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A new blue phosphorescent glass–ceramic: Rare-earth-doped calcium aluminoborate

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Abstract

A new blue phosphorescent glass–ceramic, Eu^{2+} and Nd^{3+} co-doped $CaO–Al_2O_3–B_2O_3$, was synthesized. After the irradiation with ultraviolet (UV) light, the glass–ceramic emitted blue long-lasting phosphorescence (LLP) with a spectrum peaking at about 464 nm ascribed to the characteristic $4f^65d^1 \rightarrow 8S_{7/2}$ transition of Eu^{2+}. This phosphorescence can be seen in the dark 1 h after the irradiation. However, the transparent Eu^{2+} and Nd^{3+} co-doped $CaO–Al_2O_3–B_2O_3$ glass did not show the phosphorescence. By the X-ray diffraction diffusion (XRD) data, α-$CaAl_2B_2O_7$ was demonstrated to be the crystallites in the glass–ceramic. We think that α-$CaAl_2B_2O_7$:Eu^{2+}, Nd^{3+} crystallites produced during the heat treatment of the glass contribute to the LLP of the glass–ceramic.

Keywords: Long lasting phosphorescence; Eu^{2+}; Nd^{3+}; Calcium aluminoborate; Glass–ceramic; α-$CaAl_2B_2O_7$

1. Introduction

LLP material is one kind of electron-trapping material of which the captured electron (or holes) can be thermally released from the traps at room temperature leading to the emission of activator. Since the synthesis of the $SrAl_2O_4$:Eu^{2+}, Dy^{3+} [1], a phosphor far exceeding the traditional sulfide phosphor in brightness, persistent time and chemical durability, new non-radioactive LLP materials received rapidly growing interest, especially the rare-earth-doped alkaline-earth aluminates. And in addition to the polycrystalline powder, several new LLP materials have also been reported in the form of glass [2–5], glass–ceramic [6,7], film [8] or single crystal [9]. LLP material is usually used in dark environment acting as indicating sign or craftwork and new applications of this material is developed recently, e.g., optical storage material [5].

Glass–ceramics are usually prepared by heating the glasses to produce the internally grown crystallites and famous for its excellent thermal shock resistance and good mechanical properties, etc. Moreover, rare-earth-doped glass–ceramics are promising optical material, such as Nd-doped or Er and Yb co-doped glass–ceramics [10,11]. In this article, we will introduce a new Eu^{2+}, Nd^{3+} co-doped calcium alumnioborate glass–ceramic emitting blue LLP. The XRD pattern shows that the crystallites of the glass–ceramic are α-$CaAl_2B_2O_7$. After the irradiation of UV light, the glass–ceramic emits bright purple phosphorescence with an emission peak at about 464 nm due to the characteristic d–f transition of Eu^{2+}. However, it should be noted that the transparent Eu^{2+}, Nd^{3+} co-doped calcium alumnioborate matrix glass does not emit LLP. We suggest that rare-earth doped α-$CaAl_2B_2O_7$ crystallites contribute to the blue phosphorescence.

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2. Experimental

Composition of the matrix glass was $30B_2O_3{\cdot}30Al_2O_3{\cdot}40CaCO_3{\cdot}0.05Eu_2O_3{\cdot}0.05Nd_2O_3$ (in mol%). Reagent-grade $CaCO_3$, H_2BO_3, Al_2O_3, Eu_2O_3 and Nd_2O_3 were used as starting materials. Mixed batches, with 5%H_2BO_3 excess to compensate the loss of boron during the heating, were melted in Pt crucible at 1500 °C for 60 min under an ambient atmosphere and the obtained glass was re-heated in alumina crucible at 1500 °C for 30 min under a CO atmosphere and the melt was quenched to room temperature to get transparent glass that could not emit LLP. However, when the transparent glass was heat-treated at 900 °C for 4 h with CO as protective atmosphere to prevent the oxidation of Eu^{2+}, it was turned to opaque glass–ceramic (CABEN) with blue LLP. As a comparison, $CaAl_2O_4$:Eu^{2+}, Nd^{3+} phosphor (CAEN) was prepared by the method described in Ref. [1]. XRD pattern was obtained on a Rigaku D/MAX-IIB X-ray diffractometer with Cu $K\alpha_1$ ($\lambda = 1.5405$ Å) radiation. IR spectra were measured on a Perkin-Elmer 850B Infrared Spectrophotometer. The photoluminescence (PL), excitation, phosphorescence spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer (150W Xe lamp and grating monochromator). For the measurement of phosphorescence the 300 nm light obtained from the excitation channel of the F-4500 spectrophotometer was used as excitation source. The thermluminescence (TL) curve was measured with an FJ-427A thermoluminescence-meter (Beijing Nuclear Instrument Factory). All measurements were taken at room temperature except mentioned.

3. Results and discussion

Some researcher [12] has observed both α and β forms of $CaAl_2B_2O_7$ in calcium aluminoborate glass–ceramic and found that the α phase predominated in the samples. For CABEN, the XRD data is in good agreement with JCPDS card (19-205, for α-$CaAl_2B_2O_7$), showing that the crystallites in the sample are α-$CaAl_2B_2O_7$. Fig. 1 gives the XRD pattern of CABEN.

Fig. 2 shows the excitation and emission spectra of CABEN. The former peaks at about 300 nm while the later at about 464 nm due to the 5d–4f transition of Eu^2. Wherever, the excitation and emission spectra of CAEN peak at about 336 nm and 440 nm, respectively, as shown in the inset of Fig. 2. For all the known LLP materials, Eu^{2+} is the most important activation ion. Because the 5d electron of Eu^{2+} is strongly coupled with the lattice of the host, the phosphorescence of Eu^{2+} usually changes with its host, for example, red emission in CaS [13], green in $SrAl_2O_4$ [1] and blue in $CaAl_2O_4$ [1]. The same interpretation is rational for the red shift of the emission of Eu^{2+} from CAEN (peaking at 440 nm) to CABEN (at 464 nm). It can also be observed that the excitation spectrum of CABEN locates at a higher energy band than that of CAEN.

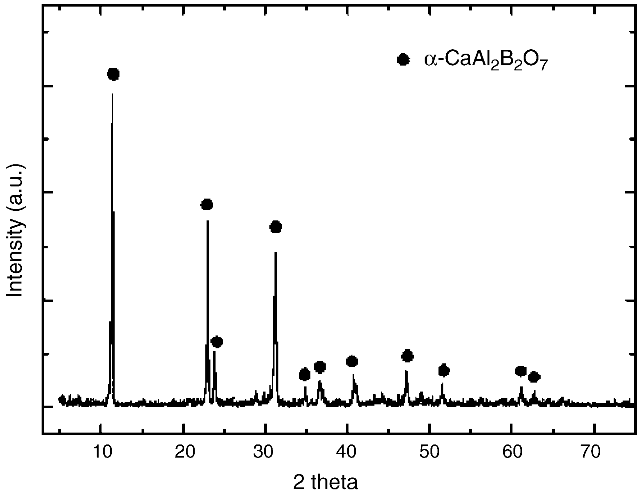

Fig. 1. XRD pattern of CABEN.

Fig. 3 shows the phosphorescent spectra measured at different time after stopping the excitation, for which the 300 nm light obtained from excitation channel of the spectrophotometer is used as pump source. The phosphorescent spectrum of CABEN is similar with its photoluminescent spectrum (see Fig. 2), indicating that the LLP of the sample is due to the characteristic emission of Eu^{2+}.

It is interesting that the transparent Eu^{2+}, Nd^{3+} co-doped calcium aluminoborate glass does not emit the blue phosphorescence until it was turned to opaque glass–ceramic, and the XRD data shows that the crystalline phase in CABEN is α-$CaAl_2B_2O_7$ (see Fig. 1). For glass–ceramic, it can be seen as such a kind material that the crystallites are embedded in the glass phase. If the crystallites are of certain function, the glass–ceramic is very possible to possess the same property. One illustration is the Er and Yb co-doped oxyfluoride glass–ceramic for upconversion:Er and Yb co-doped fluo-

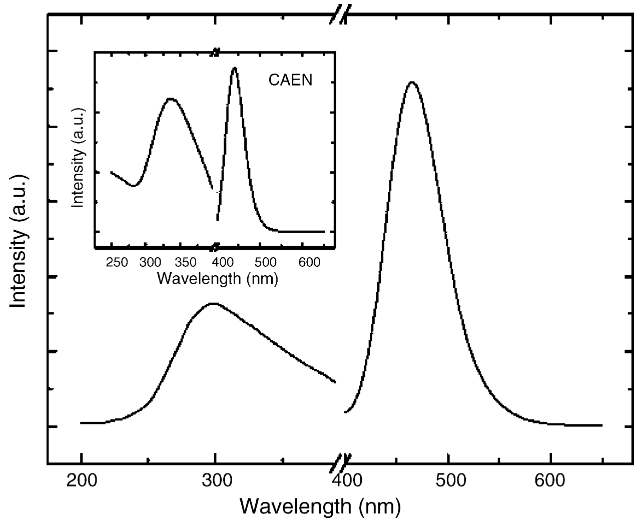

Fig. 2. The excitation and emission spectra of CABEN and the inset is those of CAEN.

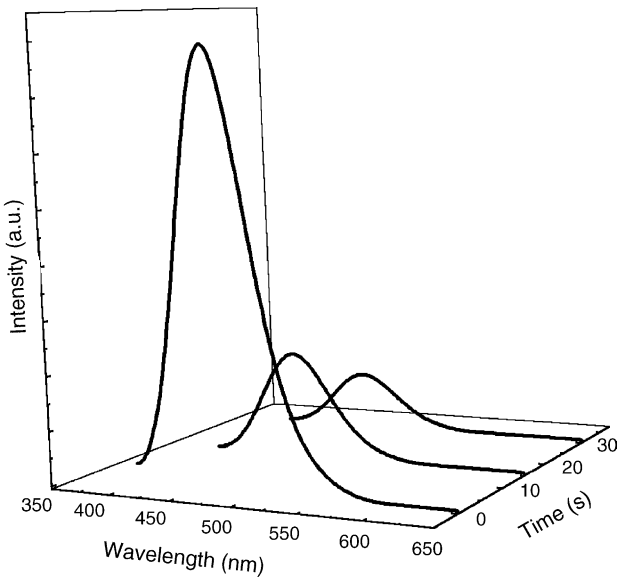

Fig. 3. Phosphorescent spectra measured at different time after stopping the excitation, for which the 300 nm light obtained from excitation channel.

ride crystallites in the oxide glass phase are responsible for the function of the material [11]. Actually, for the known LLP glass–ceramics, it is considered that the phosphorescence is due to the crystallites in the material. We thus deduce that α-$CaAl_2B_2O_7:Eu^{2+}$, Nd^{3+} is responsible for the LLP of CABEN.

The TL curve of CABEN is a broad band and given in Fig. 4, which has a maximum peak at about 336 K and a shoulder at 380 K. It is known that the TL curve is closely related with the traps in the materials, therefore, the broad band implies that the traps in CABEN has a wide distribution. The traps with TL band near room temperature should answer for the LLP of the sample.

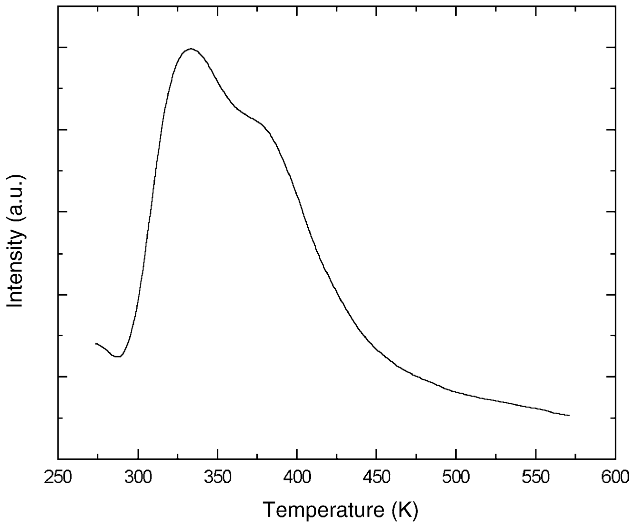

Fig. 4. The TL curve of CABEN measured after the sample have being excited by 300 nm light for 5 min. Heating rate is 2 K/s.

About the mechanism of alkaline earth aluminate LLP materials many investigations have been proposed. Abbruscato studied the mechanism of LLP of $SrAl_2O_4:Eu^{2+}$ with the case of excess of Al, and proposed that holes were trapped at lattice defects and the Eu^{2+} emission was associated with thermal deactivation of those traps [15]. Since the birth of $SrAl_2O:Eu^{2+}$, Dy^{3+} and $CaAl_2O_4:Eu^{2+}$, Nd^{3+}, considerable efforts have been made to interpret its phosphorescence mechanism. Some researchers put forward a mechanism in which it is involved that Eu^{2+} and Dy^{3+}/Nd^{3+} are reduced and oxidized into Eu^{+} and Dy^{4+}/Nd^{4+} during the excitation, respectively [1]. However, different suggestions are also proposed [14] for the reason as follows. In addition to the uncertainty of the existence of Eu^{+}, it is difficult to reduce the Eu^{2+} into univalent ion and oxidize the Dy^{3+}/Nd^{3+} into quadrivalent ion just with the irradiation of the mild near-UV or visible light at ambient condition but which is the effective excitation light for the LLP of the material.

Basing on the configurational-coordinate diagram model, we also proposed a mechanism of the rare earth doped alkaline earth aluminate LLP materials [16]. Although existing different opinions on the mechanism it is a common viewpoint that during the excitation part energy of the incident light is stored in the form of captured electrons and holes, those captured electrons and holes can be thermally released from the traps at room temperature and subsequently recombine with each other to set free the energy to result the characteristic emission of the luminescence ion, such as Eu^{2+}; because the release of the captured electrons and traps is durative, the luminescence of the materials shows the property of long life.

We suggest that this general model is also applicable for the interpretation of the mechanism of CABEN, namely, the Nd^{3+} ions in the glass–ceramic serve as a modifier for the trap of the sample and lead to the optimum depth of the traps from which it is easy for the captured electron to release at a appropriate rate resulting in the LLP of CABEN. Of course, the case for our sample should be more complicated because not only the crystallites but also the glass phase are involved. In the article we will not give much attention to the detail of the mechanism of CABEN.

To our knowledge, it is the first time to report the blue phosphorescence in rare earth doped calcium aluminoborate glass–ceramic. Furthermore, so far we have not found articles about the LLP of rare earth doped α-$CaAl_2B_2O_7:Eu^{2+}$, Nd^{3+}, which is very possible to be a new LLP material and the related studies on which has been carried.

4. Conclusion

In sum, we synthesize a new blue LLP glass–ceramic from the rare earth doped transparent calcium aluminoborate glass for which no phosphorescence is observed. α-$CaAl_2B_2O_7$ is proved to be the micro-crystalline phase of the glass–ceramic and responsible for the LLP.

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