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Synthesis, crystal structure, and luminescence properties of a new nitride polymorph, β-$Sr_{0.98}Eu_{0.02}AlSi_4N_7$

Fumitaka Yoshimura[a], Hisanori Yamane[b,*], Makoto Nagasako[c]

[a] Mitsubishi Chemical Corporation, 1060, Naruda, Odawara, Kanagawa 250-0862, Japan
[b] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan
[c] Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

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ABSTRACT

Prismatic vermilion single crystals 200 μm–2 mm in size, together with a white powder, were obtained by heating a mixture of binary nitrides containing Mg_3N_2 at 2030 °C under 0.85 MPa of N_2. Yellow, thick-platelet single crystals with sizes of 150–500 μm were also found to grow at or near the surface of the product. Single crystal X-ray diffraction demonstrated that the vermilion crystals were orthorhombic $Sr_{0.98}Eu_{0.02}AlSi_4N_7$, which has been prepared in previous studies and is termed the α phase of this compound. The yellow crystals were revealed to be a new polymorph of $Sr_{0.98}Eu_{0.02}AlSi_4N_7$ (β phase) that crystalized in a monoclinic cell (a = 8.1062(1) Å, b = 9.0953(1) Å, c = 8.9802(2) Å, β = 111.6550(5)°, space group $P2_1$) with twins that could be examined by transmission and scanning transmission electron microscopy. β-$Sr_{0.98}Eu_{0.02}AlSi_4N_7$ was found to have a three-dimensional network structure formed by the stacking of two types of layers. One is a dreier layer of $(Al/Si)N_4$ tetrahedra that consists of N vertex-sharing double chains of $(Al/Si)N_4$ tetrahedra extending in the c-axis direction with Sr and Eu atoms aligned between the chains, while the other is a layer of $(Al/Si)N_4$ tetrahedra connected by sharing N edges and vertexes. The crystal structure of β-$Sr_{0.98}Eu_{0.02}AlSi_4N_7$ is similar to those of certain oxynitrides, such as $Sr_3Al_{3+x}Si_{13-x}N_{21-x}O_{2+x}$:$Eu^{2+}$ ($x \approx 0$) and $Sr_{4.9}Eu_{0.1}Al_{5+x}Si_{21-x}N_{35-x}O_{2+x}$ ($x \approx 0$). The peak wavelength and full width at half maximum in the emission spectrum obtained from single crystals of β-$Sr_{0.98}Eu_{0.02}AlSi_4N_7$ under excitation at 400 nm were 541 and 66 nm, respectively.

1. Introduction

Following the development of near-ultraviolet and blue light emitting diodes (LEDs), combinations of phosphors and LEDs have been used to realize solid state white LED lamps and liquid crystal display backlights. Phosphors that can be excited with near-ultraviolet and blue light have been investigated for such applications [1,2], and various novel multinary aluminum silicon nitrides and oxynitrides have been considered as host crystals for the phosphors [3–8]. Visible light emissions with a wide variety of colors have been realized by doping Eu^{2+} and Ce^{3+} at Ca^{2+}, Sr^{2+}, Ba^{2+}, and La^{3+} sites in these nitrides and oxynitrides. In addition, the properties of the phosphors themselves are believed to vary with the coordination environments of the cations doped into the host crystals.

A Eu^{2+}-doped strontium aluminum silicon nitride, $SrAlSi_4N_7$:Eu^{2+}, has been previously studied for use in phosphors. Hecht et al. synthesized $SrAlSi_4N_7$ and reported that the crystal structure of this compound is tetragonal (a = 11.742(2) Å, b = 21.391(4) Å, c = 4.966(1) Å, space group $Pna2_1$), based on single crystal X-ray structure analysis [9]. They synthesized a powder sample of $Sr_{0.98}Eu_{0.02}AlSi_4N_7$ and measured the emission spectrum of this compound, which exhibited red emission with a broad peak at 635 nm under 450 nm light excitation. This same work found that the emission peak wavelength changed from 630 to 660 nm when the Eu concentration was increased to 20 mol%. Ruan et al. demonstrated that $SrAlSi_4N_7$:Eu^{2+} was more likely to be produced at a nitrogen gas pressure of 0.48 MPa when increasing the AlN proportion in the starting materials [10]. Fukuda et al. synthesized $(Sr_{0.9}Eu_{0.1})_2Al_{3-x}Si_{7+x}N_{13+x}O_{1-x}$ ($-0.12 \le x \le 0.31$), in which Si and N atoms were partly substituted with Al and O, respectively, having the $SrAlSi_4N_7$ structure, and studied the effects of x on the lattice constants [11,12]. The peak wavelength of the emission spectrum acquired during 450 nm excitation shifted from 613 to 629 nm with increasing x values. Ruan et al. and Zhan et al. synthesized $Sr_{1-x}Ce_xAl_{1+x}Si_{4-x}N_7$, in which Ce^{3+} was doped as an activator, from $SrAlSi_4N_7$ and reported yellow light emission with peak wavelengths between 550 and 565 nm [13,14]. Eu^{2+} and Ce^{3+} ions have also been co-doped into $SrAlSi_4N_7$ and the emission wavelength was found to be adjusted by dual emissions from the Eu^{2+} and Ce^{3+} [15,16]. In

* Corresponding author.
E-mail address: yamane@tagen.tohoku.ac.jp (H. Yamane).

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addition, a phosphor that emits orange light with a peak wavelength of 597 nm was fabricated by activating Yb^{3+} ions in $SrAlSi_4N_7$ [17]. It has also been reported that Pr^{3+}, Sm^{3+}, and Tb^{3+} ions are activated in $SrAlSi_4N_7$ as luminescent centers [18].

In the present study, we synthesized a new polymorph of $SrAlSi_4N_7$:Eu^{2+} in the form of single crystals, together with single crystals of the previously reported form of $SrAlSi_4N_7$:Eu^{2+} from a mixture of starting materials and Mg_3N_2. The previously known compound $SrAlSi_4N_7$ and the new polymorph are denoted herein as the α and β forms, respectively. The synthesis, crystal structure, and luminescence properties of the β phase were investigated and compared with those of the α phase. The crystal structure of the β phase was found to be related to the structures of some oxynitrides reported in previous studies [19–25].

2. Experimental

'Sr_3N_2' (Materion Co., 99.5%), Mg_3N_2 (Materion Co., 99.9%), EuN (Materion Co., 99.9%), AlN (Tokuyama, 99%) and α-Si_3N_4 (Ube Industries, SN-E10, > 99%) powders were used as starting materials. 'Sr_3N_2' was actually a mixture of Sr_2N, SrN_2, SrN and SrH. The respective quantities were 155.4 mg of 'Sr_3N_2', 70.8 mg of Mg_3N_2, 5.4 mg of EuN, 77.1 mg of AlN and 191.2 mg of α-Si_3N_4, and these were mixed with an alumina mortar and pestle under Ar (Tokyo Koatsu Co., Ltd. > 99.9999%)) in a glove box. The mixed powder was transferred into a boron nitride crucible with a lid (Showa Denko, 99.5%, inner diameter 18 mm, depth 18 mm) and heated in a graphite resistance furnace (VESTA, Shimadzu Mectem Inc.) from room temperature to 800 °C under 8×10^{-3} Pa of N_2 (Taiyo Nippon Sanso Co., 99.9995%) at a heating rate of 20 °C/min. From 800–2030 °C, the sample was heated under 0.85 MPa of N_2 at the same rate. After heating at 2030 °C and 0.85 MPa of N_2 for 4 h, the sample was cooled to 1200 °C at −20 °C/min and then cooled to room temperature in the furnace by shutting off the electric power to the heater, maintaining the N_2 pressure at 0.85 MPa.

The morphology of the product was observed with an optical microscope and by scanning electron microscopy (SEM, Keyence, VE-8800SP1614). Elemental analysis of single crystals selected from the product was performed by electron-probe microanalysis (EPMA, JEOL). A thin slice specimen of a single crystal was prepared using a focused ion beam/SEM dual-beam system (FIB/SEM, Helios NanoLab 600i). Selected area electron diffraction (SAED) patterns and transmission electron microscopy images along with atomic resolution images of the specimen were taken with probe aberration-corrected scanning transmission electron microscopy (STEM, JEOL JEM-ARM200CF) in conjunction with a cold-field emission electron source. The probe convergence angle and the inner/outer detector angle used for high-angle annular dark-field (HAADF) imaging were 22 and 90/370 mrad, respectively.

Single crystal X-ray diffraction (XRD) data were measured with a diffractometer and Mo Kα radiation (λ = 0.71073 Å, Bruker, D8 QUEST). Data collection and unit-cell refinement were performed with the APEX2 software package [26]. Multiscan absorption corrections were applied using the SADABS or TWINABS programs in the package [26]. An initial structural model of the new polymorph was obtained by a direct method using the SIR2004 program [27]. The structural parameters of the crystals were refined using the SHELXL-2014 program [28]. The VESTA program was employed to draw the structures [29]. An XRD pattern for the powder separated from the product by elutriation was acquired with an X-ray diffractometer using Cu Kα radiation (Bruker, D2 PHASER). Photoluminescence (PL) excitation and emission spectra were obtained from single crystal grains set in a copper holder with a quartz-glass window at 25–300 °C using a fluorescence spectrophotometer (FP-6500, JASCO) equipped with a 150 W xenon lamp.

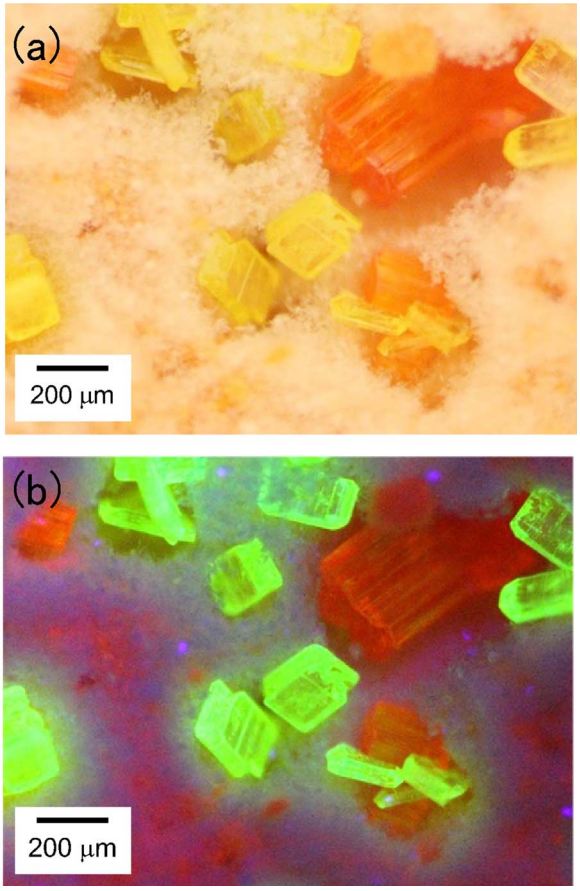

Fig. 1. Optical micrographs taken under white light (a) and 400 nm light (b) for the surface of the sample prepared by heating at 2030 °C and 0.85 MPa of N_2 for 4 h.

3. Results and discussion

3.1. Synthesis and chemical analysis

The product was primarily composed of vermillion prismatic single crystals (with 200 μm–2 mm sides) together with a white powder. Yellow thick-platelet single crystals 150–500 μm in size also grew at and near the surface of the product, as shown in Fig. 1(a). The vermillion single crystals emitted red light while the yellow single crystals emitted green light under excitation at 400 nm (Fig. 1(b)). The single crystal XRD analysis presented in the next section confirms that the vermillion crystals were the α phase previously reported by Hecht et al. [9]. The powder XRD pattern for the white powder is similar to that for AlN, although the individual reflections in the pattern cannot be explained by the structure of AlN (see Supporting information, Fig. S1). The yellow single crystals were the new polymorph, the β phase.

Although the original reaction mixture was 14 mass% Mg_3N_2, Mg was not detected in the single crystals of either the α or β phases nor in the powder by EPMA. The mass loss of the sample after synthesis was 25 mass%, indicating the vaporization of all the Mg_3N_2 and most likely some amounts of Sr-N and Eu-N. In the case that Mg_3N_2 was not added to the mixture of raw ingredients, vermilion single crystals (α phase) with sizes on the order of tens of μm were obtained, together with the white powder, while the yellow crystals of the β phase were absent. Therefore, even though Mg was not contained in the single crystals of the β phase, Mg or Mg-N presumably played a crucial role in the crystallization of the new polymorph.

The chemical compositions obtained from the analysis of fracture cross-sections of a vermillion crystal (the α phase) and a yellow crystal (the β phase) by EPMA were Sr 24.9(3), Eu 0.8(1), Al 9.1(1), Si 33.9(4) and N 27(1) mass% (total 95.6 mass%), and Sr 25.4(6), Eu 1.2(1), Al