Long lasting phosphorescence of Eu²⁺-activated MO-B₂O₃ glasses

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In this letter, Eu²⁺-activated MO-B₂O₃ (M=Ca, Sr, and Ba) glasses are prepared in reductive atmosphere and their long lasting phosphorescence properties are studied. The intensity of the phosphorescence for the glasses is Sr>Ca>Ba. The light-induced electron paramagnetic resonance signal is observed after the irradiation of an ultraviolet lamp, which is due to the electron trapped by oxygen vacancy. The energy depth of the glasses is calculated using Hoogenstraaten's method.

OCIS codes: 160.2750, 160.2540, 160.4670.
doi: 10.3788/COL201109.071602.

Materials with long lasting phosphorescence (LLP) have been typically used in the dark for its indicating or beautifying effect. Currently, most commercial LLP products consist of polycrystalline powder. Compared with crystalline materials, glasses have particular merits, including being homogenous, transparent, and easy to fabricate into various shapes from big plate to thin fiber. The use of glasses with LLP has enriched the application of LLP materials. In 1998, Qiu *et al.* have reported on LLP of Eu²⁺-doped alkaline earth aluminborate glasses[1,2]. On the other hand, Hosono *et al.* have observed LLP in Tb³⁺-doped 60ZnO-20B₂O₃-SiO₂ glasses[3]. Since then, the subject of LLP glasses has attracted considerable attention from researchers[4,5]. However, although several viewpoints have been suggested for the mechanism of the LLP glasses[1−5], gaining a full understanding of these is not yet to be achieved.

Rare earth ions have typically been utilized as activators for luminescent glasses[6,7]. In this letter, the LLP properties of Eu²⁺-activated MO-B₂O₃ (M=Ca, Sr, and Ba) glasses are studied. The intensity of the phosphorescence for the glasses is Sr>Ca>Ba. The light-induced electron paramagnetic resonance (EPR) signal is observed after irradiation of 254-nm light. This is attributed to the electron trapped by oxygen vacancy (Vo) of the glasses. The energy depth of the glasses is calculated using Hoogenstraaten's method. We find that the deeper the trap depth, the brighter the phosphorescence.

Analytical grade B₂O₃, CaCO₃, SrCO₃, BaCO₃, and Eu₂O₃ (99.99%) were used as raw materials. The compositions of the glasses were 35MO-65B₂O₃ (M=Ca, Sr, or Ba), and the concentration of the doped Eu was 0.01 mol.-%. The calculated mixtures of raw materials were ground thoroughly and then melted in an alumina crucible at 1,400 °C in the CO atmosphere for 30 min. Transparent glasses were obtained by quenching the liquids on a stainless steel plate at room temperature. The body color of the Eu²⁺-doped glasses was faint yellow. All the samples were cut, polished, and subjected to optical measurements.

LLP emission spectra and decay curves were detected immediately after 254-nm ultraviolet (UV) lamp irradiation for 3 min using a spectrofluorometer (F-4500, HITACHI, Japan) equipped with a monochromator. The EPR spectra were measured at X-band (9.438 GHz) with EPR spectrometer (JES-FE3AX, Japan). The samples were irradiated using a 254-nm UV lamp for 5 min before the measurement. Thermoluminescence (TL) spectra were measured on a TL meter (FJ-427A, Beijing) with a heating rate of 2 K/s. All the samples were heated at 500 °C for thermal bleaching before TL measurement. All measurements except for the TL spectra were performed at room temperature.

The photoluminescence (PL) spectra of MO-B₂O₃: Eu²⁺ (M=Ca, Sr and Ba) are shown in Fig. 1. It is obvious that the emission peak of the samples is 448 nm (for Ca), 430 nm (for Sr), and 440 nm (for Ba). Although there are some differences in the emission peak positions of the glasses, the PL of the samples is due to the characteristic d-f transition of Eu²⁺. After the irradiation of a 254-nm UV lamp for 5 min, the blue phosphorescence of the samples persisted for more than 30 min. The decay curves of the LLP of the glasses are given in Fig. 2, as exhibited by the phosphorescent brightness of the samples and is in the order of Sr>Ca>Ba.
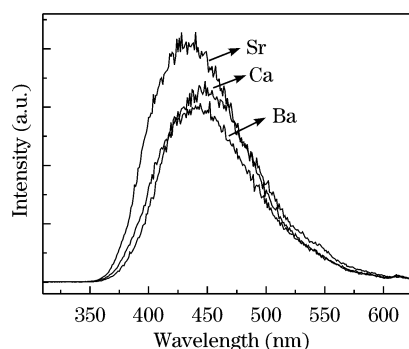
The EPR spectra of the Eu²⁺-activated MO-B₂O₃

Fig. 1. PL spectra of Eu²⁺-activated MO-B₂O₃(M=Ca, Sr, and Ba) glasses.
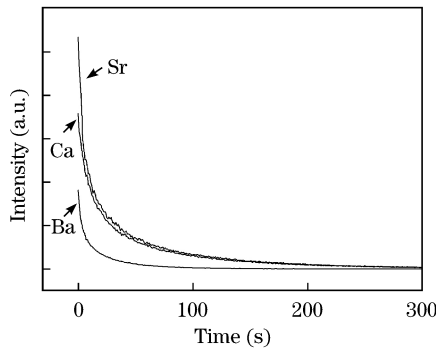
Fig. 2. Decay curves of LLP of the Eu^{2+}-doped B_2O_3-MO (M = Ca, Sr, and Ba) glasses. The samples are first excited with a 254-nm UV Lamp for 5 min.
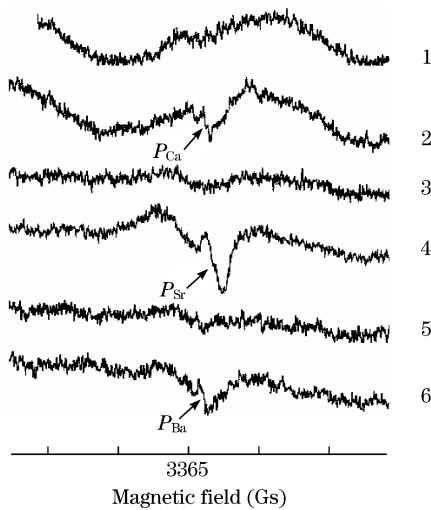

Fig. 3. EPR spectra of the glasses, curves 1 and 2 for Ca, curves 3 and 4 for Sr, and curves 5 and 6 for Ba. Curves 1, 3, and 5 are measured before UV excitation, while curves 2, 4, and 6 are obtained after UV excitation.
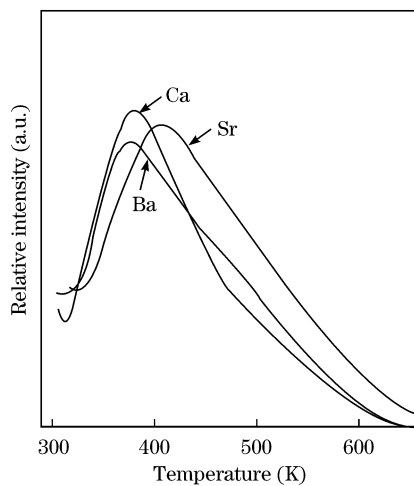

Fig. 4. TL spectra of B_2O_3-MO (M=Ca, Sr and Ba) glasses with a heating rate of 2 K/s.

(M=Ca, Sr and Ba) glasses before and after the irradiation of UV lamp are shown in Fig. 3. For each sample, a new light-induced EPR signal was brought after the excitation, which was marked P_{Ca}, P_{Sr} or P_{Ba}, as re-

spectively shown by curves 2 for (Ca), 4 (for Sr), and 6 (for Ba) in Fig. 3. Curves 1, 3, and 5 are the EPR spectra for Ca, Sr, and Ba glasses before the excitation, respectively. The value of the g factor of P_{Ca}, P_{Sr} or P_{Ba} are 2.0013, 1.9947, and 2.0022, respectively, and are smaller than that of the g factor of free electron, which is 2.0023.

The broad TL curves of the glasses are given in Fig. 4, in which the TL peaks are located at 382 K (for Ca), 408 K (for Sr), and 375 K (for Ba).

The EPR method has been used to characterize the trapped charges in LLP material by the excitation light-induced EPR signal[4,6]. If the g value of the new EPR signal is smaller than that of a free electron, that is, 2.0023, the signal is due to the trapped electron. However, if the g value is bigger than 2.0023, the new signal is ascribed to the trapped holes. Therefore, the induced EPR signals in Fig. 3 measured after the UV-irradiation are due to the induced electrons. For the Eu^{2+}-activated MO-B_2O_3 (M=Ca, Sr, and Ba) glasses in this letter, during the melting step, the reductive atmosphere can cause Vo in MO-B_2O_3 (M=Ca, Sr, and Ba) glasses, and those vacancies act as an electron-trapping center. There are two types of Vo in the oxide glasses, the vacancy associated with network forming cations, such as B^{3+}, Al^{3+}, and Si^{4+}, and the vacancy coordinated with network modifying cations. Unfortunately, it is difficult to determine the type of Vo in the present glasses. Vo is closely associated with the LLP phenomenon in several glass systems that could act as electron center, that is, F or F^+ center in the cases of trapping one or two electrons[8]. Due to the fact that it is easy for the Eu^{2+} to lose an electron, it can serve as hole center in the glasses.

Therefore, the mechanism for Eu^{2+}-activated MO-B_2O_3 (M=Ca, Sr, Ba) can be suggested. During the excitation process, the induced electrons and holes are trapped by the electron- and hole-centers, Vo and Eu^{2+},
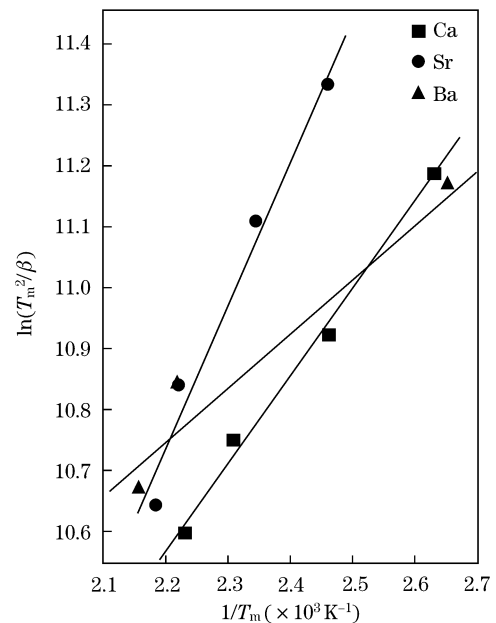

Fig. 5. The plots of $\ln(T_m^2/\beta)$ versus $1/T_m$ of the glasses. The heating rates are 2, 3, 4, and 5 K/s, respectively. Prior to taking each measurement, the sample is heated at 673 K for 30 min to empty the samples of residual electrons.

respectively. After irradiation, the captured electrons are thermally released from the electron-center at room temperature and then migrate to the hole center, $(Eu^{2+})^*$, which is a special state of Eu^{2+} formed by trapping a hole, and this electron hole recombination process results in the LLP of the glasses. However, the depiction is rough, and further studies should be carried out on various areas, for instance, on the details of Vo. As discussed above, there are two types of Vo in oxide glasses associated with the network forming cations and network modifying cations. However, which kind of Vo contributes to the LLP phenomenon remains unclear.

The intensity of the LLP of the Eu^{2+}-activated MO-B_2O_3 (M=Ca, Sr, and Ba) glasses is Sr>Ca>Ba (Fig. 2). Meanwhile, the temperature of the TL peak is Sr(408 K)>Ca(382 K)>Ba(375 K). In order to investigate the activation energy of the sample, the method developed by Hoogenstraaten is utilized[9], which is shown as

$$\ln\left(\frac{T_m^2}{\beta}\right) = \frac{E}{kT_m} + \ln\left(\frac{E}{ks}\right), \qquad (1)$$

where T_m is the peak temperature corresponding to the maximum TL intensity, β is the heating rate, E is the activation energy of the electron trap, s is the escape frequency, and k is the Boltzmann's constant. From Eq. (1), the plot of $\ln(T_m^2/\beta)$ versus $1/T_m$ is linear, and E can be obtained from the slope. When choosing different heating rates, the results of the different glasses based on Eq. (1) are shown in Fig. 5. The as-obtained activation energy of the glasses is 0.11 eV (for Ca), 0.20 eV (for Sr), and 0.076 eV (for Ba). Therefore, this kind of alkali earth ion has an obvious effect on the depth of the trap of the samples. Finally, compared with the phosphorescence of the samples, it has been found that the deeper the trap depth, the brighter the LLP of the present studied glasses.

In conclusion, Eu^{2+}-activated MO-B_2O_3 (M=Ca, Sr, and Ba) glasses are prepared in reductive atmosphere. These glasses emit blue LLP that can be observed in the dark even after 30 min after excitation in 254-nm light. For the samples, the order of the brightness of the phosphorescence is Sr>Ca>Ba, which is consistent with that of the trap depth of the glasses. Thus, the electron trapping center has been proven by the ERP results.

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