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A single-phase full-color phosphor based on $\text{Ba}_3\text{MgSi}_2\text{O}_8$ co-activated with Eu^{2+} , Tb^{3+} , and Mn^{2+}

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Abstract

We present a rapid and energy-efficient microwave-assisted approach to prepare a single-phase full-color phosphor based on $\text{Ba}_3\text{MgSi}_2\text{O}_8$. The samples were prepared using a citric acid based sol-gel preparation pathway with a microwave-assisted heating step, which reduces the time required for the final heat treatment to less than 30 minutes. Thermogravimetric analysis was utilized to optimize the solution-based preparation prior to microwave heating. The structural properties of the obtained luminescent materials have been thoroughly investigated by means of X-ray powder diffraction and Rietveld analyses. To study the optical behavior, the excitation and emission spectra were recorded. Full-color emission is achieved using Eu^{2+} (blue), Tb^{3+} (green), and Mn^{2+} (red) as the activator ions. The thermally robust emission was investigated using temperature-dependent luminescence spectroscopy. The energy-transfer processes within the samples were studied using time-dependent spectroscopy, and the quantum yield of this true color phosphor as a function of the composition was determined.

Keywords: Phosphors, solid-state lighting, microwave preparation, merwinite, full-color

1. Introduction

Solid-state lighting based on phosphor-converted light-emitting diodes (pc-LEDs) is replacing both low-efficiency incandescent and mercury-containing fluorescent light sources due to lower energy consumption and longer lifetimes.[1, 2, 3, 4, 5, 6] Among the many classes of materials recently investigated for potential lighting applications, a significant number of reports have appeared on oxide hosts including aluminates[7, 8, 9], aluminosilicates[10, 11] and silicates.[12, 13] Within the silicates, $\text{Ba}_3\text{MgSi}_2\text{O}_8$ has been the focus of much research effort since the late 1960's[14, 15], mostly due to its good thermal stability of luminescence, high quantum yield, abundant constituents, and the potential for full-color emission. Phosphors based on $\text{Ba}_3\text{MgSi}_2\text{O}_8$ co-activated with Eu^{2+} and Mn^{2+} emitting blue and red light have been studied extensively. Earlier reports of tri-band (*i.e.*, blue, green and red) luminescence[12, 16, 17] from Eu^{2+} and Mn^{2+} co-activated samples have significant amounts of orthosilicate (Ba_2SiO_4) impurities, which exhibit a broad and

very efficient emission band centered around 505 nm.[18, 19] However, a true full-color emitting phosphor based on $\text{Ba}_3\text{MgSi}_2\text{O}_8$ has not yet been reported.

The elucidation of the $\text{Ba}_3\text{MgSi}_2\text{O}_8$ structure has also been in the center of much discussion. Originally described by Klasens *et al.* as isostructural to the monoclinic calcium analogue *merwinite* ($\text{Ca}_3\text{MgSi}_2\text{O}_8$),[20] the $\text{Ba}_3\text{MgSi}_2\text{O}_8$ structure was later been found to be closely related to the orthorhombic *glaserite* structure type of $\text{K}_3\text{Na}(\text{SO}_4)_2$. [19, 21] Recently, Park *et al.* used a combined neutron and X-ray diffraction study to determine the true structure, and found that $\text{Ba}_3\text{MgSi}_2\text{O}_8$ crystallizes in a structure with a trigonal space group $P\bar{3}$ (No. 147).[22]

As for most oxide phosphors, preparation usually relies on heating intimate mixtures of solid precursors at high temperatures on the order of hours, often under reducing atmospheres to stabilize the desired valence state of the dopant ions (textite.g., Eu^{2+} or Ce^{3+}). Microwave-assisted preparations, reported as early as the 1980s [23, 24], offer a energy efficient alternative to these more classical pathways at a fraction of the time. Recently, several different materials have been prepared employing microwave-assisted solid-state pathways, such as skutterudites[25], intermetallics[26, 27], and oxide phosphors.[28, 29, 30, 31, 32] We present the first true full-color phosphor $\text{Ba}_3\text{MgSi}_2\text{O}_8$ co-activated with Eu^{2+} , Mn^{2+} and Tb^{3+} , prepared by a rapid microwave-assisted sol-gel pathway. The phase purity and structural parameters have been carefully investigated and the relations between the optical and structural properties are uncovered by means of diffraction experiments and extensive optical studies, including the photoluminescence quantum yield and the thermal robustness.

2. Materials and Methods

Samples of $\text{Ba}_{2.97-x}\text{Eu}_{0.03}\text{Tb}_x\text{Mg}_{1-x}\text{Li}_x\text{Si}_2\text{O}_8$ were prepared *via* microwave-assisted sol-gel reactions. In a typical synthesis, a 2:1 mixture by volume of MilliPore (18 M Ω ·cm) water to ethanol was adjusted to a pH of 2-3 through the addition of several drops of glacial acetic acid (EMD). Subsequently, a 5-6 times excess in terms of metal cations amount of citric acid (99.5%, Alfa Aesar) was added and the solution was stirred until clear (~10 min at 500 rpm). Then, under constant stirring, stoichiometric amounts of BaCO_3 (99.95%, Alfa Aesar), $\text{Mg}(\text{NO}_3)_2$ hexahydrate (98%, Alfa Aesar), Tetraethylorthosilicate (TEOS, Sigma-Aldrich), $\text{Tb}(\text{NO}_3)_3$ pentahydrate (99.9%, Sigma-Aldrich), $\text{Eu}(\text{NO}_3)_3$ pentahydrate (99.9%, Sigma-Aldrich), MnCO_3 (99.9%, Sigma-Aldrich), and Li_2CO_3 (Sigma-Aldrich) were dissolved and the solution was allowed to slowly evaporate at 65°C until a transparent gel formed. This gel was then dried at 125°C overnight and finely ground. The ground powder was then heated to 400°C and held for 4 h, and finally heated to 650°C and held for 6 h. The resultant powder was reground and heat-treated in a microwave setup, as described elsewhere.[28, 29, 26]

Laboratory powder X-ray diffraction (XRD) data were obtained using Cu K_α radiation (Philips

X'Pert) over the angular range $15^\circ \leq 2\theta \leq 90^\circ$ with a step size of 0.016° . Full profile fits employing the Le Bail method[33] were obtained using TOPAS Academic.[34] TGA was carried out using a ThermoGravimetric Analyzer (METTLER TGA/sDTA851e) under N_2 /air scanning the temperature range between 25°C and 1000°C at a heating rate of $10^\circ\text{C}/\text{min}$.

Photoluminescence (PL) spectra were obtained on a Perkin Elmer LS55 spectrophotometer, scanning a wavelength range of 325 nm to 825 nm. The samples were thoroughly ground and subsequently mixed within a silicone resin. A small amount of this mixture was administered onto a $10 \times 10 \text{ mm}^2$ piece of glass and cured at 150°C for 15 minutes. Photoluminescence quantum yield (PLQY) was measured with excitation wavelengths of 351 nm and 405 nm using an argon laser and an experimental protocol as described by Greenham *et al.*[35] Further details of PLQY measurements as well as the procedure to determine the temperature-dependence of the photoluminescence properties are detailed elsewhere.[28] Luminescence life-time measurements were performed using the Time-Correlated Single Photon Counting (TCSPC) technique.[36] Approximately 200 femtosecond (fs) excitation pulses with wavelength 440 nm were generated by doubling the fundamental frequency of fs – Ti:Sapphire laser (Coherent Mira 900) pulses in a commercial optical harmonic generator (Inrad). The laser pulse rate was reduced to 200 KHz by a home-made acousto-optical pulse picker in order to avoid any saturation effects. The TCSPC system is equipped with an ultrafast micro-channel plate photomultiplier tube detector (Hamamatsu R3809U-51), an electronics board (Becker & Hickl SPC-630), and has an instrument response time of about 60-65 picoseconds. The triggering signal for the TCSPC board was generated by sending a small fraction of the laser beam onto a fast (*i.e.*, 400 MHz bandwidth) Si photo-diode (Thorlabs Inc.). The fluorescence signal was dispersed in a monochromator (Acton Research SPC-500) after passing through a pump blocking, long wavelength-pass, autofluorescence-free, interference filter (Omega Filters, ALP series). The monochromator is equipped with a CCD camera (Roper Scientific PIXIS-400), allowing for monitoring of the time-averaged fluorescence spectrum. Luminescence transients were not deconvolved with the instrument response function since their characteristic time-constants were much longer than the width of the system response to the excitation pulse.

3. Results and discussion

As a first step, we have investigated the formation process of the desired $\text{Ba}_3\text{MgSi}_2\text{O}_8$ phase, prepared by the microwave-assisted sol-gel pathway, using thermogravimetric analyses. The TGA curve of a representative gel sample dried at 125°C is presented in Fig. 1.

The total weight loss of the sample is $\sim 80\%$, mostly due to the thermal decomposition of the citric acid, citrate complexes, and volatile precursors. Most of the mass loss occurs up to 600°C while very little additional loss is seen when increasing the temperature to 1000°C . The TGA curve contains a total of two significant weight loss stages; one located between room-temperature and

below 200°C, where the corresponding DTA curve reveals an endothermic peak, and another weight loss between 200°C and ~650°C, where the DTA shows several exothermic peaks. These results are comparable to the our earlier studies on the sol-gel preparation of orthosilicates.[32] In short, the weight loss occurring below 200°C is due to the desorption of residual water and surface agents in the dried gel. The main combustion of the chelating agent in the specimen occurs in a multi-step process, starting at around 250°C and is mostly finished at 600°C. The DTA curve shows two broad exothermic peaks in this temperature region. Therefore, in order to completely decompose the citric acid and citric acid complexes before microwave heating, the phosphor samples were heated to 650°C. This heating step reduces the amount of residual carbon impurities that would be present if the dried gel was processed in the microwave without a preheating step. Preventing carbon impurities is important because carbon residue in the samples leads to discoloration that is correlated with dramatic decreases in optical performance. Concomitant sample preparations that did not make use of a rapid microwave step and instead relied on conventional furnace heating yielded multiphase samples with a marked tendency for the stable orthosilicate Ba₂SiO₄. We believe the rapid final preparation step also helps retain the relatively volatile Li in the final product.

3.1. Ba₃MgSi₂O₈, co-activated with Eu²⁺ and Tb³⁺

As mentioned in the introduction, green emission observed in Ba₃MgSi₂O₈ samples activated with Eu²⁺ is due to a significant amount of an orthosilicate (Ba₂SiO₄:Eu²⁺) impurity.[18] This impurity phase shows a strong, broad emission band in the green region, centered around 505 nm. Several attempts have been made to systematically tune the intensity of the green emission of Ba₂SiO₄:Eu²⁺,[37] but the amount of Ba₂SiO₄:Eu²⁺ unpredictably varies from sample to sample, making this scheme difficult for the preparation of full-color emitting materials.

To circumvent this issue, we have co-activated Ba₃MgSi₂O₈ with Eu²⁺ ions to achieve emission in the blue, with Tb³⁺ ions, which are known to yield green emission due to the $f \rightarrow f$ transitions within the trivalent terbium ion. Nominally, we replaced the divalent barium with a trivalent cation. Therefore, appropriate amounts of Mg²⁺ were substituted with Li⁺ to maintain charge neutrality. Mg²⁺ and Li⁺ were used due to their very similar ionic radius ($r_{\text{Li}^+} = 0.76 \text{ \AA}$ and $r_{\text{Mg}^{2+}} = 0.72 \text{ \AA}$ for CN = 6) and similar chemical behavior. The laboratory X-ray diffraction patterns of the investigated Eu²⁺ and Tb³⁺ samples are found in Fig. 2. Amounts of up to 10 mol-% terbium and lithium can be introduced without the formation of any significant impurities. The relatively significant solubility is interesting to note given the dissimilar ionic radii of Tb³⁺ and Ba²⁺. However, when analyzing the structure as determined elsewhere using neutron diffraction,[22] bond valence sums show that for three unique barium sites, two sites are underbonded (1.1 and 1.6 for Wyckoff positions 1b and 2d, respectively) and one site is over bonded (2.3 for the 6g site). The overbonded site suggests the 6g site might be too small for the barium, thereby enabling the 10 mol-% terbium solubility limit observed in the current work.

All specimens investigated here (*i.e.*, prepared *via* a microwave-assisted sol-gel method) exhibit very good phase purity, as demonstrated by a full-profile pattern fit (Le Bail fit) of a specimen co-activated with 1% Eu^{2+} and 10% Tb^{3+} (Fig. 3). Negligible amounts of secondary silicates are present. We have also found that omission of the charge compensator ion or replacing Si^{4+} with Al^{3+} leads to a more side product formation, even at low terbium concentrations. The Le Bail fit shows that the major phase is $\text{Ba}_3\text{MgSi}_2\text{O}_8$, and only minor amounts of silicate impurities, which are not observed to influence the optical properties significantly, are present. Samples prepared using the microwave-assisted pathway, despite the much shorter reaction time, showed better phase purity than reference samples prepared using conventional pathways.

The excitation spectrum of $\text{Ba}_3\text{MgSi}_2\text{O}_8$ activated with 1% Eu^{2+} (Fig. 4(a)) exhibits a broad band with peaks at 335 nm and 358 nm, and a shoulder ~ 405 nm. These bands are due to the $4f^7 \rightarrow 5d^14f^6$ transitions within the Eu^{2+} ions. The excitation band reaches into the near-UV part of the spectrum, revealing the possibility to excite $\text{Ba}_{2.97}\text{Eu}_{0.03}\text{MgSi}_2\text{O}_8$ with near-UV light emitting diodes currently used in solid-state lighting. The emission spectrum under 395 nm excitation consists of a very intense band centered around 435 nm (FWHM ~ 35 nm). Both emission and FWHM values are in good agreement with earlier reports.[14, 15, 21]

It has been shown that the crystal field depression, also called the spectroscopic redshift, $D(Q, A)$, can be expressed by the following equation:

$$D(Q, A) = E_{Afree}(n, Q) - E_{abs}(n, Q, A) \quad (1)$$

where $E_{Afree}(n, Q)$ is a constant for each lanthanide ion and $E_{abs}(n, Q, A)$ is the observed value for the lowest $f \rightarrow d$ absorption.[38, 39] The variables n , Q and A represent the number of electrons in the f -shell, the oxidation state, and the effect of the host crystal, respectively. Using the tabulated data of $E_{Afree}(n, Q) = 34000 \text{ cm}^{-1}$ for Eu^{2+} and the value that we have determined for $E_{abs}(n, Q, A)$ (*i.e.*, $= 24691 \text{ cm}^{-1}$ at 405 nm), $D(Q, A)$ is calculated to be 9308 cm^{-1} for the microwave-prepared sample, which is in excellent agreement with the tabulated value in the literature.[40]

When trivalent terbium ions are introduced into the host lattice, several sharp excitation peaks in the region between 300 nm and 500 nm are observed (Fig. 4(b)). The overlap in the emission spectrum of $\text{Ba}_{2.97}\text{Eu}_{0.03}\text{MgSi}_2\text{O}_8$ with the excitation bands of Tb^{3+} are due to several $f \rightarrow f$ excitation pathways within the terbium ions. When excited with 365 nm radiation, samples activated with 10% of Tb^{3+} exhibit green emission with multiple sharp bands observed between 500 nm and 700 nm. These peaks have been assigned to several $^5D_4 - ^7F_J$ transitions in the Tb^{3+} ion.[41]

Due to the spectral overlap between the emission spectrum of Eu^{2+} and parts of the excitation spectrum of Tb^{3+} , we can expect energy transfer between these two ions if both are introduced into the host lattice. The emission spectra of a sample co-activated with 1% Eu^{2+} and 10% Tb^{3+}

are presented in Fig. 4(c). Under 395 nm excitation, features from both dopant ions are present, including the broad blue emission band due to Eu^{2+} and the sharp transitions of the Tb^{3+} ion. The excitation spectra for the most intense band (*i.e.*, 544 nm for Tb^{3+}) show strong similarities to the excitation spectrum of the solely europium-activated $\text{Ba}_3\text{MgSi}_2\text{O}_8$, suggesting an energy transfer effect between the two dopants, where the europium ions act as both sensitizer and activator.

The limits of introducing Tb^{3+} on the optical properties are shown in Fig. 5. The observed emission spectra exhibit a broad emission in the blue as well as emission bands attributed to Tb^{3+} , with the most prominent emission centered ~ 544 nm. As expected, the relative intensity of the green emission increases with the addition of more terbium into the host lattice. The broad and intense emission centered around 505 nm is characteristic of the impurity $\text{Ba}_2\text{SiO}_4\text{:Eu}^{2+}$, [14] thus confirming the maximum amount of Tb^{3+} before impurity formation, observed using XRD. We are interested in samples without Ba_2SiO_4 , and have therefore limited the amount of terbium to a maximum of 10 mol% in all further investigated samples.

Another important metric for relevant luminescent materials is their thermal stability. The temperature-dependent emission spectra between 77 K and 473 K are presented in Fig. 6 and Table 1. Several observations are important. There is no significant shift in the position of the emission band maximums originating from both dopant ions. While the $f \rightarrow f$ transitions usually show only very little temperature dependence in regards to their position, $5d \rightarrow 4f$ transitions very often show a strong shift with an increase in temperature.[29] Additionally, it is observed that the emission intensity is strongly temperature dependent. At room-temperature, the intensity has dropped to about 50% of the value observed at 77 K. In general, we refer to the temperature at which the luminescence intensity is 50% of the 77 K value at $T_{1/2}$. Finally, the bands originating from the two dopant ions show a different thermal robustness, meaning that the intensity of the green emission (Tb^{3+}) decays faster than the blue Eu^{2+} emission. This results in different quenching temperatures determined from the emission spectra, namely $T_{1/2}(\text{total}) = 313$ K, $T_{1/2}(\text{Eu}^{2+}) = 323$ K and $T_{1/2}(\text{Tb}^{3+}) = 285$ K, which leads to a change in color temperature and CIE coordinates, as shown in Table 1.

Since emission intensities are not satisfactory to fully determine thermal quenching behavior[42], we have elucidated the temperature-dependence of the photoluminescence lifetime of the Eu^{2+} emission. Although there are three potential emission sites in the lattice due to the ions present, only the decay behavior at the maximum of the blue emission band at 440 nm has been investigated. The transfer efficiency between the europium and the terbium ions at 77 K has been investigated in an attempt to detect the presence of any non-radiative pathways (*i.e.*, phonon and multi phonon relations). The average decay time, $\tau_{\text{avg.}}$, can be calculated from decay curves using a ratio of the integrated intensities as follows: [43]

$$\tau_{avg.} = \frac{\int_0^{\infty} tI(t)dt}{\int_0^{\infty} I(t)dt} \quad (2)$$

The obtained decay curves for samples doped with Eu^{2+} and co-doped with Eu^{2+} and Tb^{3+} are presented in Fig. 7. The average decay time of the $5d^14f^6 \rightarrow 4f^7$ transition within the Eu^{2+} ions without terbium is found to be ~ 285 ns (*i.e.*, 290 ns from the single-exponential fit and 281 ns from the calculation according to Eq. 2), which is comparable to values found for similar host lattices.[44] The experimentally determined lifetime can be expressed as:

$$\frac{1}{\tau} = \frac{1}{\tau_0} + A_{nr} + P_t \quad (3)$$

where τ_0 is the radiative lifetime of the monitored emission, A_{nr} is the decay rate due to non-radiative pathways, and P_t is the energy transfer rate.

If there exists a non-radiative energy transfer pathway between the Eu^{2+} ions, which would act as both the activator and the sensitizer for Tb^{3+} , the fluorescence lifetimes monitored at 77 K of the emission at 440 nm should decrease. In Eu^{2+} and Tb^{3+} co-activated samples, the decay time decreases to an average value of ~ 240 ns due to the energy transfer between the Eu^{2+} and Tb^{3+} ions. In addition, the decay curve of the emission monitored at 440 nm deviates slightly from a mono-exponential decay. A bi-exponential fit yields two different decay constants, $\tau_1 = 42$ ns and $\tau_2 = 238$ ns, suggesting there are at least two different pathways for energy transfer between dopant ions present. A possible reason for this behavior is that the energy transfer efficiency between Eu^{2+} and Tb^{3+} ions varies with the crystallographic site each ion occupies. The efficiency of the energy transfer can be expressed by:

$$\eta_T = 1 - \frac{\tau_s}{\tau_{s0}} \quad (4)$$

where τ_s is the decay time in the presence of the donor and τ_{s0} is the decay time in the absence of the donor.[45] A transfer efficiency of $\sim 20\%$ between Eu^{2+} with 10% $\text{Tb}^{3+}/\text{Li}^+$ was calculated using the average lifetime values observed here.

For an allowed transition, such as the $5d^14f^6 \rightarrow 4f^7$ transition within Eu^{2+} ions, the decay time should be independent of the temperature until elevated temperatures, where more non-radiative pathways become accessible. As shown in Fig. 7, the decay behavior of the solely europium-activated sample shows almost no deviation from a mono-exponential decay until 353 K, proving that the $4f^7 \rightarrow 5d^14f^6$ transition is robust at elevated temperatures. The values found here are lower than the quenching temperatures found by Blasse *et al.*[14] The temperature-stability changes notably with the inclusion of terbium ions into $\text{Ba}_3\text{MgSi}_2\text{O}_8$. As can be seen from Fig. 7,

both the decay curve deviates from a mono-exponential decay, even at 77 K, and the average life-time decreases notably with an increase in temperature. This is explained by the presence of more non-radiative pathways available due to the introduction of the dopant ions (*i.e.*, Tb^{3+} and Li^+), leading to a quicker depopulation of the excited states. This is in strong accordance with the measured trend in emission intensity.

3.2. $\text{Ba}_3\text{MgSi}_2\text{O}_8$, co-activated with Eu^{2+} , Tb^{3+} , and Mn^{2+}

To achieve a full-color phosphor, *i.e.*, a material with emission bands covering the complete visible range of the electromagnetic spectrum, $\text{Ba}_3\text{MgSi}_2\text{O}_8$ was co-activated with Tb, Mn, and Eu ions, where Eu acts as both a sensitizer and activator. Optimization of the sol-gel preparation route yielded samples with $\sim 100\%$ phase purity, as shown in Fig. 8. Only trace amounts of barium orthosilicate were detected.

To obtain tri-band emission for white light emission, different concentrations of Eu^{2+} , Tb^{3+} and Mn^{2+} have been incorporated into the host structure. Changing the dopant concentration allows tuning of the green emission band. A concentration of $\sim 2\text{-mol}\%$ Eu^{2+} and $\sim 1.5\text{-}2\text{-mol}\%$ Mn^{2+} was found as the optimized dopant concentration for the most efficient samples. Small amounts of Tb^{3+} were then added to obtain the desired emission band in the green part of the visible spectrum, and the obtained photoluminescence data under near-UV excitation is presented in Fig. 9. It is evident that the more Tb^{3+} is added to the host, the more intense the green emission. The red emission becomes more intense in terms of relative intensity values, but this effect is negligible, as adding amounts greater than 10% of Tb^{3+} seems to have little effect on the emission intensity of the green emission band at around 542 nm, and the red emission increases only slightly.

The outer lying d -orbitals of Eu^{2+} are very sensitive to changes in the bond length and associated with changes in the crystal field splitting. The crystal field splitting (Dq) can be expressed by the following equation:

$$Dq = \frac{1}{6}Ze^2\frac{r^4}{R^5} \quad (5)$$

where Z is the valence of the coordinating anion, e is the elemental charge, r is the radius of the d -wavefunction and R is the bond length between the activator ion and the coordinating anion.[46] In the current work, a clear shift towards longer wavelengths with the addition of Tb^{3+} into the europium-activated host is observed. The formula implies that through the introduction of the smaller Tb^{3+} (*i.e.*, $r_{\text{Ba}^{2+}}=1.47\text{ \AA}$, $r_{\text{Tb}^{3+}}=1.095\text{ \AA}$, CN = 9) on the Ba^{2+} site(s), the bond length of Eu—O between the surrounding oxygen ligands and the Eu^{2+} ions decreases. An 11 nm red shift in the emission maximum of the europium emission is observed. Interestingly, the $d \rightarrow d$ of the Mn^{2+} ion seems unaffected by this, as no significant shift in the emission wavelength is observed.

As shown by the raw data in Table 2 and the CIE chromaticity diagram in Fig. 10, an increase in the terbium concentration moves the color coordinates closer to the desired white point (0.33,

0.33). However, due to the solubility limit of Tb^{3+} and Li^+ in the host structure, a blue hue remains in the emitted radiation. The most efficient full-color emission and the closest to emission to full-color white occurs in samples activated with the optimized 2% Eu^{2+} , 10% Tb^{3+} and 2% Mn^{2+} . Therefore, all further optical studies have been carried out on these specimens.

The room-temperature emission and excitation spectra of samples with the composition $\text{Ba}_{2.64}\text{Eu}_{0.06}\text{Tb}_{0.3}\text{Mg}_{0.68}\text{Mn}_{0.02}\text{Li}_{0.3}\text{Si}_2\text{O}_8$ are presented in Fig. 11. The sample shows a broad and intense emission band in the blue, centered around 440 nm, which originates from the $5d \rightarrow 4f$ transition within the europium ion. The green emission band, with a maximum at around 542 nm, cooperates with the broad, red emission due to the $d \rightarrow d$ transitions of the Mn^{2+} ion to complete the full color emission. This comparison of the excitation spectra recorded at the respective maximum of the three emission bands reveals that there is energy-transfer present, due to the observation that all three excitation spectra exhibit the same fine structure as the sample with only Eu^{2+} .

The thermal robustness of the full-color emitting samples has been investigated. The emission spectra under 395 nm excitation between 77 K and 473 K, normalized to the absolute maximum of the emission intensity at 77 K is shown in Fig. 12. The degradation in intensity of Eu^{2+} , Tb^{3+} , and Mn^{2+} samples is equally pronounced as in the case of Eu^{2+} and Tb^{3+} co-activation. At room-temperature, the total integrated emission intensity has dropped to $\sim 50\%$ of the value at 77 K, with $T_{1/2}$ values of 265 K for the blue, 275 K for the green, 355 K for the red, and 300 K for the total emission of the sample, which are lower than earlier reports.[47, 14]

Dorenbos has shown that in alkaline-earth compounds, the thermal quenching of the Eu^{2+} luminescence is mostly due to the promotion of an electron from the divalent europium to the conduction band of the host lattice.[47] Using the relation provided, the activation energy of the thermal quenching process (ΔE) can be calculated using the following expression:

$$\Delta E = \frac{T_{1/2}}{680} \text{ eV} \quad (6)$$

where $T_{1/2}$ is the experimentally obtained quenching temperature for the respective transition. Using the values obtained from the temperature-dependent studies in the present work, an activation energy of 0.390 eV for the blue, 0.404 eV for the green, 0.522 eV for the red, and 0.442 eV for the combined full-color emission is calculated.

A comparison of the temperature-dependent lifetime curves of samples with different dopant ions reveals that the decrease in efficiency is mostly due to the strong diminishing of the Eu^{2+} lifetime in combination with terbium. Although a rather high transfer efficiency was determined at low temperatures, the addition of terbium and lithium ions to the host leads to very significant decrease in the average lifetime of the europium emission, due to more efficient non-radiative relaxation pathways. Figure 13(b) shows the calculated average lifetimes as a function of temperature,

and it becomes evident that the strong decrease is mostly due to Eu-Tb pair interactions.

Finally, the quantum yield of the prepared samples has been experimentally determined. The room temperature quantum yield is $\sim 10\%$, and the addition of certain flux materials, such as NH_4F , increases this value to 15% . However, more impurities were present, which can be seen from the steep drop in emission intensity at 473 K , where the quantum yield has fallen to $\sim 2.5\%$. Further optimization of the flux materials used might mitigate impurities without decreasing the efficiency.

4. Conclusions

We have successfully employed a microwave-assisted sol-gel pathway to prepare the widely studied silicate-based phosphor, $\text{Ba}_3\text{MgSi}_2\text{O}_8$, co-activated with europium, terbium and manganese. Through the combination of the sol-gel method and microwave heating, we have obtained samples with very high phase purity not obtainable using furnace-based preparation methods. For the first time, we demonstrate that $\text{Ba}_3\text{MgSi}_2\text{O}_8$ exhibits tri-band (*i.e.*, red, green and blue) emission due to the dopant ions and not due to impurity phases such as Ba_2SiO_4 . The light produced is a cool white light with warmer colors limited by the solubility limit of Tb^{3+} in $\text{Ba}_3\text{MgSi}_2\text{O}_8$. The optical characterization has shown that the quantum yield and temperature-stability of the samples can be improved. One such method is through cation substitution.[48] The present work successfully demonstrates co-doping as a means of tuning the color of a phosphor to achieve a broad emission spectra. Further optimization, *e.g.*, through the use of fluxes and compositional tuning with ions such as strontium and calcium, may improve the efficiency, leading to more full-color strategies for applications in solid-state white lighting devices.

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Figure and table captions

Fig. 1 Thermogravimetric analysis of the decomposition of the dried gel (125°C) of $\text{Ba}_{2.64}\text{Eu}_{0.06}\text{Tb}_{0.3}\text{Mg}_{0.68}\text{Mn}_{0.02}\text{Li}_{0.3}\text{Si}_2\text{O}_8$. The dotted line represents the DTA curve recorded simultaneously.

Fig. 2 Laboratory X-ray diffraction data of $\text{Ba}_{2.97-x}\text{Eu}_{0.03}\text{Tb}_x\text{Mg}_{1-x}\text{Li}_x\text{Si}_2\text{O}_8$ with different terbium (lithium) concentrations. The dashed lines indicate the positions of the most intense Bragg peaks of the silicate impurities observed with 15 mol-% terbium.

Fig. 3 Le Bail fitting of laboratory ($\text{Cu K}\alpha$) X-ray diffraction data of $\text{Ba}_{2.67}\text{Eu}_{0.03}\text{Tb}_{0.3}\text{Mg}_{0.7}\text{Li}_{0.3}\text{Si}_2\text{O}_8$ demonstrates only negligible amounts of other silicates can be found in the samples.

Fig. 4 PL and PLE spectra for $\text{Ba}_3\text{MgSi}_2\text{O}_8$ samples with (a) 1% Eu^{2+} , (b) 10% Tb^{3+} and (c) 1% Eu^{2+} and 10% Tb^{3+} . All spectra have been recorded at room-temperature.

Fig. 5 Photoluminescence spectra under 365 nm excitation of $\text{Ba}_3\text{MgSi}_2\text{O}_8$ samples with varying terbium concentrations. The europium content has been fixed at 1-mol%. The inset in each plot shows an image of the emission color under 365 nm excitation.

Fig. 6 Temperature-dependent emission spectra for a typical $\text{Ba}_3\text{MgSi}_2\text{O}_8$ sample, co-activated with 1% Eu^{2+} and 10% Tb^{3+} . The bar on the right represents the spectral color of the emitted light. The emission intensity has been normalized to the maximum value at 77 K.

Fig. 7 Low-temperature photoluminescence decay curves for $\text{Ba}_3\text{MgSi}_2\text{O}_8$ samples with (a) 1% Eu^{2+} , (b) 1% Eu^{2+} and 10% Tb^{3+} and (c) the comparison of both curves.

Fig. 8 Le Bail fitting of laboratory X-ray diffraction data of $\text{Ba}_{2.67}\text{Eu}_{0.03}\text{Tb}_{0.3}\text{Mg}_{0.69}\text{Mn}_{0.01}\text{Li}_{0.3}\text{Si}_2\text{O}_8$ show negligible amounts of Ba_2SiO_4 impurities.

Fig. 9 PLE spectra for $\text{Ba}_3\text{MgSi}_2\text{O}_8$ samples doped with 2% Eu^{2+} , 2% Mn^{2+} and various amounts of Tb^{3+} . The spectra have been recorded at room-temperature.

Fig. 10 Commission Internationale de l'éclairage x-y coordinates of $\text{Ba}_3\text{MgSi}_2\text{O}_8$ samples doped with Eu, Tb, and Mn.

Fig. 11 Room-temperature PL and PLE spectra for $\text{Ba}_{2.64}\text{Eu}_{0.06}\text{Tb}_{0.3}\text{Mg}_{0.68}\text{Mn}_{0.02}\text{Li}_{0.3}\text{Si}_2\text{O}_8$.

Fig. 12 Temperature-dependent photoluminescence spectra for $\text{Ba}_3\text{MgSi}_2\text{O}_8$ samples doped with 2% Eu^{2+} , 10% Tb^{3+} and 2% Mn^{2+} .

Fig. 13 Temperature-dependent photoluminescence lifetime data, and temperature dependence of the photoluminescence lifetime for the different $\text{Ba}_3\text{MgSi}_2\text{O}_8$ samples, doped with (a) 1%

Eu^{2+} , (b) 1% Eu^{2+} 10% Tb^{3+} , (c) 1% Eu^{2+} 10% Mn^{2+} and (d) 2% Eu^{2+} , 10% Tb^{3+} and 2% Mn^{2+} .

Table 1 Spectroscopic properties of a typical $\text{Ba}_3\text{MgSi}_2\text{O}_8$ sample, co-activated with 1% Eu^{2+} and 10% Tb^{3+} .

Table 1 Spectroscopic properties of a typical $\text{Ba}_3\text{MgSi}_2\text{O}_8$ sample, co-activated with 2% Eu^{2+} , 10% Tb^{3+} and 2% Mn^{2+} .

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Fig. 1:

Fig. 2:

Fig. 3:

Fig. 4:

Fig. 5:

Fig. 6:

Fig. 7:

Fig. 8:

Fig. 9:

Fig. 10:

Fig. 11:

Fig. 12:

Fig. 13:

Table 1

T (K)	integrated Intensity	CIE x	CIE y	Ra
77	1	0.20	0.16	66
295	0.59	0.19	0.14	59
473	0.06	0.19	0.15	62

Table 2

T (K)	norm. Int.	(Eu ²⁺)	(Tb ³⁺)	(Mn ²⁺)	CIE x	CIE y	Ra
77	1	1	1	1	0.24	0.22	83
295	0.51	0.41	0.40	0.63	0.29	0.26	65
473	0.13	0.07	0.09	0.20	0.35	0.33	84

TOC Graphic: