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The origin of bimodal luminescence of β-SiAlON:Eu^{2+} phosphors as revealed by fluorescence microscopy and cathodoluminescence analysis

Lin Gan [a,b], Zhi-Yong Mao [b,c], Xiong-Hui Zeng [d], Yu-Qiang Zhang [e], Yang Zhao [b,c], Fang-Fang Xu [a,*], Ying-Chun Zhu [c], Xue-Jian Liu [d]

[a] *State Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China*
[b] *University of Chinese Academy of Sciences, Beijing 100049, PR China*
[c] *Inorganic Coating Materials Research Center, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China*
[d] *Electron Microscope Lab, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, PR China*
[e] *The Research Center of Structural Ceramic Engineering, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China*

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ABSTRACT

Eu^{2+}-doped SiAlON phosphors with the composition of $Eu_xSi_{6-z}Al_zO_zN_{8-z}$ $(0.5 \leq z \leq 3)$ at a fixed $x = 0.01$ were synthesized by the gas pressure sintering method. Dependence of luminescence properties on the phase compositions in β-SiAlON:Eu^{2+} phosphors has been examined via fluorescence microscope and scanning electron microscope equipped with a cathodoluminescence spectrometer and an energy dispersive spectrometer. Bimodal emission (green and violet) from β-SiAlON phase is observed in the samples with $z \geq 2$, indicating co-existence of two different kinds of coordination for Eu^{2+} ions in the host lattice.

1. Introduction

As a new class of inorganic phosphors, rare earth (RE)-doped oxynitride and nitride luminescence materials have received increasing attention in recent years because of their excellent optical properties and great potentials for application in light-emitting diodes (LEDs) [1–3]. β-SiAlON ceramics is a high performance structural material due to its superior thermal stability, chemical inertness and high mechanical strength [4]. It is a solid solution isostructurally derived from β-Si_3N_4 through equivalent replacement of Si–N bonds by Al–O bonds [5]. The chemical formula of the solid solution can be written as $Si_{6-z}Al_zO_zN_{8-z}$ $(0 < z \leq 4.2)$, where z represents the number of Al–O bonds substituting for Si–N bonds. In the last decade, β-SiAlON has been discovered as a promising host for RE luminescent materials. Although β-SiAlON has no apparent crystallographic sites for RE ions, Hirosaki et al. [6] first reported the green-emitting Eu^{2+}-doped β-SiAlON. Then Xie et al. [7] systematically studied the optical properties of the Eu^{2+}-doped β-SiAlON with various z values $(0.1 \leq z \leq 2)$ and Eu^{2+} doping concentrations (0.02–1.5 mol%). Though both theoretical calculation [8,9] and experimental observation [10] indicated that Eu^{2+} ions could be stabilized inside the channels of β-SiAlON lattice, there is still no critical data available with respect to the accurate coordination of Eu^{2+} ions in β-SiAlON host. Nevertheless, this has not hindered successful applications of Ce^{3+}-, Yb^{2+}- and Pr^{3+}-doped β-SiAlON phosphors in LEDs [11–13].

β-SiAlON is an interesting host for RE dopants because of the possibility of modifying its chemical composition in a large range from a nitrogen-rich host to an oxygen-rich one without changing its crystal structure. The luminescence of Eu^{2+} and Ce^{3+} ions comes from 5d → 4f electronic transitions, which strongly depends on the structure and composition of the host lattice. With the increase of z value, the increased O/N ratio and lattice parameters can both have influence on the emission. Therefore, the luminescence of Ce^{3+} or Eu^{2+}-doped β-SiAlON can be tuned by variation of the z value. It is known that Eu^{2+} gives long wave green emission peaked at about 535 nm due to strong nephelauxetic effect and large crystal field splitting resulted from the nitrogen-rich covalent host for β-SiAlON with low z values. However, emission spectra of β-SiAlON:Eu^{2+} with a minor band or shoulder peaked at about 460 nm have been reported by Xie et al. [7] and Li et al. [8]. They both suggested that the secondary phases should be responsible for this emission. Later, Zhu et al. [14] reported bimodal emission

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[*] Corresponding author. Tel.: +86 21 52412574; fax: +86 21 52415615.
E-mail address: ffxu@mail.sic.ac.cn (F.-F. Xu).

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of Eu^{2+}-doped β-SiAlON with $1 \leq z \leq 4$, which had an additional violet emission band located at about 415 nm besides the dominant green band. The excitation spectra monitored at these two emission peaks respectively showed completely different shapes. So they attributed this phenomenon to the co-existence of two different coordination environments for Eu^{2+} in β-SiAlON matrix, i.e. nitrogen-rich and oxygen-rich. However, the authors did not provide enough evidences to exclude possible contributions to the violet emission from the minor doped AlN polytypoid phases which were detected in all these bimodal emitting samples by X-ray diffraction (XRD) analysis. According to our previous study, formation of AlN polytypoid impurity phases is inevitable in the RE-doped β-SiAlON phosphors with $z \geq 1$ synthesized by high temperature solid-state reaction [15]. To clarify the source of each emission, microanalysis of luminescence is required. Fluorescence microscope can intuitively show the full color emitting overview for micron-sized phosphor particles under ultraviolet (UV) excitation. Cathodoluminescence (CL), an accessory spectrometer attached to a scanning electron microscope (SEM) can acquire luminescence spectra emitted from individual particles since the electron beam can excite the sample in nanoscale [16].

In this work, we aim to investigate the luminescence characters of Eu^{2+}-doped β-SiAlON correlated with phase compositions. In particular, each emission band possibly aroused from different phases or micro-regions were tracked down via using fluorescence microscope and SEM-CL. Bimodal emission from β-SiAlON phases was explicitly observed in samples with high *z* values and the luminescent mechanism was investigated.

2. Experimental procedures

Four β-SiAlON:Eu^{2+} phosphor samples with nominal compositions of $Eu_xSi_{6-z}Al_zO_zN_{8-z}$ (z = 0.5, 1, 2 and 3, respectively; x = 0.01) were synthesized from α-Si_3N_4 (SN-E10, Ube Industries, Japan), AlN (Type F, Tokuyama Corp., Japan), Al_2O_3 (99.99%, Shanghai Yuelong, China) and Eu_2O_3 (99.99%, Aladdin, China) powders. The raw material powders were mixed homogeneously in an agate mortar and then granulated using a test sieve. The powder mixture was then loaded into boron nitride crucibles and heated in a gas pressure sintering (GPS) furnace at 1900 °C for 5 h under a N_2 gas pressure of 0.6 MPa. After firing, the samples were cooled down naturally to the room temperature in the furnace. The fired samples were ground in the agate mortar for further characterization.

Phases of the synthesized powders were identified by X-ray diffraction (XRD, AXS D8 Focus, Bruker, Germany) analysis using Cu Kα radiation (λ = 1.5406 Å) at 40 kV, 40 mA with a graphite monochromator. A step size of 0.02° was used with a scan speed of 6°/min. Photoluminescence (PL) spectra were measured by a fluorescence spectrophotometer (FluoroMax-4, Horiba, Japan) at room temperature. Morphology and luminescence of the particles were observed by a fluorescence microscope (BX71, Olympus, Japan). Transmission electron microscopy (TEM) observation and corresponding energy dispersive spectrometry (EDS) analysis were performed using a 200 kV field-emission TEM (JEM-2100F, JEOL, Japan) equipped with an energy dispersive spectroscopy (INCAEnergy, Oxford Instruments, UK). CL and composition measurements were carried out at room temperature using a SEM (Quanta 400 FEG, FEI, USA) equipped with a CL system (MonoCL3+, Gatan, USA) and an EDS (Genesis, EDAX, USA).

3. Results and discussion

Fig. 1 shows the XRD patterns of the synthesized samples with various *z* values and a fixed x = 0.01 in their nominal compositions. It can be seen that the sample with z = 0.5 consists of phase pure β-SiAlON, while small amount of AlN polytypoid secondary phases (12H or 15R) are identified in the samples with $z \geq 1$. Additionally, upon increasing the *z* value, the diffraction peaks of β-SiAlON (see inset in Fig. 1) gradually shift to lower diffraction angles, indicating continuous expansion of the crystal lattice due to the partial replacement of the shorter Si–N (1.74 Å) bonds by the longer Al–N (1.87 Å) and Al–O (1.75 Å) bonds.

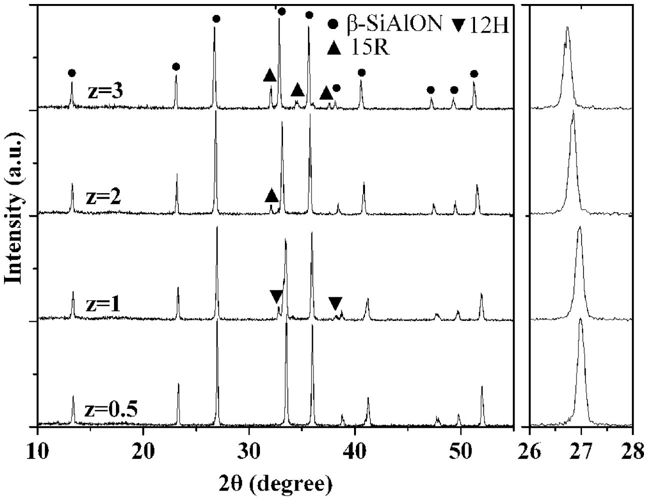

Fig. 1. XRD patterns of the synthesized Eu^{2+}-doped β-SiAlON phosphors with various *z* values.

The luminescence properties of Eu^{2+}-doped β-SiAlON have been found to be strongly affected by *z* value. Fig. 2 shows the PL spectra of the four samples under 305 nm UV excitation at room temperature. All samples show broad band emission corresponding to the $4f^65d \rightarrow 4f^7$ transition of Eu^{2+} [17,18]. No line emission peaks (between 590 and 615 nm) of Eu^{3+} have been observed, indicating Eu^{3+} in the Eu_2O_3 raw material has been completely reduced to Eu^{2+} during the firing process. The samples with z = 0.5 and 1 exhibit a single broad emission band (green), whereas bimodal emission (green and violet) is observed for z = 2 and 3, where the violet emission is peaked at 430 and 415 nm, respectively. The green emission peaks of samples with increasing *z* value are located at 533, 538, 540 and 520 nm, respectively. The red shift with *z* increasing from 0.5 to 2 can be attributed to the Stokes shift caused by the deceased rigidity of the β-SiAlON lattice with increasing *z* value [7], while the abnormal blue shift with

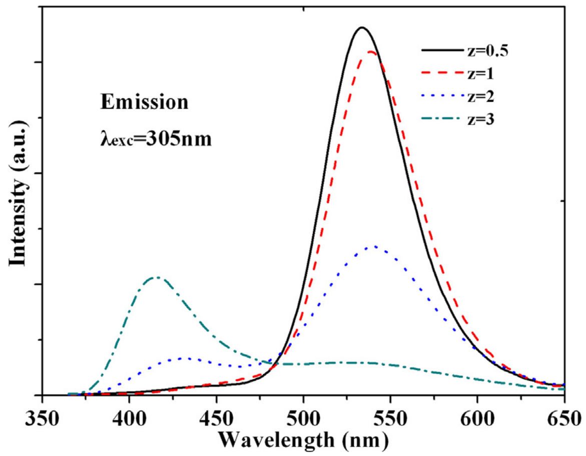

Fig. 2. Emission spectra of the synthesized Eu^{2+}-doped β-SiAlON phosphor powders with various *z* values.