Preparation and Characterization of Zn/Mg Co-doped aluminate phosphor for white LEDs

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Abstract. The Eu^{2+} activated Zn/Mg co-doped aluminate phosphors for white LEDs was prepared by the solution combustion method at 600˚C successfully. The crystal structure model of the phosphor was built, and the band structure and density of states of phosphor were calculated using CASTEP program based on density functional theory. The crystal structure, morphology and luminescent properties of samples were analyzed by the X-ray diffraction (XRD), scanning electron microscope (SEM) and spectrofluorometer, respectively. The results show that sample has a single emission band and centered at 470nm under ultraviolet (UV) 330nm excitation, which corresponds to $4f^65d\rightarrow4f^7$（$^8S_{7/2}$）transition of Eu^{2+}. The crystal structure of the doped phosphors is the same as simple phosphors. The phosphors show the maximum emission peak intensity when the ratio of Sr and Ca is 2:1 and the ratio of Mg and Zn is 3:1, and the dispersion was improved obviously.

Introduction

White light-emitting diodes (WLEDs) were given great expectation due to their less heat, high brightness, long life and other advantages[1-2]. Today commercial WLEDs mainly composed of UV InGaN tube and tricolor phosphors for white light[3-4]. $BaMgAl_{10}O_{17}$: Eu^{2+} (BAM) blue phosphor was used commonly. The traditional preparation of BAM phosphor is high temperature solid-state method. This method can not only cause a reunion of the samples in the sintering process, but also destroy the surface morphology of phosphor when grinding which leads to reduction of luminescent properties[5-6]. Therefore, it’s necessary to develop aluminate phosphor of excellent performance, simple preparation technology for WLEDs.

$SrMgAl_{10}O_{17}$ (SAM) phosphor is considered to be a substitute for BAM phosphor because of its possessing high quenching temperature, good thermal stability and so on[7-10]. Solution combustion method[11] can make the phosphor under a state of molecular reactions, avoid the incompleteness of the high temperature solid-state method caused by big gap of solid - solid contact. Besides, solution combustion method has advantages of short reaction time, low energy consumption and so on. But SAM phosphor prepared by simple combustion method has low luminescence properties because of poor dispersion. Therefore, scholars have proposed a lot of methods to improve luminescence properties, thermal stability and so on. Doping has been widely used because of easy operation and low cost[12,13].

In this paper, $SrMgAl_{10}O_{17}$ phosphor was prepared by solution combustion method and luminescent properties of samples was improved by ions doping. The formation process of $SrMgAl_{10}O_{17}$ was investigated through observation of luminescence properties of samples formed by the method at varied Ca/Sr ratios and choose the best ratio. Within that context, luminescence properties and dispersion $SrMgAl_{10}O_{17}$ formed by the method at varied Zn/Mg ratios. Through the analysis of XRD, PL and SEM, it has been found that the luminescence properties, dispersion and crystallinity have been improved. The crystal structure model of SAM is constructed, and band structure of doping phosphor and no-doping phosphor has been calculated, and a brief analysis.

Experimental

$SrMgAl_{10}O_{17}$ samples were synthesized solution combustion method. $Mg(NO_3)_2 \cdot 6H_2O$, $Ca(NO_3)_2$, $Zn(NO_3)_2$, $Al(NO_3)_3 \cdot 9H_2O$, $Sr(NO_3)_2$, $CO(NH_2)_2$, H_3BO_3, Eu_2O_3 were used for the synthesis of $SrMgAl_{10}O_{17}$ phosphor. A stoichiometric mixture of nitrate raw materials and the mass fraction of 5% Eu_2O_3; the molar ratio 1.5:1 and 1:100 of $CO(NH_2)_2$ and H_3BO_3 of nitrate, the mole ratio 1:5 and 1:8 of HNO_3 and CH_3CH_2OH of the product. A stoichiometric mixture was dissolved in a constant temperature water bath at 80 ˚C and removes the mixture after 40 - 60 min to get the white collosol. Then the collosol was fired in a muffle furnace at 600 ˚C for 5 min,to produce the $SrMgAl_{10}O_{17}$ samples.

Preparation of samples by X-ray diffractometer (XRD, Bruker D2, lambda = 0.15406nm, step 0.02 °, the scanning range of 10~80°) characterization of its crystal structure. With Japan HATACHI company SU8010 type ice emission scanning electron microscope (FE-SEM) to observe the sample particle morphology. Use the HORIBA JobinYvon Fluorolog fluorescence spectrometer tests the excitation spectra and emission spectra of the sample. All tests are completed at room temperature.

Results and discussion

Theoretical calculation analysis

SAM is a hexagonal system, compose by the close packing of spinel block ($MgAl_{10}O_{16}$) and mirror surface layer ((SrO) , as saw in Fig.1. The space group is $P6_3/mmc$. SAM has a β $-Al_2O_3$ structure, and has excellent performance due to strong chemical bonds in lattice[7,10].

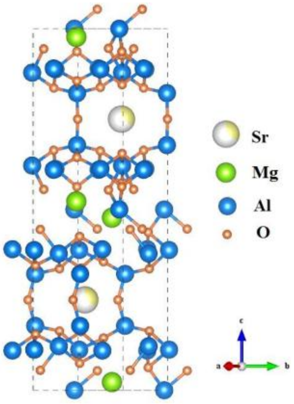
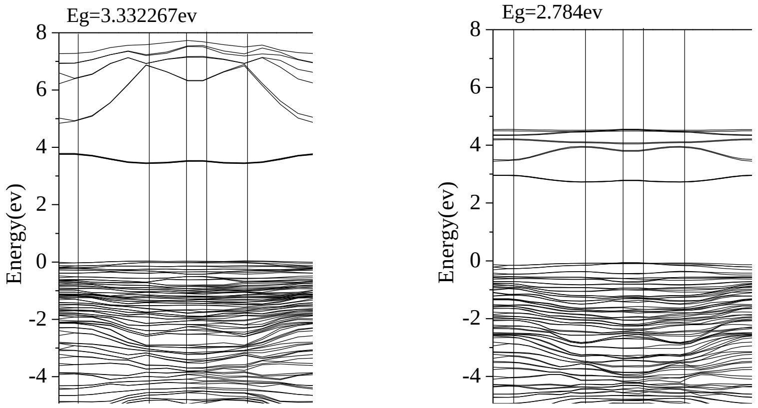


Fig.1. The crystal structure model of SAM

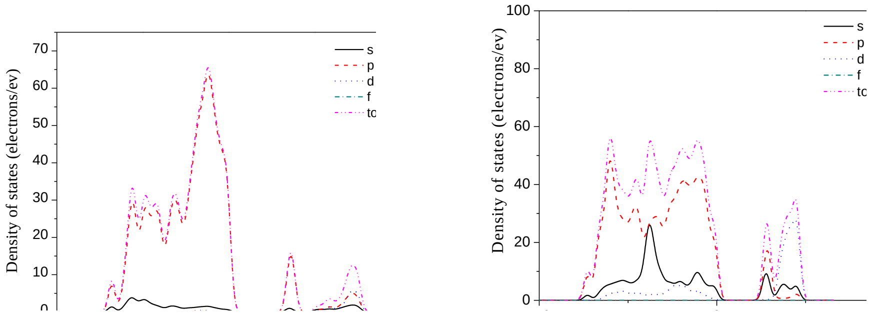
Fig. 2 (a) shows the band structure of SAM, Fig.2 (b) for the shows the band structure of pure SAM under 2:1 Sr/Ca ratio and 3:1 Mg/Zn ratio. It’s different between the band structure of pure SAM (band gap 3.332eV) and the band structure of doped SAM (band gap 2.784eV). It has been seen that a decrease of the band gap with doped SAM is advantageous to the electron transition, makes energy transfer between activator ions more easily.

Fig.3 (a) and Fig.3 (b) show the crystal density of pure SAM and the crystal density of doped SAM, respectively (0 ev as Fermi level). In Fig. (a) , obvious peaks exist in the area of the valence band of pure SAM, illustrates that electronics near the Fermi level are relatively concentrated, while the energy levels in the region of the conduction band is relatively discrete. In Fig. (b), it can be seen that the electric distribution of valence band area of doping SAM is more uniform, hybrid discrete energy levels of the conduction band area decreased. It's obvious that the transition in the electric energy level of doping SAM is more easier.



(a) The band structure of SAM (b) The band structure with doped SAM

Fig.2. The band structure of SAM



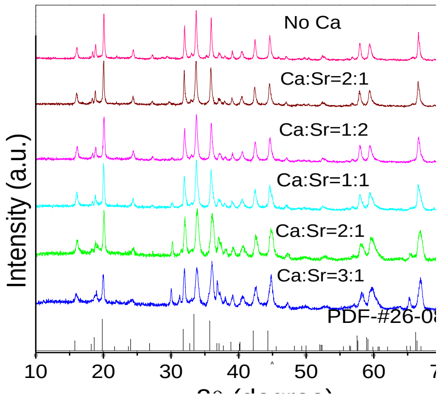
(a) Crystal density of SAM （b）Crystal density of doped SAM

Fig.3. Crystal density of SAM

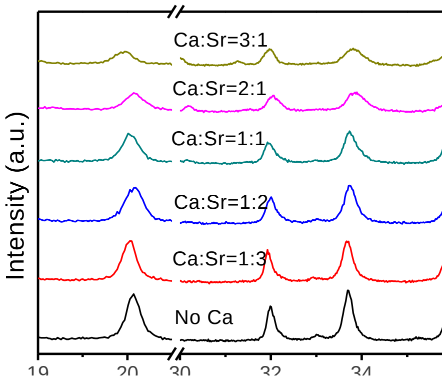
XRD analysis

Fig. 4 shows the XRD patterns of $SrMgAl_{10}O_{17}$ samples with different ratio of Ca and Sr. All of the observed peaks matched well with the standard data card (PDF-#26-0879). Ca ions were supposed to substitute the Sr sites according to their similar ions of radius and have no effect on the crystal structure of SAM. But the samples include impurity phases when the Sr/Ca ratio less than 2:1, appeared some impurities of samples due to excessive Ca ions. In Fig.2, it can be found that the diffraction peaks have shifted when adding Ca ion gradually. It is because that the radius of Sr ion (0.120nm [15]) is larger than the radius Ca ion (0.104 [15]), which makes crystal lattice, contraction field strength increase, and then the diffraction peaks red shift. The intensity of the diffraction peak is weakened gradually when the ratio of Sr: Ca larger than 2:1, suggests that the change of crystal structure.

Fig. 5 shows the XRD patterns of $SrMgAl_{10}O_{17}$ samples with different ratio of Zn and Mg. All of the observed peaks matched well with the standard data card (PDF-#26-0879). The Zn ions were supposed to substitute the Mg sites according to their similar ions of radius. It can be seen that the intensity of the diffraction peak decreased gradually when the ratio of Sr: Ca larger than 3:1. Combined Fig.4 and Fig.5, we can see that Ca/Sr co-doping can affect the crystal structure of SAM phosphor, the right amount of Ca/Sr, Zn/Mg will not change the crystal structure of the SAM phosphor.



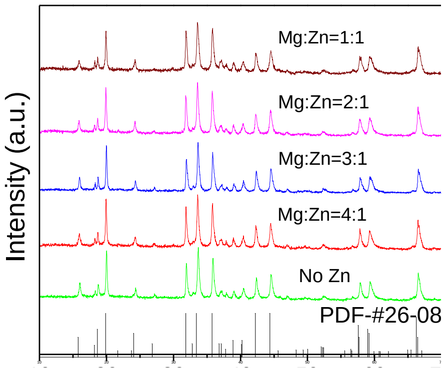
(a)



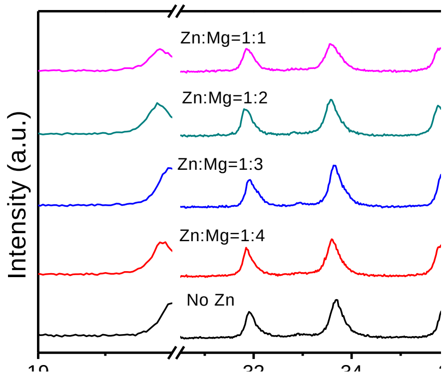
(b)

Fig. 4（a） XRD patterns of Ca and Sr doped SAM

Fig .4（b） Shifting and broadening of peaks for changing ratio of Ca and Sr



(a)



(b)

Fig.5（a） XRD patterns of Mg and Zn doped phosphors particles

Fig.5（b） Shifting and broadening of peaks for changing ratio of Mg and Zn

SEM analysis

Fig.6 (a) shows the SEM of $SrMgAl_{10}O_{17}$ phosphors. It shows that the shape of the sample is limited to hexagonal lamellar structure. The shape of the sample is nonuniform, and the size is not consistent. The reunion phenomenon is relatively serious because of sintering phenomenon. Fig.6 (b) shows the SEM of $SrMgAl_{10}O_{17}$ phosphors of 1:2 Ca/Sr ratio. It can be found that the morphology of samples did not significantly change, suggested that a small amount of Ca ions will not affect the structure of the phosphors in $SrMgAl_{10}O_{17.}$ Luminescence properties of SAM phosphor have been improved but also have reunion phenomenon (saw Fig.7). Fig.6 (c) shows the SEM of $SrMgAl_{10}O_{17}$

phosphors of 3:1 Mg/Zn ratio. It can be seen that the surface morphology has been improved obviously with Zn doping compared to Fig.6 (a), and shows rod structure. Indicating that adding Zn ion can improve the dispersivity of SAM phosphor because of improving the dispersion of the sample[16].

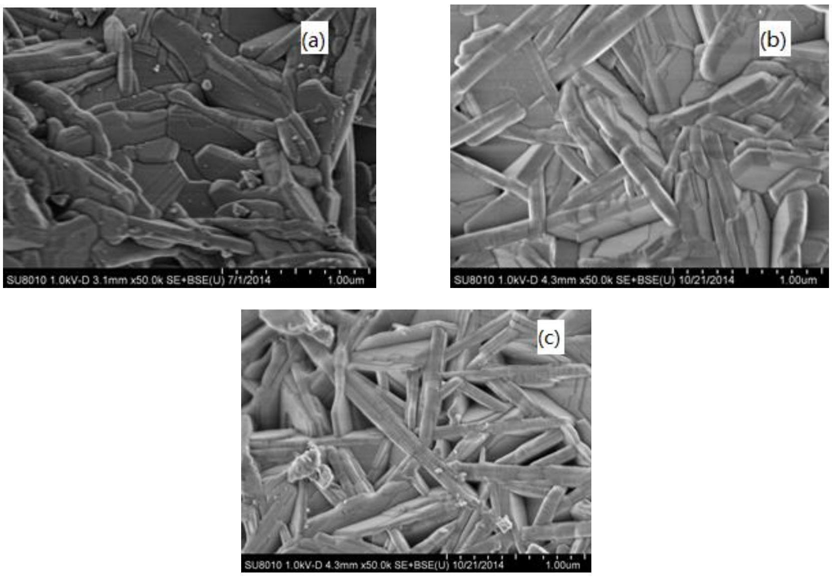


Fig.6. SEM images of samples：(a) SAM; (b) Ca and Sr; (c) Zn and Mg

Luminescence properties analysis

Fig. 7 is the emission spectrum of the samples. When doped with Ca ions and changed the proportion of Sr/Ca, the emission spectrum shape of the sample was roughly same, however, the location of the emission peak and luminescence intensity is different. When the Sr/Ca ratio began to increase, the luminescence intensity of samples increased the red shift. The luminescence intensity reaches maximum and peaks at 470nm when the Sr/Ca ratio attains to 2:1. When continue to increase the content of Ca, the luminescence intensity gradually weakened and the emission peak appears a blue shift. Because of doping Ca ions, the crystal structure of power has changed. When gradually increase the proportion of Ca ion and ionic radius of the larger Sr (0.120 nm) are ionic radius smaller Ca (0.104 nm) after the replacement, crystal shrinking crystal field strength increase, Eu^{2+} 5d level division to strengthen, so that the 4f - 5d level energy decreases, and lead to red shift phenomenon, emission spectrum and luminescence intensity increased. When adding excessive Ca, will produce a certain amount of impurities, led to the luminescence intensity weakens.

Doped with Zn ions and change Mg/Zn ratio at the same time, the emission spectrum of sample shape and emission peak position mainly invariant, but differences between luminescence intensity can be seen from the Fig. 8. When Zn/ Mg ratio of 1:3, the luminescence intensity of samples reached a maximum; Continuing to increase the content of Zn, the luminescence intensity gradually reduces. Because Zn^{2+} to Eu^{2+} will be the energy transfer between Eu^{2+} $^8S_{7/2}$ stimulated by 4f5d excited state to ground state level transition, and Zn^{2+} to be able to absorb the energy transmitted to Eu^{2+} at the same time, thus improve the luminescence intensity of the sample. When the content of Zn excess, the energy difference between the ground state and excited state is reduced, it is easier to produce the radiative transition, make more power back to the ground state, led to the luminescence intensity weaken. Through comparing Fig. 7 and Fig. 8 found, Zn/Mg doping ratio of 1:3 is slightly higher than the luminescence intensity is not mixed with recent luminescence intensity, shows that the addition of suitable amount of Zn ion can be certain improvement the luminescence intensity .

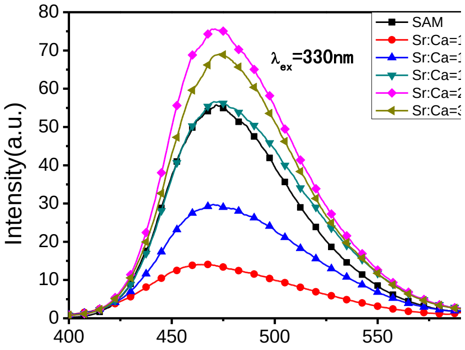


Fig.7. Photoluminescence emission spectra（λ_{ex}=330nm）of changing the ratio of Ca and Sr

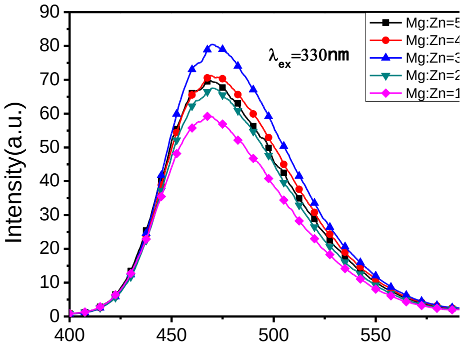


Fig.8. Photoluminescence emission spectra（λ_{ex}=330nm）of different ratios of Mg and Zn

Summary

Zn/Mg co-doped $SrMgAl_{10}O_{17}$ phosphor was successfully prepared by solution combustion method at 600 ˚C. They were characterized with regard to their luminescence properties, purity and dispersion. The sample obtained by Zn/Mg co-doped $SrMgAl_{10}O_{17}$ phosphor showed better luminescence intensity, dispersion, and crystallite than $SrMgAl_{10}O_{17}$ phosphor. The crystal structure model of $SrMgAl_{10}O_{17}$ has been built, the band gap and crystal density were calculated. The $SrMgAl_{10}O_{17}$ phosphor shows best luminescence properties when the ratio of Ca/Sr is 1:2 and the ratio of Zn/Mg is 1:3. The emission spectra shows the most high intensity at 470nm under UV excitation, which suggested that this phosphor is an excellent phosphor for white LEDs.

Acknowledgements

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