces a local piezoelectric field that leads to de-trapping and subsequent recombination of carriers in luminescent centers, and ultimately light emission (Fig. 32b).

The piezoelectricity-induced carrier de-trapping model has been optimized to account for the ML of materials that harbor multiple traps with different activation energies (Section 4.7). A thermoluminescence (ThL) study of $\text{CaZr}(\text{PO}_4)_2:\text{Eu}^{2+}$ (Fig. 33a) suggested that at least four types of traps contribute to the ML, including $[\text{Eu}_{\text{Ca}}]^{+}$ or oxygen vacancies V_{O} (Section 2.2) [103]. The Hoogenstraaten method [260] allows one to estimate of the activation energy in each of the traps identified in the peaks 1–4 of $\text{CaZr}(\text{PO}_4)_2:\text{Eu}^{2+}$ (Fig. 33a), i.e., 0.687, 0.829, 1.171 and 1.873 eV, respectively. Following UV irradiation, some of the excited electrons in the conduction band of Eu^{2+} are captured by the shallower traps. Moreover, some of these trapped electrons will migrate to other traps, driven by thermal energy, to generate a broad distribution of trapped states. In some cases, one can expect a continuum of trap levels whose populations are equilibrated by the thermal energy. As we discussed earlier, mechanical stimulation generates a stress-

Fig. 30. Mechano-electro-optical triangle interactions and related effects. Adapted with permission from Ref. [89], Copyright 2005, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Fig. 31. Dependence of EL intensity and ML intensity on the Ca composition of $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3:\text{Pr}^{3+}$. Insets: EL and ML spectra of $\text{Ba}_{0.4}\text{Ca}_{0.6}\text{TiO}_3:\text{Pr}^{3+}$ (left); BSEM image and EDS line-scan spectrum of $\text{Ba}_{0.4}\text{Ca}_{0.6}\text{TiO}_3:\text{Pr}^{3+}$ (middle); schematic illustration on ML mechanism of diphase $(\text{Ba,Ca})\text{TiO}_3:\text{Pr}^{3+}$ with a sandwich structure (right). Adapted with permission from Ref. [143], Copyright 2010, The Electrochemical Society.

Fig. 32. Schematic diagram of ML mechanism of piezoelectricity-induced carrier de-trapping.

induced piezoelectric field that de-traps the captured electrons, where after they enter the conduction band (Fig. 33b). Electrons within shallow traps should de-trap to the conduction band during exposures to weak piezoelectric fields. De-trapping electrons from deeper traps on the other hand would require stronger piezoelectric fields, where they may transition first to adjacent shallower traps before entering the conduction band. Finally, the recombination of electrons that enter the conduction band with luminescent centers will lead to the emission of light. ML materials harboring trap states over a wide range of energy (from shallow to deep) should be sensitive to mechanical stimuli over a broad range of energy [103], a feature that could drive the development of multiscale ML stress sensors (Section 6.1).

The piezoelectricity-induced carrier de-trapping model can account for the ML properties of a broad range of materials, including $\text{Ca}_2\text{Al}_2\text{SiO}_7:\text{Ce}^{3+}$ [82], $(\text{Sr,M})\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) [90,95], $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ [92], $\text{BaSi}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ [97], $\text{SrMg}_2(\text{PO}_4)_2:\text{Eu}^{2+}$ [100], $\text{CaZnOS}:\text{Mn}^{2+}$ [102], $\text{CaZr}(\text{PO}_4)_2:\text{Eu}^{2+}$ [103], $(\text{Ba,Ca})\text{TiO}_3:\text{Pr}^{3+}$ [143], $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ [152], and $\text{ZnS}:\text{Mn}^{2+}$ [87]. This model can also account for the identical ML spectra and PL spectra of most ML materials (Section 4.2). Finally, the model rationalizes the indirect transfer of carriers between traps and luminescent centers, i.e., via conduction band or charge transfer state [Figs. 12d, 23, 32 and 33b] [15,16,82,97,100–103,143,178].

Fig. 33. Multiple trap levels and ML in $\text{CaZr(PO}_4)_2\text{:Eu}^{2+}$: (a) ThL curve; (b) schematic illustration of ML process. Adapted with permission from Ref. [103], Copyright 2013, Optical Society of America.

Interestingly, Zhang et al. have reported that significant differences exist between the ML and PL spectra of calcium niobates (Fig. 34) [112]. In particular, they showed that the prominent blue and green peaks of the PL spectra of $\text{CaNb}_2\text{O}_6\text{:Pr}^{3+}$, $\text{Ca}_2\text{Nb}_2\text{O}_7\text{:Pr}^{3+}$ and $\text{Ca}_3\text{Nb}_2\text{O}_8\text{:Pr}^{3+}$ are lost in the corresponding ML spectra. They attributed this phenomenon to a tunneling pathway that provides a direct relaxation pathway of electrons from a deep energy trap to a low-excited state level of an adjacent luminescent center. On exposure to a high piezoelectric field, this transfer mechanism promotes a small population of electrons to the conduction band [112]. The piezoelectricity-induced carrier de-trapping model predicts that carriers may transfer to traps and luminescent centers via two different pathways, namely an indirect pathway that proceeds via the conduction band and a charge transfer state, or else by direct tunneling.

5.1.3. Material exploitation based on piezoelectricity and carrier traps

The roles of carrier traps in “storing” energy in ML materials, and in generating mechanically-induced piezoelectric fields were discussed in Sections 5.1.1 and 5.1.2. Essentially, the release of stored energy in the carrier traps leads to light emission. Some of the best-performing ML materials are piezoelectric and harbor carrier traps, including ZnS:Mn^{2+} and $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$ – these materials are prepared by incorporating luminescent ions into a piezoelectric material [15,16,173,255]. Zhang et al. prepared novel ML materials using this synthetic approach (Fig. 35), namely $\text{Ca}_2\text{Nb}_2\text{O}_7\text{:Pr}^{3+}$ [112], $\text{Sr}_2\text{Nb}_2\text{O}_7\text{:Pr}^{3+}$ [126,127], and $\text{NaNbO}_3\text{:Pr}^{3+}$ [129,130]. The ML of these materials results from complex interactions between the doped activator and the piezoelectric host. These complexities, which include site tolerance and luminescence quenching, should be anticipated and optimized for specific dopants and hosts. The second strategy to prepare high performance ML materials involves screening families of persistent phosphors that harbor traps and exhibit piezoelectricity. Adoption of this strategy led to the discovery of $\text{Ca}_2\text{Al}_2\text{SiO}_7\text{:Ce}^{3+}$ [82], $\text{CaAl}_2\text{Si}_2\text{O}_8\text{:Eu}^{2+}$ [94], $\text{M}_2\text{MgSi}_2\text{O}_7\text{:Eu}^{2+}$ ($\text{M} = \text{Ca, Sr}$) [90,92], $\text{BaSi}_2\text{O}_2\text{N}_2\text{:Eu}^{2+}$ [96,97], and $\text{Sr}_3\text{Sn}_2\text{O}_7\text{:Sm}^{3+}$ [101]. As we discussed in Section 4.7, these materials emit both ML and persistent luminescence, and so one could employ appropriate methods to isolate the ML signal temporally from the total emission (Section 4.7), or improve the signal/noise ratio of ML by increasing the intensity of the ML component of the total emission (Section 6.1).

Piezoelectricity, as it relates to ML, may arise directly from the non-centrosymmetric crystal structure of host materials, or indirectly from a change in the local crystal structure near a defect or impurity [83,97,101,102,112,150,186,194,207,255–257,261–263]. Relationships between specific structural properties of the material and the differentiated piezoelectricity that generate ML are unknown. Certain materials, for example $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$, $\text{BaSi}_2\text{O}_2\text{N}_2\text{:Eu}^{2+}$, CaZnOS:Mn^{2+} , $\text{Ca}_2\text{Nb}_2\text{O}_7\text{:Pr}^{3+}$ and $\text{NaNbO}_3\text{:Pr}^{3+}$ emit light in response to a variety of mechanical stimuli (deformation and friction) (Section 4.3). Typically, the recorded ML images of the composite disks embedded with these materials during compression show a fusiform distribution of light intensity (Figs. 11c and 13d). While current approaches to prepare new ML materials are quite successful (Section 5.1), they could be improved by integrating new principles and concepts that would arise from deeper understanding of ML phenomena. To reach this goal, we need to establish productive collaborations between theoreticians and experimentalists to understand how structural characteristics modulate the piezoelectric properties of doped materials and the efficiency of ML of activators.

5.2. Triboelectricity-induced ML

Centrosymmetric semiconductors including $\text{ZnGa}_2\text{O}_4\text{:Mn}^{2+}$, $\text{MgGa}_2\text{O}_4\text{:Mn}^{2+}$ and $\text{ZnAl}_2\text{O}_4\text{:Mn}^{2+}$ (space group $Fd\bar{3}m$) are not piezoelectric, and consequently they do not emit ML during deformation. However, these materials generate an intense triboluminescence during contact-friction [84,85,221,264], a finding that led the Xu group to study the mechanism of this interesting ML behavior. The authors showed that the contact voltage generated on rubbing a $\text{ZnAl}_2\text{O}_4\text{:Mn}^{2+}$ composite with a frictional rod depended on the material composition of the rod. Moreover, they found that the ML intensity depended on the contact (surface) voltage (Fig. 36a and b), which led to them to conclude that the triboluminescence of $\text{ZnAl}_2\text{O}_4\text{:Mn}^{2+}$ arises from triboelectricity.

Fig. 34. (a)–(c) Spectral discrepancy between PL and ML of CaNb₂O₆:Pr³⁺, Ca₂Nb₂O₇:Pr³⁺, and Ca₃Nb₂O₈:Pr³⁺, respectively. (d) Schematic diagram of the tunneling pathway in ML process. Reproduced with permission from Ref. [112], Copyright 2016, American Chemical Society.

Since ZnAl₂O₄:Mn²⁺ is a highly efficient EL material, they further proposed that the triboluminescence occurs via triboelectricity-induced EL (Fig. 36c) [221]. In other words, it was argued that the captured electrons in ZnAl₂O₄:Mn²⁺ were de-trapped and accelerated to impact-excite the luminescent centers by a triboelectricity-induced electric field (Section 5.1.1). We note however, there is no experimental evidence to support the occurrence of EL under a triboelectric field. Therefore, the triboelectricity-induced carrier de-trapping model may also explain the triboluminescence of ZnAl₂O₄:Mn²⁺, ZnGa₂O₄:Mn²⁺ and MgGa₂O₄:Mn²⁺ [Section 5.1.2] [84,85]. To summarize, the mechanisms of piezoelectric- and triboelectric-mediated luminescence are very similar – in fact, one can use the schematic diagrams shown in Figs. 29 and 30, to explain both the piezoelectricity and triboelectricity-induced carrier de-trapping models, i.e., simply by switching the words “piezoelectric field” and “triboelectric field”.

Fig. 35. Schematic illustration of a design strategy to create ML in piezoelectrics based on doping luminescent centers. Reproduced with permission from Ref. [112], Copyright 2016, American Chemical Society.

6. Performance optimization

6.1. Enhancement of ML intensity

Elastomeric polymers embedded with ML particles have been compared to mechano-optically sensitive skin. The ML intensity of a 2D composite film firmly attached to the surface of a target structure contains information on the distribution of stress in the target structure. While offering advantages over conventional stress sensing devices, the low ML intensity of composite materials could undermine their potential to monitor the structural health of buildings and bridges during daylight hours. To date, efforts to increase the intensity of ML of materials have focused on the crystal structures and trap levels of the ML material, for example by optimizing protocols to synthesize ML particles and coatings [17,19,137,150,152,164,166,208,240,265–275] that include adjusting the composition deficiency (Section 2.2) [142,150,151,173], exposing the material to SHI irradiation (Section 4.7.1) [247], by substituting host ions in the crystal [94,95,194,265–267] and co-doping crystals with rare earth or transition metal ions [87,88,91,92,123,231,248,249,268–270,273–275].

6.1.1. Substitution of host ions

The ML of $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ is significantly enhanced by partially substituting Sr^{2+} for Ca^{2+} (to 40 mol%) (Fig. 37) [194]. This enhancement arises from a change in crystal symmetry. The crystal structures of $\text{CaAl}_2\text{Si}_2\text{O}_8$ and $\text{SrAl}_2\text{Si}_2\text{O}_8$ share a similar framework although they have different symmetries, i.e., $\text{CaAl}_2\text{Si}_2\text{O}_8$ has a lower symmetry (triclinic, space group $P1$) compared to $\text{SrAl}_2\text{Si}_2\text{O}_8$ (monoclinic, space group $I2/c$) (Fig. 37b). A lower symmetry is known to favor ML – for example, the ML of $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ ($x = 0$) is stronger than that of $\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ ($x = 1$) (Fig. 37a). The substitution of Sr^{2+} for Ca^{2+} at 40 mol% in $\text{CaAl}_2\text{Si}_2\text{O}_8$ changes the cell edge (b and c) and cell volume, and increases atomic disorder in the crystal lattice (Fig. 37c). We have argued that these distortions increase piezoelectricity in the crystal and thereby increase ML [194]. The substitution of host ions in the crystal can also increase the intensity of ML, in part by creating additional traps at energy levels associated with ML in the crystal. ML materials of this class include $(\text{Ba,Ca})\text{TiO}_3:\text{Pr}^{3+}$ [143], $(\text{Sr,M})\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ ($\text{M} = \text{Ba, Sr, Ca}$) [95,265], $\text{CaZnOS}:\text{Mn}^{2+}, \text{Li}^+$ [274], $(\text{Sr,Ca,Ba})_2\text{SnO}_4:\text{Sm}^{3+}, \text{La}^{3+}$ [266] and $\text{Sr}_3(\text{Sn,Si/Ge})_2\text{O}_7:\text{Sm}^{3+}$ [267].

6.1.2. Ion co-doping

One can increase the ML intensity of a material by co-doping the host crystal with rare earth (RE) or transition metal ions. Examples of co-doped ML materials include $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}(\text{Dy}^{3+}/\text{Dy}^{3+}, \text{Nd}^{3+})$ [123,231,268], $\text{ZnS}:\text{Mn}^{2+}(\text{Te}^{2+})$ [87,88], $\text{SrAl}_2\text{O}_4:\text{Ce}^{3+}(\text{Ho}^{3+})$ [91], $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}(\text{Dy}^{3+})$ [92], $(\text{Ba,Ca})\text{TiO}_3:\text{Pr}^{3+}(\text{RE}^{3+})$ ($\text{RE}^{3+} = \text{Y}^{3+}, \text{La}^{3+}, \text{Nd}^{3+}, \text{Gd}^{3+}, \text{Yb}^{3+}, \text{Lu}^{3+}$) [248,269], $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}(\text{Ho}^{3+})$ [270], $(\text{Sr,Ca,Ba})_2\text{SnO}_4:\text{Sm}^{3+}(\text{La}^{3+})$ [266], $\text{Ba}_2\text{Zr}_2\text{Si}_3\text{O}_{12}:\text{Eu}^{2+}(\text{Dy}^{3+})$ [128] and $\text{LiNbO}_3:\text{Pr}^{3+}(\text{Gd}^{3+})$ [275]. Co-doping increases the ML intensity by increasing the number of traps in these materials [87,88,91,92,248,267,269,270,275]. Co-doping strategies to increase the ML of a material depend critically on the co-dopants. The most successful strategy has been to empirically use Eu^{2+} as activators and Dy^{3+} as co-dopants [153]. For example, Dy^{3+} co-dopants

Fig. 36. (a) and (b) Dependences of ML intensity and surface voltage on different materials of friction rods. (c) Schematic depiction on ML mechanism of $\text{ZnAl}_2\text{O}_4:\text{Mn}^{2+}$ via triboelectricity-induced EL model. Reproduced with permission from Ref. [221], Copyright 2004, The American Physical Society.

Fig. 37. ML improvement induced by the change of crystal symmetry. (a) Dependence of ML intensity on the composition of $\text{Ca}_{1-x}\text{Sr}_x\text{Al}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$. (b) Crystal structures of $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$ and $\text{SrAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}$. (c) Dependence of cell parameters on composition. Adapted with permission from Ref. [194], Copyright 2010, The Electrochemical Society.

in $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ enhance the ML intensity by almost two orders of magnitude (Fig. 38a). Materials co-doped with Dy^{3+} exhibit a new high-intensity low-temperature ThL peak – this finding suggests that co-doping increases the intensity of ML for example in $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+},\text{Dy}^{3+}$ by creating a high-density of shallow depth traps (Fig. 38b,c).

Effective co-dopants can also be paired by screening libraries of materials that are co-doped with specific ions. Exhaustive screens of this type have identified the following ML materials: $\text{CaAl}_2\text{Si}_2\text{O}_8:\text{Eu}^{2+}(\text{RE})$, where $\text{RE} = \text{La}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}$ [270] and $(\text{Ba},\text{Ca})\text{TiO}_3:\text{Pr}^{3+}(\text{RE})$, where $\text{RE} = \text{Y}, \text{La}, \text{Ce}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{Yb}, \text{Lu}$ [248]. Here, we summarize findings of a study conducted by Zhang et al. who explored the effects of co-dopants on the ML of $(\text{Ba},\text{Ca})\text{TiO}_3:\text{Pr}^{3+}(\text{RE})$ [248]. Using RE_2O_3 as the raw material, the authors synthesized $(\text{Ba},\text{Ca})\text{TiO}_3:\text{Pr}^{3+}(\text{RE})$ using solid-state reaction in air. According to the reduction potential, the RE ion may oxidize to RE^{4+} or else co-exist as a mixture of RE^{3+} and RE^{4+} – for example, $\text{Ce}-\text{Ce}^{4+}$, $\text{Tb}-\text{Tb}^{3+}/\text{Tb}^{4+}$, and $\text{Dy}-\text{Dy}^{3+}/\text{Dy}^{4+}$. The ML intensity of the co-doped material depends on the type of doped RE ions, with Y^{3+} , La^{3+} , Nd^{3+} , Gd^{3+} , Yb^{3+} and Lu^{3+} exhibiting markedly improved ML intensity (Fig. 39a). The intensity of PL in these co-doped ML materials is reduced, which would indicate that the RE ions introduce new traps that capture carriers, or else behave as non-radiative centers (Fig. 39b). A ThL

Fig. 38. Enhanced ML arising from the generation of new traps. (a) ML responses and (b) ThL curves of $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ (CMSE) and $\text{Ca}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}(\text{Dy}^{3+})$ (CMSED). Reproduced with permission from Ref. [92], Copyright 2007, The Electrochemical Society.

analysis of the trap properties showed that co-doping with effective RE ions significantly increased the concentration of traps in the material (Fig. 39d) but hardly changed the trap depth (Fig. 39c) – the only exception to this trend was in self-quenching Ce^{4+} co-doped materials. This study suggests that increasing the concentration of traps of suitable depth in a material can significantly improve the efficiency of ML (Fig. 39d).

6.2. Regulation of ML color

ML materials have been integrated into touch-sensitive light sources and displays. However, these ML materials generate low levels of light with a limited range of color output that undermine their commercial potential. Strategies to enhance the intensity output of ML materials were discussed earlier, and so here we focus the discussion on strategies to regulate the color of ML emission. The simplest method to control the color of the ML is to mix different types of phosphors in a composite material. Other approaches include manipulating the composition and structure of the phosphor, for example by doping the phosphor with different luminescent ions [15,16,91,93,99,102,104,105,107,108,111,134,125,131], by substituting host ions in the crystal [95,194,276], by integrating energy transfer centers to red-shift the emission [15,16,20,88,104,134], by manipulating the concentration effect of luminescent centers [149], and finally by adjusting the stress condition [15,88,104,105,110,134]. Next, we survey methods identified above to regulate ML color (Fig. 40) – methods based on mixing different ML phosphors will be discussed in Section 7.6.1.

6.2.1. Doping with different luminescent ions

Materials doped with different luminescent ions emit distinct ML colors, from the UV to the NIR, for example, ZnS:Mn^{2+} (yellow) [15] vs. ZnS:Cu (blue, green, orange) [134], $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ (green) [16] vs. $\text{SrAl}_2\text{O}_4:\text{Ce}^{3+}$ (UV) [91], $\text{CaYAl}_3\text{O}_7:\text{Eu}^{2+}$ (blue) [93] vs. $\text{CaYAl}_3\text{O}_7:\text{Ce}^{3+}$ (deep blue) [99], and CaZnOS:Mn^{2+} (red) [102] vs. CaZnOS:Cu (cyan) [107] vs. $\text{CaZnOS:Tb}^{3+}/\text{Eu}^{3+}/\text{Pr}^{3+}/\text{Sm}^{3+}/\text{Er}^{3+}/\text{Dy}^{3+}/\text{Ho}^{3+}/\text{Nd}^{3+}/\text{Tm}^{3+}/\text{Yb}^{3+}$ (from violet to NIR) [108,111,125,131].

6.2.2. Energy transfer

Light emitted by an ML material can be red-shifted via energy transfer from a sensitizer (donor) to an activator, where the sensitizer absorbs photons at short wavelengths and the activator emits photons at longer wavelengths [277,278]. Examples of energy

Fig. 39. Effects of rare earth ion co-doping on (a) ML intensity, (b) PL intensity, (c) trap depth, and (d) ThL intensity of $(\text{Ba,Ca})\text{TiO}_3:\text{Pr}^{3+}(\text{RE})$ (RE = Y, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). Adapted with permission from Ref. [248], Copyright 2014, The Royal Society of Chemistry.

Fig. 40. Schematic illustration of technologies of ML color manipulation in an individual material.

transfer include ZnS:Mn²⁺ (yellow) [15] vs. ZnS:Mn²⁺,Te²⁺ (red) [88], ZnS:Cu (blue, green, orange) [134] vs. ZnS:Cu,Mn²⁺ (orange) [104], and SrAl₂O₄:Eu²⁺ (green) [16] vs. SrAl₂O₄:Eu²⁺,Er³⁺ (NIR) [20] vs. SrAl₂O₄:Eu²⁺,Nd³⁺ (NIR) [124].

6.2.3. Substitution of host ions

The substitution of a host ion in an ML material changes the strength of crystal field around the luminescent centers, thereby shifting the color of the ML emission. For example, the peak wavelengths of ML of the Ba²⁺-, Sr²⁺- and Ca²⁺-substituted hosts, i.e., SrBaMgSi₂O₇:Eu²⁺, Sr₂MgSi₂O₇:Eu²⁺ and SrCaMgSi₂O₇:Eu²⁺, are red-shifted from 440 to 499 nm (Fig. 41) [95]. The emission of these ML materials originates from the 5d-4f transition of Eu²⁺, which is susceptible to the strength of the crystal field (Section 4.2.1). Different crystal field strengths around the Eu²⁺ ion may result in diverse splitting of the 5d state – electronic transitions from the degenerated 5d state will thereby give rise to multiple emission bands that collectively broaden the emission band, and change the color compared to the unsubstituted material. In the previous examples, ion substitution in (Sr,M)MgSi₂O₇:Eu²⁺ (where M = Ba, Sr and Ca) leads to lattice shrinking, and the creation of a stronger crystal field around Eu²⁺ – the magnitude of this field increases according to the radius of the ion, i.e., Ba²⁺ > Sr²⁺ > Ca²⁺. The energy of the 5d-4f transition of Eu²⁺ decreases at high strengths of the crystal field and results in the observed red-shifted emission [95,276]. A similar explanation has been proposed to account for an opposite blue-shift (from 428 to 403 nm) of partially substituted CaAl₂Si₂O₈:Eu²⁺ (Sr²⁺ partially substituted for Ca²⁺) [194].

6.2.4. Adjusting stress conditions

The color of the ML emitted by ZnS is sensitive to the nature of the doped transition metal ions (Section 6.2.1) and to the presence of energy transfer sensitizers (Section 6.2.2). Examples of doped and co-doped ZnS materials include ZnS:Mn²⁺ (yellow) [15], ZnS:Cu (blue, green, orange) [134], ZnS:Mn²⁺,Te²⁺ (red) [88], ZnS:Cu,Mn²⁺ (orange) [104], ZnS:Al³⁺,Cu (green) [105] and ZnS:Al³⁺,Cu,Mn²⁺ (cool white) [105]. The ML color of doped ZnS series can also be regulated by using particular types of stress (Section 4.2.1). Interestingly, the ML color of the semiconductor BaZnOS:Mn²⁺ is also affected by the stress condition, with friction generating an orange emission, and compression a red-colored emission [110]. Intriguingly, the color of the ML of other host materials and lanthanide ions doped ML materials are not affected by the stress condition.

6.2.5. Concentration effect of luminescent centers

Zhang et al. have shown a possibility to tune the ML color of CaZnOS:Mn²⁺ from yellow to red by adjusting the concentration of the activator Mn²⁺ (Fig. 42) [149]. In particular, increasing the concentration of Mn²⁺ dopants in CaZnOS progressively shifts the color of the PL from yellow through orange to red. Interestingly, they also recorded a similar color-shift for friction-induced ML of CaZnOS:Mn²⁺ (Fig. 42a-c). By analyzing the ML spectra as a function of Mn²⁺ concentration, the authors established that the color-shift for the PL and ML originated from a Mn²⁺-dependent red-shift of the emission peak (Fig. 42d,e). The authors further suggested that the red-shift arose from the formation of Mn²⁺ pairs, which have a lower energy level compared to that at lower concentrations of Mn²⁺ [149]. While high concentration of activators in the host are known to quench luminescence severely [279–281], Zhang's study showed that the ML of CaZnOS over a wide concentration of Mn²⁺ activators (0.1 to 10 mol%) is intense enough to be observed by the naked eye in a dark room (see Movie in Ref. [149]).

Fig. 41. ML images and spectra of $\text{SrBaMgSi}_2\text{O}_7:\text{Eu}^{2+}$ (SBMSE), $\text{Sr}_2\text{MgSi}_2\text{O}_7:\text{Eu}^{2+}$ (SMSE), and $\text{SrCaMgSi}_2\text{O}_7:\text{Eu}^{2+}$ (SCMSE). Reproduced with permission from Ref. [95], Copyright 2009, The Japan Society of Applied Physics.

Fig. 42. Color manipulation of ML from $\text{CaZnOS}:\text{Mn}^{2+}$ by the Mn^{2+} concentration effect. Photographs of $\text{CaZn}_{1-x}\text{Mn}_x\text{OS}$ (0 ≤ x ≤ 0.1): (a) under daylight lamp lighting, (b) under 254 nm UV lamp excitation, and (c) under manual friction. (d) Normalized tribo-ML spectra of $\text{CaZn}_{1-x}\text{Mn}_x\text{OS}$ (0.005 ≤ x ≤ 0.1). (e) Red-shift of tribo-ML spectra. Reproduced with permission from Ref. [149], Copyright 2015, American Chemical Society.

7. Applications

ML materials have been engineered to function as mechano-optical sensors for multiscale analysis and imaging of stress, and to probe structural defects in static and dynamic target structures [7,15,16,21,22,24,132,133,148,178,179,229,231,245,254,282–308]. ML images, recorded in real-time using a sensitive CCD camera, can be further analyzed to generate dynamic maps of the stress distribution and crack-propagation in a target structure, for example a dynamic component of a machine. Integrated ML stress-sensing systems were introduced by the Xu group, and have been applied in diverse studies, including monitoring the structural health of concrete buildings and bridges, and imaging stress distribution in artificial bones and joints during the application of an external load [20–24,132,239,245,299,300,308]. Other groups have integrated ML materials as excitation sources for touch-sensitive lighting and optical displays [104,129,130,134–136,148,309–314]. Next, we present an overview of recent research on the application of ML materials and associated devices for real-world applications in industry and medicine – some of the high impact applications are schematized illustrated in Fig. 43.

7.1. Stress sensors

ML materials convert mechanical energy to light emission. ML materials may emit light in response to one or more types of mechanical stimuli, including touch, impact, vibration, friction, stretching, compression, bending, and twisting (Fig. 44). In the case of trap-controlled materials, the mechanical stimulus is believed to increase the piezoelectric field or triboelectric field – ML is emitted once the field strength exceeds a threshold value (Section 5). This mechanism of ML emission is valid for individual ML particles, and for ML particles integrated in thin films or embedded in elastic polymers. An important requirement for these composite systems is that the ML intensity correlates quantitatively with the amplitude of stress in a target structure. Thus, an ML composite film that is bonded tightly to the surface of a target structure emits light as a result of the transfer of energy associated with stress in the target structure to the ML particles in the film. This novel system allows one to in real-time monitor the structural health of load-bearing structures, for example in buildings and bridges (Section 4.3) [7,15,16,157,158,228,244]. Furthermore, by calibrating the ML-stress relationship for the ML composite material (Section 4.4.1), it is possible to compute quasi-real time maps of the actual stress distribution in the target structure, and to extract quantitative information on the amplitude, direction and propagation of stress and strain.

For example, the Xu group has employed ML composite materials to study the dynamics of axial force during bolt-tightening [133]. In this study, a washer bearing a surface-attached $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ polymer film, was subjected to compression using a bolt-tightening device (Fig. 45a). The authors recorded simultaneously the ML intensity and the axial force during the entire course of the bolt-tightening study. As expected, the ML intensity increased synchronously with the axial force (Fig. 45b). The authors also showed that the integrated ML intensity (i.e., ML area) scaled linearly with the square of the axial force (inset of Fig. 45c), although the peak of the ML intensity depended on the speed of bolt-tightening (Fig. 45c). In summary, this study demonstrated the power of imaging the ML of composite films to analyze changes of stress distribution in the washer during bolt-tightening. Moreover, since the fastening of the bolt joint is driven by the axial force rather than by the torque, this ML-based imaging approach could be integrated into a feed-back circuit for real-time monitoring and control of bolt-tightening tasks.

In another study, Kim et al. described a new class of ML-based sensors to measure torque (Fig. 46) [179,254,289]. In particular, the authors painted a torque shaft with an ML coating composed of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}, \text{Dy}^{3+}$ or $\text{ZnS}:\text{Cu}$. They used a CCD camera and a PMT to record the ML intensity of these coatings during the application of torque (Fig. 46b and c–f). In one configuration, the authors

Fig. 43. Schematic illustration showing diverse applications of ML.

Fig. 44. Intense ML triggered by various mechanical stimuli. (a) Impact- and (b) friction-induced ML photographs of ZnS:Mn^{2+} film. Reproduced with permission from Ref. [15], Copyright 1999, American Institute of Physics. (c) Ultrasonic-wave-driven ML image of $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$ powders. Reproduced with permission from Ref. [23], Copyright 2012, Elsevier B.V. (d) Compression-excited ML photograph of $(\text{Ba,Ca})\text{TiO}_3\text{:Pr}^{3+}$ composite pellet. (e) Stretching- and (f) gas-flow-driven ML images of ZnS:Cu composite film. Reproduced with permission from Ref. [178], Copyright 2013, American Institute of Physics. (g) Instantaneous ML observation of crack propagation in $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}, \text{Dy}^{3+}, \text{Nd}^{3+}$ specimen. Reproduced with permission from Ref. [231], Copyright 2003, Acta Materialia Inc.

Fig. 45. Axial force sensor based on ML. (a) Schematic diagram of experimental system to measure ML, torque and axial force simultaneously. (b) Correspondence between ML and axial force at a tightening speed of 25 round min^{-1} (rpm). (c) Dependence of ML area on axial force at different tightening speeds (inset: linear dependence of ML area on square of axial force). Reproduced with permission from Ref. [133], Copyright 2010, SPIE.

recorded the ML of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ shortly after exposing the shaft to a brief pulse of UV (the periodic irradiation condition) [179]. In the second configuration, they recorded the ML signals of $\text{ZnS}:\text{Cu}$ while exposing the shaft to a constant intensity of UV, i.e., the constant irradiation condition discussed in Section 4.9.3 [179]. The authors showed that the ML intensity of the stress sensor using the periodic irradiation condition was synchronous with step-wise increases of torque (Fig. 46c). Furthermore, they found that the ML response of the sensor to a sinusoidal waveform of torque on the shaft was also sinusoidal, and in-phase with the applied torque (Fig. 46d). As expected, the ML intensity of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ decreased with time using the periodic irradiation condition, owing to the depletion of trapped carriers (Section 4.5.1). The authors developed an approach to account for the loss of trapped carriers in the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ as a function of time, and used this modified ML signal to calculate the torque throughout the study [179]. In the case of the novel (constant) illumination condition, they recorded a uniform ML intensity, regardless of whether the torque was applied stepwise or sinusoidally (Fig. 46e and f). Thus, the ML signal recorded during constant UV-illumination provides a simple and direct measure of torque. Interestingly, the authors found that the ML response of the $\text{ZnS}:\text{Cu}$ sensor was phase-delayed with respect to the applied torque using the constant illumination condition (Section 4.9.3) – this result is very different from that recorded for $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ using the periodic irradiation condition (Fig. 29). Although the authors did not investigate the origin of the phase-delayed ML signal in their system, we believe that this property is of sufficient interest to warrant further study.

Fig. 46. Torque sensor based on ML. (a) Schematic illustration of experimental device of torque sensor. Reproduced with permission from Ref. [254], Copyright 2014, IOP Publishing Ltd. (b) ML images of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ -based device under the applied torque. (c) and (d) ML responses of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Dy}^{3+}$ -based device to a step torque and a sinusoidal torque, respectively. (e) and (f) ML responses of $\text{ZnS}:\text{Cu}$ -based device to a step torque and a sinusoidal torque, respectively. Reproduced with permission from Ref. [179], Copyright 2014, Elsevier B.V.

7.2. Imaging stress distributions

Currently, structural defects in a target structure are detected using stress sensors that generate single-point readouts of the stress or strain at the point of testing [315]. However, strain gauges and piezoelectric sensors are not suitable in situations where one requires rapid and high-resolution analysis of stress distributions in the target structures [316–319]. In our view, the ideal sensor for these dynamic studies would use a 2D-optical probe that provides high-spatial and temporal resolution maps of stress distributions in the target structure [320–326]. ML coatings are promising candidates for this type of stress-sensing application. Thus, once bonded firmly to the surface of the target structure, these 2D sensors act as an artificial mechano-optical sensitive skin, transducing stresses and strains from the target structure to ML particles embedded in the coating material. The ML in the composite material can be imaged using a sensitive CCD camera in real-time and over a wide dynamic range of stress. ML imaging offers several advantages over single point, electric signal detection approaches – for example, stress distributions can be computed from ML images in real-time, at high spatial resolution and over a larger test area. Moreover, the ML signal from high-performance ML materials is robust, reproducible and repeatable, and computer algorithms may be used to convert images of the ML intensity to quantitative high-resolution maps of the stress distribution in the target structure over a broad range of applied stress. In the following sections, we review recent work on applications of ML materials to map stress distributions in damaged structures, in components of dynamic machines [7,16], and in living systems, including studies on the stress distribution of artificial bone during the application of compressive loads [22]. Also, we directed to the following publications for discussions on other image-based applications of ML [160,173,209,227,229,290–295].

7.2.1. Stress/strain distribution for metal

The ML images of a $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ composite film coated on a hole-drilled aluminum plate shown in Fig. 47 were recorded during the application of tensile force on the plate [132]. The intensity of the ML of the $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ film during the application of tensile forces to the surface of the plate was recorded using a high-speed CCD camera (Fig. 47a). The stress distribution in the plate was computed by subtracting the background signals from the raw ML intensity image, and then converting the corrected ML intensities to stress values using an ML intensity-stress calibration plot (Fig. 47b). Inspection of the ML and stress images shown in Fig. 47 shows that the calculated stress distribution around the hole in the plate is almost identical to the corresponding images of the ML intensity (Fig. 47b) and the FEM simulation (Fig. 47c). Dynamic imaging of the ML generated from ML composite materials offers distinct advantages over single point electrode-based approaches in recording stress distributions, including the ability to generate high-resolution and real-time images of stress distribution in a large test area of the target structure. Moreover, by using a WiFi-enabled CCD camera, one can image the ML of the composite material on remote target structures 24 h a day.

7.2.2. Stress detection within artificial bones and joints

In an exciting new development in the field of ML, the Xu group described an application of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ particles for ML-based imaging of stress distributions in artificial bone during the application of compressive loads. In this study, Xu and Hyodo applied an ML composite coat containing $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ particles to the surfaces of artificial bones and joints [22]. After drying, they mounted the bone and subjected the joint region to compressive loads of 100–1800 N at a rate of 7000 N sec^{-1} to mimic natural load on a human femur. Real-time images of the ML for the entire bone revealed significant differences in the distribution of ML intensity (stress) as a function of time and position during the application of the load (Fig. 48). In particular, the stress was initially localized to the site of compression, where after it propagated down the femur. This study led the authors to propose that ML analyses of stress distributions in artificial bones and joints would help to identify invisible fractures and uneven distribution of stress before they are implanted into the patient. Related ML-based quality control procedures could be used to assess stress distributions in other artificial

Fig. 47. ML technology for visualization of stress distribution around visible hole defect of aluminum plate. (a) Real-time ML image of an aluminum specimen ($225 \times 25 \times 3 \text{ mm}^3$) with a central hole (10 mm diameter) coated with a $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ composite film under the tensile test. (b) Stress distribution image transformed from the linear dependence of ML intensity and stress. (c) Stress distribution calculated by FEM. Reproduced with permission from Ref. [132], Copyright 2008, The Visualization Society of Japan.

Fig. 48. Dynamic ML images of a femur model covered with ML paint under a compressive load. Reproduced with permission from Ref. [22], Copyright 2012, Elsevier Ltd.

implants, including dental implants and prosthetic devices. This study highlights the potential of ML-based materials and ML-imaging in biomedical engineering and medicine. Moreover, discoveries of new ML materials that emit ML from 800 to 1700 nm, a wavelength region that has high transmission through tissue, could be exploited for *in vivo* analysis stress distributions and to identify defects in surgically-implanted devices in small animals (Section 7.8).

7.2.3. Pressure mapping of personalized handwriting

In a novel application of ML, Wang et al. described an ML imaging technique to improve the security of electronic signatures (Fig. 49) [148]. The authors argued that no two individuals would apply the same pressure to a substrate (paper or an electronic display) during the writing of a common signature. Dynamic imaging of the ML of a flexible polymer matrix impregnated with ZnS:Mn^{2+} particles on a substrate allowed the authors to analyze differences in the pressure applied during the writing of the signature, and to quantify differences in the rate of applying pressure for individual letters. Images of the ML intensity distribution show that the ML intensity scales with the pressure applied during the writing of each word. ML images recorded for different students when writing the word “piezo” revealed characteristic force patterns (Fig. 49c–g) and dynamics for each individual (Fig. 49h). The authors proposed that their findings could lead to the development of a unique and high-level stealth security system.

7.2.4. Visualization of invisible defects

ML imaging techniques have been used to detect invisible defects and cracks within metal structures. Invisible defects in a structure would change the distribution of stress in the structure – these defects are usually identified by imaging X-rays and ultrasonic waves. While useful, these approaches do not generate information related to changes in the stress distribution in the damaged structure. As we have seen earlier, ML composite materials and sensitive ML imaging techniques can be engineered to overcome this limitation. To highlight this point, we describe a recent application of ML imaging to map stress distributions of a metal plate bearing engineered structural defects [245]. In this study, three incomplete holes were drilled into one face of the metal plate to create three small circular wells that were invisible when viewed from the opposite (smooth) side of the plate (Fig. 50). Next, a polymer film embedded with $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+}$ particles was attached firmly to the smooth surface of the metal plate (Fig. 50a and b) and ML images were recorded from the smooth side of the plate during the application of tensile force (Fig. 50a). The pseudo-3D color image of ML intensity of the plate during tension reveals strong ML emission signals that correspond to the positions of the three drilled wells (Fig. 50c) – the highest level of stress was recorded around the upper and deepest-drilled well. In summary, this study shows that ML-based imaging of mechano-optical responsive films allows for quantitative and real-time mapping of internal defects within the structure, and moreover, the ML signal provides a means to quantify stress distributions around multiple defects in the test sample during the application of a mechanical stimulus [325]. Thus, ML imaging technologies hold great promise for remote monitoring of the structural health of static and dynamic mechanical and structural components. For example, one could employ ML-based imaging of ML composite films to detect invisible cracks and other defects in pipes before they are assembled either underground or hidden in the infrastructure of a building.

7.3. Visualization of crack propagation

7.3.1. Fast-moving crack propagation

Several studies have reported applications of ML imaging techniques to visualize and track high-speed crack propagation in engineered materials ($15\text{--}250\text{ m s}^{-1}$) [231,232,296,327–335], i.e., far faster than those recorded using conventional crack monitoring techniques ($10^{-3}\text{--}10^{-2}\text{ m s}^{-1}$) [336–338]. For example, Sohn et al. coated a thin film harboring $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+},\text{Dy}^{3+}$ particles to the surface of test samples, and imaged crack propagation during their fracture by using a sensitive high-speed camera [296]. In one study, the authors recorded the ML of the $\text{SrAl}_2\text{O}_4\text{:Eu}^{2+},\text{Dy}^{3+}$ film applied to the surface of a disc that was engineered with a crack initiation point (Fig. 51) – the ML of the film was recorded at a rate of 8000 frame s^{-1} during the application of the mechanical load. One can discern from the time-series of ML intensity images of this study that the ML intensity increases with time along the direction of the propagating crack (left panel of Fig. 51). Next, the authors extracted the instantaneous ML intensity of each image as

Fig. 49. Pressure mapping of personalized handwriting. (a) Schematic diagram of experimental system. (b) ML mapping of 2D planar pressure. (c) ML image of a handwritten letter “e”. (d) Intensity distribution of ML image in pseudo-color and (e) relative ML intensity in a line profile. (f) and (g) Dynamic ML frames under the fast and slow signing speeds, respectively. (h) ML demonstrations of different signing behaviors of four signees: (i) strong pressure applied continuously; (ii) weak pressure applied continuously; (iii) strong pressure applied at the turning points and the end; (iv) strong pressure applied at the end. Reproduced with permission from Ref. [148], Copyright 2015, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Fig. 50. ML technology for detecting invisible defects. (a) Metal plate coating with ML film on the front surface. (b) Three non-penetrated holes introduced on the backside of metal plate. (c) Pseudo-3D color image of ML distribution observed from the front surface. Reproduced with permission from Ref. [245], Copyright 2013, IEEE.

a measure of the strain rate (middle panel of Fig. 51), and used the integrated ML intensity to calculate the value of the strain energy on the crack tip (right column of Fig. 51). By analyzing plots of the strain rate and strain, the authors successfully identified the location of the propagating crack tip in real-time (marked with vertical yellow lines in Fig. 51). Time-resolved imaging of ML of composite films has also been applied to measure the velocity of crack propagation in ceramic materials including studies on zirconia (Mg-PSZ) [296], yttria-tetragonal zirconia polycrystals (Y-TZP) [331], Si_3N_4 and SiC [339].

7.3.2. Slow-moving crack propagation

The Xu group has used novel ML imaging technologies to quantify the movement of a slow-moving crack in engineered materials [245,340]. In one of these studies, a stainless steel plate harboring a notch was coated with an ML film embedded with $\text{SrAl}_2\text{O}_4\cdot\text{Eu}^{2+}$ particles (Fig. 52a). They employed time-series imaging of the ML of a composite film attached to a plate during the application of a cyclical load to map the slow progression of the crack tip from the notch. For example, they determined from the ML image shown in Fig. 52b that the crack extended 1.6 mm from the engineered notch following 30,000 cycles of tensile fatigue. Notably, slow-moving cracks of this type cannot be not detected using strain gauge techniques even in cases where a micro-crack is visible (Fig. 52c).

7.4. Structural health diagnosis

Catastrophic failures of social infrastructure are increasingly common – in many cases these failures are linked to aging structures and supports, earthquakes and even shoddy construction. Two pertinent examples here include the collapse of the Mississippi River Bridge in 2007, and the destruction of purpose-built defenses during the massive earthquake and tsunami in Japan in 2011. These events have led to widespread concerns about the current health of essential social infrastructure, including bridges and buildings. One approach to address these concerns would be to test the structural integrity of key infrastructure on a regular basis. Ideally, any defective component of a structure that was identified from these tests would be replaced to extend the life of that structure. This goal is clearly unrealistic due to the high cost and the massive scale of such an endeavor, and may not even be possible using current fault monitoring technologies. On the other hand, ML-imaging approaches that employ thin film or polymer coatings could provide a simple, effective and low-cost solution to enable remote, long-term monitoring of critical or suspect components of load-bearing structures. In its simplest form, the monitoring technology would involve adhering an ML film to a component of the infrastructure, and recording images of the ML from the film using a WiFi-enabled CCD camera, much like the ones used for home surveillance. The Xu group has employed ML-imaging technologies of this type to monitor and diagnose the structural health of macroscopic infrastructure, including bridges [25,245,341–343], buildings [244,344–346], welding points along pipelines [347,348], and high-pressure vessels [24,346,348]. Moreover, these systems are engineered to operate 24/7 at remote sites. By encasing the ML-sensor area and camera in a black box that also includes an UV-excitation source to recharge ML materials within the film. The increased sensitivity of these purpose-built devices would allow one to integrate multi-sensitive ML materials in the film to assess a broad range of applied load [48,49,283,349–356].

In the first study of this type, the Xu group detected and analyzed structural defects in concrete supports of an in-service bridge

Fig. 51. High-speed ML images of crack propagation (left panel), ML converted strain rate (middle panel), and ML converted strain distribution (right panel). Reproduced with permission from Ref. [296], Copyright 2007, American Institute of Physics.

Fig. 52. ML-based visualization of fatigue crack propagation. Reproduced with permission from Ref. [245], Copyright 2013, IEEE.

(Fig. 53) [21,157,348]. In this study, several sheets of ML film ($700 \times 400 \text{ mm}^2$) embedded with $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ microparticles were attached to a visible crack ($\sim 600 \text{ mm}$) on a concrete girder of the bridge. Vehicles passing over the defective girder applied a load that increased the ML of the film, which was recorded in real-time using a sensitive CCD camera. The recorded ML images identified the location and profile of the active crack, while images of the stress distribution of the load were calculated from the instantaneous ML (Fig. 53a–c). Additional processing of these ML images was used to calculate the crack mouth opening displacement (CMOD), which is usually measured with a strain gauge (conventional electrical feedback) (Fig. 53d). Interestingly, this ML-imaging study also identified defects from seemingly healthy regions of the structure, for example those shown in Fig. 53e and f (a-b and a-c lines). Collectively, ML-based image analysis of both visible and hidden defects provides a means to conduct a total diagnosis of the structural health of key components of remote infrastructure.

To quantitatively evaluate the stress concentration on a large-scale infrastructure, the Xu group further performed the onsite test and dynamic strain imaging on the Urban Expressway (near Kanenokuma Interchange Entrance) in Fukuoka, Japan (Fig. 54) [308]. Fig. 54a shows an outside image of the inspected urban expressway, and Fig. 54b shows a future image of onsite inspection on the intersection of a U-rib. Fig. 54c and d shows the ML and strain images before the repair work when the peak value of the absolute strain was about $200 \mu\text{ST}$ that was caused by a passing vehicle and detected by the strain gauge. In that case, the maximum strain at the U-rib was evaluated to be $922 \mu\text{ST}$, i.e., a value 4.6 times the strain nearby (region A). Fig. 54e–f shows that, after the repair, the maximum strain at the previous “region A” became $530 \mu\text{ST}$, which is 2.9 times the absolute peak strain nearby (about $180 \mu\text{ST}$

Fig. 53. ML-based monitoring on active crack of bridge. (a)–(c) ML images of active crack during the vehicles passing the bridge: no vehicle, light vehicle, and heavy vehicle, respectively. (d) Acceleration, CMOD, temperature and ML luminance during the crossing of a heavy vehicle. (e) Photograph and (f) ML image corresponding to the specific region of frame (c). Reproduced with permission from Ref. [21], Copyright 2012, SPIE.

caused by a passing vehicle). The decrease of 40% in stress concentration verifies the effectiveness of this scalable ML sensor on both the quantitative imaging of stress concentration and the unprecedented visible quantitative evaluation of the repair work. It further confirms that, with using this scalable paint sensor, it becomes possible for full-field quantitative strain imaging and effective prediction of the danger region for efficient maintenance, which are the most challenge issues for infrastructural health.

A related ML-imaging technology was also employed by the Xu group to study cracks within a high-pressure steel vessel (Fig. 55) [24]. In this study, a mechano-sensitive film embedded with $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ microparticles was attached firmly to the outer surface of a hydrogen storage cylinder that had been engineered with an internal U-notch to mimic a crack tip. The ML of the probe on the cylinder was imaged during a fatigue test, during which the hydraulic pressure alternated between cycles of pressurization and release. The ML images of the attached film were recorded in real-time using a CCD camera, and then analyzed to generate dynamic maps of the distribution of stress around the engineered crack (Fig. 55a). These images show that the crack extended from the initial tip in the cylinder and increased in depth during each pressure cycle (on–off). The stress distributions calculated from the ML intensity images of this study were consistent with maps of the strain pattern calculated from a FEM simulation at different depths around the crack (Fig. 55b and c). Moreover, the deepening of the crack was accompanied by increases in the ML intensity and the strain – at the end of this study, the authors recorded the increases in the distance between the two ML peaks and the associated strain-concentration points. Since the ML intensity correlates linearly with the strain concentration at the crack tip, the distance of two ML peak intensities on the outer surface of vessel can be used to calculate the depth of the internal crack, i.e., based on the inverse dependence of the distance on the crack depth (Fig. 55d).

Fig. 54. Scalable ML sensor for onsite quantitative strain imaging and effective danger-level diagnosis of a highway joint section. (a) Outside view of the inspected urban expressway. (b) Future image of onsite inspection on infrastructure. Images of ML (c) and strain (d) show a high stress concentration with a maximum strain of about 1000 μST before repair. Images of ML (e) and strain (f) show the above concentration with a maximum strain down to about 500 μST after repair. Reproduced with permission from Ref. [308], Copyright 2018, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Fig. 55. ML-based evaluation on the inner crack of high-pressure vessel. (a) Photograph and schematic illustration of high-pressure hydrogen vessel coated with three ML sheets. (b) Strain pattern calculated by FEM for vessel model with different crack depths. (c) ML intensity pattern corresponding to different cycles of fatigue testing. (d) Linear dependence of the distance between two strain-concentration points on the crack depth. Reproduced with permission from Ref. [24], Copyright 2015, Hydrogen Energy Publications, LLC.

7.5. Excitation sources

Several studies have shown the ML emitted within a composite material is capable of exciting optically-emitting acceptor molecules in photocells [357] – this feature has been used to trigger photochemical reactions [23,300], and to excite fluorescent probes [239].

7.5.1. ML-driven photocell

In one study, the Xu group developed a photocell device where photons produced during the ML photons serve as an intermediary in the mechano-electro transformation device (Fig. 56) [357]. In particular, the authors used an epoxy-resin pellet embedded with $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ particles as an ML-based photon excitation source to drive a commercial silicon solar cell, i.e., the device transformed the ML-generated photons to an electric current (Fig. 56a). The authors showed that the photocurrent output of this novel photocell was regulated quantitatively by the amplitude of the mechanical load applied to the ML pellet (Fig. 56b).

7.5.2. ML-induced photocatalyst reaction

To this point, we have highlighted specific applications of ensemble populations of ML microparticles embedded in thin films and elastic polymer coatings. In the following section, we discuss applications of individual nanometer-scale ML particles. The Xu group has shown that the ML power generated by single ML nanoparticles is on the order of a nW. Moreover, like their micron-scale counterparts, the ML intensity of a single ML nanoparticle scales linearly with the amplitude of the mechanical stimulus [138,175,234]. This property suggests that the ML signal emitted by ensemble populations of ML particles within a thin film originates from mechano-optical coupling events within the fundamental structural unit of the ML material, i.e., micro- or nanocrystals. In other words, the ML material generated within a composite coating or film does not require any specialized assembly of the smaller ML particles.

Fig. 56. (a) Schematic representation of ML-driven photocell. (b) Consistent relation between load signal and photocurrent response. Reproduced with permission from Ref. [357], Copyright 2007, The Japan Society of Applied Physics.

The Xu group has proposed that the ML generated from an ML material could be used to drive a photochemical reaction associated with the activation of a pro-drug (Fig. 57) [23,300]. To this end, the authors proposed a new class of hybrid ML material that contains ML nanoparticles and a photosensitizer whose photo-products activate a pro-drug. The photons that activate the photosensitizer in the hybrid material are produced during ultrasound excitation of the hybrid material. Next, they envisaged the ML-mediated excitation of the photosensitizer would produce reactive oxygen species (ROS) to activate a pro-drug. This proposal, while purely theoretical at this stage, could have practical applications in human health, for example, focused ultrasound excitation of the hybrid material targeted to a tumor could be used to activate a photodynamic therapy probe, or ROS-activated anti-cancer drugs. Ultrasound, we note, is used routinely to image fetal development and to assess the structure and health of internal organs. Plausible hybrid materials include $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, $\text{CaYAl}_3\text{O}_7:\text{Eu}^{2+}$ and $\text{CaZnOS}:\text{Mn}^{2+}$, as these materials are known to emit ML in response to ultrasound [23,102,174], and titanium oxide as the photosensitizer, as it generates oxygen radicals during its photo-excitation and has an action spectrum that overlaps with the wavelengths emitted by $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$, $\text{CaYAl}_3\text{O}_7:\text{Eu}^{2+}$ and $\text{CaZnOS}:\text{Mn}^{2+}$. In summary, while ML materials have obvious applications as stress sensors in machine condition monitoring and structural health diagnosis, it is also possible that they can provide new information and capabilities in biomedicine, including high-contrast imaging, analysis of biomechanical force and novel approaches to drug delivery and activation [23].

7.5.3. Pump light for fluorescent probe molecules

Fluorescent probes that emit visible light have been used extensively to image tumor cells *in vitro* and in tissue models of human cancer. Unfortunately, these probes are not very useful for the *in vivo* of tumors, because visible light does not transmit very far in living tissue. This problem can be overcome to some degree by using ultrasound-mediated excitation of ML materials to excite fluorescent probes in tissue (Fig. 58) [239]. In a proof of practice demonstration, the Xu group prepared a composite material composed of $\text{CaYAl}_3\text{O}_7:\text{Eu}^{2+}$ and fluorescein. The application of a compressive force to the sample generated an ML signal from $\text{CaYAl}_3\text{O}_7:\text{Eu}^{2+}$ that was centered at 440 nm – these photons led to the excitation of fluorescein molecules in the composite, which shifted the emission to the green fluorescence (523 nm) (Fig. 58a–c). While far from optimized, this demonstration of a mechanically-induced energy transfer demonstrates the potential of using ultrasound to excite fluorescent probes deep within living tissue. In a related study, Jeong et al. showed that the green ML of $\text{ZnS}:\text{Cu}$ microparticles was effective in exciting adsorbed molecules of 4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran, a fluorescent dye that emits a red fluorescence [309]. Since ML materials emit light from the UV to the NIR (Table 1), one could prepare other hybrid ML-fluorescent materials whose mechanically-induced fluorescence would excite fluorescent molecules in the first (600–950 nm) and second (1100–1400 nm) optical windows of biological tissue. These hybrid materials would represent a new class of self-illuminating fluorophores that could find applications as probes for *in vivo* imaging of diseased states [358,359].

Fig. 57. (a) Schematic illustration of ML-induced photocatalyst reaction on the hybrid structure comprising ML material and photocatalyst. Reproduced with permission from Ref. [300], Copyright 2009, Elsevier B.V. (b) Concept on ultrasonic-induced ML to excite photo-functional materials inside a living body. Reproduced with permission from Ref. [23], Copyright 2012, Elsevier B.V.

Fig. 58. Energy transfer from ML material to non-ML molecule. (a) Fluorescent microscopy image of $\text{CaYAl}_3\text{O}_7:\text{Eu}^{2+}$ particles. (b) Fluorescent microscopy image of composite pellet containing $\text{CaYAl}_3\text{O}_7:\text{Eu}^{2+}$ particles and fluorescein isothiocyanate isomer-I (FITC). (c) ML image of composite pellet under a compressive load. (d) PL spectrum of $\text{CaYAl}_3\text{O}_7:\text{Eu}^{2+}$ ($\lambda_{\text{ex}} = 326$ nm, dotted line), PL excitation spectra of FITC ($\lambda_{\text{em}} = 523$ nm, broken line), and PL emission spectrum of FITC ($\lambda_{\text{ex}} = 492$ nm, solid line). Reproduced with permission from Ref. [239], Copyright 2011, The Royal Society of Chemistry.

7.6. Light sources and displays

Several groups have developed ML composite materials as substrates for mechanically-driven surface displays. Research in this area has centered on the design of intense ML composite materials, each of which may emit light of a certain color and when combined, should emit white light.

7.6.1. Full-color manipulation by mixing ML materials

The ML spectrum is characterized by a peak wavelength, and a bandwidth, often on the order of a 100 nm. ML materials exhibit peak wavelengths in the visible (400–650 nm), and so they have a characteristic color when viewed by the human eye (Table 1). Jeong et al. showed that the ML emission from composite materials harboring multiple types of ML particles is additive, and approximates to white light [104,134,178,210]. The authors showed that the actual color emitted by these composite films was dependent on the concentration ratios of the green-emitting ML material ($\text{ZnS}:\text{Cu}$) and the orange-emitting material ($\text{ZnS}:\text{Cu},\text{Mn}$) (Fig. 59) [104]. Jeong et al. also embedded multiple types of ML particles in a horsetail-shape composite film that functioned as a wind-powered multi-colored ML light source (Fig. 44f) [178]. The authors mixed three types of commercial $\text{ZnS}:\text{Cu}$ materials in the horsetail-shape film that emitted either blue, green or orange ML [134]. They showed that certain combinations of the three materials in the horsetail shaped film produced white light when exposed to a stream of air. In a separate study, Jeong et al. used gas-flow to simulate the action of wind on the horsetail structure (Fig. 60) [134]. Interestingly, they found that by changing the velocity of gas-flow through the structure they could control the brightness and the color of the ML. In particular, they found that a gas flow rate of 80 L min^{-1} (1pm) produced blue, green and orange ML at relative ML intensities corresponding to 83.3, 125.5 and 15.8 cd m^{-2} , respectively (Fig. 60a–c). Next, Jeong et al. examined the color output of a film embedded with mixtures of blue- and orange-emitting ML materials. Under defined conditions of gas flow, they showed that specific binary mixtures of the orange- and blue-emitting $\text{ZnS}:\text{Cu}$ at ratios of 9:1, 8:2 and 7:3 produced white lights that were characterized as either warm, neutral or cool, corresponding to color temperatures of 3560, 4620 and 8000 K, respectively (Fig. 60d). The photograph shown in Fig. 60e shows the bright cool-white ML that was generated by gas-flow-over using a film composed of a mixture of the two materials at a ratio of 7:3. While promising, the production of pure white light from mechanically-driven ML of mixtures of ML materials is limited by sub-optimal responses of ML materials to mechanical stimuli, and by the low efficiency of the ML of these materials. In fact, the authors measured a lower ML output for the red-emitting ML material compared to the blue- and green-emitting ML materials. Jeong's studies on the development of mechanically-driven white light sources highlights the need to develop more efficient red-emitting ML materials.

7.6.2. Wind-driven ML light displays

In an extension to the previous study, Jeong et al. described a wind-driven ML display to generate spatial patterns of ML (Fig. 61) [134]. These patterns arise from wind-driven vibrations within an array of fabricated posts, each composed of different mixtures of ML materials (Fig. 61a). The ML of these posts was realized by gas flow, which triggered different amplitudes of vibration and bending of individual posts in the array (Fig. 61b–e). The authors showed that the color of the ML within the array could be controlled by embedding posts with either the green-emitting $\text{ZnS}:\text{Cu}$, or with mixtures of $\text{ZnS}:\text{Cu}$ ML materials – in this way the

Fig. 59. Color manipulation of stretching-driven ML from the mixed phosphors emitting different ML colors. (a) Schematic illustration of color tunable ML composite films by physically mixing ZnS:Cu and ZnS:Cu,Mn particles. (b) Stretching-driven ML spectra of ZnS:Cu (green) and ZnS:Cu,Mn (orange). (c) CIE coordinate-color graph corresponding to various orange/green ratios (0:10–10:0). (d) Photograph of ML-patterned composite film: yellow (8:2), orange (10:0), and green (0:10). Reproduced with permission from Ref. [104], Copyright 2013, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 60. Wind-driven multi-colored ML from a mixture of ZnS:Cu emitting different colors. (a)–(c) Blue, green, and orange ML images driven by gas flow, respectively. (d) CIE coordinate-color graph corresponding to various orange/blue ratios (10:0–0:10). (e) Gas-flow-driven cool white ML image (7:3). Reproduced with permission from Ref. [134], Copyright 2014, The Royal Society of Chemistry. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

authors could illuminate particular posts with green or white light, as indicated by the illumination of the letters “ML” in green, against a white ML background (Fig. 61f–h). They also noted that one could increase the resolution of these display units by increasing the density of posts in the array. This proof of principle study demonstrates the potential of using ML composite materials as wind-driven color displays. However, as noted by Jeong et al. [134], these applications are undermined by the poor mechano-responsiveness and low emission yields of currently available ML materials.

7.6.3. Electro-mechanical dual-powered displays

In another study on ML based display units, Jeong et al. employed the EL and ML properties of ZnS:Cu [104], to develop a dual-powered, electro-mechanically triggered ML light display (Fig. 62) [135]. In this study, the authors sandwiched a layer of ZnS:Cu microparticles between two PDMS plates each embedded with Ag nanowire (AgNW) electrodes (Fig. 62a). The bird and flower shaped patterns were generated by electrically stimulating AgNWs located at the bottom PDMS plate (Fig. 62b–e). Moreover, by using the electro-mechanically dual-powered mode, the authors could generate simultaneous dual emission patterns (EL/ML) in AgNW regions, while ML emission occurred only in the non-AgNW regions (Fig. 62b–e). Accordingly, by controlling the amplitudes of the electrical and mechanical stimuli (Sections 4.2.1 and 7.6.1), and by mixing the colors of EL and ML materials (Fig. 62f and g), the authors were able to generate multiple colored patterns in the device, i.e., by combining contributions from the single probe EL, the single probe ML, and the dual probe EL/ML (Fig. 62b–e).

7.6.4. Magnetic-induced ML lighting and displays

Hao et al. detailed an approach to generate ML for optical displays and lighting using magnetostriction (Fig. 63) [136,360]. In a proof-of-concept study (Fig. 63a), the authors mixed a conventional magnetic material Fe-Co-Ni alloy with an ML material (metal ions doped ZnS microparticles) in a PDMS elastomer. First, they fabricated an elastic composite material in the form of a rod,

Fig. 61. Patterned, wind-driven ML colorful displaying. (a) Schematic illustration of wind-driven ML display device. (b) Image of ML distribution in the vibrating rod matrix. (c)–(e) Photographs and (f), (g) ML images of two patterned display devices. (h) ML spectra captured from spots A and B in frames (f) and (g). Reproduced with permission from Ref. [134], Copyright 2014, The Royal Society of Chemistry.

Fig. 62. Electro-mechanically dual-powered displays. (a) Schematic illustration of device fabrication. (b)–(e) Patterned EL, EL/ML and ML images upon different electro-mechanical excitations. (f) Spectra and (g) CIE coordinates of EL, EL/ML and ML corresponding to frames (b), (c) and (e), respectively. Reproduced with permission from Ref. [135], Copyright 2016, Elsevier Ltd.

followed by additional patterning to generate an array of the ML material (Fig. 63b and c). The authors generated magnetostriction in the PDMS rod by exposing the device to a magnetic field – this perturbation triggered ML in the PDMS-embedded ML particles, i.e., magnetic-induced ML (Fig. 63d). The authors generated a green emitting “PU” display (Fig. 63e), and a bright cool white ML lighting (Fig. 63f) in the image by embedding different ML materials within the rod structures, including green-emitting ZnS:Al^{3+} , Cu and cool white-emitting ZnS:Al^{3+} , Cu, Mn^{2+} . Significantly, the authors generated the magnetic-induced ML at a low magnetic field (3.5 kOe, 50 Hz) and at room temperature (Fig. 63d).

7.6.5. Wearable devices

With the advent and development of the “Internet of Things” (IoT), many efforts have been made to develop wearable devices for the human body that respond to various stimuli. Accordingly, different wearable ML devices with 1D, 2D and 3D structures have been prepared on the basis of the synthetic ML materials (Figs. 64 and 65) [361–366]. For example, Jeong et al. and Peng et al. manufactured the 1D ML fibers by integrating an elastomeric fiber-frame, the composite of PDMS and ZnS:Cu, and an adhesive surface-layer (Fig. 64a and c) [361,362]. Subsequently, these two groups separately engineered the 2D ML fabrics by weaving the ML fibers or other fabricated strategies (Fig. 64b and d) [361,362]. On the other hand, wearable ML devices showing multi-dimensions can also be produced using 3D printing techniques. By employing the ink composed of PDMS, ZnS-based ML particles and a curing retarder, Magdsssi et al. printed ML devices of 2D and 3D geometries by the direct-writing means (Fig. 65a and b) [363]. More attractively, the authors further demonstrated that the printing patterned multi-material ML devices emitted an anisotropic ML when undergoing compression applied in different directions (Fig. 65c) [363]. Furthermore, Song et al. direct-writing printed skin-driven ML devices, which shows potential applications in photonic skin with the augmented animations expressions (Fig. 65d) [364].

7.7. Anti-counterfeiting

In the face of increasingly serious counterfeiting problems, there is a pressing need to develop advanced anti-counterfeiting

Fig. 63. Magnetic-induced ML display and lighting. (a) Principle of magnetic-induced ML by coupling magnetostriction and ML. (b) SEM image of the interface of magnetic elastomer layer (Fe-Co-Ni alloy + PDMS polymer) and ML phosphor layer (metal ions doped ZnS + PDMS polymer). (c) Experimental setup of magnetic-induced ML. (d) Transient characteristic of magnetic-induced ML. (e) Displaying of green emitting logo driven by magnetic field (upper: off; lower: on). (f) Cool white ML driven by magnetic field. Reproduced with permission from Ref. [136], Copyright 2015, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

technology. In 2014 Dai Nippon Printing commercialized a printing technology based on the ML material of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ – the ML coating on paper emits light under tearing or bending, providing a novel encryption pattern which is different from the traditional PL, UCL and PersL modes used for anti-counterfeiting. However, the tri-modal emission of $\text{Sr}_2\text{Al}_2\text{O}_4:\text{Eu}^{2+}$ (i.e., PL, PersL and ML) is identical (green), which results in a low-level visual encryption. The development of multi-color, multi-temporal and multi-modal luminescence in a single material represents a significant challenge. Recently, Zhang et al. demonstrated the superior integration of four-modal (thermo-/mechano-motivated and up-converted/down-shifted), bi-temporal (fluorescent and delayed) and colorful (red-orange-yellow-green) emissions in the NaNbO_3 piezoelectric lattice via optical multiplexing of Pr^{3+} and Er^{3+} dopants (Fig. 66) [129,130]. In this system, Pr^{3+} ions are introduced to create photo-chargeable traps, which participate in the red delayed emission under the thermo- and mechano-stimuli. Er^{3+} ions, the typical UCL dopants, are codoped to endow NaNbO_3 with the green fluorescent emission under the NIR excitation (Fig. 66a). Furthermore, the red-emitting Pr^{3+} and green-emitting Er^{3+} both display a collective PL mode under UV excitation, showing a color-tunable emission via excitation wavelength fine-selectivity. Zhang et al. also showed that the versatile $\text{NaNbO}_3:\text{Pr}^{3+}, \text{Er}^{3+}$ particles are suitable for embedding into thermoplastic polyurethane (TPU) films to achieve waterproof, flexible/wearable and high-stretchable features (Fig. 66b and c), and synchronously to enable excellent multi-dimensional identifiability with the help of the simple tools (including LED of smartphone, pen-writing, cooling-heating stimuli, and UV/NIR lights) (Fig. 66d).

7.8. NIR-ML imaging

NIR fluorescence imaging techniques are gaining favor as probes for *in vivo* analysis of biological structures, and for high-contrast detection of biomarkers in blood and biopsy samples [358,359]. NIR probes that emit fluorescence over the wavelength range of 800–1700 nm provide additional contrast for these *in vivo* imaging studies, because NIR wavelengths penetrate deeper in living tissue compared to visible light. Moreover, gated detection of the emission of NIR probes with long-lived excited states can further enhance the contrast of fluorescence detection, in part by rejecting contributions from the short-lived excited states of background probes in the sample [367]. ML materials are attractive probes for *in vivo* NIR imaging as their emission is tunable from 650 to 1500 nm, and

Fig. 64. (a) SEM image of an ML fiber consisting of a cross-shaped elastomeric fiber-frame, the composite of PDMS and ZnS:Cu, and a silicon adhesive surface-layer. (b) Photograph of ML-emitting fabric undergoing hand-stretching. Reproduced with permission from Ref. [361], Copyright 2017, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim. (c) SEM image of an ML fiber consisting of a cylindrical elastomeric fiber-frame, the composite of PDMS and ZnS:Cu, and a PDMS surface-layer. (d) ZnS-based colorful ML fabrics based on (i) ML fibers, (ii) ML ribbons and (iii) ML dots. Reproduced with permission from Ref. [362], Copyright 2017, The Royal Society of Chemistry.

Fig. 65. (a) Direct printing of ML pattern devices (in process); (b) Printed ML devices with different patterns; (c) Dual light-emitting patterned ML concentric-square device: (i) without and (ii) with UV-light irradiation, ML responses under (iii) horizontal and (iv) diagonal compression-release. Reproduced with permission from Ref. [363], Copyright 2018, The Royal Society of Chemistry. (d) Skin-driven colored ML patterns responded to (i) lips corner, (ii) canthus, and (iii) cheek muscle movements. Reproduced with permission from Ref. [364], Copyright 2018, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Fig. 66. (a) Crystal structure of NaNbO_3 piezoelectric lattice and co-doping of Pr^{3+} and Er^{3+} in Na^+ sites. (b) Schematic structure of $\text{NaNbO}_3:\text{Pr}^{3+},\text{Er}^{3+}/\text{TPU}$ composite film. (c) Load-elongation relation of composite film (initial size of $4\text{ cm} \times 4\text{ cm} \times 250\text{ }\mu\text{m}$). The insets show photographs of film (bottom) and water droplets on film (upper) at different elongations. (d) Illustration of thermo-mechano-opto-responsive bi-temporal colorful luminescence of composite film: I. Thermo-/mechano-motivated red emission (delayed emission); II. NIR-excited green-emitting UCL (fluorescent emission); III. UV-excited color-tunable emission (fluorescent emission + delayed emission). Reproduced with permission from Ref. [129], Copyright 2018, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

can be triggered deep in tissue by using non-invasive medical ultrasound (Table 1). Certain trap-controlled materials containing rare earth ions are known to emit ML from the visible to the NIR – the ML of $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+},\text{Er}^{3+}$ for example extends to 1530 nm [20]. Moreover, it has been shown that the NIR ML of Nd^{3+} -doped materials include line emissions in the second optical window of biological tissue (NIR2, as shown in Fig. 67) [124,125,368,369]. The ability to generate NIR light from ML materials using ultrasound excitation [23,102,174,326], coupled with the greater transmission of NIR photons through living tissue could lead to exciting developments in medicine, including high-contrast *in vivo* imaging of tumors and other diseased states. Moreover, by coating NIR-emitting materials to anatomical structures or prosthetic devices in animal models of human bone disease, one can envisage using ML-based biomechanical imaging in the NIR2 window to study the effect of load on stress distributions in implanted joints and bones, and to identify defects or failing structures within the living system.

8. Conclusions and outlooks

We have summarized an extensive body of research on trap-controlled ML materials and their mechano-optical composites. The full potential of trap-controlled materials for applications in structural health monitoring, analysis of faults and crack-propagation, and in biomedical imaging will require a concerted interdisciplinary research effort to optimize specific mechanical, optical properties. In this summary, we identify specific challenges that must be addressed to improve the performance of ML materials to fully enable their application as mechano-optical sensors and light sources. The first challenge is to increase the brightness and the mechano-responsiveness of high-performance ML materials. Currently, only a few of the ~ 40 known trap-controlled ML materials are classified as high-performance ML materials. Consequently, there is a pressing need to enhance the performance of these ML materials and to identify new materials that exhibit several of the following properties: control the color of the ML emission over a broad range of wavelengths; increase the efficiency of ML emission; increase the mechano-optical conversion efficiency; increase multi-mechano-sensitivity; demonstrate the dependence of the ML intensity on the amplitude of various stress parameters; increase the reproducibility or self-recovery of ML materials; optimize the physical and chemical properties of ML to enhance their mechanosensitive properties; increase water stability.

Approaches to improve the efficiency of ML emission of trap-controlled materials, for example the brightness, focus on modifying the methods of synthesis and the compositions of ML materials and their composites. Even so, the ML brightness of most optimized ML materials is too low for most in-field applications, for example remote monitoring of the health of building infrastructure. In fact,

Fig. 67. (a) Emission spectra of CaZnOS:Nd^{3+} upon excitations by compression, friction and 600 nm-light, showing the characteristic emission from Nd^{3+} . (b) NIR ML photographs of handwriting on CaZnOS:Nd^{3+} sample. (c) Bio-imaging of tissues by detecting NIR ML of CaZnOS:Nd^{3+} passing through the pork tissues with different thicknesses. Reproduced with permission from Ref. [125], Copyright 2018, American Chemical Society.

the ML signals of current trap-controlled materials are, for the most part, only visible to the naked eye in a darkened room. Greater progress is being made in the design of ML composite materials that respond to multiple mechanical perturbations – these ML materials are particularly valued for multiscale analysis of stress distributions, and as touch-sensitive light displays.

$\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ is considered the best and the highest-performing ML material, and it serves as a benchmark to evaluate the ML properties of new materials. $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ particles embedded in elastic polymers emit a strong and recoverable ML during cycles of multiple mechanical stimuli. Importantly, the ML intensity of these composite films correlates quantitatively with the distribution of stress induced by diverse mechanical stimuli. This relationship allows one to map 2D stress distributions, for example by attaching thin sheets of the ML polymer to the surface of the target structure, i.e., the ML polymer serves as an ML mechano-optical “skin” that can both sense and see changes in strain/stress in the target structure. Significantly, $\text{SrAl}_2\text{O}_4:\text{Eu}^{2+}$ exhibits multi-mechano-sensitivity and has proven useful for quantitative sensing of diverse mechanical perturbations in static and dynamic systems. Given recent improvements in the synthetic methods used to prepare ML materials and their composites, we anticipate that a flurry of high-performance ML materials will emerge over the next few years. Comparative quantitative analyses of the ML properties of these materials will require careful and calibrated characterization of their optical, mechano-optical and physical properties. To this end, we anticipate a need to develop a suite of standardized, high-performance ML reference materials, and associated instrumentation and measurement conditions that will allow researchers to compare and quantify specific optical and mechanical properties of new ML materials to those of reference ML materials.

The second challenge to advance ML materials for diverse applications in industry, consumer products and biomedicine is to understand the mechanisms that underlie ML phenomena in trap-controlled materials. This breakthrough will require close collaboration between experimentalists and theorists. In our view, some of the popular views on the origin of the ML of trap-controlled materials are based on incomplete characterization of the ML material in question, and in some cases they invoke too many assumptions and approximations [243,370–381]. For instance, there is no theory to explain the dynamic relationship between crystal structure, local electronic states, trap levels and ML. Moreover, it is commonly believed that ML arises from the cooperation of the stress-induced electric field (piezoelectric or triboelectric fields) and thermal energy. The mechanism of ML is far more complicated than that proposed for persistent luminescence, as the ML signal includes unknown contributions from the probabilities of de-trapping, re-trapping and the recombination of trapped carriers under an applied stress. In fact, even in the case of the best-studied ML materials, we do not understand how differences in the crystal structure and trap levels contribute to the ML signal.

ML phenomena are intrinsically coupled to structural and piezoelectric properties of the material. The multi-mechano-sensitivity of certain ML materials is linked to properties of the lattice behavior, for example, since piezoelectric properties differ for each direction of the crystal, the ML response will depend on the direction and nature of the applied mechanical stimulus. The stress threshold of ML signal saturation of the material also depends on the local piezoelectric field strength and the trap depth. ML brightness on the other hand, depends on the number of traps that give rise to ML – these traps are different from those that give rise to persistent luminescence. At this time, we cannot directly determine piezoelectric constants along the different lattice directions, the local piezoelectric constant near a crystal defect, or the depth and concentration of traps associated with ML. Consequently, most groups use indirect methods to establish relationships among ML intensity, multi-mechano-sensitivity, stress threshold, crystal structure and defects. Fortunately, computer simulation methods are quite effective in modelling and predicting deformations and defects in crystal structures, and so future advances in our understanding the mechanism of ML may depend on encouraging collaborations between computational and experimental scientists. A deeper understanding of the mechanism of ML in trap-controlled

materials could emerge from experimental-theoretical collaborations that consider a wider range of trap-controlled materials, rather than the handful of true high-performance ML materials. In summary, we believe that a thorough understanding of the nano- and microscopic properties of ML materials coupled with detailed characterization of ML materials and their mechano-optical properties will help the field move from a discovery based approach to prepare high-performance ML materials to one guided by rational design.

The third challenge is to advance practical applications of ML materials. We have summarized diverse applications of ML materials, including the detection of “invisible” cracks in solid materials, tracking crack propagation in dynamic mechanical systems, and imaging the distribution of stress in artificial bones and joints. The introduction of ML composite materials, in which micro- or nanoscale ML particles are embedded within thin films or in elastic polymers has accelerated the application of ML materials as stress sensors. These coating materials can be applied as a spray or polymer sheet to any target structure. Images of the ML of these coatings, recorded with a sensitive CCD camera, enable remote monitoring of stress distributions in target structures, including bridges and buildings. The most striking applications of ML imaging technologies comprising ML composite materials, network CCD cameras and image analysis systems were reported by the Xu group on imaging cracks/strain/stress distributions of concrete and steel components in the working bridges. ML-based sensor systems also hold promise to identify structural damage, cracks and leaks on the internal face of pipes and tubing.

Our review included a discussion of emerging and novel applications of ML materials and ML composite materials, including mechanically-driven light sources and displays, self-illuminating probes, and approaches to map stress distributions in artificial bones and joints. Finally, we summarized applications of multi-mechano-responsive ML composite materials for mechanically-driven lighting units and displays whose ML emission can be tuned over a broad range of emission wavelength (UV to NIR).

Most applications of ML materials record ML signals in terms of a relative intensity – consequently, it is difficult to compare the performance of different ML devices, or to properly assess claims of the superior ML properties of new materials. Relevant here is the widespread use of relative measures of the ML intensity, which makes it difficult to compare the ML intensity of ML materials between labs. For example, the ML intensity is sensitive to power of the optical excitation, the time-delay between photoexcitation and recording of the ML signal, the rate of compression and related properties of the mechanical perturbation, and finally environmental factors. These instrumentation and measurement factors must be exactly defined and adhered to strictly for meaningful and quantitative comparisons of the ML properties of new materials. To this end, we believe that the ML field will advance more quickly if it adopts robust standardization and testing protocols that allow researchers to report ML responses of ML materials to defined mechanical perturbations absolute terms, or at least in terms of a referenced or calibrated signal.

We started this review by drawing attention to the pioneering discovery made by Francis Bacon on fractoluminescence. His discovery set in motion an interest in the ML materials and ML phenomena that have endured for more than four centuries – most of these studies have focused on the fractoluminescence and triboluminescence of natural materials and chemicals. Fractoluminescence is an irreversible process, which greatly limits its application to fracture sensing. The discovery of trap-controlled ML materials and ML composite materials that exhibit robust, repeatable and reproducible ML within their non-destructive limit has led to a resurgence of interest in ML phenomena. In fact, the number of ML probes and ML-based devices for real-world applications reported since 1999 outnumbers that reported between 1605 and 1999. Looking ahead, we anticipate that research on ML over the next 20 years will lead to an exponential increase in the number of high-performance ML materials, driven in part by a better understanding of ML mechanisms in trap-controlled materials. These developments will further drive applications of ML materials and their composite materials to solve real-world problems.

Acknowledgments

This work was supported by the grants awarded to J.C. Zhang from the National Natural Science Foundation, China (11774189 and 11404181), grant awarded to X. Wang from the National Natural Science Foundation, China (51572195), grants awarded to C. N. Xu by JSPS KAKENHI, Japan (JP25249100, JP16F16076 and JP17H06374), and grants awarded to G. Marriott from the Tsinghua-Berkeley Shenzhen Institute, China and the NIH, United States (5R21CA199512-02). We thank all ML team members of AIST.

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Jun-Cheng Zhang obtained his BS degree from Qingdao University in 2005. He completed his MS and PhD degrees from Tongji University in 2008 and 2011, respectively. From 2010 to 2011, he researched as a visiting PhD student at Kyushu University and National Institute of Advanced Industrial Science and Technology (AIST, Xu Lab), Japan. In 2010, he was awarded a doctoral scholar newcomer award from the Ministry of Education, China. He joined the College of Physics at Qingdao University in 2011, and became a distinguished professor in 2015. His research interests include the development, mechanism, and application of luminescent materials and devices.

Xusheng Wang obtained his BS degree from Zhengzhou University in 1982, and his MS degree from Xidian University in 1985. He received his PhD degree in Xi'an Jiaotong University in 1997. From 1996 to 1997, he worked as a visiting researcher in Kyushu University, Japan. From 2000 to 2003, he worked as a special researcher in Tokyo Institute of Technology, Japan. From 2003 to 2005, he worked as a special researcher in National Institute of Advanced Industrial Science and Technology (AIST, Xu Lab), Japan. He joined Tongji University as a full professor in 2005. His research interests involve the design and application of devices based on ferroelectrics and multifunctional materials.

The Marriott laboratory conducts innovative research at the interface of bioengineering, chemistry, biophysics, nanotechnology and chemical biology. The long-term goal of our studies is to understand molecular mechanisms that underlie complex processes, including motility, tumour metastasis and stem cell differentiation. These studies benefit from outputs of a long-standing program of research on the design, synthesis and application of optical probes and photo-actuators for high-contrast imaging and control of protein interactions, and early detection of tumours. **Gerard Marriott** received a BSc (Hons) in Biochemistry from Birmingham University in the UK in 1980, and a PhD from the University of Illinois in 1987 under the tutorship of Gregorio Weber, a pioneer in biological spectroscopy. Marriott was awarded prestigious fellowships from the Alexander von Humboldt Stiftung and the Japan Society for the Promotion of Science working with Profs. Thomas Jovin and Kazuhiko Kinoshita, respectively. His postdoctoral research led to the introduction and application of a new optical approach to control the activity of proteins, and the development of time-delayed fluorescence lifetime imaging microscopy. As a C3-professor at the Max Planck Institute for Biochemistry in Martinsried, he applied caged proteins to understand the molecular basis of muscle contraction and cell motility and quantitative and dynamic fluorescence microscopy techniques to map functional dynamics of protein complexes during muscle contraction and cell motility. He was recruited to the University of Wisconsin-Madison in 1999 to lead a new biophotonics initiative. In 2009 he moved to UC-Berkeley where his group works on: the engineering of human platelets and exosomes as living vehicles for targeted delivery of imaging probes and immuno-therapeutics to cancer cells. He

also has interests in developing novel biosensors for fluorescence anisotropy imaging, and high-contrast NIR1 and NIR2 in vivo imaging of cancer cells, and smart biomaterials to control properties of the tumour microenvironment, and biosensors suitable for wearable devices and at-home diagnostics. He was the JSPS visiting professor in 2016 at National Institute of Advanced Industrial Science and Technology (AIST, Xu Lab), Japan. Marriott holds guest professorships at the South-East University Nanjing, and at Tsinghua University, Shenzhen.

Chao-Nan Xu received a BS in electronics from Xi'an Jiaotong University in China in 1984, and a PhD in material sciences from Kyushu University in Japan in 1991. She is the funding chair of Mechanoluminescence Technology Consortium, the Principal Research Manager, and the leader of the research team at National Research Institute of Advanced Industrial Science and Technology (AIST) since 2001. She also serves concurrently as the full Professor of New Material Lab at Kyushu University since 2005. Prof. Xu discovered the intensive new type of elasticoluminescence, and established the hybrid concept of inorganic/organic composite coating (skins) and the principle for quantitative analysis of stress/strain and faults. She also made discovery of grain size effect for gas sensitivity. Her breakthroughs in innovative materials and novel applications open the new era in 400-years history of mechanoluminescence. She pioneered the new repeatable mechanoluminescent materials and their novel applications particularly in lighting, health care, and stress/strain visualization. Her research interests include functional materials, sensors and their applications.