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A new route for the synthesis of β-sialon: Eu^{2+} phosphors using pyrophyllite powders

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Abstract

Eu^{2+} ion doped β-sialon ($Si_{6-z}Al_zO_zN_{8-z}$:xEu^{2+}) phosphors were prepared from pyrophyllite-based mixtures by a carbothermal reduction and nitridation method first. Then, the effects of z values and the Eu concentration on the structure and the photoluminescence (PL) properties were investigated. β-Sialon was successfully synthesized as a dominant phase even at the low temperature of 1500 °C, while Si_3N_4 and AlN weakly coexisted as secondary phases. The PL excitation spectra exhibited the broad spectra covering up to 500 nm, and the greenish-yellow emission was observed at around 580 nm. At $z=1$ and $x=0.012$, excellent emission intensity could be attained.

Keywords: A. Powders: solid state reaction; C. Optical properties; Oxynitrides

1. Introduction

Recently, rare-earth metals doped α- and β-sialon powders have been widely investigated as phosphors for white light emitting diodes (LEDs).

β-Sialon basically has a hexagonal crystal system ($P6_3$ or $P6_3/m$ space group), which is a derivative of β-Si_3N_4. The Si–N pairs of β-Si_3N_4 are partly substituted by Al–O pairs, resulting in the β-sialon formula of $Si_{6-z}Al_zO_zN_{8-z}$ (z: the number of Al–O pairs, 0∼4.2) [1,2]. Wide investigations on the effects of z values suggested that $z<2$ values were favorable to a pure phase and a strong green emission of Eu^{2+} doped β-sialon [3–7].

As the requirement of very high temperature and nitrogen pressure for the synthesis of β-sialon powders results in high cost and low productivity, low temperature processes have been strongly demanded. For example, Lee et al. synthesized β-sialon powders at the low temperature of 1350 °C using pyrophyllite ($Al_2Si_4O_{10}(OH)_2$) [8,9]. Meanwhile, Křest′an et al. prepared β-Si_3N_4 powders at 1510 °C from pyrophyllite-based mixtures by a carbothermal reduction and nitridation method (CRN), and then β-sialon was achieved by adding Al_2O_3 to these β-Si_3N_4 powders and hot-pressing the mixed powders [10,11]. However, the preparation of Eu^{2+} doped β-sialon phosphors using pyrophyllite has not been investigated yet.

In this work, Eu^{2+} doped β-sialon powders were prepared from pyrophyllite-based mixtures by CRN, and their luminescent properties were investigated first.

2. Experiment

Eu^{2+} doped β-sialon ($Si_{6-z}Al_zO_zN_{8-z}$:xEu^{2+}, $0<z<4.2$) powders were prepared by CRN using the mixture of pyrophyllite (Seongsan Co., Ltd.), Si_3N_4 (E10, Ube), Eu_2O_3 (Grand Chemical & Material Co., Ltd.), AlN (Tokuyama Co.), and carbon black powders (OCI Co.). To enlarge the specific surface area of pyrophyllite, small particles (below 5 μm) were selected by Stokes's law [12]. The estimated chemical composition of pyrophyllite is given in Table 1. The mixtures with different z values were pressed into pellets. These pellets were heated at 600 °C for 3 h in a vacuum furnace, and then fired at 1500 °C for 5 h under high purity nitrogen atmosphere. The chemical composition and the crystal structure were determined with an X-ray fluorescence spectrometry (XRF, ZSX-100e, Rigaku, Japan) and an X-ray

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Table 1
Chemical composition of pyrophyllite (under 5 μm, wt%).

Ignition-loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	TiO_2	P_2O_5	Total
4.40	76.34	18.49	0.03	0.08	0.02	0.21	0.06	0.23	0.13	100

Table 2
Compositions of starting mixtures (mass ratio).

Sample	z	Pyrophyllite	Si_3N_4	Carbon black	AlN	SiO_2	Al_2O_3	Eu_2O_3
A	1	–	6.28	2.33	0.81	0.46	0.44	0.2
B	1	6.81	1.87	2.33	–	–	–	0.18
C	0.25	3	10.41	2.33	–	–	–	0.32
D	0.15	2	12.62	2.33	–	–	–	0.36

diffractometer (XRD, SIEMENS D5005) using CuKα radiation ($\lambda = 1.5406$ Å). PL properties were measured by a photoluminescence (PL) system (PSI Darsa 5000) with a 500 W xenon lamp as an excitation source.

3. Result and discussion

β-Sialon powders can be synthesized from the mixture of Si_3N_4–AlN–Al_2O_3, Si_3N_4–AlN–SiO_2, or Si_3N_4–AlN–Al_2O_3–SiO_2 [8,9]. Meanwhile, about 95% of pyrophyllite is composed of SiO_2 and Al_2O_3 (Table 1); therefore, β-sialon powders can be effectively prepared from the mixture of only pyrophyllite and Si_3N_4 under carbon and nitrogen atmosphere (i.e. CRN). To investigate the effects of pyrophyllite on the synthesizing temperature, $Si_{6-z}Al_zO_zN_{8-z}$:$0.003Eu^{2+}$ powders were prepared at $z = 1$ and 1500 °C from a pyrophyllite-based mixture (Sample B) and a reference mixture (Sample A) that was composed of commercially available starting materials as given in Table 2. Pyrophyllite can be converted to β-sialon by CRN following Eq. (1), and z values were controlled by changing only an amount of Si_3N_4 in the mixture

$$Al_2Si_4O_{10}(OH)_2\ (s) + 9C\ (s) + 3N_2 \leftrightarrow Si_4Al_2O_2N_6\ (s) + 9CO\ (g) + H_2O\ (g) \quad (1)$$

The XRD patterns of samples A and B are shown in Fig. 1. In the case of sample B, the β-sialon phase dominantly appeared, while the XRD peaks of Si_3N_4 and AlN were weakly observed. On the other hand, for sample A, the β-sialon phase was not produced, whereas the strong AlN, weak Si_3N_4, and weak SiC peaks were observed. This demonstrated that pyrophyllite promoted the reaction process for the synthesis of β-sialon. As pyrophyllite is mainly composed of SiO_2 and Al_2O_3, the reaction distance between Si and Al in sample B is much shorter than that in sample A, lowering the synthesizing temperature. There are some polytypoids for β-sialon (15R, 12H, 21R, 27R, and 2H), but their XRD peaks do not just coincide with those in Fig. 1.

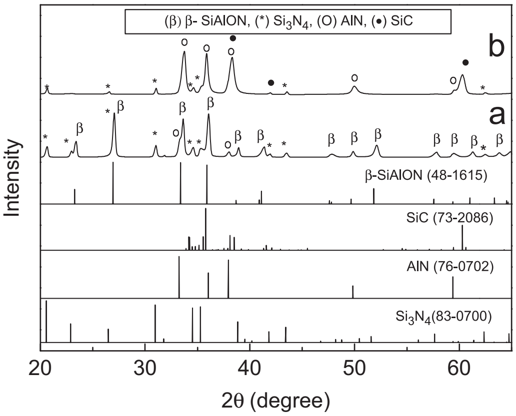

Fig. 1. XRD patterns of (a) Sample B and (b) Sample A.

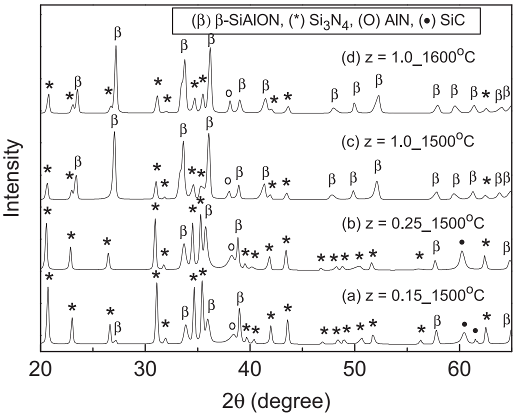

Fig. 2. XRD patterns of pyrophyllite-based mixture with various z values after firing.

β-Sialon powders were prepared from the pyrophyllite-based mixtures with various z values (Samples B–D in Table 2) at 1500 °C, and the resulting XRD data are shown in Fig. 2(a)–(c). β-Sialon was synthesized as a dominant phase at $z = 1$, while weak peaks of Si_3N_4 and AlN were observed as secondary phases. With decreasing z

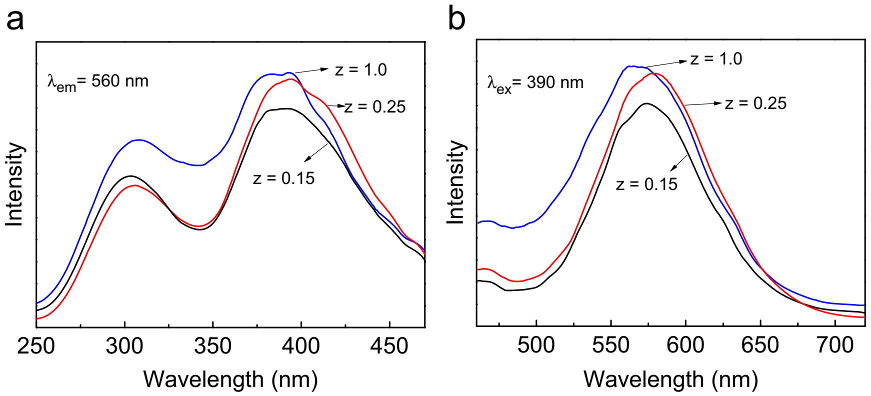

Fig. 3. (a) PLE and (b) PL spectra of β-sialon powders ($Si_{6-z}Al_zO_zN_{8-z}$:0.003Eu^{2+}) with various z values.

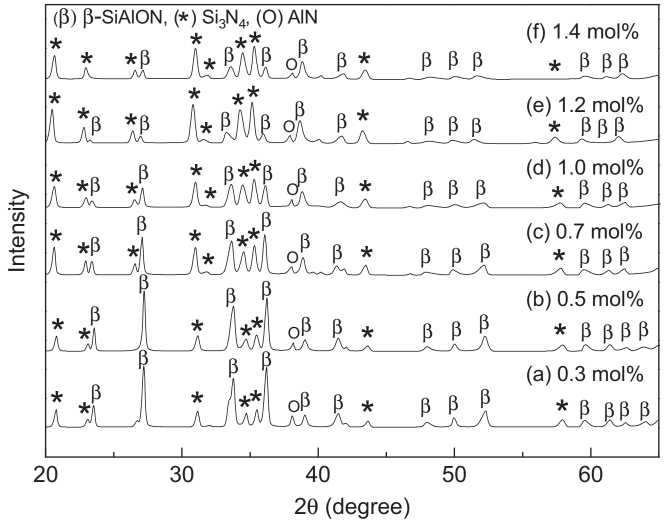

Fig. 4. XRD patterns of pyrophyllite-based mixture as a function of the Eu concentration prepared at 1600 °C.

value up to 0.15, the β-sialon phase gradually decreased, whereas the Si_3N_4 phase continuously increased and became a dominant phase.

As z values were decreased in the starting mixtures as given in Table 2, the amount of Si_3N_4 was largely increased. This caused the additional increase in unreacted Si_3N_4 peaks of XRD at lower z values. Meanwhile, we have tried to prepare β-sialon powders with $z \geq 1.5$, but it was impossible due to a too small amount of Si_3N_4 in starting mixtures. To promote the reaction process at $z=1$, the firing temperature was increased up to 1600 °C (Fig. 2(d)), but XRD did not exhibit a significant change. It was reported by Xie et al. that pure or mixed β-sialon phases could be achieved by a gas-pressure sintering (GPS) at 2000 °C under 1.0 MPa N_2 pressure, depending on the Eu concentration and z values [5]. Compared with this previous work, our results demonstrated that pyrophyllite enabled β-sialon to be synthesized as a dominant phase at the low temperature of 1500 °C, even though weak secondary phases coexisted.

The photoluminescence excitation (PLE) and PL spectra of β-sialon powders ($Si_{6-z}Al_zO_zN_{8-z}$:0.003Eu^{2+}) as a function of z values are shown in Fig. 3. The PLE spectra exhibit two strong excitation bands and shoulders at around 305, 390, and 450 nm, respectively. The corresponding PL spectra excited by 390 nm show the greenish-yellow emissions at around 580 nm, which are assigned to $4f^65d \rightarrow 4f^7$ transitions of Eu^{2+} ions. These broad emission bands revealed that Eu^{3+} ions, which might result in the sharp emission peaks at the red region, were successfully reduced to Eu^{2+} ions under nitrogen atmosphere. β-Sialon has a hexagonal structure with continuous channels parallel to the c-directions, on which Eu^{2+} ions are possibly coordinated [7]. These PLE spectra were similar to those reported by Xie et al. [5]. However, our greenish-yellow emissions at around 580 nm were significantly different from their green emissions at around 538 nm. This distinction was possibly attributed to the different crystal field splitting surrounding Eu^{2+} ions from each other. The crystal field splitting and the number of splitting levels of 5 d orbits of Eu^{2+} ions closely depended on the host structure; therefore, the different crystal circumstances (local distortion, atomic distance and interaction, reactions between the host and secondary phases, etc.) led to the gap of the emission wavelength. With increasing z value the emission peak (570 nm) at $z=1$ exhibited an apparent blue-shift compared to those (580 nm) at $z=0.15$ and 0.25. These results were contrary to the previous works [3,5] that reported the red-shift at higher z values. They suggested that the high z values caused the large lattice expansions due to the difference in the bond length: 1.75 Å for Al–O, 1.87 Å for Al–N, and 1.74 Å for Si–N. This caused less rigidity of β-sialon, leading to the red-shift. However, in this work the β-sialon powders were prepared by a different method using pyrophyllite from above previous works by GPS. The β-sialon phase in this work is more developed with the increase in the z value (Fig. 2) in contrast to the above previous works, leading to the different crystal field surrounding Eu^{2+} ions.

Besides the greenish-yellow emissions around 580 nm, weak blue emission shoulders were observed around 450 nm. It was suggested that the blue emissions were

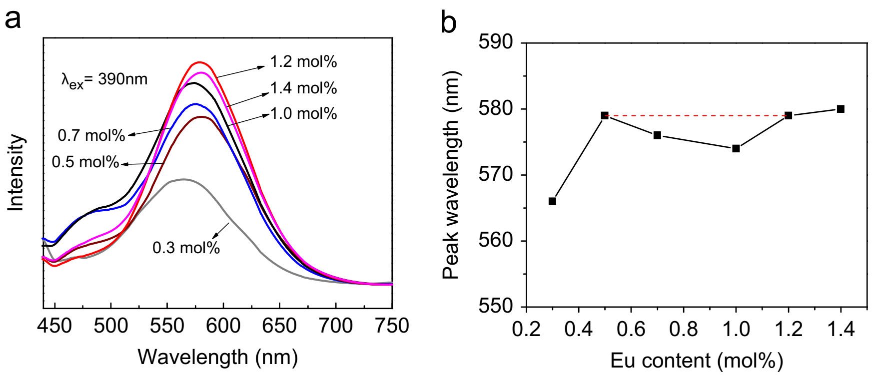

Fig. 5. (a) PL and (b) the emission peak wavelength of β-sialon powders ($z=1$) as a function of the Eu concentration prepared at 1600 °C.

ascribed to secondary polytypoid phases such as 12H [5], but it was unclear whether they originated from the polytypoids and/or the secondary phase (AlN). Polytypoid phases are not detectable in this work, and AlN:Eu^{2+} powders are known to emit a blue emission at around 470 nm [13]. When the firing temperature was increased from 1500 to 1600 °C, the PL intensity was increased by about 160%, even though their XRD patterns exhibited insignificant difference as described in Fig. 2. This indicated that the elevated temperature probably contributed to the elimination of micro-defects and/or the enhancement of the incorporation of Eu^{2+} ions in β-sialon.

The XRD patterns of β-sialon powders prepared as a function of the Eu content are shown in Fig. 4. As the Eu content increased, the amount of β-sialon gradually decreased, whereas the Si_3N_4 peaks continuously increased. There were only insignificant changes in AlN peaks. The ways how Eu^{2+} ions affected the phase transition is unclear at this stage. It has not been definitely understood what sites they occupy in β-sialon yet, even though it was suggested that Eu^{2+} ions were coordinated on channels parallel to the *c*-directions [7]. Xie et al. reported that higher *z* values reduced the Eu^{2+} solubility, and also the high Eu concentration caused the formation of the secondary sialon polytypoid phases at the same *z* value [5]. For our experiments it was evident that Eu^{2+} ions hindered the substitution of Al–O for Si–N pairs.

The PL spectra and the emission peak wavelength of β-sialon powders as a function of the Eu content are depicted in Fig. 5(a) and (b), respectively. The PL spectra show the strongest intensity at 1.2 mol%. Even though β-sialon powders prepared at lower Eu concentration were purer than those prepared at higher Eu concentration, their emission was lower than the latter. These findings were completely different from the previous work that concluded that purer β-sialon powders were favorable for the higher PL intensity [5]. The reason for this unexpected result can be speculated by considering two competing factors: the phase purity and the incorporated activator (Eu^{2+}) concentration. The lower phase purity evidently causes the decrease in the PL intensity, but increased incorporated Eu concentration, which contributes to the enhancement of the PL intensity, can surpass the effects of the low phase purity. According to Fig. 4, the main XRD peak positions of β-sialon apparently shifted to lower angles with the increase in the Eu concentration, indicating the expansion of the crystal lattice. This implied that more Eu^{2+} ions occupied the specific sites such as channels along the *c*-axis, because Eu^{2+} ionic size is rather large.

The emission peak shows the red-shift with the increase in the Eu concentration as shown in Fig. 5. However, the β-sialon powders at 0.7 and 1.0 mol% showed slightly deviated positions from the others (0.5. 1.2, and 1.4 mol%), because their PL spectra were composed of the blue emission shoulders as well as the main emission peaks. The probability of the energy transfer of Eu^{2+} ions from the higher to lower 5 d energy levels increases with increasing Eu concentrations. This causes the lower emission energy for the energy transition from the lowest 5 d level to the 4 f ground state, resulting in the red-shift.

4. Conclusion

$Si_{6-z}Al_zO_zN_{8-z}$:$x$$Eu^{2+}$ phosphors were prepared from pyrophyllite-based mixtures by CRN. Their structure and photoluminescence (PL) properties closely depended on the *z* value and the Eu concentration. β-Sialon was successfully synthesized as a dominant phase even at the low temperature of 1500 °C due to the short reaction distance between Si and Al in pyrophyllite. The PL excitation spectra were broad, covering up to 500 nm, and the greenish-yellow emission was observed at around 580 nm. The strongest emission intensity could be attained at $z=1$ and $x=0.012$.

Acknowledgments

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