J. Ceram. Sci. Technol., **12** [1] 1-8 (2021) DOI: 10.4416/JCST2020-00017 available online at: http://www.ceramic-science.com © 2021 Göller Verlag

The Effects of Eu_2O_3 Additive Amounts and Addition Methods on the Synthesis of β -SiAlON Multiphase Materials from Fly Ash Acid Slag

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Abstract

 β -SiAlON:Eu phosphors prepared from acid slag of fly ash at low temperatures were studied. The effect of the amounts and addition methods of Eu₂O₃ additives was discussed. The phase compositions of the products were characterized with X-ray diffraction (XRD) spectroscopy. The photoluminescence (PL) properties of the Eu-doped β -SiAlON phosphors were studied by means of photoluminescence spectroscopy. The morphology of the products was characterized with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results confirmed that the alumina extracted acid dissolution slag could produce β -SiAlON: Eu multiphase phosphors at 1400 °C. The optimum Eu concentration was approximately 0.08. The PL spectrum emission range is located in the violet/blue spectral range.

Keywords: SiAlON, fly ash, carbothermal reduction, nitridation, Eu2O3

I. Introduction

In recent years, with the development of phosphor research, several research workers have found that nitrides are very suitable for white light-emitting diode (LED) applications. Rare earth element-doped β-SiAlON phosphors occupy a unique position among nitride phosphors. Compared with similar α -SiAlON phosphors ¹⁻⁵, β -SiAlON phosphors have higher chemical stability. Due to the lack of special sites for rare earth ions in the structure, researchers have paid less attention to these complexes. Therefore, rare earth-doped β-SiAlON phosphors obviously have high research value and are worth further study ⁶⁻¹². Using scanning transmission electron microscopy (STEM), Koji Kimoto et al. 13 observed directly that a Eu dopant atom exists in a continuous atomic channel in the β -SiAlON structure. However, there are few similar studies, and more data are needed to determine the influence of the doped ions.

 β -SiAlON:Eu²⁺ has the advantages of high chemical stability, high luminescence intensity, small thermal quenching and narrow half-peak width. It is a very suitable fluorescent material. In the past, it was reported that the raw materials used for the preparation were usually high-purity powders (such as Si₃N₄, AlN and rare earth oxides), and the synthesis temperature was very high (1 900 – 2 000 °C). The raw material cost, energy consumption and equipment requirements are high. Therefore, it is of great significance to search for cheaper raw materials and lower preparation temperatures. Fly ash acid slag, which is the slag obtained after alumina or aluminum salts are extracted from

* Corresponding author: lifangfei_jlu@163.com co-corresponding author: weicundi_jlu@163.com fly ash, can satisfy the above requirements $^{14-18}$. Fly ash acid slag is usually considered a kind of solid waste, and it is difficult to recycle and utilize.

Researchers are trying to reduce the preparation temperature and raw material cost, but it is very difficult to balance these two factors. X.W. Zhu et al. 19 synthesized Eu²⁺-doped β -SiAlON phosphors with $1 \le z \le 4$ by means of gas pressure sintering at 1 900 °C. This synthesis temperature is common for β-SiAlON phosphor preparation. Hua Yang et al. ²⁰ synthesized β-SiAlON:Eu phosphors using an SBA-15 hard template at 1 380-1 450 °C. This synthetic temperature is much lower than traditional methods, but the raw materials are not cheap enough. Naoto Hirosaki et al.²¹ synthesized a β -SiAlON green phosphor from Si_3N_4 and AlN at 1 900 °C with z close to 0.14, as calculated from the XRD measurement. Jeong Ho-Ryu *et al.*²² obtained Eu²⁺-doped β -SiAlON phosphor at 2000 °C. High energy consumption is also a large problem for the application of this method. Qian Liu et al. 23 obtained β-SiAlON:Eu²⁺ phosphors from high-purity Si $(OC_{2}H_{5})_{4}$ and Al $(NO_{3})_{3}$ ·9H₂O at 1 370 – 1 500 °C with an electrospinning method combined with carbothermal reduction nitridation. Both the preparation method and the raw materials incur high costs. Kukhyun Jun et al. 24 prepared β -SiAlON:Eu²⁺ (*z* = 1) phosphors from pyrophyllite-based mixtures at 1 500 °C by means of carbothermal reduction and nitridation. Although the preparation temperature was not as high, the raw materials in this research were not cheap enough.

In this experiment, the acid slag of circulating fluidized bed (CFB) fly ash and carbon black were used as raw

materials to significantly reduce the cost of raw materials. The multiphase powder of β -SiAlON was prepared by means of carbothermal reduction and nitridation. The preparation temperature and raw material cost are low. β -SiAlON:xEu (x = 0, 0.002, 0.005, 0.008, 0.01, 0.02, 0.05, 0.08, 0.10) phosphors were obtained. The effects of Eu content, excitation voltage and excitation wavelength on the photoluminescence (PL) properties of the samples were analyzed.

II. Materials and Methods

β-SiAlON:Eu phosphors were prepared from a mixture of CFB fly ash acid slag, carbon black (model N550, oil absorption 2.01, Jilin Petrochemical Co. Ltd.) and Eu₂O₃ (99.99 %, Sinopharm Chemical Reagent Co. Ltd.). The chemical composition of the CFB fly ash acid slag from Zhungeer coal mine in China is as follows: SiO₂, 61.80 wt%; Al₂O₃, 21.84 wt%; TiO₂, 2.08 wt%; CaO, 0.76 wt%; MgO, 0.09 wt%; Fe₂O₃, 0.26 wt%; K₂O, 0.27 wt%; Na₂O, 0.18 wt%; and LOI (Loss on ignition), 12.50 wt%. The samples were prepared with an optimal molar ratio of C:Si = 3.02 with different Eu doping contents (*x* = 0, 0.002, 0.005, 0.008, 0.01, 0.02, 0.05, 0.08, 0.10) weighed and mixed by means of dry-milling in a mortar. Then, the starting powders were calcined in a boxtype furnace. The reaction temperature was 1 400 °C and was maintained for 6 h under nitrogen flow (flow rate of 2 L/min). The samples were cooled to room temperature in the furnace and characterized at room temperature.

The phase analysis of the β -SiAlON phosphors was carried out by means of X-ray diffraction (XRD, DX-2700, China). The photoluminescence properties were measured at room temperature with a fluorescence spectrophotometer (F-380, China) with a Xe lamp as an excitation source. The morphology of the β -SiAlON phosphors was investigated with scanning electron microscopy (SEM, S-570, Japan) and transmission electron microscopy (TEM, JEM-2100F, Japan).

III. Results and Discussion

(1) Phase compositions of products

Fig. 1 shows the XRD patterns of the CFB fly ash and acid slag. According to the XRD spectra, the phase compositions of acid slag and fly ash have an obvious evolutionary relationship. Apart from the loss of the acid-soluble phase and the enrichment of the inert phase, the change in the intensity of the mullite phase can indicate the dissolution of a large number of aluminum elements. The positions and shapes of amorphous peaks are basically unchanged, but the relative intensities are improved, which is related to the enrichment of silicon. The enrichment of silicon is related to the dissolution of the amorphous skeleton, suggesting that the dissolution of the amorphous skeleton may be less affected and to a large extent remains in the acid slag.

The XRD spectra of the samples are shown in Fig. 2. The phase compositions of all of the samples are β -SiAlON, SiC and corundum. Although the content of TiO₂ is not low, there are no related phases observed in the XRD spectra, as they may be concealed by other phases. As the Eu

doping content increases, the phase compositions of the samples remain basically unchanged, and the relative contents are changed, as shown in Fig. 2(a) and (b). In particular, the characteristic peaks of corundum are significantly weakened, which may be related to the decrease in the melting point of the whole system and the formation of more SiAlON solid solutions from corundum. The relationship between the normalized intensities of the major phase XRD characteristic peaks and different Eu additive amounts is shown in Fig. 2(d). With the increase in Eu_2O_3 , the intensities of β -SiAlON first increase until the Eu additive amount reaches 0.01, then decrease until the additive amount reaches 0.05, and finally increase. The change in SiC is opposite to that of β -SiAlON. The intensities of corundum remain approximately constant during this period. With the increase in Eu₂O₃, the intensities of the XRD peaks decrease, which is probably due to the decrease in the melting point of the system with the increase in Eu₂O₃, resulting in more liquid phase at high temperature and a lower crystallization degree under the same cooling conditions. It also implies that if we want to obtain better PL performance, that is, to obtain a better lattice structure, the addition of Eu₂O₃ should not be too much, while insufficient addition will make the PL performance negligible. It can be inferred that there is an optimal addition range. The lattice constants of the SiAlON phase characteristic peaks of XRD spectra are calculated according to Eq. (1) and Eq. (2) ^{25, 26}.



Fig. 1: XRD patterns of raw materials (a) CFB fly ash (b) alumina extracted acid dissolution slag.

$$a = 0.7603(6) + z \cdot 0.00296(4) \text{ nm}, \tag{1}$$

$$c = 0.2907(8) + z \cdot 0.00255(6) \text{ nm}, \tag{2}$$

The z value of $Si_{6-z}Al_zO_zN_{8-z}$, which is the chemical composition of the SiAlON phase, is calculated to be approximately 2, between 2.0 and 2.4. The results are in agreement with relevant literature ¹⁹ about the range of z value.



Fig. 2: XRD patterns of (a) and (b) products with different Eu additive amounts (c) products with different Eu addition methods (d) the relationship between major phase XRD characteristic peaks normalized intensities and the Eu additive amount.

Fig. 2(c) shows the effect of different Eu addition methods on the XRD patterns of the β -SiAlON:xEu (x = 0.05) sample. The raw materials of sample 1, namely slag and carbon black, are mixed with the rare earth oxide Eu₂O₃ and then carbothermally nitrided. The raw material of sample 2, namely slag and carbon black, are carbothermally nitrided first, then mixed with the rare earth oxide Eu₂O₃, and then calcined twice. The major crystalline phases of both samples are β -SiAlON, SiC and corundum. There is less SiC and amorphous glass phase in sample 2 based on the XRD patterns. This result will affect the PL properties of the samples.

(2) The effect of the excitation voltages and excitation wavelengths

Fig. 3(a) shows the emission spectra of the sample of β -SiAlON:*x*Eu (x = 0.01) excited by different excitation voltages. The emission spectra of the sample are not ob-

vious when the excitation voltages are 200-600 V, and the emission spectra of the sample are obvious when the excitation voltages are 700-900 V. Therefore, it is necessary to select a suitable high excitation voltage in the testing process. Fig. 3(b) shows the emission spectra of the β -SiAlON:*x*Eu (*x* = 0.01) sample under different excitation wavelengths (230-350 nm). The relationships between the excitation wavelengths and the peak position of the emission spectra and the relative peak intensities of the emission spectra are shown in Fig. 4. As the excitation wavelength increases, the relative peak intensity of the emission spectrum first increases and then decreases after reaching 330 nm, which means that there is an optimal excitation wavelength of approximately 330 nm. Except for the initial points, the peak positions of the emission spectra remained at approximately 420 nm, which means that the PL color of the synthesized powders is not sensitive to the change in the excitation wavelength.



Fig. 3: (a) Emission spectra of the sample of β -SiAlON:xEu (x = 0.01) excited by different excitation voltages (b) emission spectra of sample β -SiAlON:xEu (x = 0.01) under different excitation wavelengths (230–350 nm).



Fig. 4: The relationships between excitation wavelengths and (a) peak positions of emission spectra (b) peak relative intensities of emission spectra.

(3) The effect of the Eu additive amount

The excitation and emission spectra of the β -SiAlON: x Eu (x = 0, 0.002, 0.005, 0.008, 0.01, 0.02, 0.05, 0.08, 0.10)samples are shown in Fig. 5. The excitation peaks are at approximately 340 nm, and the variations in the peaks of different samples are very small. The emission spectra of the samples have two peaks located at approximately 440 nm and 470 nm. The relationships between the relative peak intensities of the emission spectra and the peak position data of the peaks corresponding to different Eu additive amounts are described in Fig. 6. Fig. 6(a) shows that the peak intensities of the emission spectra are affected by the Eu additive amount in the samples. The peak intensities increase with increasing Eu additive amount, except for a few points (x = 0.005, 0.008). The peak intensities decrease when the Eu additive amount exceeds 0.08. This may be related to the decrease of the SiC phase in the samples, which has negative effects on the PL properties. The change in peak intensities is consistent with the change in SiC XRD intensity shown in Fig. 2(d). The crystallinity of the samples and the content of SiC will affect the PL intensity of the samples; in particular, the SiC content will have a considerable negative impact on the PL performance. The content of silicon carbide should be controlled and reduced. The effect of concentration quenching is responsible for the peak intensity ⁶. The intensities of the peaks at 470 nm are weaker than those of the peaks at 440 nm when the Eu additive amount reaches 0.08. Fig. 6(b) shows that the peak wavelengths of the emission spectra are affected by the Eu additive amount in the samples. The first peak wavelengths decrease with increasing Eu additive amount and are basically maintained at approximately 439 nm. The second peak wavelengths were maintained at approximately 470 nm.

In this paper, the emission spectra depend not only on the coordination environments of rare earth ions in β -SiAlON but also on the influence of oxides in sample powders. In the samples from starting mixtures with Si₃N₄, the



Fig. 5: (a) Excitation and (b) emission spectra of the samples β -SiAlON:xEu (x = 0, 0.002, 0.005, 0.008, 0.01, 0.02, 0.05, 0.08, 0.10).



Fig. 6: The relationships between Eu additive amount and (a) peak intensities of emission spectra (b) peak wavelengths of emission spectra.

emission spectrum of β -SiAlON:Eu²⁺ with an increase in the z value may show a redshift because the Al-O and Al-N bonds are longer than the Si-N bonds²². However, the Stokes shift effect competes with the nephelauxetic effect ²², and the emission spectrum of β -SiAlON:Eu²⁺ with an increase in the z value may show a blueshift in other studies ¹⁹. Upon excitation, emission occurs due to the Eu²⁺ 4f⁶5d¹ \rightarrow 4f⁷ transition ²⁷. In this study, the *z* values were approximately 2 (between 2.0 and 2.4) and the emission spectrum was located in the blue-purple region. This result is similar to the results of related literature ^{19, 20}, and the luminescence mechanism may be more relevant to the nephelauxetic effect and the different kinds of N/O coordination around Eu²⁺ ions ¹⁹. In this study, the silicon source in the starting mixture is fly ash acid slag, which is different from Si₃N₄. It leads to more coproducts, such as SiC and corundum.

(4) The effect of different Eu addition methods

Fig. 7 shows the effect of different Eu addition methods on the emission spectra of the β -SiAlON:*x*Eu (x = 0.05) sample. The relative intensity of the emission spectra of the sample 2 is much higher than that of the sample 1, which may be related to the decrease in SiC content, the higher crystallinity of the samples and other factors. SiC was found to have adverse effects on the PL properties of the samples. It can be considered that secondary calcining is beneficial to the improvement in PL properties.



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Fig. 7: The effect of different Eu addition methods on the emission spectra.



Fig. 8: The SEM images of (a) acid slag (b) sample β -SiAlON:xEu (x = 0) (c) sample β -SiAlON:xEu (x = 0.05) (d) sample β -SiAlON:xEu (x = 0.05) calcined twice (e) sample β -SiAlON:xEu (x = 0.10), the TEM images of (f) sample β -SiAlON:xEu (x = 0.05) (g) sample β -SiAlON:xEu (x = 0.05) calcined twice (h) sample β -SiAlON:xEu (x = 0.10).

(5) Product morphology

Fig. 8 shows the typical morphology of different samples. The SEM morphology of the samples is similar to the morphology described in relevant literature about SiAlON $^{28-32}$, Si₃N₄ and SiC $^{33-36}$. The SEM image of acid slag is shown in Fig. 8(a). The particles are irregular. Fig. 8(c) and (d) compare the morphology of the samples nitrided after mixing with Eu₂O₃ and before mixing with Eu₂O₃. Rod-like grains can be found at the surface of sample 1, with small fragments, while the surface of sample 2 is smooth, which will lead to a difference in the PL spectra. Fig. 8(b), (c), and (e) compare the morphology of the samples with different Eu contents. There were particles accompanying the formation of fibers at the surface in Fig. 8(b). Agglomerated rod-like grains are shown in Fig. 8(c). There are particles accompanying nearly spherical grains at the surface in Fig. 8(e). The doping of rare earth oxides will reduce the number of fibers. Fig. 8(f), (g), and (h) compare the TEM images of samples with different Eu contents and the clinker mixed with Eu₂O₃. The TEM morphology of the samples is similar to those described in the relevant literature about Si_3N_4 and SiC^{37} . With the increase in the Eu content, the edge of the sample becomes smoother, and the sharp corners become rounded. The clinker is rounder than the slag (ignoring the fragments at the surface). The fragments may be related to grinding and dispersion in the sample preparation process, not to the real state of the sample. This implies that fibers are widely present in all samples. The morphology of fibers in samples is close to that of SiC, so it can be inferred that there is more SiAlON transformed from SiC. SiC maintains the morphology of the fibers in this kind of sample, which will have adverse effects on the PL properties.

IV. Conclusions

Eu-doped β -SiAlON multiphase phosphors with different Eu additive amounts were prepared from fly ash acid slag under nitrogen flow (the flow rate was 2 L/min) at 1 400 °C for 6 h. The major crystalline phases of the samples are β-SiAlON, SiC and corundum. The excitation voltages should be as high as 700 V or above. The optimum Eu additive amount was approximately 0.08 based on the PL spectra. More or less Eu additive will have adverse effects on the PL properties of the samples. The SiC content will have a considerable negative impact on the PL performance. The PL spectrum emission range is located in the violet/blue spectral range, with two maximum peaks at approximately 440 nm and 470 nm. The relative intensity of the emission spectra of the sample calcined twice is much higher than that of other samples because of lower SiC content and other factors. SiC was found to have adverse effects on the PL properties of the samples. The samples consist of particles and fibers. The morphology of the products is similar to that of the β -SiAlON powder described in the relevant literature. SiC maintains the morphology of the fibers. The addition of Eu₂O₃ will reduce the number of fibers.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (NSFC, grant No. 41702036 and grant No. 41472035).

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