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On the Existence of Europium Aluminum Oxynitrides with a Magnetoplumbite or β-Alumina Type Structure

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In the literature confusion exists concerning the structure type, the valence of europium, and the amount of nitrogen incorporation of the compound europium aluminum oxynitride. By using X-ray diffraction and luminescence measurements, we show that europium aluminum oxynitride has the magnetoplumbite structure. Eu is present in its divalent state, and a negligible amount of nitrogen is present. © 1999 Academic Press

INTRODUCTION

Aluminates with a β-alumina or related magnetoplumbite type structure are well known because of their extensive crystal chemistry as well as attractive optical and electrical properties (1–5). Recently, we described the preparation and characterization of a novel material with a β-alumina type structure, viz., the oxynitride $BaAl_{11}O_{16}N$, which is deduced from $NaAl_{11}O_{17}$ by substitution of $(NaO)^-$ by $(BaN)^-$ (6, 7). A comparison of $BaAl_{11}O_{16}N$ with $BaMgAl_{10}O_{17}$, which results after substitution of $(BaMg)^{4+}$ for $(NaAl)^{4+}$, is given in Ref. (8). In line with these results, the possible existence of $Eu^{2+}Al_{11}O_{16}N$ with a β-alumina type structure can be envisaged, similar to the compound $Eu^{2+}MgAl_{10}O_{17}$ (3).

In the literature europium aluminum oxynitride has been reported to possess a β-alumina type structure, but with composition $EuAl_{12}O_{18}N$, indicating Eu^{3+} instead of Eu^{2+} (9). However, in two independent papers the same compound $EuAl_{12}O_{18}N$ was said to have the magnetoplumbite structure instead (10, 11). It can be considered as deduced from $Eu^{2+}Al_{12}O_{19}$ with the magnetoplumbite structure (3, 12) by substitution of $(Eu^{2+}O)^0$ by $(Eu^{3+}N)^0$. In contrast to his paper (11), in his Ph.D. thesis Wang mentions that europium aluminum oxynitride contains divalent Eu in combination with a negligible content of incorporated nitrogen (13). In view of the above-mentioned results, it is obvious that with respect to europium aluminum oxynitride serious confusion exists about (1) the structure type, (2) the valence of the Eu ion, and (3) the degree of nitrogen incorporation.

In this paper we focus on these questions. For comparison, also the europium aluminum oxide ($EuAl_{12}O_{19}$) and europium magnesium aluminum oxide ($EuMgAl_{10}O_{17}$) were taken into account.

EXPERIMENTAL

The materials were prepared in the same way as described by us for Eu-doped alkaline-earth aluminum oxynitrides by weighing out the compositions $EuAl_{12}O_{19}$, $EuMgAl_{10}O_{17}$, and $EuAl_{11}O_{16}N$ (8). The starting materials Eu_2O_3 (Rhône-Poulenc, 99.99%). γ-Al_2O_3 (Sumitomo AKPG, >99.995%) $MgCO_3$ (Riedel de Haen, >99%), and AlN (Starck grade C, >97%) were mixed in the appropriate amounts and fired at 1973 K in an N_2/H_2 atmosphere. The samples were characterized with powder X-ray diffraction (Philips 5100 diffractometer, Fe$K\alpha$ radiation) and luminescence spectroscopy (Perkin-Elmer LS50B spectrophotometer). Details about the measuring conditions can be found in Ref. (8).

RESULTS AND DISCUSSION

The lattice parameters determined for $EuAl_{12}O_{19}$ and $EuMgAl_{10}O_{17}$ agree with literature values (Table 1).

The ratio between the lattice parameters (c/a) nicely fits in the dependence of it on the ionic radius of the metal ion as found for various alkaline-earth hexaaluminates (Fig. 1) with a magnetoplumbite type structure (for $EuAl_{12}O_{19}$) or a β-alumina type structure (for $EuMgAl_{10}O_{17}$). The c/a value determined for our europium aluminum oxynitride ($c/a = 3.952$, Table 1) appears to be characteristic for the magnetoplumbite type structure (Fig. 1). The same

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TABLE 1
Lattice Parameters Determined for Europium Aluminum Oxides, Europium Magnesium Aluminum Oxides, and Europium Aluminum Oxynitrides

Weighed-out composition	a (Å)	c (Å)	c/a	Reference
$EuAl_{12}O_{19}$	5.568(1)	22.000(5)	3.951(2)	This work
	5.571	22.01	3.951(3)	12
$EuMgAl_{10}O_{17}$	5.624(1)	22.399(8)	3.982(3)	This work
	5.609	22.42	3.997(3)	3
$EuAl_{11}O_{16}N$	5.565(1)	21.994(2)	3.952(1)	This work
$EuAl_{12}O_{18}N$	5.557	22.00	3.959(3)	9
	5.564	22.00	3.954(3)	10
	5.568	22.009	3.953(1)	11, 13

TABLE 2
Luminescence Properties Determined for Europium Aluminum Oxide, Europium Magnesium Aluminum Oxide, and Europium Aluminum Oxynitride

Weighed-out composition	Emission peak (nm)	Excitation peaks[a] (nm)	Stokes shift[b] (10^3 cm^{-1})
$EuAl_{12}O_{19}$	403	278, 322	6.2
$EuMgAl_{10}O_{17}$	480	235, 345, 386	5.1
$EuAl_{11}O_{16}N$	410	278, 327	6.2

[a] The excitation spectra were recorded at the emission maximum.
[b] The Stokes shift is calculated by taking the difference between the position of the emission peak and the excitation peak with the lowest wavenumber.

conclusion can be drawn from the c/a ratios reported for the europium aluminum oxynitrides mentioned in the literature ($c/a = 3.953$–3.959, Table 1). Secondary phases are observed in our material with the weighed-out composition of $EuAl_{11}O_{16}N$. This is logical since we aimed to synthesize a material with the β-alumina type structure, whereas we obtained a material with the magnetoplumbite type structure.

The structure assignment is confirmed by the luminescence properties measured for our material (Table 2).

The emission and excitation spectra of europium aluminum oxynitride (Fig. 2) resemble those of $EuAl_{12}O_{19}$ with the magnetoplumbite type structure but are different from those measured for $EuMgAl_{10}O_{17}$ with a β-alumina type structure (Fig. 2). The wavelength with maximum emission intensity is in accordance with expectation from the relationship between it and the ionic radius of the metal ion, as found for various alkaline-earth hexaaluminates (Fig. 3). The same is true for the Stokes shift (Fig. 4). The gradual decrease of the Stokes shift for larger host-lattice ions can be explained with the configuration coordinate model as a consequence of obstructed shrinkage of the Eu^{2+} ion during excitation (5), whereas a stepwise decrease takes place corresponding with a change in crystallographic modification.

As an additional result, the observed broad band in the emission spectrum (Fig. 2) unambiguously shows that the major amount of Eu in our europium aluminum oxynitride is present in the divalent state (5). With respect to $EuAl_{12}O_{19}$, the wavelength of maximum intensity is shifted with about 7 nm for europium aluminum oxynitride, possibly indicating the incorporation of some nitrogen (8).

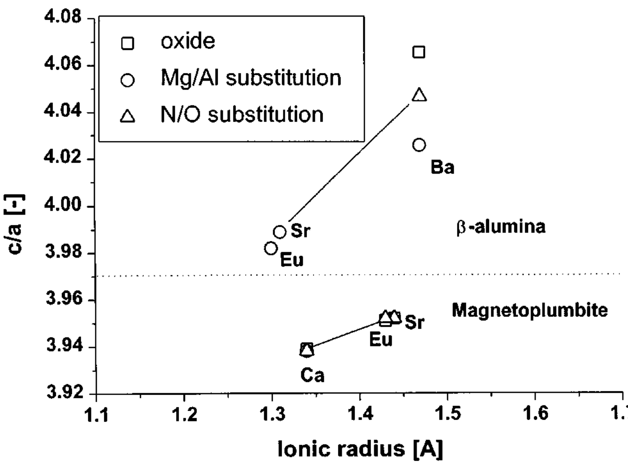

FIG. 1. c/a ratio of europium aluminum oxide, europium magnesium aluminum oxide, europium aluminum oxynitride, and related alkaline-earth hexaaluminates as a function of the ionic radius (14). Data for the alkaline-earth hexaaluminates were taken from Ref. (8).

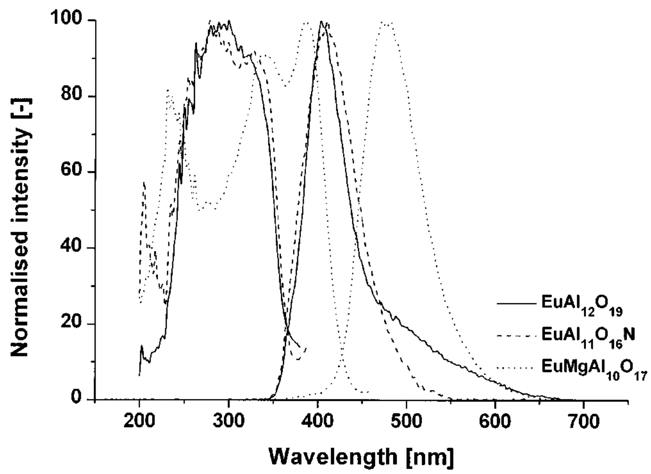

FIG. 2. Emission spectra ($\lambda_{exe} = 254$ nm) and excitation spectra (λ_{max} is wavelength with maximum emission intensity) of europium aluminum oxide, europium magnesium aluminum oxide, and europium aluminum oxynitride.

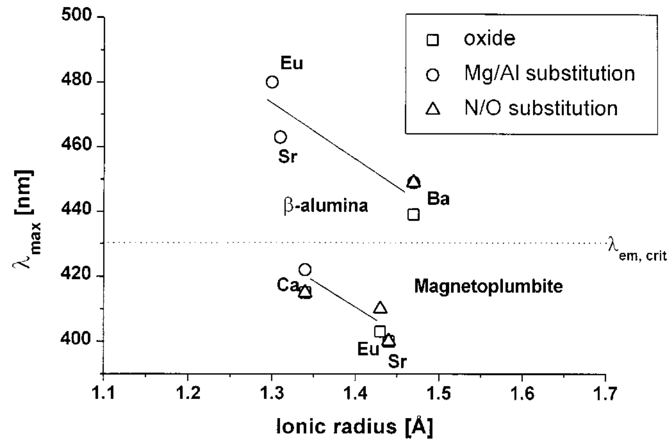

FIG. 3. Wavelength of maximum emission intensity of europium aluminum oxide, europium magnesium aluminum oxide, europium aluminum oxynitride, and related Eu-doped alkaline-earth hexaaluminates as a function of the ionic radius (14). Data for the Eu-doped alkaline-earth hexaaluminates were taken from Ref. (8).

The chemical composition of europium aluminum oxynitrides therefore is closest to $EuAl_{12}O_{19}$, possibly with a very small amount of nitrogen incorporated in it. In agreement with this, a negligible nitrogen content was also concluded for strontium aluminum oxynitride (the ionic radius of Sr^{2+} is about the same as that of Eu^{2+}(14)) with the magnetoplumbite-type structure (8).

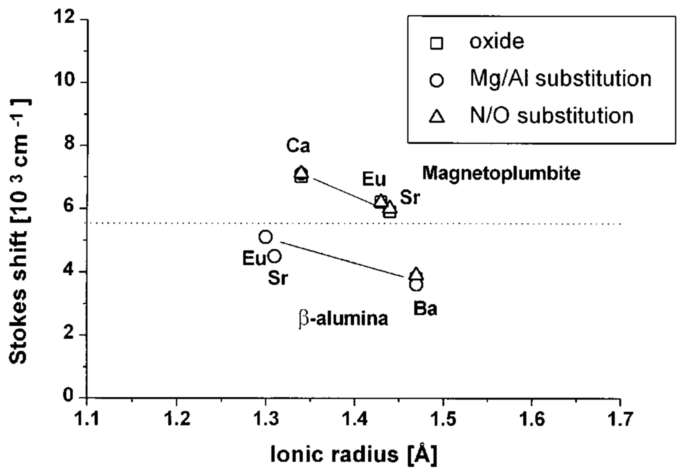

FIG. 4. Stokes shift of europium aluminum oxide, europium magnesium aluminum oxide, europium aluminum oxynitride, and related Eu-doped alkaline-earth hexaaluminates as a function of the ionic radius (14). Data for the Eu-doped alkaline-earth hexaaluminates were taken from Ref. (8).

CONCLUSIONS

Concerning the existence of europium aluminum oxynitrides, it can be stated that the crystallographic modification is magnetoplumbite, that the major part of Eu is present in the divalent state, and that the amount of incorporated nitrogen is small, thus resembling the already known compound $EuAl_{12}O_{19}$ with a magnetoplumbite type structure.

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