Crystal Structures and Properties of Europium Aluminum Oxynitride Eu$_2$AlO$_{3.75}$N$_{0.1}$ and Europium Aluminum Oxide EuAl$_2$O$_4$

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Ⓢ Supporting Information

ABSTRACT: The reactions among Eu$_2$O$_3$, AlN, and Al$_2$O$_3$ with the ratios Eu:Al = 2:1 and 1:2 at 1200 °C for 10 h yielded Eu$_2$AlO$_{3.75}$N$_{0.1}$ and EuAl$_2$O$_4$, respectively. The powder X-ray diffraction pattern of the new oxynitride could be indexed as a monoclinic structure with the space group $I2$ (No. 5) (a = 3.7113(2) Å, b = 3.6894(2) Å, c = 12.3900(8) Å, and β = 90.6860(5)°). This structure was found to be a novel distorted Ruddlesden−Popper type. For EuAl$_2$O$_4$, isostructural with monoclinic SrAl$_2$O$_4$ (space group $P2_1$, No. 4), a structural refinement was performed, indicating that the cell parameters were a = 8.44478(11) Å, b = 8.82388(12) Å, c = 5.15643(7) Å, and β = 93.1854(12)°. ^{151}Eu Mössbauer spectra revealed that the divalent and trivalent Eu ions coexisted in Eu$_2$AlO$_{3.75}$N$_{0.1}$, while Eu ions were in the divalent state in EuAl$_2$O$_4$. A photoluminescent mechanism due to 4f^7 (^{8}S$_{7/2}$) ↔ 4f^{6}5d^1 of europium in EuAl$_2$O$_4$ was proposed on the basis of the calculated band structure, the band gap obtained from UV−vis diffuse reflectance spectra, and the photoluminescence spectra.
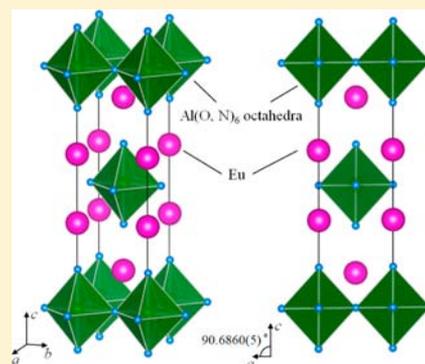
INTRODUCTION

Non-oxide materials have attracted attention due to their peculiar chemical and physical properties. For oxynitrides, oxide and nitride anions with close ionic radii and electronegativity values often substitute each other in the same site of the lattice, forming solid solutions.[1−9] Among such materials, some cation-doped metal oxynitrides display luminescent properties. In particular, Si−Al−O−N system materials known as SiAlON have received increased interest as potential candidates for phosphors in commercial white light-emitting diodes (LEDs).[5−9]

From the viewpoint of synthesizing oxynitrides and their industrial applications, studies on preparation methods are also attracting attention due to the difficulty in the synthesis process. Oxynitrides are usually synthesized by heating oxide/metal in the flow of NH$_3$ gas as the nitrogen source[3,4,9] or by reaction between oxide and nitride under a high-pressure N$_2$ atmosphere.[6−8,10] However, the former method is strongly influenced by the purity and the flow rate of NH$_3$ gas, and the latter requires a high-pressure system. Furthermore, these methods cannot control the ratio of the starting materials, and also the possible range of reaction temperatures is limited.

In order to resolve these problems, we have attempted to prepare new oxynitrides by reactions between oxides and nitrides in a silica tube. A similar technique has been widely applied to preparations of non-oxide materials such as sulfides.[11−14] The encapsulation syntheses of some oxynitrides have also been reported, mainly using an evacuated nickel tube.[15,16] When metal oxide and nitride are heated together in an evacuated closed system, we can expect two types of reactions. One is the reaction between oxide and nitride to form oxynitride. Another is the decomposition of the starting nitride, resulting in the formation of low-valent oxides or oxynitrides. In particular, the latter reaction is peculiar to this technique, and unique compounds are expected to be prepared by selecting appropriate starting materials and preparation conditions.

In this study, we have chosen the Eu−Al compounds as the target system and succeeded in obtaining a new oxynitride, Eu$_2$AlO$_{3.75}$N$_{0.1}$, and the photoluminescent EuAl$_2$O$_4$.

EXPERIMENTAL SECTION

Europium sesquioxide (Eu$_2$O$_3$, Nippon Yttrium, 99.9%), aluminum mononitride (AlN), and alumina (Al$_2$O$_3$, Kanto Chemical, 99%) were used as starting materials. The AlN compound was prepared by heating powders of Al (Kojundo Chemical Laboratory, 99.9%) at 1100 °C for 10 h in the flow of NH$_3$ gas. The mixture of starting materials was ground, pressed into a pellet, and sealed in an evacuated silica tube. The tube was heated at 1200 °C for 10 h.

Powder X-ray diffraction (XRD) measurements were carried out with Cu Kα radiation on a RINT2200 diffractometer (Rigaku) equipped with a graphite monochromator. The Eu oxidation states were investigated through the ^{151}Eu Mössbauer spectrum measurements with a VT-6000 (Labo. Equip. Co., Japan). Quantitative analysis

of nitrogen and oxygen in a prepared sample was performed with the oxygen/nitrogen combustion analyzer EMGA-920 (Horiba). Quantitative analysis of the cation composition was performed with a wavelength-dispersive X-ray fluorescence (XRF) spectrometer, ZSX PrimusII (Rigaku). Thermogravimetric (TG) analysis for the product EuAl$_2$O$_4$ was performed with the Bruker TG-DTA 2000S system. The sample and reference (Al$_2$O$_3$) were placed in Pt cells heated in air to 1000 °C at a rate of 5 °C/min and maintained for 6 h. The optical second-harmonic generation (SHG) responses were tested for the compounds using a Continuum Minilite YAG:Nd laser (λ 1064 nm). UV−vis diffuse reflectance spectra were measured with a V-570 instrument (JASCO). Photoluminescence spectra were measured on the same spectrometer in the range from excitation wavelength plus 20 to 700 nm. The detection of photoluminescence was tried with excitation light at wavelengths of 220, 250, 300, 350, 400, 450, and 500 nm.

Rietveld analysis was performed using the program RIETAN-FP.[17] The crystal structures were visualized with the program VESTA.[18] The calculations of the electronic structures, densities of states (DOS), and quadrupole coupling constants for EuAl$_2$O$_4$ were carried out using the WIEN2k program package.[19] This program employs the full potential linearized augmented plane wave + local orbitals (FP-LAPW + lo) method based on density functional theory (DFT). We used the generalized gradient approximation (GGA) + Hubbard U parameter for the Eu 4f electrons. In the calculation, the convergence parameter was set to be $R_{MT}k_{max}$ = 7.0, and the muffin-tin (MT) spheres are R_{MT}(Eu) = 2.30 bohr, R_{MT}(Al) = 1.42 bohr, and R_{MT}(O) = 1.73 bohr. We used 8 × 8 × 14 meshes, which generated 224 k points in the first Brillouin zone.

■ RESULTS AND DISCUSSION

In this study, the ratios of Eu:Al were investigated for 2:1 and 1:2. In the case of Eu:Al = 2:1, a new oxynitride named Eu2−Al1−O−N was obtained, and its composition and crystal structure were investigated. For Eu:Al = 1:2, EuAl$_2$O$_4$, known as a luminescent material, was prepared, and its characterizations were performed. The crystal structure of EuAl$_2$O$_4$ was determined for the first time.

Preparation of Eu2−Al1−O−N. The reactions with the mixing ratio Eu$_2$O$_3$:AlN = 1:1 (Eu:Al = 2:1) were investigated with the silica tube technique. The XRD patterns of the Eu2−Al1−O−N phase are shown in Figure 1. The pattern of the new phase is similar to that of Eu$_2$AlO$_3$N, and other impurity phases are also observed, as shown in Figure 1a. The products were obtained as a pellet, and part of the surface was covered by
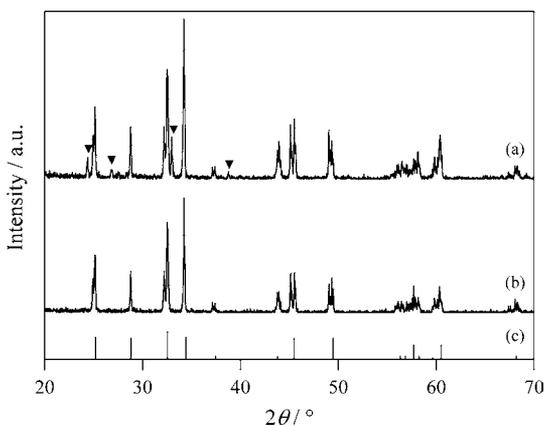
orange impurities, which could not be identified. The impurities were removed from the pellet by using sandpaper, and the pure phase Eu2−Al1−O−N was obtained, which was black, having no photoluminescent properties. Silicon in the quartz tube often reacts with the sample to form silicon compounds. However, the silicon concentration in the product was below the detection limit of the XRF measurement. The compositions of oxygen and nitrogen were determined to be 15.3 and 0.4 mass %, respectively, by combustion analysis. These results with the condition of Eu:Al = 2:1 gave the empirical formula Eu$_2$AlO$_{3.75}$N$_{0.1}$, in which the average oxidation state of Eu was calculated to be 2.4.

The Eu:Al ratio was maintained at 2:1 in the product, because the Eu:Al ratio of the product agreed well with that of the mixture in the molar ratio Eu$_2$O$_3$:AlN = 1:1 through the XRF measurements. An amorphous phase of Al compounds is often formed as impurities of a crystalline compound. If such an amorphous Al compound exists, the main product should have Al deficiencies. However, an Al deficiency is not observed from the Rietveld analysis. Then, with the aim of investigating the phase stability and composition of the product, we attempted to prepare Eu$_2$AlO$_4$ using stoichiometric starting materials Eu$_2$O$_3$, Al$_2$O$_3$, and Al without AlN. As a result, the Ruddlesden−Popper (layered perovskite) phase was not observed at all. Furthermore, preparations of compositions Eu$_2$AlO$_{3.75}$ and Eu$_2$AlO$_{3.90}$ having the ratio Eu^{II}:Eu^{III} = 3:2 were also tried in the same way. In both XRD patterns, impurities with considerable peak intensities were detected in addition to a Ruddlesden−Popper phase. From these results, we conclude that the composition of Eu2−Al1−O−N is determined to be Eu$_2$AlO$_{3.75}$N$_{0.1}$. The amount of the anion deficiency of Eu$_2$AlO$_{3.75}$N$_{0.1}$ is as large as that for the Ruddlesden−Popper phase. Such a large amount of the anion deficiency was found to exist in Nd$_{1.8}$Sr$_{0.72}$NiO$_{3.72}$.[20] In the case of Eu$_2$AlO$_{3.75}$N$_{0.1}$, the existence of nitrogen and a large anion deficiency would stabilize a Ruddlesden−Popper phase.

Although the XRD profile of the pure phase was similar to that of tetragonal Eu$_2$AlO$_3$N,[21] most of the diffraction peaks split and the pattern could be indexed with the monoclinic system (see Figure 1b,c). Then, instead of Eu, Sm and Gd, which are neighbors of Eu in the periodic table, were used as the oxide for the reactions with AlN in order to elucidate the tendency of the phase formation. The XRD patterns of the products did not show any phase similar to the pattern of Eu2−Al1−O−N (Figure 2). Therefore, the new phase is unique to Eu, and this suggests that the formation of the new phase depends on the stability of Eu(II). Since the starting compound is the trivalent oxide Eu$_2$O$_3$, part of the Eu is reduced during the reaction.

^{151}Eu Mössbauer Spectrum of Eu2−Al1−O−N. Figure 3 shows the ^{151}Eu Mössbauer spectrum of the Eu2−Al1−O−N phase. Two large absorption peaks are observed, indicating that Eu ions with two oxidation states coexist. The Eu ions occupy a 4c site of the space group I2 (C2), as discussed later. Because the site symmetry is 1, a nonzero quadrupole interaction is expected.[22] The quadrupole interaction is given by

$$H_Q = (e^2qQ)/(4I(2I-1))[3I_z^2 - I(I+1)$$
$$+ \eta(I_x^2 - I_y^2)] \tag{1}$$

where I is the nuclear spin, Q is the quadrupole moment, $eq = V_{zz}$, and $\eta = (V_{xx} - V_{yy})/V_{zz}$ (V_{ii} is the electric field gradient tensor).[23] Since the Eu site has no symmetry, 12 possible

Figure 1. XRD patterns of (a) Eu2−Al1−O−N with the orange impurity phase and (b) pure Eu2−Al1−O−N and reported patterns of (c) Eu$_2$AlO$_3$N (JCPDS Card No. 47-0099). Solid inverted triangles show the main peaks of the impurity phase.
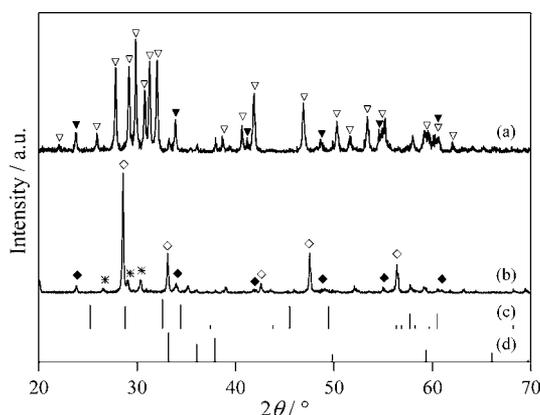
Figure 2. XRD patterns of the products obtained by the ratios (a) Sm_2O_3:AlN = 1:1 and (b) Gd_2O_3:AlN = 1:1 and reported patterns of (c) Eu_2AlO_3N (JCPDS Card No. 47-0099) and (d) AlN (JCPDS Card No. 25-1133). Legend: (▽) Sm_2O_3 (JCPDS Card No. 42-1464); (▼) $SmAlO_3$ (JCPDS Card No. 29-0082); (◇) Gd_2O_3 (JCPDS Card No. 12-0797); (◆) $GdAlO_3$ (JCPDS Card No. 46-0395); (*) $Gd_4Al_2O_9$ (JCPDS Card No. 46-0396).
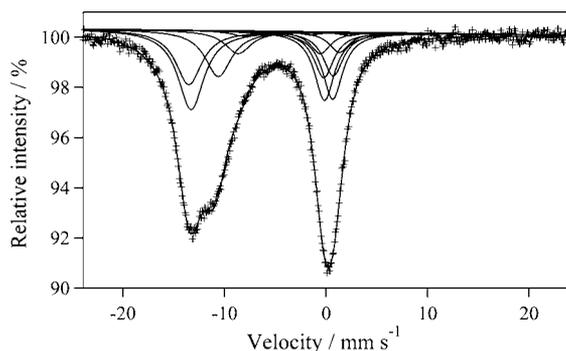
Figure 3. ^{151}Eu Mössbauer spectrum of Eu2−Al1−O−N at 20 K.

transitions exist due to the quadrupole interaction. Thus, the spectrum was fitted by using 12 Lorentzian functions for each of the two absorption peaks. Table 1 gives the ^{151}Eu Mössbauer parameters. The isomer shifts, −11.981(13) and 0.282(9) mm/s relative to EuF_3, are assigned to Eu^{II} and Eu^{III}, respectively.[24] Since the spectrum was measured at a low temperature (20 K), the recoil-free fractions of Eu^{II} and Eu^{III} are almost equal and the ratio Eu^{II}:Eu^{III} was determined to be 3.0:2.0 from the areas of the two peaks. The average oxidation number of Eu calculated from the ratio is 2.4, which is exactly the same as that estimated from the compositional analyses.

The synthesis reaction is estimated to be

$$Eu^{III}_2O_3 + AlN \rightarrow aEu^{II}_{1.20}Eu^{III}_{0.80}AlO_{3.75}N_{0.1}$$
$$+ xN_2\uparrow + \alpha \qquad (2)$$

where α is the composition of impurities removed from the pellet and the values of a and x are unknown because of the undetermined quantity of impurities.

Crystal Structure of Eu2−Al1−O−N. The crystal system was determined to be monoclinic by indexing the XRD peaks. However, all of the known compounds R_2AlO_3N (R = La−Nd, Sm, Eu), with compositions similar to that of $Eu^{II}_{1.20}Eu^{III}_{0.80}AlO_{3.75}N_{0.1}$, have tetragonal structures with space group $I4/mmm$ or $I4mm$.[15,21,25] These compounds crystallize in the Ruddlesden−Popper-type structure expressed by the chemical formula $A_{n+1}B_nX_{3n+1}$ (A, B = cation, X = anion) with $n = 1$. As the XRD peaks with reflection conditions $h + k + l = 2n$ for hkl in the unique axis b are observed, it has a body-centered lattice. Furthermore, the multiplicity of the crystallographic Al site must be equal to or less than 2 because a unit cell contains only two Al atoms. From these conditions, possible space groups are narrowed down to $I2$ (cell choice 3 of $C2$, No. 5), Im (cell choice 3 of Cm, No. 8), and $I2/m$ (cell choice 3 of $C2/m$, No. 12). These space groups can be classified into subspace groups of $I4/mmm$. The YAG laser radiation to the powder samples showed SHG signals, indicating exclusion of centrosymmetric $I2/m$, although the intensity of the signal was weaker than that for the quartz. Space groups $I2$ and Im were investigated using the Rietveld method.

First, we attempted the space group $I2$. Initial crystal parameters of the structural refinement were referenced to those of Nd_2AlO_3N ($I4mm$).[25] The $4c$ site (0, 0, 0.3649) is used as the initial position of Eu, assuming that Eu^{II} and Eu^{III} are located randomly. The Al site was set as the $2a$ site, (0, 0.0, 0). Because it is too difficult to verify the site occupancies of O and N from XRD data, O and N are assumed to occupy disordered anion sites. The anion sites were (0, 0.5, 0) of the $2a$ site, (0, 0.5, 1/2) of the $2b$ site, and (0.5, 0.5, 0.6700) of the $4c$ site. Anion vacancy is also disordered; that is, the occupancy of all these sites was uniformly 0.9625. The refined results are shown in Table 2 and Figure 4. The R_{wp} and S values converged to 8.36% and 1.30, respectively. For Nd_2AlO_3N, Al−O/N bonds (2.086 Å for Al−O and 2.130 Å for Al−N) perpendicular to $Al(O/N)_2$ layers are obviously longer than those (1.855 Å for Al−O) parallel to the layers. The tendency of these distances is also observed in the refined structure, as shown in Table 3. In addition, three kinds of Al−O/N bonds parallel to the layers exist, and one of them (1.70(5) Å) is much shorter than the other distances (1.857(3) and 1.99(5) Å). Thus, a large distortion of $Al(O/N)_6$ octahedra was observed in the monoclinic system.

Then, the space group Im was studied. The initial crystal parameters are also referenced to those for Nd_2AlO_3N. As all of the atoms occupy the $2a$ sites, equivalent Eu sites and O/N sites increase in number to 2 and 4, respectively. The other refinement conditions were the same as that for $I2$. The R_{wp} and S values converged to 8.33% and 1.29, respectively. A large distortion of $Al(O/N)_6$ octahedra with a very short Al−O/N distance (1.700 Å) was also observed.

A significant difference between the results of $I2$ and Im was not observed. Thus, we reconsidered the result of the ^{151}Eu Mössbauer spectrum, because this is strongly affected by the coordination environment of europium. In the case of $I2$, the spectra can be analyzed using 12 Lorentzian functions for each

Table 1. ^{151}Eu Mössbauer Parameters for Eu2−Al1−O−N at 20 K

species	δ (mm/s)	$eV_{zz}Q_g$ (mm/s)	η	I_0 (%)	Γ (mm/s)
Eu^{II}	−11.981(13)	−16.9(2)	0.47(2)	−12.70(11)	3.14(4)
Eu^{III}	0.282(9)	−5.6(3)	0.83(9)	−11.1(2)	2.41(6)

Table 2. Crystallographic Data for $Eu^{II}_{1.20}Eu^{III}_{0.80}AlO_{3.75}N_{0.1}$ at Room Temperature

space group						$I2$ (No. 5, setting 3)
a/Å						3.7113(2)
b/Å						3.6894(2)
c/Å						12.3900(8)
β/deg						90.6860(5)
R_{wp}/%						8.36
S						1.30

atom	site	g	x	y	z	B/Å^2
Eu	4c	1.0	0.4968(2)	0.504(13)	0.85755(4)	0.607(10)
Al	2a	1.0	0	0.0	0	0.88(6)
O/N1	2a	0.9625	0	0.539(14)	0	0.3(2)
O/N2	2b	0.9625	0	0.52(2)	1/2	1.7(2)
O/N3	4c	0.9625	0.498(2)	0.51(2)	0.6660(4)	0.83(11)
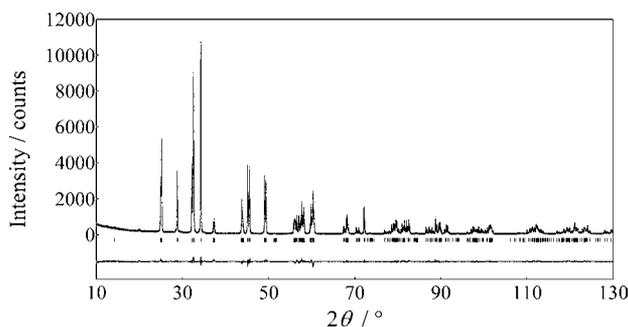
Figure 4. Powder X-ray diffraction pattern fitting for $Eu^{II}_{1.20}Eu^{III}_{0.80}AlO_{3.75}N_{0.1}$. The calculated and observed patterns are shown by the top solid line and the cross markers, respectively. The vertical marks in the middle show positions calculated for Bragg reflections. The lower trace is a plot of the difference between calculated and observed intensities.

Figure 5. Crystal structure of $Eu^{II}_{1.20}Eu^{III}_{0.80}AlO_{3.75}N_{0.1}$.

Table 3. Selected Bond Distances of $Eu^{II}_{1.20}Eu^{III}_{0.80}AlO_{3.75}N_{0.1}$

species	distance (Å)	species	distance (Å)
Eu–O/N1	2.5575(12) × 1	Eu–O/N1	2.5710(12) × 1
Eu–O/N2	2.52(5) × 1	Eu–O/N2	2.59(5) × 1
Eu–O/N3	2.374(5) × 1	Eu–O/N3	2.61(5) × 1
Eu–O/N3	2.63(5) × 1	Eu–O/N3	2.64(5) × 1
Eu–O/N3	2.66(5) × 1		
Al–O/N1	1.70(5) × 1	Al–O/N1	1.99(5) × 1
Al–O/N2	1.857(3) × 2	Al–O/N3	2.057(5) × 2

of the two absorption peaks corresponding to Eu^{II} and Eu^{III}, as shown in Table 1, due to having only one europium site. On the other hand, Im has two crystallographic sites for europium. In this case, Eu^{II} must occupy two sites, since the ratio Eu^{II}:Eu^{III} is greater than 1. Because this analysis could not distinguish accurately the two sites, space group $I2$ having one europium crystallographic site was adopted. The refined crystal structure of $Eu^{II}_{1.20}Eu^{III}_{0.80}AlO_{3.75}N_{0.1}$ with space group $I2$ is shown in Figure 5. The basic crystal structure is confirmed to be similar to that for Eu_2AlO_3N.

However, this refined crystal structure differs from the previously reported Ruddlesden–Popper structures with the chemical formula A_2BX_4. Generally, tilts with rotations of corner-sharing BX_6 octahedra yield distortions from the ideal tetragonal A_2BX_4 structure ($I4/mmm$).[26,27] Recently, Harris reexamined the rigid octahedral tiltings and classified them into 10 structures using a Landau expansion of the free energy.[28]

For these A_2BX_4 structures, the conventional unit cell volumes ($Z \geq 4$) with octahedral tiltings are 2 times more than that of the ideal structure ($Z = 2$). On the other hand, while the crystal structure of $Eu^{II}_{1.20}Eu^{III}_{0.80}AlO_{3.75}N_{0.1}$ is distorted due to monoclinic symmetry, the number of the chemical formula per the conventional unit cell is $Z = 2$. In this structure, the $Al(O/N)_6$ octahedron has a tilt with no rotation. The unique tilt of the $Al(O/N)_6$ octahedron may be attributable to deficiencies and disorders between O and N anions and/or more covalent Al–O/N bonds in comparison with ionic Al–O bonds.

Preparation of $EuAl_2O_4$. Although $EuAl_2O_4$ is known as a promising photoluminescent material with green emission,[29] the crystal structure has not been reported due to the difficulty in preparing a sample with good crystallinity. A pure phase of $EuAl_2O_4$ was obtained when the molar ratio of the starting compounds was Eu_2O_3:Al_2O_3:AlN = 2:3:2. From this result, the reaction is presumed to be

$$\frac{1}{2}Eu^{III}_2O_3 + \frac{3}{4}Al_2O_3 + \frac{1}{2}AlN \rightarrow bEu^{II}Al_2O_4 + yN_2 \uparrow + \beta \tag{3}$$
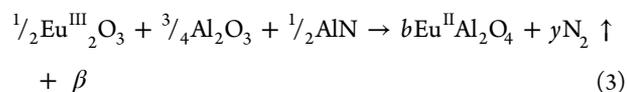
where β is the composition of impurities removed from the pellet, and the values of b and y are unknown because of the undetermined quantity of the impurities. In order to confirm the nitrogen amount in the product, TG analysis was performed at 1000 °C. If the chemical composition of the entire product is $EuAl_2O_4$, the theoretical weight gain should be 2.96% of the product due to the chemical reaction $4Eu^{II}Al_2O_4 + O_2 \rightarrow 4Eu^{III}AlO_3 + 2Al_2O_3$. The actual weight gain is 2.96%,

which is the same as the theoretical value. Therefore, the composition of the product is determined to be $EuAl_2O_4$. We also attempted to prepare $EuAl_2O_4$ from Eu_2O_3, Al_2O_3, and Al in order to clarify the effect of AlN. In the reaction, $EuAlO_3$ was formed as the main product with a small amount of $EuAl_2O_4$. Thus, we confirmed that the use of AlN is necessary for the preparation of $EuAl_2O_4$. The calculated Gibbs free energy change of the reduction reaction of Eu_2O_3 to EuO by AlN or Al indicates that AlN is not better than Al as a reducing agent.[30] Thus, AlN is expected not to be suitable as the starting material for the preparation of $EuAl_2O_4$ from the point of view of thermodynamic equilibrium. Therefore, AlN probably has a great advantage for the reaction in terms of the chemical kinetics. The reaction rates are expected to be mainly related to the particle surface conditions of AlN and Al owing to decomposition of AlN and/or passivity of Al.

Crystal Structure of $EuAl_2O_4$. The XRD profile of the product shown in Figure 6 is very similar to that of $SrAl_2O_4$,[31]
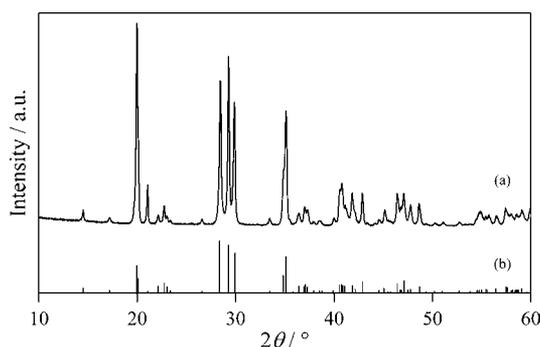
Figure 6. XRD pattern of (a) $EuAl_2O_4$ and reported pattern of (b) $SrAl_2O_4$ (JCPDS Card No. 34-0379).

suggesting that they are isostructural. The $SrAl_2O_4$ phase has a monoclinic structure with the space group $P2_1$ (No. 4). $EuAl_2O_4$ gave SHG signals, supporting the notion that it has the non-centrosymmetric space group $P2_1$. The intensity of the SHG signal for the $EuAl_2O_4$ was stronger than that for the quartz. Then, with the atomic parameters of $SrAl_2O_4$ as initial values, the structure of $EuAl_2O_4$ could be refined (Table 4 and Figure 7). The R_{wp} and S values converged to 6.45% and 1.31, respectively. The refined crystal structure is shown in Figure 8, and selected bond distances are given in Table 5. The cell parameters of $EuAl_2O_4$ ($a = 8.44478(11)$ Å, $b = 8.82388(12)$ Å, $c = 5.15643(7)$ Å, and $\beta = 93.1854(12)°$) are very close to those of $SrAl_2O_4$ ($a = 8.447$ Å, $b = 8.816$ Å, $c = 5.163$ Å, and $\beta = 93.42°$),[31] due to the almost identical ionic radii of Eu^{2+} and Sr^{2+}. The Al–O and Eu–O lengths are also similar to those for $SrAl_2O_4$ (1.730−1.772 Å for Al–O, 2.508−3.114 Å for Sr–O). The bond valence sum (BVS) method was applied to estimate the valence of cations using $r_0(Eu^{2+}-O^{2-}) = 2.147$ Å and $r_0(Al^{3+}-O^{2-}) = 1.644$ Å. The calculated bond valences for Eu1 and Eu2 were +1.78 and +1.84, respectively. These values are similar to those expected for divalent europium and are consistent with the result obtained from Mössbauer spectra, as mentioned later. The calculated bond valences for Al1, Al2, Al3, and Al4 were +3.26, +3.09, +2.79, and +2.99, respectively, indicating that aluminum is in a trivalent state.

[151]Eu Mössbauer Spectrum of $EuAl_2O_4$. As described above, Eu atoms in $EuAl_2O_4$ occupy two crystallographic sites with no symmetry elements, and the [151]Eu Mössbauer spectrum consists of 2 sets of 12 overlapping peaks due to quadrupole

Table 4. Crystallographic Data for $EuAl_2O_4$ at Room Temperature[a]

space group		$P2_1$ (No. 4, setting 1)			
a/Å		8.44478(11)			
b/Å		8.82388(12)			
c/Å		5.15643(7)			
β/deg		93.1854(12)			
R_{wp}/%		6.45			
S		1.31			

atom	site	x	y	z	B/Å^2
Eu1	2a	0.4926(2)	0.0	0.2517(3)	0.66(5)
Eu2	2a	0.0267(2)	0.9928(3)	0.2005(3)	0.57(5)
Al1	2a	0.1935(13)	0.8178(11)	0.709(2)	0.68(8)
Al2	2a	0.8014(14)	0.8317(11)	0.738(2)	0.68(8)
Al3	2a	0.7034(14)	0.6576(12)	0.235(2)	0.68(8)
Al4	2a	0.6837(13)	0.1656(13)	0.798(2)	0.68(8)
O1	2a	0.270(2)	0.185(2)	0.428(4)	0.47(12)
O2	2a	0.738(2)	0.334(2)	0.599(4)	0.47(12)
O3	2a	0.3239(12)	0.502(3)	0.344(2)	0.47(12)
O4	2a	0.2633(13)	0.975(2)	0.879(2)	0.47(12)
O5	2a	0.170(2)	0.294(2)	0.936(3)	0.47(12)
O6	2a	0.217(2)	0.665(2)	0.891(3)	0.47(12)
O7	2a	0.489(2)	0.221(2)	0.874(2)	0.47(12)
O8	2a	0.992(2)	0.877(2)	0.635(3)	0.47(12)

[a]Fitting of the isotropic atomic displacement parameters, B, of Al and O was carried out as one kind, respectively.
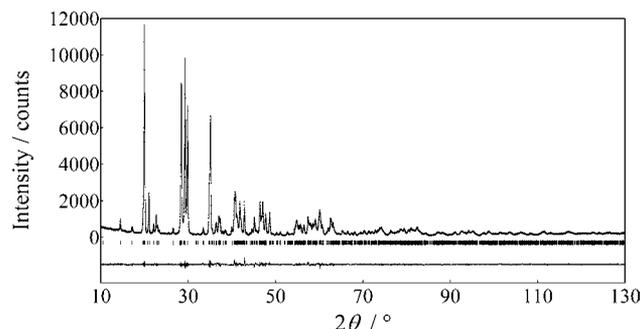
Figure 7. Powder X-ray diffraction pattern fitting for $EuAl_2O_4$. The calculated and observed patterns are shown by the top solid line and the cross markers, respectively. The vertical marks in the middle show positions calculated for Bragg reflections. The lower trace is a plot of the difference between calculated and observed intensities.
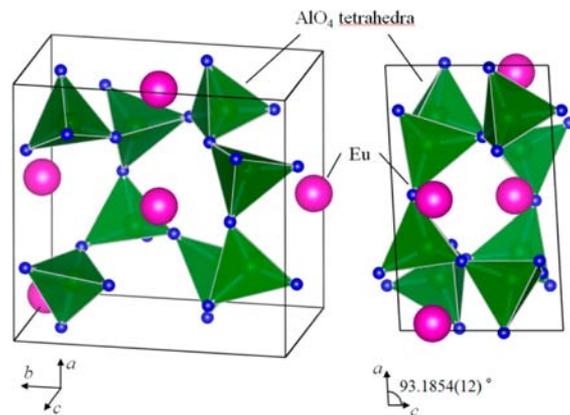
Figure 8. Crystal structure of $EuAl_2O_4$.

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dx.doi.org/10.1021/ic4013334 | *Inorg. Chem.* 2013, 52, 12972−12979

Table 5. Selected Bond Distances of EuAl$_2$O$_4$

bond	distance (Å)	bond	distance (Å)
Eu1−O1	2.69(2)	Eu2−O1	2.87(2)
Eu1−O2	2.59(2)	Eu2−O2	2.60(2)
Eu1−O3	2.527(11)	Eu2−O4	2.670(11)
Eu1−O4	2.661(11)	Eu2−O5	2.49(2)
Eu1−O6	2.977(13)	Eu2−O6	2.58(2)
Eu1−O7	2.56(2)	Eu2−O8	2.499(14)
Eu1−O7	2.754(14)	Eu2−O8	3.088(14)
Al1−O2	1.73(2)	Al3−O1	1.75(2)
Al1−O4	1.73(2)	Al3−O4	1.74(2)
Al1−O6	1.65(2)	Al3−O5	1.86(2)
Al1−O8	1.80(2)	Al3−O7	1.78(2)
Al2−O1	1.65(2)	Al4−O2	1.88(2)
Al2−O3	1.87(2)	Al4−O3	1.62(2)
Al2−O5	1.72(2)	Al4−O6	1.77(2)
Al2−O8	1.76(2)	Al4−O7	1.79(2)

interactions. Since it was too difficult to estimate the ^{151}Eu Mössbauer parameters adequately, we used the quadrupole coupling constants and asymmetry parameters obtained from the DFT calculations as the initial parameters in Table 6 (see

Table 6. Quadrupole Coupling Constants and Asymmetry Parameters for the Eu Ions of EuAl$_2$O$_4$ Calculated Using WIEN2k^a

species	$eV_{zz}Q_g$ (mm/s)	η
Eu(1)	−20.1	0.65
Eu(2)	17.7	0.50

^{a}The Hubbard U parameter is set at 8.2 eV.

Table 7. ^{151}Eu Mössbauer Parameters for EuAl$_2$O$_4$ at Room Temperature

species	δ (mm/s)	$eV_{zz}Q_g$ (mm/s)	η	I_0 (%)	Γ (mm/s)
Eu(1)	−13.40(10)	−15.6(4)	0.65(16)	4.5(10)	2.84(12)
Eu(2)	−12.83(13)	16.4(8)	0.51(15)	2.1(10)	2.0(5)

the section of band structure of EuAl$_2$O$_4$). Table 7 shows the Mössbauer parameters obtained by fittings of 2 sets of 12 Lorentzian functions to the observed data in Figure 9. The
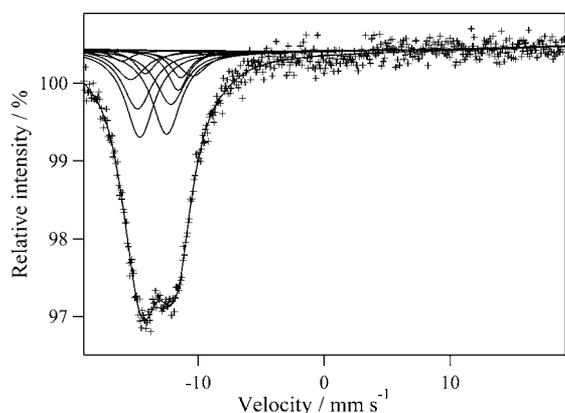
Figure 9. ^{151}Eu Mössbauer spectrum of EuAl$_2$O$_4$ at room temperature.

isomer shifts relative to EuF$_3$ of the Eu(1) and Eu(2) sites were determined to be −13.40(10) and −12.83(13) mm/s, respectively, and they confirmed that all Eu ions were in the divalent state.

Band Structure of EuAl$_2$O$_4$. Figure 10 shows the UV−vis diffuse reflectance spectrum. The absorption coefficients were
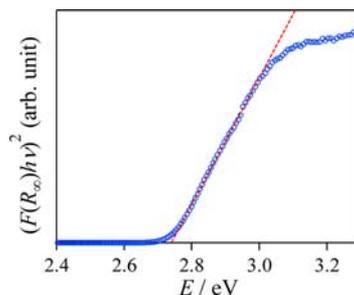
Figure 10. Diffuse reflectance spectrum of EuAl$_2$O$_4$. The Tauc plot is shown.

calculated from the reflectance data with the Kubelka−Munk function.[32] The energy of the optical band gap was determined to be 2.74 eV from the Tauc plot (see Figure 10).[33] The fact that the photon energy ($h\nu$) is proportional to the square of $F(R_\infty)h\nu$ indicates the predominance of the direct, allowed transition, in agreement with the result of our DFT calculations (see below).

In the DFT calculations of insulators with strongly correlated electrons, the energy of the band gap is very sensitive to the Hubbard U parameter. In the case of EuAl$_2$O$_4$, the band gap energy E_g calculated with the WIEN2k program increased with the U parameter. Thus, we adjusted the U parameter so that the calculated E_g value became equal to the observed value (2.7 eV), and it was determined to be 8.2 eV. Figure 11a shows the total density of states and partial DOS for Eu 4f electrons and total electrons of Eu, Al, and O. From the partial DOS, it is found that the top of the valence band located from −0.5 to 0 eV primarily consists of up-spin states of Eu 4f and O 2p orbitals, while the lowest unoccupied state in the conduction band is mainly composed of hybridized states between O 2p and Eu 5d orbitals. Figure 11b,c shows the energy dispersions for the up-spin and down-spin states, respectively. The dispersions reveal that the lowest state in the conduction band is located at the Γ point and that the tops of the valence band are positioned at the X point. However, the difference between the highest energies at the Z and Γ points is small (<0.01 eV) because of the flatness of the valence band, suggesting the predominance of the direct, allowed transition (Γ → Γ) in the photoluminescent properties.

Photoluminescent Properties of EuAl$_2$O$_4$. The photoluminescent properties were measured on powder samples of pure Eu^{II}Al$_2$O$_4$. Figure 12 shows the excitation and emission spectra. A peak is observed at 515 nm in the emission spectrum, and two peaks are shown at around 380 nm and at 430 nm in the excitation spectra. The result of emission is consistent with earlier studies.[29,34,35] On the other hand, the feature of the excitation spectra in our study differs from those by Zorenko et al.[34] and Meister et al.[35] More than two peaks are visible in these spectra measured using non-single-phase EuAl$_2$O$_4$ including some impurities such as EuAlO$_3$ and Al$_2$O$_3$. However, it is considered that the peaks at 380 and 430 nm observed in Figure 12 are both due to intrinsic optical excitations in
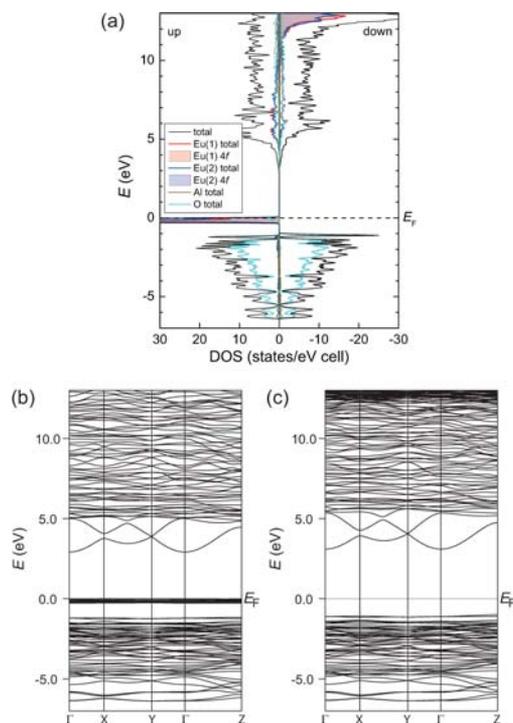
Figure 11. Total and partial density of states (DOS) (a) and energy dispersions of $EuAl_2O_4$ for the up-spin electrons (b) and for the down-spin electrons (c). The zero energy is placed at the highest occupied state.
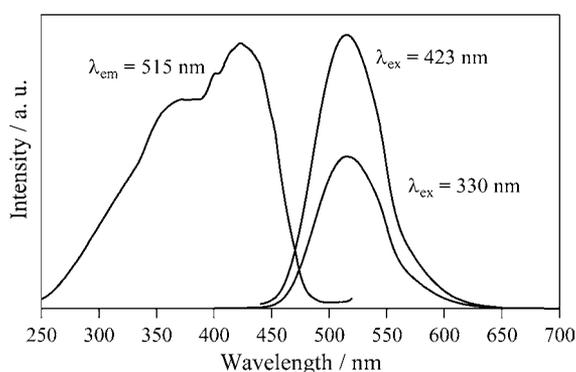
Figure 12. Excitation spectrum of luminescence at 515 nm and emission spectra under excitation at 423 and 330 nm of $EuAl_2O_4$.

$EuAl_2O_4$, because the normalized intensities of the peaks at 380 and 460 nm increase with Eu concentration in $Eu_xSr_{1-x}Al_2O_4$ solid solutions.[35]

Figure 13 illustrates a possible luminescence mechanism for $EuAl_2O_4$. From the DOS and the energy dispersions in the
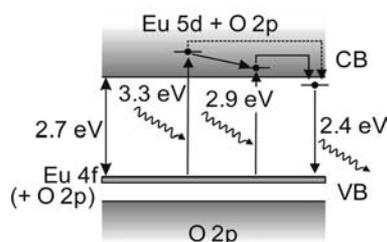
Figure 13. Luminescence mechanism for $EuAl_2O_4$.

band structure of $EuAl_2O_4$ (see Figure 11), the excitation at 430 nm ($E \approx 2.9$ eV) and the emission at 515 nm ($E \approx 2.4$ eV) are attributable to the direct, allowed transitions ($4f^7$ ($^8S_{7/2}$) $\leftrightarrow$ $4f^6 5d^1$) between Eu 4f valence bands (VBs) and conduction bands (CBs) by hybridization with O 2p and Eu 5d orbitals near the Γ point. The emission (430 nm) via the excitation at 380 nm ($E \approx 3.3$ eV) was reported to disappear due to energy transfer to the emission at 515 nm.[36] It is supposed that the origin of the excitation at 380 nm is also related to the transitions from the Eu 4f VB to the O 2p and Eu 5d CBs. This model accounts for the luminescence mechanism for $EuAl_2O_4$.

CONCLUSIONS

We succeeded in synthesizing the new compound $Eu_2AlO_{3.75}N_{0.1}$ and the phosphor $EuAl_2O_4$ by reactions among Eu_2O_3, AlN, and Al_2O_3 at 1200 °C in evacuated silica tubes. The decomposition of the aluminum nitride in the tubes induced the formations of these compounds with lower valent cations, Eu^{2+}. This novel silica tube technique should be useful in forming such low-valent oxides and oxynitrides.

For $Eu_2AlO_{3.75}N_{0.1}$, the ratio Eu^{II}:Eu^{III} was determined to be 3.0:2.0 from the ^{151}Eu Mössbauer spectrum, and it has a novel Ruddlesden−Popper-type structure with monoclinic space group $I2$.

The crystal structure of $EuAl_2O_4$ is almost the same as that of $SrAl_2O_4$ with monoclinic space group $P2_1$. An emission peak of the photoluminescence was observed around 515 nm, and excitation peaks were observed around 430 nm with a shoulder around 370 nm. The excitations and the emissions are explicable in terms of the direct, allowed transitions ($4f^7$ ($^8S_{7/2}$) $\leftrightarrow$ $4f^6 5d^1$) from the calculated band structures and the measured band gap.

ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving structural data of $Eu_2AlO_{3.75}N_{0.1}$ and $EuAl_2O_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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