Greenish-yellow Light-emitting, Long-lasting Phosphorescence in Eu^{2+}-doped $CaO–CaBr_2–SiO_2$ Phosphor System

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Novel greenish-yellow light long-lasting afterglow material, Eu^{2+}-doped $CaO–CaBr_2–SiO_2$ phosphor system, is prepared by the conventional high-temperature solid-state method. Photoluminescence (PL) spectrum reveals that it exhibits a strong blue emission band centered at 469 nm with some asymmetry on the long wavelength side, while this phosphor emits greenish-yellow light and shows strong long-lasting phosphorescence after it is excited with 365-nm UV light. The phosphorescence lasts for more than 1 h in the light perception of the dark-adapted human eye ($0.32\,mcd/m^2$). The possible phosphorescence mechanism is also investigated.

Recently, tremendous progress has been achieved in the development of long-lasting afterglow phosphors based on varied host lattice, such as sulfides, aluminates, silicates, titanates, oxysulfides, etc.[1–5] But most of them are proved to be more or less deficient in the practical application, such as their relative narrow excitation band, poor afterglow intensity, short duration time, even their poor physical and chemical stability or complicated synthesis technique. Therefore, it is necessary to develop novel host matrix used for long-lasting phosphorescence (LLP) materials with better comprehensive performance. Remarkably, as the multiplex compound of halide and silicate, alkaline earth halosilicate crystal has lower synthesis temperature and higher physical and chemical stability, furthermore, rare earth-activated halosilicate has been proved to be an efficient phosphor.[6–8] In the halosilicate host, the luminescence of Eu^{2+} consists of the $4f^65d^1–4f^7(^8S_{7/2})$ broad-band emission, which belongs to electric-dipole-allowed transition and has the properties of large absorption of UV light and broad emission ranging from the ultraviolet to infrared region depending on different crystal-lattice environment.[9] In our present work, we have synthesized an interesting greenish-yellow light-emitting LLP material, Eu^{2+}-doped $CaO–CaBr_2–SiO_2$ via the conventional solid-state reaction method. Their luminescent properties, including the PL and LLP properties, as well as their mechanism are also studied.

On the basis of the formula of an efficient green-emitting phosphor $Ca_3SiO_4Cl_2{:}Eu^{2+}$, we designed the chemical composition of the Eu^{2+}-doped $CaO–CaBr_2–SiO_2$ phosphor system as $Ca_3SiO_4Br_2{:}Eu^{2+}$.[7] Accordingly, this bromosilicate phosphor system, Eu^{2+}-doped $CaO–CaBr_2–SiO_2$, was synthesized by a high-temperature solid-state synthesis method. The starting materials, $CaCO_3$ (A.R.), $CaBr_2{\cdot}2H_2O$ (A.R.), and SiO_2 (A.R.) were weighted by a molar ratio of $CaCO_3$, $CaBr_2{\cdot}2H_2O$, and $SiO_2 = 2{:}1.1{:}1$. A small amount of Eu_2O_3 was added in the mixture as activator, and a little excessive $CaBr_2$ (10%) is necessary, for loss of weight at high temperature, because the melting point of $CaBr_2$ is only 810 °C. All starting materials were mixed in an agate mortar and then placed in corundum crucibles. The samples were fired at 850 °C for 3 h, and highly pure carbon particles were used as reducing agent, by which the sample was covered during firing. X-ray diffraction pattern of the sample was recorded by using a Shimadzu XRD-6000 X-ray powder diffractometer (Cu Kα radiation, 40 kV, 30 mA and a scanning speed 2.0°/min). The PL spectrum was obtained at room temperature with a Hitachi F-4500 spectrophotometer with a photomultiplier tube operating at 400 V and a 150-W Xe lamp. The LLP emission spectrum and afterglow intensity decay curve were measured on the same Hitachi F-4500 spectrophotometer, and their measuring procedures were as follows. The excitation light of the sample was blocked when the sample had been excited for 5 min, and the afterglow emitted from the sample was measured by using the phosphorescence mode for afterglow spectra and time scan mode for decay curves.

Figure 1 shows the typical XRD pattern of $(CaO–CaBr_2–SiO_2){:}Eu^{2+}$ phosphor system. As seen in Figure 1, the XRD pattern of $(CaO–CaBr_2–SiO_2){:}Eu^{2+}$ phosphor indicates that it belongs to the well-formed crystalline structure, although it does not match any data in the JCPDS base after careful comparison. We propose that the $CaO–CaBr_2–SiO_2$ system will be potentially a kind of novel bromosilicate structure built up with the framework of Ca^{2+}, SiO_4^{4-}, and Br^-, and its detailed structure information will be developed in our future work. The point of this letter is to report the interesting PL and LLP properties in the novel $CaO–CaBr_2–SiO_2$ host lattice.

The PLE and PL spectra of $(CaO–CaBr_2–SiO_2){:}0.03Eu^{2+}$ are shown in Figure 2. An excitation band measured by monitoring the emission of 469 nm is broad, ranging from 250 to 450 nm, which indicates that the phosphor can be effectively excited by the long wavelength UV and visible light. Upon 365-nm UV excitation, the phosphor shows a very strong blue emission band with a peak at 469 nm. The emission band appears to be asymmetric on the long wavelength side, which indicates that there is a possible emission peak in the long wavelength region. The

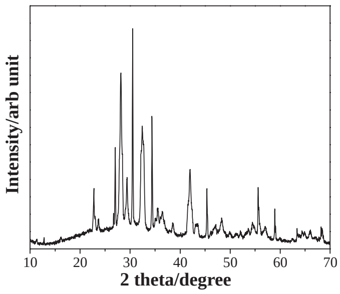

Figure 1. X-ray diffraction pattern of the typical $(CaO–CaBr_2–SiO_2){:}Eu^{2+}$ phosphor system.

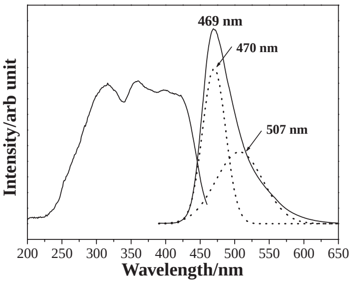

Figure 2. PLE (left) and PL (right) spectra of (CaO–$CaBr_2$–SiO_2): $0.03Eu^{2+}$ phosphor ($\lambda_{em} = 469$ nm for excitation and $\lambda_{ex} = 365$ nm for emission), and the dotted line denotes the Gaussian fit of the PL spectrum.

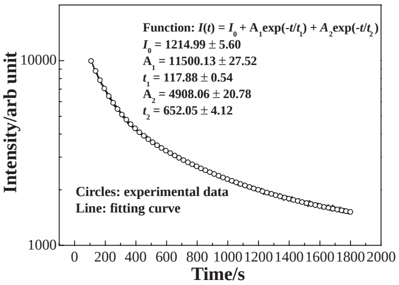

Figure 3. Afterglow decay curve of (CaO–$CaBr_2$–SiO_2):$0.03Eu^{2+}$ phosphor. Sample was irradiated by 365-nm UV for 5 min before measurement.

dotted line in Figure 2 denotes the Gaussian fit of the PL spectrum with maxima at 470 and 507 nm, respectively. It can be presumed that Eu^{2+} ions occupy two types of sites in the CaO–$CaBr_2$–SiO_2 lattice, forming two corresponding emission centers, namely Eu_I and Eu_2 sites.

In this letter, we reported, for the first time to the best of our knowledge, the LLP properties in the halosilicate host, although the PL in the halosilicate host has been intensively investigated since Burrus reported the PL properties of Eu^{2+} in halosilicate.[6] Figure 3 shows the afterglow intensity decay for (CaO–$CaBr_2$–SiO_2):$0.03Eu^{2+}$ phosphor in the range of 100–1800 s after the 365-nm UV has been removed. As shown in Figure 3, the afterglow intensity of Eu^{2+} decreases quickly at first and then very slowly. These two decay components can be well fitted to a double-exponential function as

$$I(t) = I_0 + A_1 \exp(-t/t_1) + A_2 \exp(-t/t_2), \qquad (1)$$

where I and I_0 are the luminescence intensity, A_1 and A_2 are constants, t is the time, and t_1 and t_2 are the decay times for the exponential components, respectively. The fitting results are shown in Figure 3. Because of the significant slow decay component, (CaO–$CaBr_2$–SiO_2):$0.03Eu^{2+}$ phosphor system shows obvious greenish-yellow LLP in the dark for more than 1 h after the shutting of excitation source.

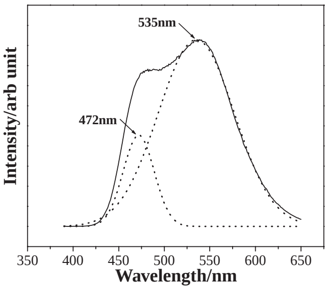

Figure 4. LLP spectrum of (CaO–$CaBr_2$–SiO_2):$0.03Eu^{2+}$ phosphor at 100 s after the 365-nm excitation source is switched off, and the dotted line denotes the Gaussian fit of the afterglow spectrum.

As shown in Figure 4, we have measured the LLP spectrum of (CaO–$CaBr_2$–SiO_2):$0.03Eu^{2+}$ phosphor at 100 s after the 365-nm excitation source is switched off. Similar to the above fluorescence emission spectrum, the LLP spectrum also indicates that there are two possible emission peaks. The dotted line in Figure 4 denotes the Gaussian fit of the afterglow spectrum with maxima at 472 and 535 nm, respectively. The peak at about 472 nm corresponds to the emission originating from Eu_I site, while peak at 535 nm corresponding to Eu_2 site. But their relative emission intensity is just opposite to the fluorescence emission spectrum, and stronger greenish-yellow emission peak in the afterglow spectrum can be observed.

We proposed that the LLP properties in (CaO–$CaBr_2$–SiO_2):Eu^{2+} are due to the thermostimulated recombination of holes and electrons, which leave electrons or holes in a metastable state at room temperature.[10] The vacancies of Br^- (V_{Br}') are created in the high temperature during the synthesis process and form the positive hole traps, which are significant to LLP acting as the defect centers. Introduction of V_{Br}' defect into the (CaO–$CaBr_2$–SiO_2):Eu^{2+} system results in the creation of the trapping energy level which locates at a suitable depth, so that the holes or electrons formed in the sample matrix by light illumination were trapped by defect centers, released by heat at room temperature and recombined with electrons or holes trapped by other defect centers. On the basis of the above process, the released energy is transferred to the rare earth ions and finally leads to the characteristic rare earth ion emission.[2] On the other hand, because the two types of Eu^{2+} emission centers existed in the same phosphor system, two different colors LLP can be observed simultaneously. However, owing to the smaller gap in energy between the excited state and the defect trap energy of Eu_2 center than that of Eu_I center, the trap energy of Eu_2 centers is smaller than that of Eu_I centers, which leads to the higher detrapping probability of Eu_2 emissions centers. So we can observe the stronger greenish-yellow LLP coming from the Eu_2 centers than blue emission from the Eu_I centers.

In conclusion, we have synthesized an interesting Eu^{2+}-doped CaO–$CaBr_2$–SiO_2 phosphor system. Under 365-nm UV excitation, it exhibits a strong blue emission band centered at 469 nm, while significantly the greenish-yellow light emitting LLP can be visible with the naked eye (0.32 mcd/m^2) for over 1 h after the removal of irradiation source. This finding has enlarged the host of the family of long-afterglow phosphors available.

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