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## Thermally stimulated luminescence from rare-earth-doped barium copper oxides

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We report the first thermally stimulated luminescence (TSL) and emission-spectra measurements of x-ray-induced defects in  $\text{Ho}_{1.5}\text{Ba}_{1.5}\text{Cu}_2\text{O}_x$  and  $\text{GdBa}_2\text{Cu}_3\text{O}_x$  in the temperature interval 80–300 K. The Gd-doped oxide exhibits a single TSL glow peak at 195 K with concomitant single-band emission with maximum at 500 nm. Two TSL glow peaks (160 and 172 K) are observed in  $\text{Ho}_{1.5}\text{Ba}_{1.5}\text{Cu}_2\text{O}_x$ , whose spectral emission is characterized by complex, temperature-dependent maxima at 450 and 660 nm. Possible defect mechanisms are discussed.

The discovery of superconductivity in oxygen-deficient perovskites La-Ba-Cu-O [ $T_c \sim 30$  K (Ref. 1)] and Y-Ba-Cu-O [ $T_c \sim 90$  K (Refs. 2–4)] has initiated intense experimental and theoretical research efforts to understand their properties. It is clear already that the method of preparation,<sup>5,6</sup> i.e., material stoichiometry, sintering temperature, etc., is very important in establishing favorable superconducting parameters. The role of oxygen although not fully understood, is important in this process. It is suggested<sup>7</sup> that the oxygen deficiency in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is partially accommodated by oxygen vacancies on the copper planes between the barium layers of the orthorhombic unit cell. Unlike pure metallic superconductors these new materials are composed of ceramic oxides with a band gap<sup>8</sup> and defect sites (oxygen vacancies), and, consequently, may be highly susceptible to radiation damage. In this Brief Report we report the first results of thermally stimulated luminescence (TSL) studies of x-irradiated oxide superconductors.

Two-phase samples of  $\text{Ho}_{1.5}\text{Ba}_{1.5}\text{Cu}_2\text{O}_x$  ( $T_c = 46$  K),  $\text{Eu}_{1.5}\text{Ba}_{1.5}\text{Cu}_2\text{O}_x$  ( $T_c = 95$  K), and single-phase  $\text{GdBa}_2\text{Cu}_3\text{O}_x$  ( $T_c = 95$  K) were studied by TSL techniques in the temperature interval 80–300 K. These materials were prepared and characterized by methods given in Refs. 9 and 10. Radiation damage was provided by an x-ray machine operating at 40 kV p.p. and 25 mA producing an exposure rate at the sample site of  $1.4 \times 10^3$  R min<sup>-1</sup>. The TSL apparatus has been previously described.<sup>11</sup>

Shown in Fig. 1 are the TSL glow curves for  $\text{Ho}_{1.5}\text{Ba}_{1.5}\text{Cu}_2\text{O}_x$  and  $\text{GdBa}_2\text{Cu}_3\text{O}_x$  resulting from x-ray exposures at 80 K of  $1.4 \times 10^4$  R and  $2.8 \times 10^4$  R, respectively. The Ho-doped sample exhibits peaks at 160 and 172 K, whereas the Gd-doped sample is characterized by a single peak at 195 K. Typical background photomultiplier tube (PMT) current is  $1 \times 10^{-9}$  A. For x-ray exposures as large as  $4.2 \times 10^4$  R the Eu-doped sample yielded no TSL emission. Moreover, we found that the intensity of TSL in Ho- and Gd-doped samples appeared to be correlated with the amount of time each sample had been maintained in vacuum ( $\sim 10^{-5}$  Torr). For example, TSL glow curves taken under identical conditions showed

dramatic decreases in just three days, and after two weeks exhibited no intensity at all. It is possible that the Eu-doped sample had undergone complete degradation before we attempted TSL measurements, and, consequently, we cannot conclude unambiguously that it does not luminesce. Nevertheless, such rapid loss of TSL sensitivity is very unusual in any luminescent material. We note, however, that these samples are opaque and that our measurements correspond to surface rather than bulk luminescence. Thus, our present TSL results probably reflect a greater sensitivity to sample properties than the usual bulk measurements.

The Ho- and Eu-doped samples contain both the green semiconducting and black superconducting phases. On the other hand, the Gd-doped sample is 90–95% pure superconducting<sup>12</sup> as determined by the Meissner-effect amplitude (20% of  $-\frac{1}{4}\pi$  perfect diamagnetism) and shielding currents which correspond to 90–95% of the specimen

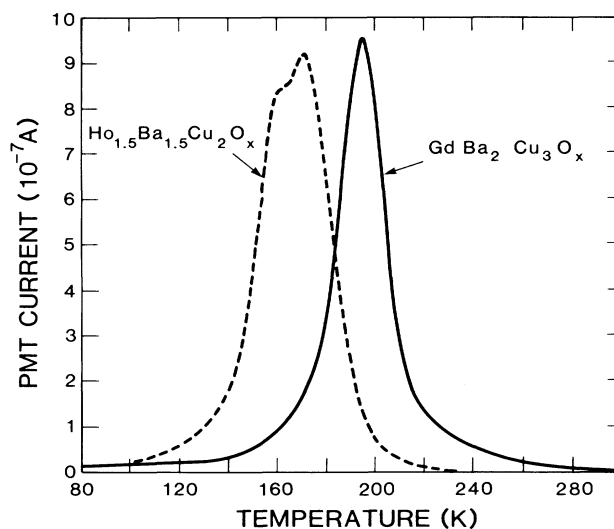


FIG. 1. TSL glow curves for x-irradiated  $\text{Ho}_{1.5}\text{Ba}_{1.5}\text{Cu}_2\text{O}_x$  ( $1.4 \times 10^4$  R) and  $\text{GdBa}_2\text{Cu}_3\text{O}_x$  ( $2.8 \times 10^4$  R).

volume. Apparently the TSL is not solely attributable to the semiconducting phase since both the Ho- and Gd-doped samples luminesce. However, a second sample of  $\sim 99\%$  pure superconducting  $\text{GdBa}_2\text{Cu}_3\text{O}_x$  did not exhibit luminescence. These results suggest that TSL is due to surface properties rather than any particular phase, and that these properties exhibit sample-to-sample variations that account for our observations.

Clues to the origin of TSL are provided by the concomitant emission spectra. The Gd-doped sample exhibits narrow emission [a full width at half maximum (FWHM) of 40 nm] that peaks at 500 nm as shown in Fig. 2. Emission spectra have not been corrected for spectrometer response. The average temperature  $\langle T \rangle$  during this emission scan was 196 K; i.e., during the time required to scan from 200 to 700 nm at a rate of  $200 \text{ nm min}^{-1}$  with a sample heating rate of  $0.05 \text{ K sec}^{-1}$ , the sample temperature increased from 192 to 204 K. Complex emission spectra are observed from the Ho-doped sample as indicated in Fig. 3. For  $\langle T \rangle = 135 \text{ K}$ , peaks occur at 450 nm (FWHM of 145 nm) and 660 nm. As  $\langle T \rangle$  increases the 450 nm peak shifts to longer wavelength (495 nm) and becomes narrower (FWHM of 125 nm) whereas the 660-nm peak disappears. Apparently the 660-nm emission peak is associated with only the 160 K TSL glow peak of Fig. 1. Likewise, the 172-K glow peak seems to be characterized by a single emission peak at 495 nm. However, the overlap of the two glow peaks (160 and 172 K) makes this assignment somewhat tentative.

If we make the analogy to simpler oxide systems, e.g.,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ , and  $\text{BeO}$ , we would expect  $V$ -type (trapped holes) and  $F$ -type (trapped electrons) centers to exist in  $x$ -irradiated rare-earth-doped copper oxides. For example, irradiated  $\text{BeO}$  exhibits TSL emission<sup>13</sup> at 525 and

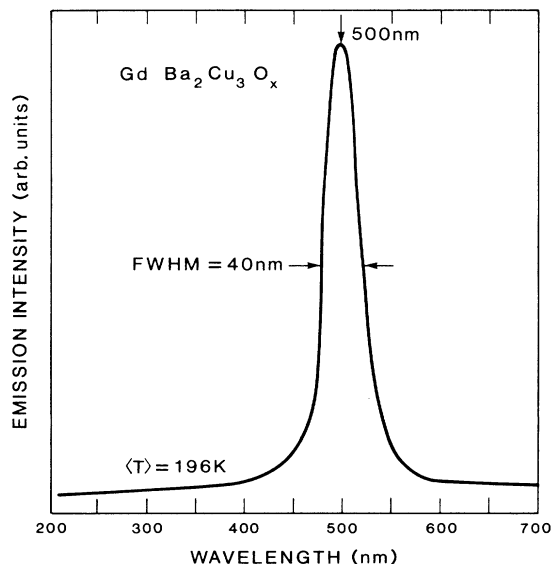


FIG. 2. Emission spectra characterizing the 195-K TSL glow peak of Fig. 1.  $\langle T \rangle$  corresponds to average temperature during emission scan. Typically the sample temperature changes by 8–10 K during one  $200 \text{ nm min}^{-1}$  scan.

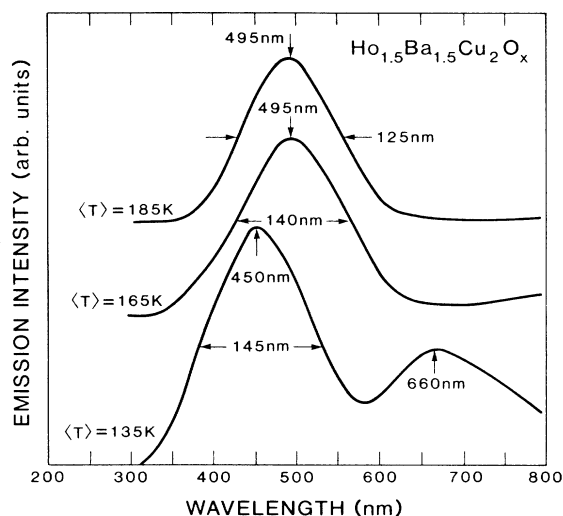


FIG. 3. Characteristic emission spectra of the two-peaked TSL glow curve of Fig. 1.  $\langle T \rangle$  corresponds to average temperature during emission scan. Horizontal arrows represent full widths at half maximum intensity.

320 nm due to recombination of thermally released holes with electrons at  $F$  centers (two electrons trapped at oxygen vacancy) and  $F^+$  centers (one electron trapped at oxygen vacancy), respectively. Therefore, one possibility for explaining the Ho-doped emission is to assign the 660- and 450-nm peaks to  $F$  and  $F^+$  centers, respectively. The 160 and 172-K TSL glow peaks correspond to energetically different trapped holes that, upon thermal excitation, are released and recombine with  $F$  and/or  $F^+$  centers producing the observed emission. Initially there exists both  $F$  and  $F^+$  centers. As holes become thermally unstable they recombine with one of the  $F$ -center electrons producing an  $F^+$  center and 660-nm emission. Also, some of the holes may recombine with  $F^+$ -center electrons yielding 450-nm emission as shown in Fig. 3 for  $\langle T \rangle = 135 \text{ K}$ . Thus  $F$  centers are quickly annihilated leaving only  $F^+$  defects. As  $\langle T \rangle$  increases only that emission characteristic of  $F^+$  centers is observed. The single 500-nm peak in Gd-doped barium copper oxide may also be associated with  $F^+$  centers. Note, however, the absence of  $F$ -center emission. Either  $F$  centers do not exist in the sample, or, alternatively, they exist but are converted to  $F^+$  centers by radiationless recombination.

A second plausible explanation for the observed TSL emission is that it results from the deexcitation of rare-earth ions.  $X$  irradiation either removes or adds electrons to the ions, producing, for example, either  $\text{Ho}^{2+}$  or  $\text{Ho}^{4+}$  (or perhaps both) ions. Upon thermal excitation holes (electrons) are released that recombine with  $\text{Ho}^{2+}$  ( $\text{Ho}^{4+}$ ) producing  $\text{Ho}^{3+}$  ions in excited states, the deexcitation yielding the observed emission. Differences in the widths of the spectral lines of the Ho- and Gd-doped samples would be due to the different crystal-field environments to which each is subjected. With the paucity of available data, however, we cannot deduce the origin of the luminescence centers in these samples, and emphasize

that the aforementioned possibilities are speculative.

An interesting feature of our data is the loss of luminescence sensitivity with time, especially when the samples are maintained in vacuum. As shown by earlier work,<sup>5</sup> the oxygen-defect perovskites have a propensity to readily lose or gain oxygen. We suggest that this loss of oxygen contributes to the decreased luminescence sensitivity. Thus TSL measurements may represent a very sensitive way to investigate the problem of oxygen stability in these materials. Present work is under way to examine the effects of various environments on the luminescence sensi-

tivity.

It is noteworthy that oxygen loss should lead to an increase in oxygen vacancies which, upon irradiation, would yield a larger concentration of *F*-type centers. This would produce increased luminescence intensity rather than decreased, as observed. Alternatively, there may be other mechanisms operative which reduce the hole concentration and consequently reduce the luminescence signal.

The theoretical general-order kinetics expression<sup>14</sup> describing TSL intensity *I* as a function of temperature *T* is given by

$$I = sn_0 \exp(-E/k_B T) \left[ [(l-1)s/\beta] \int_{T_0}^T \exp(-E/k_B T') dT' + 1 \right]^{-1/(l-1)}, \quad (1)$$

where *s* is the preexponential factor, *n*<sub>0</sub> the concentration of trapped charges at *t*=0, *E* the thermal activation energy, *k<sub>B</sub>* is Boltzmann's constant, *l* the order of kinetics, and *β* is the heating rate. A least-squares fit of Eq. (1) to the experimental TSL glow curves yields *E*, *s*, and *l*. For GdBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub> the best-fit values are *E*=0.429 eV, *s*=6.16×10<sup>8</sup> sec<sup>-1</sup>, and *l*=1.3. Similarly, the obtained parameters for Ho<sub>1.5</sub>Ba<sub>1.5</sub>Cu<sub>2</sub>O<sub>x</sub> are *E*=0.265 eV, *s*=2.14×10<sup>6</sup> sec<sup>-1</sup>, *l*=1 (160-K peak); and *E*=0.290 eV, *s*=2.05×10<sup>6</sup> sec<sup>-1</sup>, *l*=1.8 (176-K peak). The approximate second-order kinetics (*l*=1.8) describing the 172-K peak indicate considerable retrapping of charged carriers prior to recombination. More elaborate details of the analysis will be presented in a subsequent publication.

In summary, we have reported the first TSL and emission spectra measurements of rare-earth-doped barium copper oxides. Possible explanations for the radiation-induced defects that produce the luminescence have been discussed. It is suggested that surface rather than bulk properties determined the TSL glow curves and that the instability of oxygen is important in this process. TSL may, in fact, be a sensitive technique by which the oxygen diffusion can be studied. Glow curve parameters describing the TSL glow peaks have been given.

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