

Blue to red color-tunable Eu-doped AlPO_4 mesoporous glass

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A tunable luminescence from red to blue in Eu-doped mesoporous AlPO_4 glass is achieved by adjusting the annealing temperature. With increasing annealing temperature, the increased Eu^{3+} ions reduction changes the luminescence of the obtained glass. The abnormal reduction of Eu^{3+} to Eu^{2+} occurs in AlPO_4 mesoporous glass at relative low annealed temperatures from 600 to 800 °C in air. The presence of Eu^{2+} ions, which are reduced from Eu^{3+} by hole-electron pairs, is revealed by XPS spectra. Our results indicate the mesoporous AlPO_4 glass is a suitable matrix to incorporate Eu ions as the tunable luminescent light sources or LEDs.

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In order to generate high color-rendering index (CRI) tunable or white light emission in LEDs, near ultraviolet (NUV) excited bi- or tri-color phosphors have attracted more attention recently^[1,2]. Both Eu^{2+} and Eu^{3+} ions have been widely used as activators in blue and red-emitting phosphors, respectively^[3,4]. Tunable and white light can be generated by combining the emission of Eu^{2+} and Eu^{3+} ^[5]. Over the past decades, many efforts have been made to manipulate the valence states of Eu ion in a single-phased host^[5–8]. Chemical modification plays a key role in host material to stabilize Eu^{2+} in air. The porous glass has shown to be attractive materials for Eu-doped solid state lighting, because of its large surface area and permission of easy infiltration of ions into its pores^[9]. Likely, the conventional sol-gel derived silicate porous glasses possess neutral rigid silica network, thus the reduction of Eu^{3+} to Eu^{2+} needs other metal ions co-doped, for instance, Al ions, to form excessive negative charge in the silica host. Nevertheless, the reduction reaction should be occurred in high temperature (above 800 °C), and the ratio of $\text{Eu}^{3+}/\text{Eu}^{2+}$ cannot be controlled^[10]. In this case, it is promising to develop an efficient approach to achieve tunable simultaneous emission of Eu^{3+} and Eu^{2+} ions in one single host matrix.

Zhang *et al.* previously reported a simple aqueous sol-gel route yielding the transparent monolith stoichiometric AlPO_4 glass possessing mesoporous structure and high surface area, the structure of which was dominated by polymerized AlO_4 and PO_4 tetrahedra^[11]. AlPO_4 provides a low optical basicity which dominates the stabilization of Eu^{2+} ions. Hereby, it emerges as a promising host for stabilizing Eu^{2+} ions. In this letter we report on the reduction of Eu^{3+} to Eu^{2+} in AlPO_4 glass at a relative low temperature (600 °C) in air. Furthermore, controllable luminescence and color tunability could be simply achieved by annealing the samples at different temperatures.

Transparent and colorless AlPO_4 mesoporous glasses were prepared via a simple aqueous sol-gel route in our previous work and characterized by BET surface area

measurements obtained from a Micro-meritics ASAP 2010 volumetric adsorption analyzer with N_2 as adsorbate at 77 K. Mesopore size distributions were calculated according to Barrett-Joyner-Halenda (BJH) method. The morphology of the porous glass surface was determined using a Zeiss scanning electron microscope (SEM)(JSM-6360LA). For the incorporation of Eu ions in AlPO_4 mesoporous glass, 200 mg of mesoporous glasses were immersed into 10 ml 0.05 mol/L $\text{Eu}(\text{NO}_3)_3$ aqueous solutions for 6 h. Then these samples were annealed at different temperatures for 8 h.

The emission and excitation spectra were performed utilizing a HORIBA JobinYvon IBH FL-322 Fluorolog 3 spectrometer equipped with a 450-W xenon arc lamp, double grating excitation and emission monochromators (2.1 nm/mm dispersion, 1200 grooves/mm), and a Hamamatsu R928 photomultiplier tube or a TBX-4-X single-photon-counting detector. All emission spectra have been normalized and arbitrarily shifted vertically for clarity. The lifetime was measured by FLS920 spectrometer. XPS measurements were operated on a Thermo Fisher Scientific K-Alpha spectrometer using non-monochromatic Al $K\alpha$ radiation with a constant pass energy of 20.0 eV. All binding energies ($\text{BE} \pm 0.2$ eV) were referred to the C 1s signal (284.6 eV). All the measurements were carried out at room temperature.

The mesoporous network offers a way to introduce rare earth ions into glass by immersing porous glass in an aqueous rare earth solution. The BET measurement indicates the AlPO_4 glass possesses a surface area as high as 464 m^2/g and an average pore diameter of about 5.0 nm, as shown in Fig. 1(a). Figure 1(b) shows the SEM image of the pore morphology and structure of the AlPO_4 mesoporous glass. The micrograph demonstrates clearly that the mesoporous structure consists of regularly bicontinuous wormlike mesopore of ~ 5.0 nm in diameter, which is consistent with the BET results.

The initial europium ions dissolved in aqueous solution were only trivalent Eu^{3+} , thus only fluorescence of Eu^{3+} was observed for $\text{Eu}(\text{NO}_3)_3$ aqueous solution, as shown

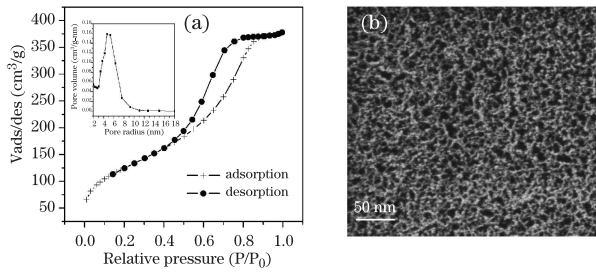


Fig. 1. (a) Adsorption–desorption isotherms of AlPO_4 mesoporous glass annealed at 600°C . The inset indicates the pore size (diameter) distribution of AlPO_4 mesoporous glass. (b) SEM of AlPO_4 sample.

in Fig. 2(a). The principal features appearing in this spectrum can be assigned to 4f-4f transitions of Eu^{3+} ions as follows: ${}^5\text{D}_1 \rightarrow {}^7\text{F}_1$ (538 nm); ${}^5\text{D}_1 \rightarrow {}^7\text{F}_2$ (558 nm); ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ (~ 595 nm); ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ (~ 615 nm). Only very weak emission from the ${}^5\text{D}_1 \rightarrow {}^7\text{F}_J$ transitions can be seen due to the occurrence of fast non-radiative relaxation of the ${}^5\text{D}_{J(1-3)}$ states by multiphonon interaction^[12]. Figure 2(b) shows the emission spectra of Eu-doped porous glass annealed at different temperatures. No emission of Eu^{2+} ions is observed as the annealing temperature is 400°C . Compared with emission spectra of aqueous solution, the weak peaks at 538 and 558 nm disappear, and the reason is the higher maximum phonon energy in the vicinity of Eu^{3+} species embedded in the amorphous phase, resulting in more-likely non-radiative energy transfer. As ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ is a magnetic dipole transition, it should not be affected by the symmetry of the Eu^{3+} environment, hence the ratio of this transition to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition, which is hypersensitive to the ion environment, is a good probe of the local symmetry^[13]. The relative luminescence intensity ratio of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ transitions of the Eu^{3+} ions is found to increase in Eu-doped glass, indicating an increasing of the asymmetry around the Eu^{3+} ions as a result of the amorphous framework. A broad emission peak around 450 nm which is attributed to the $4f^65d^1 \rightarrow 4f^7$ transition of the Eu^{2+} ions in Eu-doped glass annealed at 600°C . The excitation band at 350 nm of Eu^{2+} (Fig. 2(c)) also appeared, while six excitation bands for Eu^{3+} (Fig. 2(d)) placed at 318, 360, 380, 390, 414, and 468 nm were observed. The lack of Eu^{2+} excitation peak in Fig. 2(d) manifests little energy transfer from Eu^{2+} to Eu^{3+} in the mesoporous network. Both the emission and excitation of Eu^{2+} ions witnesses the reduction reaction of partial Eu from trivalent to divalent ions. As the growth temperature increasing, more amount of emission due to the transition of Eu^{3+} changed into a broad peak around 445 nm. The glass annealed at 800°C had a single emission with the maximum around 445 nm along with weak emissions due to Eu^{3+} . Thus, a majority of the europium ions were converted from trivalent to divalent ions even though the Eu-doped AlPO_4 was annealed in air.

Furthermore, it is well known that the Al^{3+} ions effectively disperse the rare-earth ions in the glass structure^[14,15]. Long lifetimes about 0.85 ms for Eu-doped AlPO_4 glass is obtained as clarifying in the inset graph of Fig. 2(b), which indicates more efficient emission than porous silicate glasses owing to its better dis-

persion in AlPO_4 glass^[10].

Previous studies indicate that the Al ions existence in the glass network provides a reductive environment to stabilize the Eu^{2+} ions in an oxidizing atmosphere^[5,6,10,16,17]. In the case of Eu-Al co-doped porous silicate glasses, a large number of defect centers existed, Eu-Al co-doped porous silicate glasses heated in high temperature (above 800°C), which induced reduction of Eu^{3+} by ejected electrons from oxygen associated hole centers^[17,18]. Thus, the abnormal reduction was attributed to an electron transfer from this defect to Eu^{3+} by thermal stimulation. According to the model, we infer that the more electrons carried by negative vacancies are activated as the temperature increases, the more Eu^{3+} ions will be reduced in glass. It is in good agreement with Fig. 2(b) that the amount of Eu^{3+} reduced to Eu^{2+} increases as the activated temperature increasing. In their studies, the intensity of the luminescence of Eu^{2+} was found to increase as more Al^{3+} was incorporated in glass^[16,17]. The phenomena can be explained with optical basicity theory. The higher the concentration of non-bridging oxygen, and thus the greater the “electron donor power” or optical basicity of glass. Therefore, the glass with higher optical basicity favors the higher positively charged cations to neutralize the negative charges provided by non-bridging oxygen. Duffy provided the equation for calculating optical basicity Λ_m as

$$\Lambda_m = X_A\Lambda(A) + X_B\Lambda(B) + \dots \quad (1)$$

where X_A, X_B, \dots are the molar proportions contributed by the constituent oxides, A, B, \dots to the total oxide content of the glass and $\Lambda(A), \Lambda(B), \dots$ are the optical basicity values of these individual oxides^[19]. The lowered

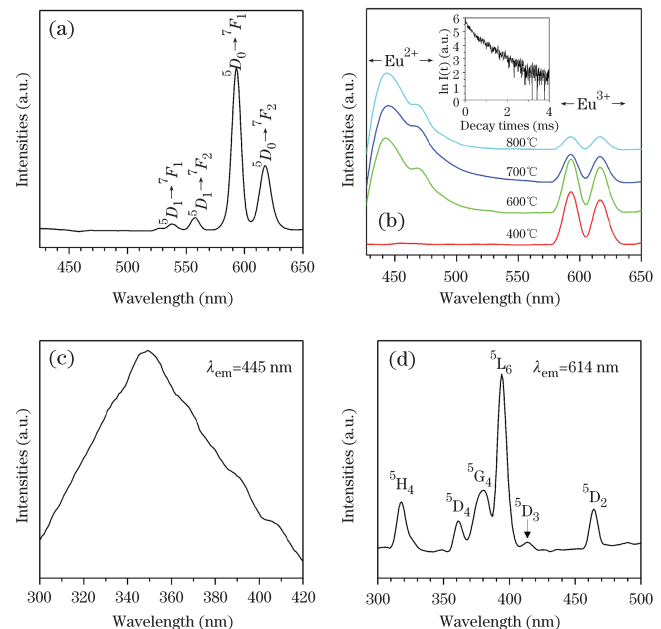


Fig. 2. Emission spectra of (a) 0.05 mol/L $\text{Eu}(\text{NO}_3)_3$ aqueous solution and (b) Eu-doped AlPO_4 mesoporous glass annealed at different temperatures ($\lambda_{ex}=395$ nm); the inset indicates lifetime decay curves of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition for Eu-doped AlPO_4 glass. Excitation spectra of Eu-doped AlPO_4 mesoporous glass annealed at 600°C monitored at (c) 445 and (d) 614 nm.

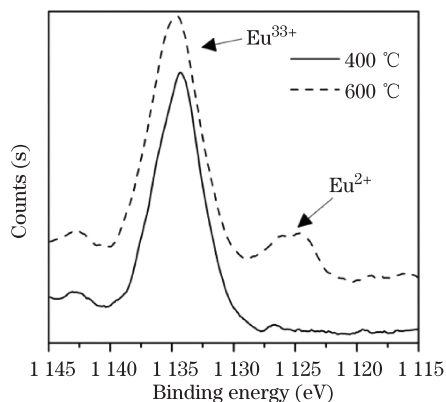


Fig. 3. XPS spectrum at Eu 3d position of Eu-doped AlPO_4 glass annealed at 400 and 600 °C in air.

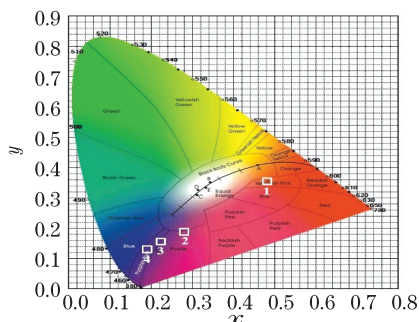


Fig. 4. CIE chromaticity diagram (under 395-nm UV lamp) of Eu-doped AlPO_4 glasses annealed at different temperature; (1)–(4) annealed at 400, 600, 700, and 800 °C in air.

basicity in Al^{3+} co-doped glasses is preferred for the stabilization of Eu^{2+} ions^[7]. It should be noted that AlO_4 is glass former of AlPO_4 glass whenever Al ions acts as network modifier in the Eu-Al co-doped glass system. Using Duffy's empirical formula, the A_m value for the AlPO_4 glass is 0.431, which is much lower than the value for the glasses investigated previously^[7]. The lower basicity induces a more efficient reductive process of Eu^{3+} ions at relative low temperature when a high temperature (above 800 °C) is required for silicate glasses doped with Al ions. The coexistence of Eu^{3+} and Eu^{2+} in AlPO_4 mesoporous glass was also proven by the XPS spectra at Eu 3d position as shown in Fig. 3. It is distinctly seen that two peaks around 1124 and 1135 eV present for the samples annealed at 600 °C. The shapes combined with binding energies of the Eu 3d signals agree well with the signals of $\text{Eu}^{2+} 3d_{5/2}$ and $\text{Eu}^{3+} 3d_{5/2}$, respectively^[20]. Only the peak of $\text{Eu}^{3+} 3d_{5/2}$ with the binding energy 1135 eV presents for the sample annealed at 400 °C. Thus, the XPS spectra agree well with the emission spectra (Fig. 3) that the reduction of Eu^{3+} ions occurs as the temperature is up to 600 °C.

The reduction process occurring at the relative low temperature offers a possibility to tailor the luminescence of Eu ions. As shown in Fig. 3, the ratio of integral intensity between Eu^{3+} and Eu^{2+} ions increases as annealing temperature increases. The calculated chromaticity coordinates of the sample annealed at different temperatures are shown in Fig. 4. The simultaneous luminescence of Eu^{2+} and Eu^{3+} can be controllable from red to blue region, which corresponds to chromaticity coordinates (x ,

y) varying from 1 (0.48, 0.36) to 4 (0.22, 0.12).

In conclusion, an efficient Eu^{3+} ions reduction process in air is observed in Eu-doped AlPO_4 glass at a lower temperature compared with previous reported glass. The chromaticity coordinates for the annealed glasses indicates a tunable luminescence of Eu^{2+} and Eu^{3+} from blue to red region is achieved by simply annealing at different temperatures. Therefore, it is remarkable that the lower basicity and dispersion effect of the glass network former AlO_4 makes the AlPO_4 glass as a suitable matrix to incorporate Eu ions as the tunable luminescent light sources or LEDs.

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