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Effect of different RE dopants on phosphorescence properties of $Sr_2Al_2SiO_7$:Eu^{2+} phosphors

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Abstract: Different rare earth (RE) ions dopants were added into the $SrAl_2SiO_7$:Eu^{2+} phosphors in order to enhance the phosphorescence properties, and the effect of the RE ions including Yb^{3+}, Ce^{3+}, Nd^{3+}, Dy^{3+} and Tm^{3+}, was comparatively investigated. It was found that Nd^{3+} addition improved the phosphorescence properties obviously among all the studied RE ions. Therefore, $Sr_{1.96-x}Al_2SiO_7$:$x$$Eu^{2+}$,$y$$Nd^{3+}$ phosphors were studied in detail, and the optimum Eu^{2+} and Nd^{3+} concentrations were determined with the afterglow time of about 20 min. The phase structures, photoluminescence (PL) properties, long-lasting phosphorescence (LLP) properties, afterglow decay curves and thermo-luminescence (TL) for the selected phosphors during the corresponding study were investigated. All the phosphors exhibited green PL emission and LLP emission. There were two TL bands located at about 325 and 380 K for the studied samples, and the relationship between RE addition and phosphorescence properties was discussed.

Keywords: phosphors; long-lasting phosphorescence; rare earths

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Long-lasting phosphorescence (LLP) phosphors belong to the energy-storing materials which can store the absorbed light energy and gradually release it as luminescence after removing the light source[1,2]. As an energy-saving material, it has been widely studied by lots of researchers due to their energy efficiency and independence from external power sources[3]. For instance, the high brightness and long afterglow phosphor $SrAl_2O_4$:Eu^{2+},Dy^{3+} can be commercially used[4,5]. However, aluminates are chemically unstable and the luminescent properties will be degraded in moisture environment. Therefore, the preparation of LLP phosphors with better performance is very important. In recent years, alkaline earth silicate phosphors with long afterglow properties are found to be the suitable host with chemical stability and water-resistant property when compared to the previous sulfide or aluminate phosphors.

Among the studied alkaline earth silicate phosphors, melilites-based compounds belong to a large family of tetragonal, noncentrosymmetric materials with formula of $M_2T_{(1)}T_{(2)2}O_7$ (M and $T_{(1)}$ usually represent the alkaline-earths or transition metals ions and $T_{(2)}$ is commonly occupied by Al, Ga, Si or Ge)[6,7]. Among all the melilites, $Sr_2Al_2SiO_7$ is studied as a new host for excellent phosphorescence property. Ding et al.[8] have reported the Eu/Dy codoped $Sr_2Al_2SiO_7$ and studied their afterglow property. In this study, we systematically investigated a series of rare earth (RE) ions dopants, which are codoped in $Sr_2Al_2SiO_7$:Eu^{2+}. The phase structures, photoluminescence (PL) properties, long-lasting phosphorescence (LLP) properties, afterglow decay curves and thermo-luminescence (TL) for the selected phosphors were investigated in detail. The optimum RE addition, and the suitable Eu^{2+} and Nd^{3+} concentrations were determined in our research.

1 Experimental

1.1 Sample preparation

Phosphor samples of $Sr_{1.96}Al_2SiO_7$:0.04Eu^{2+}, $Sr_{1.92}Al_2SiO_7$:0.04Eu^{2+},0.04RE^{3+} (RE=Yb, Ce, Nd, Dy, Tm), $Sr_{1.96-x}Al_2SiO_7$:0.04Eu^{2+},$x$$Nd^{3+}$ (x=0, 0.01, 0.04, 0.1, 0.2) and $Sr_{1.9-x}Al_2SiO_7$:$x$$Eu^{2+}$,0.1$Nd^{3+}$ (x=0.01, 0.02, 0.04, 0.08, 0.1) were synthesized through a conventional solid-state reaction under CO reducing atmosphere. $SrCO_3$ (A.R.), Al_2O_3 (A.R.), SiO_2 (A.R.), Eu_2O_3 (99.99%), Nd_2O_3 (99.99%), Tm_2O_3 (99.99%), Yb_2O_3 (99.99%), Dy_2O_3 (99.99%) and CeO_2 (99.99%) were used as starting materials according to the designed formula. H_3BO_3 (A.R.) was selected as the flux via the comparative investigations of different types of flux and the optimized amount was also fixed to keep the pure phase during the preparation. In a typical process, the starting materials are weighed in stoichiometric amounts and thoroughly

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mixed in an agate mortar by grinding. Then, the mixture was fired at 1260 ºC for 5 h. After that, the samples were furnace-cooled to room temperature and ground again into fine powders and finally the samples were obtained.

1.2 Sample characterization

Powder X-ray diffraction (XRD) data were collected on an X-ray powder diffractometer (SHIMADZU, XRD-6000, Cu Kα radiation, λ=0.15406 nm, 40 kV, 40 mA) and the continuous scanning rate (2θ ranging from 10º to 70º) is 4º (2θ)/min. Room temperature PLE and PL spectra were characterized on an F-4600 fluorescence spectrophotometer with a photomultiplier tube operating at 400 V, and a 150 W Xe lamp used as the excitation source. Afterglow decay curve and afterglow emission spectra were detected immediately after the samples were irradiated for 15 min with a 365 nm UV lamp. The TL spectra were recorded by using microcomputer TL dosimeters (FJ427-AL, Beijing Nuclear Instrument Factory, Beijing, China).

2 Results and discussion

2.1 Phase structure of $Sr_{1.96}Al_2SiO_7:0.04Eu^{2+}$

Fig. 1 shows the XRD patterns of as-prepared $Sr_{1.96}Al_2SiO_7:0.04Eu^{2+}$ along with the standard card of $Sr_2Al_2SiO_7$ (JCPDS card #74-1234). The observed peaks are well indexed to the corresponding standard cards which proves that there is no obvious other phase in the patterns based on the XRD check. We also checked the XRD patterns of the designed $Sr_{1.92}Al_2SiO_7:0.04Eu^{2+}$, $0.04RE^{3+}$ (RE=Yb, Ce, Nd, Dy, Tm) samples, and it is found that the RE dopants also do not change the phase structure.

2.2 Identification of different RE dopants on PL properties

Accordingly, PLE and PL spectra of $Sr_{1.96}Al_2SiO_7:0.04Eu^{2+}$ and $Sr_{1.92}Al_2SiO_7:0.04Eu^{2+},0.04RE^{3+}$ (RE=Yb, Ce, Nd, Dy, Tm) are shown in Fig. 2(a) and (b). Upon excitation by UV light, all the phosphors exhibit green luminescence. Typically, the PLE spectra of $Sr_{1.96}Al_2SiO_7:0.04Eu^{2+}$ consists of a broad band from 270 to 440 nm with two peaks at 330 and 360 nm, which can be ascribed to the typical f-f transitions of Eu^{2+}. The PL band of $Sr_{1.96}Al_2SiO_7:0.04Eu^{2+}$ also consists of a broad band with a peak at 515 nm which can be attributed to $4f^65d\text{-}4f^7$ of Eu^{2+} [9,10]. Since the emission of Eu^{2+} is ascribed to the f-d transition depending on the enviroment of the activators, and the emission peaks can be shifted[11]. However, samples codoped with different RE ions show similar luminescence property as $Sr_{1.96}Al_2SiO_7:0.04Eu^{2+}$. Moreover, the luminesence intensity has been obviously enhanced by the codoped RE ions except for Ce^{3+} when compared to $Sr_{1.96}Al_2SiO_7:0.04Eu^{2+}$. The decrease of the emission intensity for the Ce^{3+} codoped samples can be explained by energy transfer from Eu^{2+} to Ce^{3+} [12]. The relative emision intensities can be placed in the order of $Sr_2Al_2SiO_7:Eu^{2+},Tm^{3+}>Sr_2Al_2SiO_7:Eu^{2+},Dy^{3+}>Sr_2Al_2SiO_7:Eu^{2+},Nd^{3+}>Sr_2Al_2SiO_7:Eu^{2+},Yb^{3+}>Sr_2Al_2SiO_7:Eu^{2+}>Sr_2Al_2SiO_7:Eu^{2+},Ce^{3+}$.

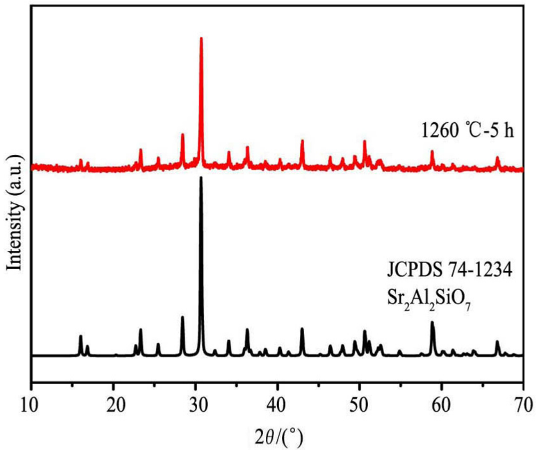

Fig. 1 XRD patterns of as-prepared $Sr_{1.96}Al_2SiO_7:0.04Eu^{2+}$ sample with the standard data of JCPDS 74-1234 for $Sr_2Al_2SiO_7$

2.3 Identification of different RE dopants on LLP properties

In order to enhance the phosphorescence properties,

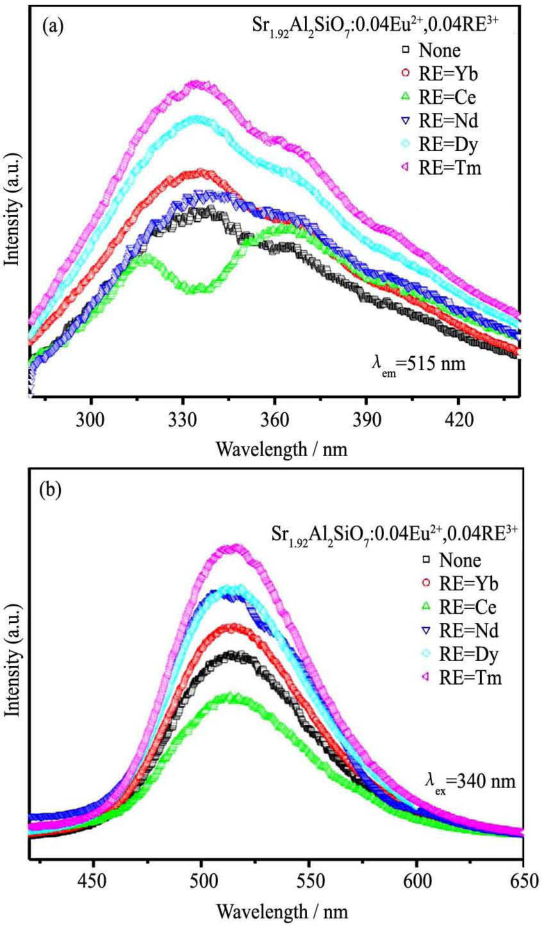

Fig. 2 PLE (a) and PL (b) spectra of $Sr_{1.96}Al_2SiO_7:0.04Eu^{2+}$ and $Sr_{1.92}Al_2SiO_7:0.04Eu^{2+},0.04RE^{3+}$(RE=Yb, Ce, Nd, Dy, Tm)