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Incorporation of Nitrogen in Alkaline-Earth Hexaaluminates with a *β*-Alumina- or a Magnetoplumbite-Type Structure

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A feasibility study is presented concerning the incorporation of N^{3-} in alkaline-earth aluminates with a magnetoplumbite- or *β*-alumina-type structure. A comparison is made with Mg^{2+}-substituted alkaline-earth aluminates with a magnetoplumbite or *β*-alumina-type structure. Various techniques such as X-ray diffraction, luminescence spectroscopy (on Eu^{2+}-doped samples), ^{27}Al magic angle spinning nuclear magnetic resonance spectroscopy, and IR spectroscopy are used in order to distinguish between the magnetoplumbite- and the *β*-alumina-type structure as well as to investigate the incorporation of N^{3-} and Mg^{2+}. The incorporation of N^{3-} is possible for materials with a *β*-alumina-type structure, resulting in $BaAl_{11}O_{16}N$, but negligible for materials with a magnetoplumbite-type structure (Sr and Ca).

Introduction

Aluminates with a magnetoplumbite-type structure are strongly related to materials with a *β*-alumina-type structure. Both structures belong to the same space group ($P6_3/mmc$) and are built of spinel blocks and intermediate layers, allowing various substitutions.[1,2] The similarities are so strong that problems are present in unequivocally assigning the structure of new materials, as has happened in the past for the barium hexaaluminates.[3]

Some specific substitutions are reported for *β*-alumina-type materials. Starting from the well-known sodium *β*-alumina (ideal formula $NaAl_{11}O_{17}$) it is possible to replace Na^+ by Ba^{2+} and simultaneously replace Al^{3+} by Mg^{2+} for charge compensation. This results in $BaMgAl_{10}O_{17}$ with a *β*-alumina-type structure.[3,4] We have investigated a different charge compensation method: replacing O^{2-} by N^{3-}.[5,6] This resulted in a new *β*-alumina-type material with the approximate composition $BaAl_{11}O_{16}N$.[7] Solid solutions are formed between the Mg/Al or N/O substituted Ba *β*-alumina-type materials and Ba phase I.[4,7] Ba phase I is a defective barium *β*-alumina-type phase with the composition $Ba_{0.83}Al_{11}O_{17.33}$.[8]

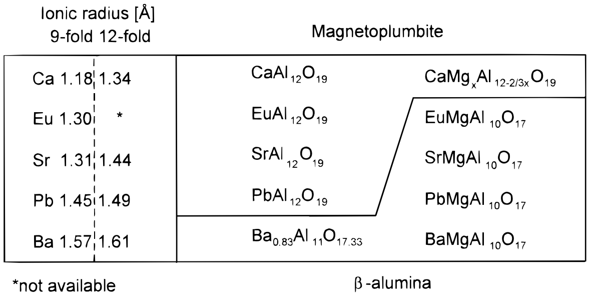

Figure 1. Schematic drawing of magnetoplumbite−*β*-alumina relations. The line represents the phase separations. The radii for the large cations in 9-fold (as in *β*-alumina) and 12-fold (as in magnetoplumbite) coordination are taken from Shannon.[9]

Depending on the ionic size of M^{2+} in $MAl_{12}O_{19}$ it is possible to transform alkaline-earth and similar hexaaluminates with a magnetoplumbite-type structure into a *β*-alumina-type structure when Al^{3+} is replaced by Mg^{2+}, resulting in $MMgAl_{10}O_{17}$.[3] This change is observed for M^{2+} = Sr, Eu, and Pb but not for M^{2+} = Ca, as is depicted in Figure 1. Thus hexaaluminates containing a large cation (Ba^{2+}) always possess a *β*-alumina-type structure, whereas with a small cation (Ca^{2+}) the structure always possesses a magnetoplumbite-type structure and hexaaluminates containing intermediate sized cations switch between both structure types.

In the present paper we report an investigation of the existence and the structure of alkaline-earth aluminum oxynitrides. These materials are expected to exist because of the similarities between the Al^{3+}/Mg^{2+} and the O^{2-}/N^{3-} substitutions as described above.[6,7]

In general, distinction between both structures is made on the basis of differences in the *c*/*a* ratio of the unit-cell parameters. The magnetoplumbites have *c*/*a*

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Table 1. Coordination of Al Ions in the Magnetoplumbite- and β-Alumina-type Structure

magnetoplumbite			β-alumina		
Wyckoff position	point symmetry	coordination	Wyckoff position	point symmetry	coordination
4f	$3m.$	tetrahedral	4f	$3m.$	tetrahedral
2b (4e)	$\bar{6}m2$ ($3m.$)	pentahedral[a]	4f	$3m.$	tetrahedral
2a	$\bar{6}m2$	octahedral	2a	$\bar{6}m2$	octahedral
4f	$3m.$	octahedral	12k	$.m.$	octahedral
12k	$.m.$	octahedral			

[a] The ideal pentahedral position in magnetoplumbites is 2b, in general 4e position (with 50% site occupancy) is observed.

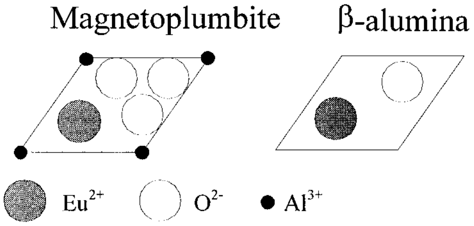

Figure 2. Cross section of the intermediate layer ($z = 0.25$) in the magnetoplumbite- and β-alumina-type structure showing the difference in coordination of the substituted Eu^{2+} and thus giving rise to a systematic difference in luminescence for these materials.

values ranging from 3.91 (ideal) to 3.97 (distorted),[10] while the c/a values of β-alumina are larger than 3.97.[3,11] Because of the existence of intermediate structures with $3.97 < c/a < 4.0$,[2,12] discrimination between both structure types based on solely XRD can be difficult for new materials. Therefore, we have used three extra techniques to distinguish between the β-alumina-type and the magnetoplumbite-type structure: luminescence of Eu^{2+}-doped materials, ^{27}Al magic angle spinning (MAS) NMR, and IR spectroscopy. Luminescence and ^{27}Al MAS NMR are suitable to detect differences concerning the coordination of Eu and Al ions, respectively, in the crystallographic structures of β-alumina and magnetoplumbite.

Substituted Eu^{2+} is assumed to incorporate in the intermediate layer. In β-alumina the intermediate layer is only filled with the alkaline-earth ion and one oxygen ion, while in magnetoplumbite this layer is filled with an alkaline-earth ion, one (pentahedrally coordinated) aluminum ion and three oxygen ions (see Figure 2). This difference in coordination of Eu^{2+} results in a systematic shift of luminescence spectra as was reported by Stevels et al.[3]

The differences in intermediate layers between the β-alumina-type and the magnetoplumbite-type structures affect the number of crystallographic sites and types of coordination for the aluminum ions in these materials, as is shown in Table 1. In both structures octahedrally and tetrahedrally coordinated Al ions are present, but the ratio $Al_{tetrahedral}/Al_{octahedral}$ is very different (8/14 in β-alumina and 4/18 in magnetoplumbite, respectively). Furthermore an important difference between both structure types is the occurrence of pentahedrally coordinated Al in the magnetoplumbite-type materials. In principle, the latter two aspects can be clarified with ^{27}Al MAS NMR. Quantitative results are, however, notoriously difficult to obtain.

The coordination differences result in different ^{27}Al MAS NMR spectra for magnetoplumbite in comparison with β-alumina, as reported by Van Hoek et al.[13] However, Van Hoek et al. were not able to detect and assign the pentahedral site in the NMR spectrum. The reason is not only the fact that the pentahedral peak might be obscured by the peaks ascribed to the other Al sites but also that only a minor amount of Al in magnetoplumbite-type materials is pentahedrally coordinated (fraction $^{1}/_{12}$). Furthermore there is a distribution in size and shape of the AlO_5 pentahedra in various materials resulting in a dispersion of NMR spectral parameters and thus hindering an easy assignment of pentahedral Al.[14−29]

The differences in crystallographic structure between magnetoplumbite and β-alumina result in different crystal lattice vibrations which can be measured by IR spectroscopy. Because the space groups of both structures are identical and all the structural differences are concentrated in the intermediate layer, the differences in IR spectra are expected to be rather small.

All four techniques (XRD, luminescence spectroscopy, ^{27}Al NMR, and IR) not only can be used to distinguish between the structure type (magnetoplumbite versus β-alumina) but also can in principle be applied to prove the N^{3-}/O^{2-} substitution.

A small change in lattice parameters is expected when N^{3-}/O^{2-} substitution is successful, as is shown previ-

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Table 2. XRD Results: Secondary Phases and Unit-Cell Dimensions[a]

weighed out composition	secondary phase (relative intensity [%])	*a* [Å] (SD)	*c* [Å] (SD)	*c*/*a* (SD)	*V* [Å^3] (SD)
$Ba_{0.83}Al_{11}O_{17.33}$		5.587 (1)	22.721 (1)	4.066 (1)	614.3 (1)
$BaMgAl_{10}O_{17}$		5.625 (2)	22.648 (5)	4.026 (2)	620.6 (3)
$BaAl_{11}O_{16}N$		5.601 (1)	22.665 (1)	4.047 (1)	615.7 (1)
$SrAl_{12}O_{19}$		5.567 (1)	22.002 (2)	3.952 (1)	590.6 (2)
$SrMgAl_{10}O_{17}$		5.621 (1)	22.421 (3)	3.989 (1)	613.6 (2)
$SrAl_{11}O_{16}N$	α-Al_2O_3 (1), AlN (<1)	5.567 (1)	22.001 (2)	3.952 (1)	590.5 (1)
$CaAl_{12}O_{19}$	α-Al_2O_3 (5)	5.559 (1)	21.900 (5)	3.939 (1)	586.2 (3)
$CaMgAl_{10}O_{17}$	$MgAl_2O_4$ (75) + unidentified phase	5.555 (1)	21.895 (6)	3.938 (2)	586.2 (4)
$CaAl_{11}O_{16}N$	$CaAl_4O_7$ (5)	5.559 (1)	21.900 (4)	3.938 (2)	586.1 (3)

[a] The unit-cell dimensions do not change significantly if 5 mol % of the metal (Ba, Ca, or Sr) is replaced by Eu.

ously.[7,30] Such a change is expected because the ionic radius of N^{3-} is larger than that of O^{2-} and because this substitution is expected to influence the defects in these materials.[7]

The N^{3-}/O^{2-} substitution will increase the covalency, resulting in electronic transitions with a lower energy for luminescent materials.[31] Due to this effect, also called the nephelauxetic effect,[31] the luminescence spectra of Eu-doped materials are expected to change with N^{3-}/O^{2-} substitution.

Also, the ^{27}Al MAS NMR resonances are different for different oxygen/nitrogen nearest neighbor coordination, as has been published for SiAlON and AlON materials.[32,33]

Another possibility to investigate the N^{3-}/O^{2-} substitution is by the determination of IR spectra, as has been performed for $LnAl_{12}O_{18}N$ (Ln = La, Ce, Nd, Pr, Sm, and Gd).[34] For these magnetoplumbite-type materials a peak near 950 cm^{-1} is observed, which is assigned to the stretching vibration of the Al−N bond.[34]

Experimental Section

Several starting mixtures were made by combining the appropriate amounts of $BaCO_3$ (Merck, >99%), $CaCO_3$ (Merck, > 99%), $SrCO_3$ (Riedel-de Haen AG, >99%), Eu_2O_3 (Rhône-Poulenc, 99.99%), $MgCO_3$ (Riedel-de Haen, >99%), AlN (Starck grade C, >97%), and γ-Al_2O_3 (Gimex AKPG, >99.995%). The weighed out compositions are shown in Table 2. Corrections were made for weight losses, and the amount of AlN is corrected for its oxygen content. The choice of Al_2O_3 starting material is based on its high reactivity.[5] The powder was wet-mixed in 2-propanol (>97%) for 2 h in an agate container with agate balls on a planetary mill. After mixing the 2-propanol was evaporated. The powder was dried in a stove for one night at 433 K, and it was subsequently ground in an agate mortar.

The powders were fired in a molybdenum crucible under a mildly flowing N_2/H_2 (90/10) gas mixture. Reactions were performed in a vertical high-temperature tube furnace at 1973 K for 2 h.

The phases, present after reaction, were determined by powder X-ray diffraction (XRD). Continuous scans were made with Cu Kα radiation from 5 to 75° (2θ), with a scan speed of 1° (2θ)/min (Philips 5100). Step scans, with a step size of 0.01° (2θ) and a counting time of 6 s/step, were made from 68 to 75° (2θ) in order to determine the presence of traces of AlN. The lattice parameters were calculated by using the following reflections: 2 0 14, 2 2 0, 2 0 13, 3 0 4, 2 0 11, 2 1 7, 1 0 11, 1 1 8, 2 0 6, 2 0 5, and 1 0 10.

The luminescence measurements were performed at room temperature, using a Perkin-Elmer LS50B spectrophotometer with a xenon flash lamp. The lamp spectrum is corrected with a double photomultiplier. For the emission, radiation with a wavelength of 254 nm was used. The wavelength with maximum emission intensity ($\lambda_{em,max}$) was used to measure the excitation spectrum.

NMR spectra were measured on a Bruker MSL 400 NMR spectrometer using a 9.4 T magnetic field, a frequency of 104.56 MHz, and magic angle spinning (MAS) at 10 or 15 kHz. Only the samples without europium are measured, because Eu is paramagnetic and therefore causes signal broadening.

A Perkin-Elmer 1600 FTIR is used to record the IR spectra in the range 5000−450 cm^{-1}. The powders were mixed with KBr (±1/100 ratio) and pressed into transparent pellets under vacuum.

Results

As is shown in Table 2, all weighed out compositions of the Mg^{2+}, or N^{3-}-substituted materials are according to the chemical composition corresponding with a β-alumina-type structure: so Mg + Al = 11 and N + O = 17.

A relatively large amount of $MgAl_2O_4$ is determined as a secondary phase in the sample with weighed out composition $CaMgAl_{10}O_{17}$ (Table 2). This suggests that almost no Mg is present in this Ca-aluminate as was already reported by Stevels et al.[3] and recently confirmed by Göbbels et al.[35] We determined a mixture of three phases ($CaMg_xAl_{12-2/3x}O_{19}$ with a magnetoplumbite-type structure (x very small, < 0.01 according to Göbbels et al.[35]), $MgAl_2O_4$, and an unidentified phase) and not a mixture of $CaMg_2Al_{16}O_{27}$ (space group $P\bar{6}m2$), $CaAl_4O_7$, and $MgAl_2O_4$ as expected according to the phase diagram determined by Göbbels et al.[35] Most probably this difference is caused by the differences in the firing procedure: our samples were fired in an N_2/H_2 gas mixture (instead of air), at a temperature of 1973 K (instead of 1923 K), and our samples were not quenched.

It is obvious that with decreasing ionic radius of the cation (Ba → Sr → Ca) the amount of secondary phases is increasing for the Mg^{2+}- and N^{3-}-substituted materials, thus suggesting that these materials do not possess a β-alumina-type structure but a magnetoplumbite-type structure. This suggestion is confirmed by the c/a ratios of the materials (see also Figure 3): the c/a ratio indicates formation of a β-alumina-type structure (c/a > 3.97) for all the Ba samples and the Sr/Mg samples, while the c/a ratio of the other materials suggests a magnetoplumbite-type structure (c/a < 3.97). The unit-cell volume can be used as an additional criterion: we

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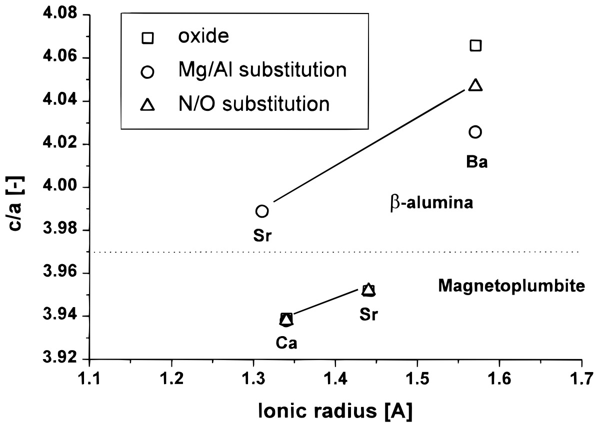

Figure 3. c/a ratio of the magnetoplumbites (12-fold coordination) and β-aluminas (9-fold coordination) as a function of the ionic radius.[9]

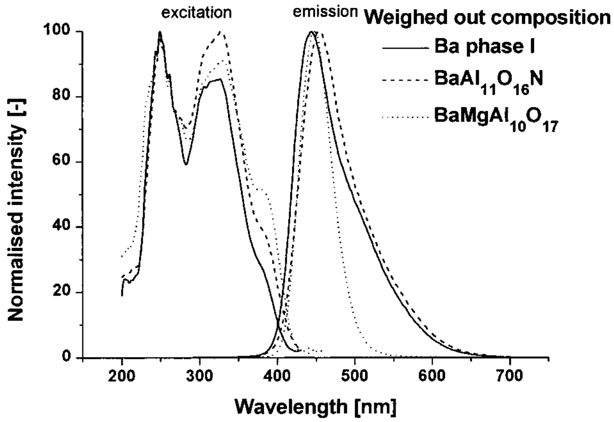

Figure 4. Normalized emission (254 nm excitation) and excitation (at emission maximum) spectra for the various Eu-doped Ba hexaaluminates.

observed that the unit cell volume of the β-alumina-type materials is larger than 600 Å^3, while it is smaller for the magnetoplumbite-type materials.

For both structure types the c/a ratio increases with increasing cation radii (Figure 3), indicating that the expansion in the direction of the c-axis is larger than along the a-axis.

Two types of luminescence spectra were determined. One type is characteristic for the Eu-doped materials $Ba_{0.83}Al_{11}O_{17.33}$, $BaMgAl_{10}O_{17}$, $BaAl_{11}O_{16}N$, and $SrMgAl_{10}O_{17}$. The other type is characteristic for the Eu-doped materials with the weighed out compositions $SrAl_{12}O_{19}$, $SrAl_{11}O_{16}N$, $CaAl_{12}O_{19}$, $CaMgAl_{10}O_{17}$, and $CaAl_{11}O_{16}N$. Both emission and excitation spectra of the various materials are depicted in Figures 4−6. A summary of these results is presented in Table 3 containing the emission and excitation peaks as well as the Stokes shift. It is possible to distinguish between the spectra of magnetoplumbite and β-alumina on the basis of the position of the emission maxima as a function of the ionic radius of the large cations (Figure 7). Therefore, a critical wavelength of the emission maxima, $\lambda_{em,crit}$, is defined that can be used to distinguish between a magnetoplumbite- and a β-alumina-type structure in the same way as does the c/a ratio with the X-ray diffraction data. As one can see in Figure 7, $\lambda_{em,crit}$ is about 430 nm. The β-alumina-type materials have an emission maximum at higher wavelength, while the magnetoplumbites have an emission maximum at lower wavelength.

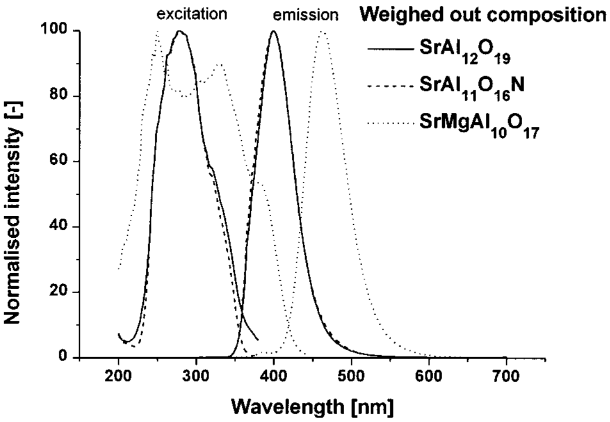

Figure 5. Normalized emission (254 nm excitation) and excitation (at emission maximum) spectra for the various Eu-doped Sr hexaaluminates.

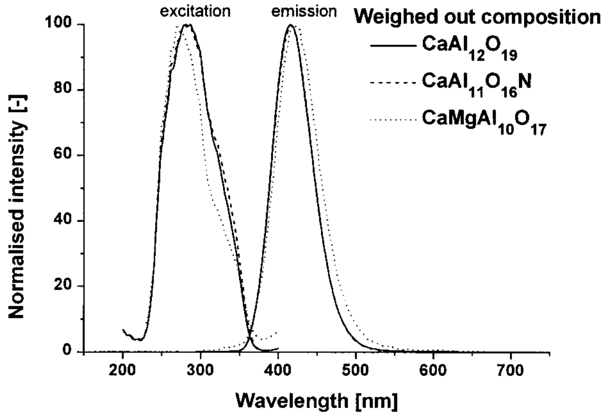

Figure 6. Normalized emission (254 nm excitation) and excitation (at emission maximum) spectra for the various Eu-doped Ca hexaaluminates.

Table 3. Luminescence Properties of the Alkaline-Earth Hexaaluminates at Room Temperature[a]

weighed out composition	emission peaks [nm] (exc at 254 nm)	excitation peaks [nm]	Stokes shift[b] [10^3 cm^{-1}]
$Ba_{0.83}Al_{11}O_{17.33}$	439, 488	∼250, ∼325, ∼380	3.8
$BaMgAl_{10}O_{17}$	449	∼250, ∼330, ∼380	3.6
$BaAl_{11}O_{16}N$	449, 488	∼250, ∼330, ∼380	3.9
$SrAl_{12}O_{19}$	400	∼280, ∼320	5.9
$SrMgAl_{10}O_{17}$	463	∼250, ∼330, ∼380	4.5
$SrAl_{11}O_{16}N$	400	∼280, ∼320	6.0
$CaAl_{12}O_{19}$	415	∼285, ∼320	7.0
$CaMgAl_{10}O_{17}$	422	∼270, ∼320	7.1
$CaAl_{11}O_{16}N$	415	∼285, ∼320	7.1

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

Discrimination between both structures is also possible on the basis of the shape of the excitation spectra: the excitation spectra of the magnetoplumbite-type materials consist of one broad peak (and shoulder), while those of the β-alumina-type materials show three peaks (see Figures 4−6). Due to the smaller crystal field the bandwidth of the excitation spectra of the magnetoplumbite-type materials is narrower than that of the β-alumina-type excitation spectra, which is in agreement with literature data.[3]

Furthermore, the Stokes shift of the materials with a β-alumina-type structure is smaller ($<5 \times 10^3$ cm^{-1}) than for the materials with a magnetoplumbite-type

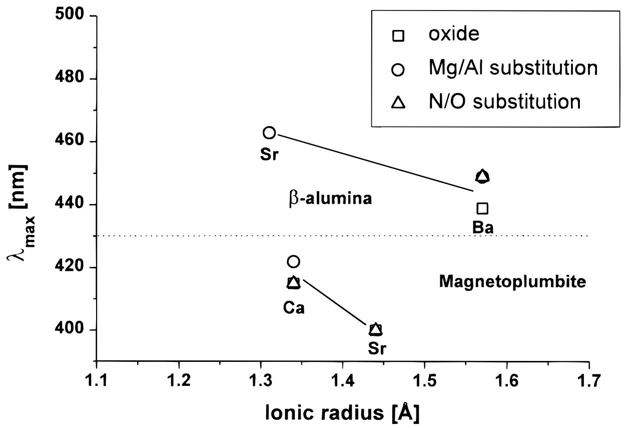

Figure 7. Emission maxima of the Eu-doped magnetoplumbites (12-fold coordination) and the β-aluminas (9-fold coordination) as function of the ionic radius.[9]

structure (>5 × 10^3 cm^{-1}, see also Table 3) as has been reported before by Stevels et al.[3]

The Mg/Al substitution has only a small influence on the shape of the excitation spectrum of the Eu-doped Ba β-aluminas, indicating small structural differences. Furthermore, as one can see in Figure 4, a shoulder is present in the emission band of Eu-doped Ba phase I which is absent in $BaMgAl_{10}O_{17}$:Eu. This indicates the presence of two Eu^{2+} sites in Eu-doped Ba phase I, while only one Eu^{2+} site is present in $BaMgAl_{10}O_{17}$, which is also observed by Stevels et al.[36] and Ronda et al.[37] The main emission band is ascribed to Eu^{2+} on the Ba^{2+} site,[36,37] but the two articles disagree about the position of the second Eu^{2+} site. To obtain more information about this second Eu^{2+} site we performed a more detailed luminescence study and neutron diffraction experiments, which will be published elsewhere.[38,39]

For the Sr hexaaluminates the Mg/Al substitution has a clear influence on the shape of the excitation spectra and on the position of the emission bands (and thus on the Stokes shift), as is shown in Figure 5 and Table 3. This clearly indicates a structural change, corresponding with the change from a magnetoplumbite- to a β-alumina-type structure as deduced from X-ray diffraction measurements.

For Ca hexaaluminate the Mg/Al substitution has little influence on the excitation and emission spectra, as is depicted in Figure 6, which means that both materials have the magnetoplumbite-type structure. These minor changes in excitation and emission spectra indicate the incorporation of only a small amount of Mg^{2+} in the Ca magnetoplumbite.

The N/O substitution has only a small influence on the luminescence spectra of the β-aluminas, indicating that the crystallographic differences between Ba phase I and $BaAl_{11}O_{16}N$ are small. It must be mentioned that in this paper luminescence is used merely as a technique to discriminate between both structure types. A more detailed discussion about the luminescence properties of the various barium β-aluminas, with emphasis on the new material $BaAl_{11}O_{16}N:Eu^{2+}$, will be presented elsewhere.[38]

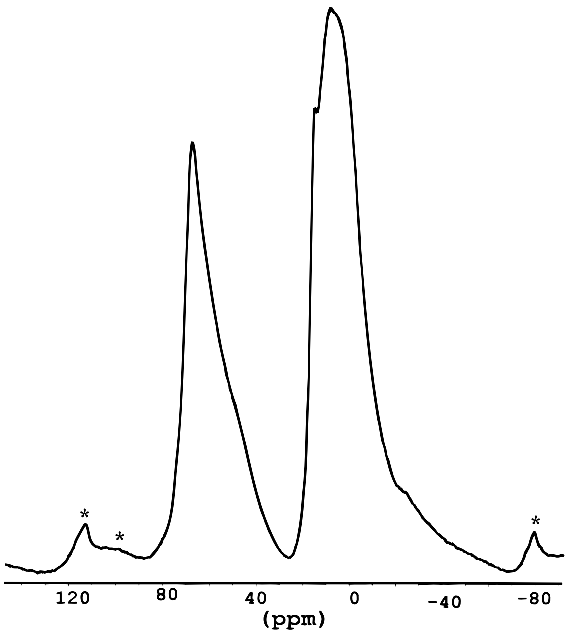

Figure 8. Solid-state ^{27}Al MAS NMR spectrum of $Ba_{0.83}Al_{11}O_{17.33}$ with the β-alumina-type structure at 9.4 T (10 kHz). The symbol * indicates a spinning sideband.

No influence of the N/O substitution on the luminescence spectra of the Sr and Ca hexaaluminates is determined, indicating no structural change and suggesting that the incorporation of N in the magnetoplumbite-type structure is ineffective.

With solid-state ^{27}Al MAS NMR two types of spectra were determined. The first type resembles the already published spectra of β-alumina-type materials[13] and is characteristic for the materials $Ba_{0.83}Al_{11}O_{17.33}$ (see Figure 8), $BaMgAl_{10}O_{17}$, $BaAl_{11}O_{16}N$, and $SrMgAl_{10}O_{17}$. It is possible to determine the ratio $Al_{tetrahedral}/Al_{octahedral}$, because it is known that the chemical shift of the resonance line of octahedral AlO_6 is between +15 and −30 ppm and of tetrahedral AlO_4 between +80 and +50 ppm.[40,41] As expected (Table 1), the ratio $Al_{tetrahedral}/Al_{octahedral}$ is about 8/14, according to the peak areas of the above-mentioned spectra. The other type of NMR spectrum resembles the already published spectrum of the magnetoplumbite $CaAl_{12}O_{19}$[13] and is characteristic for the materials with the weighed out compositions $SrAl_{12}O_{19}$ (see Figure 9), $SrAl_{11}O_{16}N$, $CaAl_{12}O_{19}$, and $CaAl_{11}O_{16}N$. As expected (Table 1), the ratio $Al_{tetrahedral}/Al_{octahedral}$ is about 4/18, according to the peak areas of these spectra. No separate signals are measured which indicate the presence of pentahedrally coordinated Al.

The spectrum of $BaAl_{11}O_{16}N$ shows an additional signal at 112 ppm; see Figure 10. In the range 90−115 ppm signals were observed for SiAlON[32] and AlON[33] materials, indicating that the additional signal at 112 ppm is likely to be caused by AlO_xN_y structural units (with $x + y = 4$).

With IR spectroscopy also two types of spectra were determined: one type characteristic for the materials

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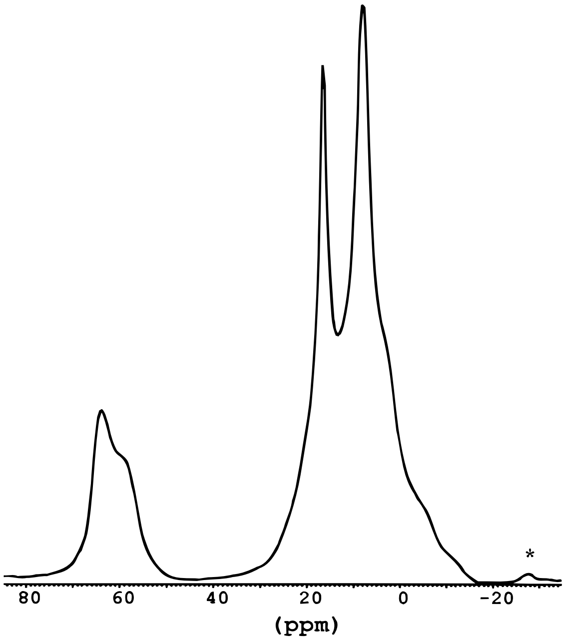

Figure 9. Solid-state ^{27}Al MAS NMR spectrum of $SrAl_{12}O_{19}$ with the magnetoplumbite-type structure at 9.4 T (10 kHz). The symbol * indicates a spinning sideband.

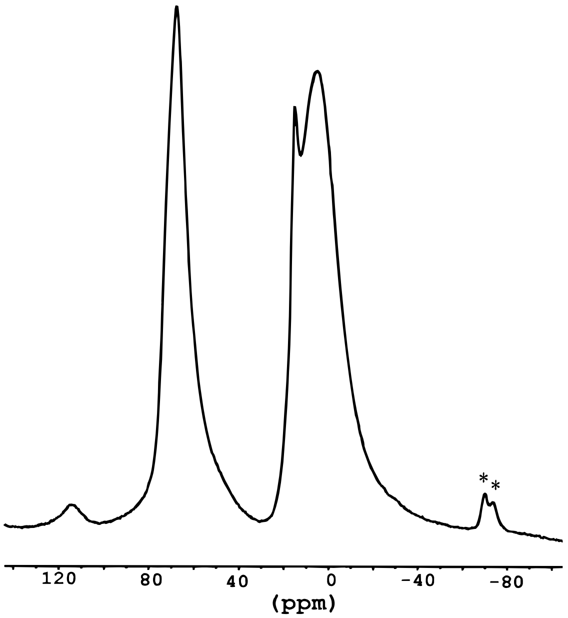

Figure 10. Solid-state ^{27}Al MAS NMR spectrum of $BaAl_{11}O_{16}N$ with the β-alumina-type structure at 9.4 T (15 kHz). The symbol * indicates a spinning sideband.

$Ba_{0.83}Al_{11}O_{17.33}$ (see Figure 11), $BaMgAl_{10}O_{17}$, $BaAl_{11}O_{16}N$, and $SrMgAl_{10}O_{17}$. The other type is characteristic for the materials with the weighed out compositions $SrAl_{12}O_{19}$ (see Figure 11), $SrAl_{11}O_{16}N$, $CaAl_{12}O_{19}$, and $CaAl_{11}O_{16}N$. The spectrum of the sample with the weighed out composition of $CaMgAl_{10}O_{17}$ could not be used because of the large amount of secondary phases. According to Wang et al. a peak at about 950 cm^{-1} in oxynitride magnetoplumbites can be assigned to the stretching vibration of Al$-$N.[34] This peak is determined for $BaAl_{11}O_{16}N$ with a β-alumina-type structure, as is shown in Figure 12. However, the suggestion that the N/O substitution takes place on similar sites for $LnAl_{12}O_{18}N$[34] and $BaAl_{11}O_{16}N$ is contradicted by the IR spectrum of $SrAl_{12}O_{19}$ (Figure 11) which also shows a peak at about 950 cm^{-1}.

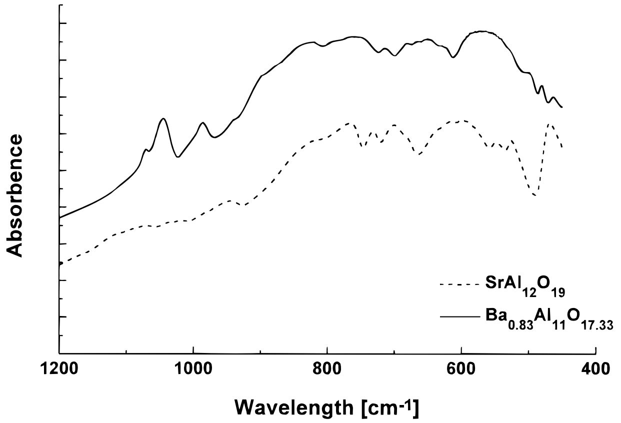

Figure 11. IR spectrum of $Ba_{0.83}Al_{11}O_{17.33}$ with the β-alumina-type structure and $SrAl_{12}O_{19}$ with the magnetoplumbite-type structure.

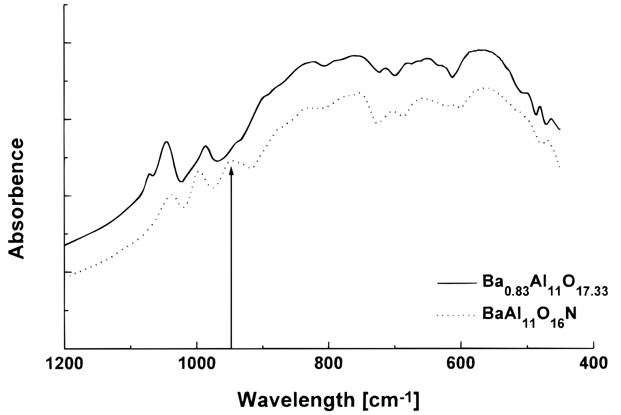

Figure 12. IR spectra of two barium β-aluminas: Ba phase I and barium aluminum oxynitride. The arrow indicates the peak that is assigned to the Al$-$N stretching vibration according to Wang et al.[34]

Discussion

Ba Hexaaluminates. Since the c/a ratio (Table 2) of the three Ba hexaaluminates is >3.97,[10] it can be stated for all materials that it is possible to synthesize $Ba_{0.83}Al_{11}O_{17.33}$, $BaMgAl_{10}O_{17}$, and $BaAl_{11}O_{16}N$ with a β-alumina-type structure. It has already been proven that the substituted materials form a solid solution with Ba phase I ($Ba_{0.83}Al_{11}O_{17.33}$),[4,6,7] thus indicating independently that all three Ba hexaaluminates possess a β-alumina-type structure. The substitution of both Mg^{2+} and N^{3-} has a significant effect on the unit-cell dimensions of the Ba hexaaluminate, as expected for materials in a solid solution. It is interesting to notice that the substitution of Mg^{2+} or N^{3-} results in an increase of the a-axis combined with a decrease of the c-axis (see Table 2). This phenomenon can be understood and is extensively discussed elsewhere.[7] Furthermore, a neutron diffraction study is performed in order to locate the position of N in $BaAl_{11}O_{16}N$, and its results will be presented soon.[39]

The shapes of the emission spectra of Eu-doped $Ba_{0.83}Al_{11}O_{17.33}$ and $BaAl_{11}O_{16}N$ are almost identical, but the emission maximum of $BaAl_{11}O_{16}N$:Eu is at a slightly higher wavelength as compared with Eu-doped Ba phase I, as is also found for $BaMgAl_{10}O_{17}$:Eu. This difference is caused most probably by the difference in defect structure. The luminescence spectra of the Eu-doped Ba hexaaluminates show two emission bands, corresponding to two Eu sites, for Ba phase I and $BaAl_{11}O_{16}N$ while just one emission band is observed for $BaMgAl_{10}O_{17}$ (at 254 nm excitation). The Eu site of Eu-doped $BaMgAl_{10}O_{17}$ is equal to the main Eu site in Eu-doped $Ba_{0.83}Al_{11}O_{17.33}$ and $BaAl_{11}O_{16}N$ because the excitation spectra of the three Ba hexaaluminates at the emission maxima are similar (Figure 4). The differences in Stokes shift (Table 3) of the main Eu site are small, indicating that the structural differences between the three Ba hexaaluminates are small.

The ^{27}Al NMR spectra of all Ba hexaaluminates are quite similar, with some minor differences, thus indicating that there are only small structural differences. In the spectrum of $BaAl_{11}O_{16}N$ at 15 kHz MAS (see Figure 10) an additional peak is observed at 112 ppm, which can be ascribed to AlO_xN_y units according to literature data of SiAlON and AlON ($x + y = 4$).[32,33]

The IR spectra of these materials do not show many differences between the various Ba β-aluminas, again indicating small structural differences.

All the techniques used here show that $Ba_{0.83}Al_{11}O_{17.33}$, $BaAl_{11}O_{16}N$, and $BaMgAl_{10}O_{17}$ have the same structure: β-alumina. Small structural differences between the three Ba hexaaluminates are also indicated by these techniques. The differences measured are caused by the differences in ionic radii between the substituted ions and the original ions (Mg^{2+} vs Al^{3+} or N^{3-} vs O^{2-}) and by the differences in the number of defects in these materials. Finally, it can be concluded that it is possible to incorporate N^{3-} in a Ba β-alumina-type structure which results in $BaAl_{11}O_{16}N$.

Sr Hexaaluminates. According to Table 2 the c/a ratios of the samples with the weighed out compositions $SrAl_{12}O_{19}$ and $SrAl_{11}O_{16}N$ are equally large and smaller than 3.97, while the c/a ratio of $SrMgAl_{10}O_{17}$ is larger than 3.97. So the samples with the weighed out compositions $SrAl_{12}O_{19}$ and $SrAl_{11}O_{16}N$ possess a magnetoplumbite-type structure, while $SrMgAl_{10}O_{17}$ possesses a β-alumina-type structure. The c/a ratio of $SrMgAl_{10}O_{17}$ (3.989) is similar to the c/a ratio published by Stevels et al.[3] Apparently the N/O substitution does not lead to a change in structure and the N incorporation does not seem possible according to the identical lattice parameters as compared to $SrAl_{12}O_{19}$ and the secondary phases determined for the sample with the weighed out composition $SrAl_{11}O_{16}N$.

The structural change due to the magnesium incorporation is confirmed by the luminescence, ^{27}Al NMR, and IR measurements. All techniques indicate that the spectrum of $SrMgAl_{10}O_{17}$ is different from the spectrum of $SrAl_{12}O_{19}$ but it resembles the spectra of the Ba hexaaluminates with a β-alumina-type structure.

From the data discussed above, we conclude that $SrAl_{11}O_{16}N$ with a β-alumina-type structure does not exist and that N is not incorporated (or only to a very small extent) in $SrAl_{12}O_{19}$ with a magnetoplumbite-type structure.

Ca Hexaaluminates. According to the c/a ratios of all three Ca hexaaluminates it can be concluded that these materials have a magnetoplumbite-type structure. Furthermore, according to the XRD results negligible Mg/Al or N/O substitution has taken place: the unit-cell dimensions are equal for all three Ca hexaaluminates, and the samples (weighed out assuming the β-alumina composition) are multiphase. The presence of a small amount of α-Al_2O_3 in $CaAl_{12}O_{19}$ is not expected on the basis of literature data,[35] but it might be caused by some Ca evaporation resulting in a Ca deficiency and thus an Al_2O_3 excess. Although the secondary phases in the sample with the weighed out composition $CaMgAl_{10}O_{17}$ sample do not agree with the expected phases as reported in literature,[35] it is clear that on base of XRD results that no or only a very small amount of Mg can be incorporated in $CaAl_{12}O_{19}$.

According to the luminescence spectra a small amount of Mg is incorporated in Ca hexaaluminate as already has been suggested by Stevels et al.[3] and by Göbbels et al.[35]

The similarity of the luminescence, ^{27}Al NMR, as well as the IR spectra between the samples with the weighed out composition $CaAl_{12}O_{19}$ and $CaAl_{11}O_{16}N$ indicates just like X-ray diffraction that it is not possible to incorporate much N in Ca hexaaluminate.

Measuring Techniques. In the present study four different techniques are used to distinguish between the magnetoplumbite- and the β-alumina-type structure and to investigate the incorporation of N or Mg: XRD, Eu luminescence, ^{27}Al MAS NMR, and IR.

The unit-cell dimensions and the secondary phases as measured by XRD are used to make this distinction: no Rietveld calculations are performed to investigate the structures.

Eu luminescence and ^{27}Al MAS NMR are used to investigate the materials on the basis of differences in atomic coordination of Eu (in doped samples) and Al, respectively.

With IR spectroscopy the differences in lattice vibrations are investigated.

All methods concur in their conclusion concerning the distinction between the magnetoplumbite- and the β-alumina-type structure. This means that only one technique is sufficient to distinguish between the two structural types.

On the other hand some problems occur with XRD and IR measurements when the incorporation of Mg or N is investigated. The XRD results did not show any incorporation of Mg in $CaAl_{12}O_{19}$, while a very small amount is incorporated according to luminescence data. Furthermore, the assignment of the 950 cm^{-1} peak to an Al−N stretching vibration in the IR spectra is doubtful because such a peak is also determined for $SrAl_{12}O_{19}$ which does not contain any N. Preferably a combination of XRD and Eu luminescence have to be used to preclude the possibility of incorporation of very small amounts of N or Mg, but this is valid only if a comparison is made with the materials without N or Mg.

Conclusions

The incorporation of N^{3-} is possible in Ba aluminate with a β-alumina-type structure, resulting in $BaAl_{11}O_{16}N$. It is not possible to incorporate N^{3-} in the other alkaline-earth (Sr and Ca) aluminates with a magnetoplumbite-type structure. As is already known, incorporation of Mg^{2+} is possible in Ba, Sr, and Ca aluminates. $BaMgAl_{10}O_{17}$ has a β-alumina type structure just like $Ba_{0.83}Al_{11}O_{17.33}$. The Sr aluminate normally possesses a magnetoplumbite-type structure, but after Mg^{2+} substitution this material adopts a β-alumina-type structure. Only a small amount of Mg^{2+} can be incorporated in Ca aluminate while the structure remains that of a magnetoplumbite-type.

Several clear criteria were used to distinguish between both structure types:

(1) The *c/a* ratio of the unit-cell dimensions (as determined by XRD) is smaller than 3.97 for materials with a magnetoplumbite-type structure, while the *c/a* ratio is larger than 3.97 for materials with a β-alumina-type structure.

(2) The unit-cell volume is larger than 600 $Å^3$ (as determined by XRD) for β-alumina-type materials while it is smaller for magnetoplumbite-type materials.

(3) The wavelength of the emission maxima (measured on Eu^{2+}-doped samples with luminescence spectroscopy) is smaller than 430 nm for materials with a magnetoplumbite-type structure, while this wavelength is larger than 430 nm for materials with a β-alumina-type structure.

(4) Differences in characteristics of the excitation spectra of Eu-doped materials, the ^{27}Al MAS NMR spectra, and the IR spectra.

(5) Differences in Stokes shift, which is $>5 \times 10^3$ cm^{-1} for magnetoplumbite-type materials and $<5 \times 10^3$ cm^{-1} for β-alumina-type materials.

The assignment of the 950 cm^{-1} peak in IR spectra to the Al−N stretching vibration is not useful to decide on the effectiveness of the N incorporation, because other vibrations are causing peaks as well in this region as has been shown for $SrAl_{12}O_{19}$. It is best to combine XRD and Eu luminescence in order to investigate the incorporation of small amounts of Mg and N, but comparative spectra of samples without Mg and N are necessary.

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