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Synthesis and crystal structure of $K_2NiF_4$-type novel
$Gd_{1+x}Ca_{1-x}AlO_{4-x}N_x$ oxynitrides

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Abstract

Novel gadolinium calcium aluminum oxynitrides, Gd\textsubscript{1+x}Ca\textsubscript{1-x}AlO\textsubscript{4-x}N\textsubscript{x}, were prepared in \( x = 0.15-0.25 \) by the solid state reaction of a nitrogen-rich mixture with AlN as an aluminum source; the mixture was sintered twice at 1500 °C for 5 h under 0.5 MPa of nitrogen gas. Shift in the optical absorption edge was observed in their diffuse reflectance spectra from 4.4 eV for the oxide (\( x = 0 \)) to 2.9 eV for the oxynitride at \( x = 0.2 \). The crystal structure of Gd\textsubscript{1.2}Ca\textsubscript{0.8}AlO\textsubscript{3.8}N\textsubscript{0.2} at \( x = 0.2 \) was refined using a synchrotron x-ray diffraction data as a layered K\textsubscript{2}NiF\textsubscript{4}-type structure with the \textit{i4mm} space group. Longer Al-O/N bond lengths in the oxynitride than those in GdCaAlO\textsubscript{4} suggest that the nitride ions are in the apical site of aluminum polyhedron, similar to those in Nd\textsubscript{2}AlO\textsubscript{3}N.

KEYWORDS: A. inorganic materials, A. rare earth alloys and compounds, B. solid state reactions, C. crystal structure, D. synchrotron radiation, D. X-ray diffraction
1. Introduction

Multinary oxynitride compounds are attracting much attention in applications such as white light emitting diodes (LEDs) [1,2], visible light driven photocatalysts [3,4], inorganic pigments [5,6] and dielectric materials [7-12]. The optical properties of the oxynitrides in the UV-vis range have been explained by the coexistence of nitride and oxide anions together because of the more covalent nature in nitride ion [13]. Much research on phosphor materials for LED applications has been conducted on silicon oxynitride and alumino-silicon oxynitrides as host materials [14-16]. However, study on (oxy)nitrides of especially aluminum is limited to systems such as AlN:Eu, spinel-type AlON:Mg,Mn, and BaAl₁₁O₁₆N:Eu [17-19]. Magnetoplumbite-type aluminum oxynitride doped with Eu was reported to be a phosphor material to have emission in multiple wavelength [20]. Neutron diffraction study showed that the emission site split because they have a slightly different coordination in the presence of both nitride and oxide ions together [21].

\[ RE_2AlO_3N \] oxynitride (\( RE = \text{La, Nd, Sm} \)) with K₂NiF₄-type structure (\( n = 1 \)) in Ruddlesden-Popper phase, \( A_{n+1}B_nX_{3n+1} \) has been prepared by firing mixtures of \( RE_2O_3 \) and AlN in a small sealed nickel tube at a high temperature (1350 °C)
under N\textsubscript{2} flow\cite{22}. Crystal structure refinement of Nd\textsubscript{2}AlO\textsubscript{5}N using its neutron diffraction data showed an ordering of nitride and oxide ions in the reduced symmetry from \textit{I4/mmm} in K\textsubscript{2}NiF\textsubscript{4} to \textit{I4mm} in Nd\textsubscript{2}AlO\textsubscript{5}N\cite{23}. The nitride ion is located at an apical site of AlO\textsubscript{5}N octahedron. There are two kinds of rare earth sites; Nd1 coordinated with O\textsubscript{8}N and Nd2 coordinated with O\textsubscript{5}N\textsubscript{4}, as shown in Fig. 1. Sr\textsubscript{2}TaO\textsubscript{5}N crystallizes in K\textsubscript{2}NiF\textsubscript{4}-type structure with \textit{I4/mmm} space group. Its nitride ions are located at equatorial sites of TaO\textsubscript{4}N\textsubscript{2} octahedron, and there is only one crystallographic Sr site, (4\textit{e})\cite{24}. Several kinds of aluminum oxides \textit{AE}E\textsubscript{R}EAlO\textsubscript{4} (\textit{AE} = Ca, Sr, \textit{RE} = La, Nd, Sm, Gd) have also been reported to crystallize in \textit{I4/mmm} space group\cite{25-27}.

The oxynitride was found out in a preparation using a nickel tube. An alternative preparation method, such as the carbon reduction nitridation method, has been applied to prepare Nd\textsubscript{2}AlO\textsubscript{5}N and Sm\textsubscript{2}AlO\textsubscript{5}N\cite{28}. La\textsubscript{2}AlO\textsubscript{5}N and Gd\textsubscript{2}AlO\textsubscript{5}N can be utilized as a multi-color emitting phosphor host material when they will be doped with divalent Eu. They have two crystallographic rare earth sites induced by O/N ordering, as mentioned above for Nd\textsubscript{2}AlO\textsubscript{5}N. Photoluminescence property of divalent Eu can be controlled by changing its coordination environment such as coordination number and O/N ratio.
In our preliminary study, La$_2$AlO$_3$N has been tried to obtain in solid state reaction but there was no appearance of the oxynitride in the products prepared using a similar method described in this paper. Gd$_2$AlO$_3$N has not yet been obtained in the carbon reduction nitridation [28], because the size of the Gd$^{3+}$ ion is not compatible with the K$_2$NiF$_4$-type structure. However, the GdCaAlO$_4$ phase is successfully prepared by the simple solid state reaction [29]. The ionic radius of Gd$^{3+}$ in 9 coordination is 0.124 nm, which is smaller than Nd$^{3+}$ (0.130 nm) and Sm$^{3+}$ (0.127 nm); however, the mixing Gd$^{3+}$ with Ca$^{2+}$ (0.132 nm) will increase their average size to stabilize K$_2$NiF$_4$ structure [30]. In this study, a series of K$_2$NiF$_4$-type gadolinium calcium aluminum oxynitrides, Gd$_{1-x}$Ca$_1$$_x$AlO$_{4-x}$N$_x$, were prepared by co-substituting Ca$^{2+}$ and O$^{2-}$ in GdCaAlO$_4$ with Gd$^{3+}$ and N$^{3-}$ simultaneously by the solid state reaction. Their crystal structure was investigated by high resolution synchrotron x-ray diffraction analysis.

2. Experimental

Gd$_2$O$_3$ (99.9%, Wako Pure Chemicals Co.), CaCO$_3$ (99.9%, Wako Pure Chemicals Co.), γ-Al$_2$O$_3$ (99.95%, Kojundo Chem. Lab. Co.), and AlN (Grade H, Tokuyama Co.) were used as starting materials. Gd$_2$O$_3$ was calcined at 1000 °C
for 10 h before mixing with other powders. The powders were dry mixed in stoichiometric ratios for \( \text{Gd}_{1+x}\text{Ca}_{1-x}\text{AlO}_{4-x}\text{N}_x \) with \( x = 0-0.3 \) in a dry nitrogen atmosphere to avoid hydrolysis of AlN with moisture. The mixed powders were uniaxially pressed at 20 MPa to form 10 mm diameter disks, which were then fired in a gas pressure furnace at 1500 °C for 5 h under a nitrogen pressure of 0.5 MPa. The aluminum source was either AlN only or a mixture of AlN and \( \gamma\text{–Al}_2\text{O}_3 \). For AlN only as the aluminum source, the cation composition, i.e., \( \text{Gd}:\text{Ca}:\text{Al} = 1+x:1-x:1 \), was maintained; however, the anionic composition was variable during the reaction. A part of AlN was expected to be oxidized during synthesis process. When AlN without \( \gamma\text{–Al}_2\text{O}_3 \) was used, the starting mixtures were fired twice with an intermediate grinding and mixing step.

The crystalline phases were characterized by powder x-ray diffraction (XRD; Ultima IV, Rigaku) with monochromatized Cu Kα radiation. XRD patterns were collected over the 2θ range of 10-120° with a step size of 0.02°. For structural refinement of \( \text{Gd}_{1+x}\text{Ca}_{1-x}\text{AlO}_{4-x}\text{N}_x \), high resolution synchrotron powder XRD experiments was performed at room temperature using a Debye-Scherrer camera installed at beamline BL02B2 of the Japan Synchrotron Radiation Institute (SPring-8). The incident beam was monochromatized to 0.035459 nm.
The finely ground powder samples were put into a 0.2 mm Ø glass capillary. The Rietveld program RIETAN-FP [31] was used for crystal structure refinement. The crystal structures were visualized using the VESTA program [32]. The nitrogen content was measured with an oxygen/nitrogen analyzer (EMGA-620W, Horiba) using Si3N4 as a reference. Diffuse reflectance spectra were measured using a spectrophotometer (V-550, Jasco) in the range of 250-750 nm.

3. Results and discussion

3.1. Preparation of Gd1+_xCa1-xAlO4-xN_x oxynitrides

The products obtained from stoichiometric mixtures using both γ-Al2O3 and AlN as aluminum source were contaminated with Gd2O3. A single phase of Gd1+_xCa1-xAlO4-xN_x with the K2NiF4-type structure was obtained only at x = 0, that is GdCaAlO4. Simultaneous substitution of Ca2+ and O2- pair with Gd3+ and N3- together led to the K2NiF4-type oxynitride products with a small impurity phase of Gd2O3. The amount of the Gd2O3 impurity phase increased with an increase in x. Diffraction lines from the (00l) planes of the K2NiF4-type structure shifted toward a smaller diffraction angle with increasing x. Elongation of the c-axis has been observed similarly from the CaNdAlO4 oxide (a = 0.36847(3) nm and c =
1.2124(2) nm) to Nd₂AlO₃N oxynitride \((a = 0.37046(2)\) nm and \(c = 1.25301(13)\) nm) [23,27]. The increase of the lattice parameter \(c\) suggests the formation of Gd\(_{1+x}\)Ca\(_{1-x}\)AlO\(_{4-x}\)N\(_x\) oxynitride with the K\(_2\)NiF\(_4\)-type structure. The appearance of Gd\(_2\)O\(_3\) impurity may indicate nitrogen deficiency in Gd\(_{1+x}\)Ca\(_{1-x}\)AlO\(_{4-x}\)N\(_x\) due to partial oxidation of AlN during the synthesis.

The K\(_2\)NiF\(_4\)-type Gd\(_{1+x}\)Ca\(_{1-x}\)AlO\(_{4-x}\)N\(_x\) oxynitride obtained from starting mixtures containing both \(\gamma\)-Al\(_2\)O\(_3\) and AlN was contaminated with the Gd\(_2\)O\(_3\) impurity phase loosing nitrogen during the reaction. Therefore, AlN only was used as the aluminum source in the starting mixtures to improve the phase purity. Single phase of Gd\(_{1+x}\)Ca\(_{1-x}\)AlO\(_{4-x}\)N\(_x\) was obtained between \(x = 0.15\) and \(0.25\) as shown in Fig. 2. AlN was expected to be partially oxidized during the synthesis process. The suitable O/N ratio was attained to form a pure oxynitride phase between \(x = 0.15\) and \(0.25\) in the reaction.

CaAl\(_2\)O\(_4\) and Gd\(_2\)O\(_3\) were observed as secondary phases at \(x = 0.1\) and \(0.30\), respectively. The product obtained at \(x = 0.2\) had an expanded \(c\)-axis \((a = 0.3658(1)\) nm and \(c = 1.2067(5)\) nm) compared to that for GdCaAlO\(_4\) \((a = 0.3658(2)\) nm and \(c = 1.1994(6)\) nm) at \(x = 0.0\). The nitrogen content of the \(x = 0.2\) oxynitride was 1.2(1) wt%, which is comparable with the theoretical nitrogen.
content of 0.9 wt% within ±3σ. The $x = 0.20$ oxynitride was expected to have an O/N ratio of 3.8/0.2 to maintain the charge neutrality. The lattice expansion may be due to partial substitution of $O^{2-}$ ($r = 0.124$ nm, c.n. = 4) by $N^{3-}$ ($r = 0.134$ nm, c.n. = 4), although $Gd^{3+}$ ($r = 0.124$ nm, c.n. = 9) is smaller than $Ca^{2+}$ ($r = 0.132$ nm, c.n. = 9) [30]. Anisotropic expansion along the c-axis implies the ordering of nitride ions in the apical sites of $AlO_5N$ octahedron, similarly to the crystal structure reported for the $Nd_2AlO_3N$ oxynitride with fully ordered nitride ions on the apical site ($2a$), as shown in Fig. 1(a) [23].

The color of the resultant oxynitrides was yellow, while $GdCaAlO_4$ was white. The absorption edges were at ca. 4.46 eV and 2.94 eV for the oxide ($x = 0$) and oxynitride ($x = 0.2$), respectively, as shown in Fig. 3. The color change occurred with the nitrogen incorporation to form a new valence band at higher energy position than O(2p) orbital level, as reported for many oxynitride pigments [5,6,13]. The edge positions of the oxynitrides obtained at $x = 0.15 \sim 0.25$ slightly shifted toward longer wavelength along with the nitrogen content, $x$. The shift in edge positions indicated a decrease in band gap of $Gd_{1+x}Ca_{1-x}AlO_4-N_x$, implying an elevated valence band level as increasing in the nitrogen content. Table 1 summarizes the optical band gap energy and lattice
parameters of the oxynitrides. Ordering of the nitride ions in the apical site of Al octahedron induces two kinds of Gd/Ca sites coordinated with N-rich or N-poor anions as shown in Fig. 1(a). Absorption edge positions can be attributed to the N-rich Gd/Ca polyhedron, because of the higher energy level of the nitrogen 2p orbital than that of oxygen. The decrease in band gap energy might be interpreted as nitrogen enrichment in the former Gd/Ca polyhedron. Crystal structure of the oxynitride at $x = 0.20$ is discussed in the next section.

3.2. Crystal structure refinement at the Gd$_{1.2}$Ca$_{0.8}$AlO$_{3.8}$N$_{0.2}$ oxynitride

The crystal structure of Gd$_{1.2}$Ca$_{0.8}$AlO$_{3.8}$N$_{0.2}$ was refined using the high resolution synchrotron XRD pattern in the K$_2$NiF$_4$-type structure with the $I4mm$ space group, starting from the reported crystallographic parameters for Nd$_2$AlO$_3$N [23]. The O/N ratios for three anionic sites were fixed at 0.95/0.05, because of their mutually similar x-ray scattering factors. Neutron diffraction has been generally used for analysis of the oxygen and nitrogen distribution in oxynitrides; however, it is not useful for the present products, because the Gd atom has a large neutron absorption cross section. The finally refined parameters from the Rietveld method are summarized in Table 2. Observed,
calculated, and difference synchrotron XRD profiles for Gd$_{1.2}$Ca$_{0.8}$AlO$_{3.8}$N$_{0.2}$ are shown in Fig. 4. The refined occupancies for Gd/Ca sites indicate a chemical composition of Gd$_{1.22(1)}$Ca$_{0.78(1)}$AlO$_{3.8}$N$_{0.2}$, which is in agreement with the nominal starting composition of Gd$_{1.2}$Ca$_{0.8}$AlO$_{3.8}$N$_{0.2}$. The bond lengths and the atomic arrangements around Al and Gd/Ca sites are summarized in Table 3 and shown in Fig. 5(a), respectively. The crystal structure of GdCaAlO$_4$ reported by L. Vasylechko, et al., [26] using a powder XRD pattern is also shown in Fig. 5(b). The oxynitride has c-axis much longer than the reported value for GdCaAlO$_4$ (1.19787 nm), while a-axis is almost similar between the oxynitride and oxide. The elongated c-axis is attributed to longer Al-O/N$_2$ bond length of 0.2160(18) nm in the oxynitride than the corresponding distance of 0.2027 nm for Al-O in the oxide. Similarly elongated bond lengths have been observed for Al-N bond length in Nd$_2$AlO$_3$N compared with NdCaAlO$_4$. The nitride ions are located at the apical sites of AlO$_5$N octahedron in Nd$_2$AlO$_3$N [23]. The bond length of Al-N was reported to be 0.1893 nm for c.n. = 4 in AlN, which is longer than that of Al-O (0.1710 nm for c.n. = 4 in γ-Al$_2$O$_3$) [33,34]. The longer bond lengths of Al-O/N$_2$ indicate the preferential occupation of nitride ions on O/N$_2$ sites in the present Gd$_{1.2}$Ca$_{0.78}$AlO$_{3.8}$N$_{0.2}$, as reported in Nd$_2$AlO$_3$N [20]. The preferential occupation
of nitride ion might elongate the chemical bond between Gd/Ca and O/N2. On the other hand, the refined bond length is 0.2617(2) nm for Gd/Ca1-O/N2 which is comparable to the reported value of 0.2609 nm in the corresponding oxide. Substitution of O\(^{2-}\) with N\(^{3-}\) can increase the bond length, while smaller Gd\(^{3+}\) cation also replaces a part of bigger Ca\(^{2+}\) cation in the oxynitride. Therefore the bond length between Gd/Ca and O/N does not change significantly from the oxide to the oxynitride. BVS calculation was performed in the oxynitride. The value is +3.06 for the Al ion and is larger than theoretical value of +3, when a random distribution of O/N ions on the anion sites is assumed. The BVS value is improved to be +3.01 in the ordering of the nitride ions only in O/N2 site, supporting the preferential occupation of nitride ions in O/N2 site. Structure refinement in \(I4/mmm\) space group showed much less agreement with \(R_{wp}\) value of 5.6 %. The refined bond length of Al-O/N2 was shorter than that of Al-O in the oxide, although the refined Gd/Ca1-O/N2 bond length was longer than that in the oxide. Both the poor fitting of the oxynitride and the decrease in the Al-O/N2 bond length of Al(O,N)\(_6\) octahedron exclude the \(I4/mmm\) space group for the structural refinement of the Gd\(_{1.2}\)Ca\(_{0.8}\)AlO\(_{3.8}\)N\(_{0.2}\) oxynitride. The present oxynitride crystallizes in \(I4mm\) space group having non-equivalent Gd/Ca1 and
Gd/Ca2 sites. Preparation and photoluminescence property of Eu doped Gd$_{1+x}$Ca$_{1-x}$AlO$_{4-x}$N$_x$ are currently being investigated.

4. Conclusions

Novel gadolinium calcium aluminum oxynitrides, Gd$_{1+x}$Ca$_{1-x}$AlO$_{4-x}$N$_x$ ($x = 0.15-0.25$), were prepared by the solid state reaction from a nitrogen-rich starting composition. Diffuse reflectance spectra showed the shift in absorption edge from oxide (4.46 eV) to oxynitride at $x = 0.2$ (2.94 eV) due to the nitrogen incorporation. The crystal structure refinement of the Gd$_{1.2}$Ca$_{0.8}$Al$_{3.8}$N$_{0.2}$ oxynitride using synchrotron XRD showed the elongation of the Al-O/N bond length in aluminum octahedron similar to the Nd$_2$AlO$_3$N, indicating that the nitride ions are preferentially in the apical site of the aluminum octahedron in the oxynitride. The preferential occupation of nitride ion on a specific anion site forms two distinct Gd/Ca sites making the oxynitride to future application for a novel muti-color emitting phosphor host material for divalent Eu doping.
References


Chem. 3 (2011) 47-52.


Table 1
Band gap energies and lattice parameters for \( \text{Gd}_{1-x}\text{Ca}_x\text{AlO}_4\cdot x\text{N}_x \).

<table>
<thead>
<tr>
<th>( x )</th>
<th>composition</th>
<th>band gap / eV</th>
<th>lattice parameters(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>( \text{GdCaAlO}_4 )</td>
<td>4.46</td>
<td>( a ) / nm</td>
</tr>
<tr>
<td>0.15</td>
<td>( \text{Gd}<em>{1.15}\text{Ca}</em>{0.85}\text{AlO}<em>{3.85}\text{N}</em>{0.15} )</td>
<td>2.96</td>
<td>( a ) / nm, ( c ) / nm</td>
</tr>
<tr>
<td>0.20</td>
<td>( \text{Gd}<em>{1.2}\text{Ca}</em>{0.8}\text{AlO}<em>{3.8}\text{N}</em>{0.2} )</td>
<td>2.94</td>
<td>( a ) / nm, ( c ) / nm</td>
</tr>
<tr>
<td>0.25</td>
<td>( \text{Gd}<em>{1.25}\text{Ca}</em>{0.75}\text{AlO}<em>{3.75}\text{N}</em>{0.25} )</td>
<td>2.91</td>
<td>( a ) / nm, ( c ) / nm</td>
</tr>
</tbody>
</table>

\(^a\) Lattice parameters were calculated from the laboratory XRD data.
Table 2
Refined structural parameters of \( \text{Gd}_{1.2}\text{Ca}_{0.8}\text{AlO}_{3.8}\text{N}_{0.2} \) in \( \text{K}_2\text{NiF}_4 \)-type structure.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>( g )</th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
<th>( B_{iso} \times 10^{-2} \text{nm}^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>2a</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0.0118(9)</td>
<td>0.56(3)</td>
</tr>
<tr>
<td>Gd/Ca1</td>
<td>2a</td>
<td>0.614/0.386(8)</td>
<td>0</td>
<td>0</td>
<td>0.3657(4)</td>
<td>0.33(6)</td>
</tr>
<tr>
<td>Gd/Ca2</td>
<td>2a</td>
<td>0.606/0.394(5)</td>
<td>0</td>
<td>0</td>
<td>0.6509(4)</td>
<td>0.35(6)</td>
</tr>
<tr>
<td>O/N1</td>
<td>4b</td>
<td></td>
<td>0</td>
<td>1/2</td>
<td>0.0151(8)</td>
<td></td>
</tr>
<tr>
<td>O/N2</td>
<td>2a</td>
<td>0.95/0.05(^a)</td>
<td>0</td>
<td>0</td>
<td>0.8329(8)</td>
<td>0.38(6)(^b)</td>
</tr>
<tr>
<td>O/N3</td>
<td>2a</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0.1689(7)</td>
<td></td>
</tr>
</tbody>
</table>

\( R_{wp} = 5.4 \% \), \( R_p = 4.1 \% \). S.G.: \( \text{l}4\text{mm} \), \( a = 0.365850(1) \text{nm} \), \( c = 1.206752(8) \text{nm} \). \(^a\)Site occupations, \( g \), for anion sites were fixed as 0.95O/0.05N. \(^b\)Isotropic displacement parameters, \( B_{iso} \), for anion sites were analyzed using a constraint: \( B(\text{O/N1}) = B(\text{O/N2}) = B(\text{O/N3}) \).
Table 3

Selected bond lengths (nm) in Gd$_{1.2}$Ca$_{0.8}$AlO$_{3.8}$N$_{0.2}$.

<table>
<thead>
<tr>
<th></th>
<th>Bond Length (nm)</th>
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<tbody>
<tr>
<td><strong>Gd$<em>{1.2}$Ca$</em>{0.8}$AlO$<em>{3.8}$N$</em>{0.2}$</strong></td>
<td>S.G.: I4mm</td>
</tr>
<tr>
<td>Al (2a)</td>
<td>O/N1 (4b)</td>
</tr>
<tr>
<td></td>
<td>O/N2 (2a)</td>
</tr>
<tr>
<td></td>
<td>O/N3 (2a)</td>
</tr>
<tr>
<td>Gd/Ca1 (2a)</td>
<td>O/N1 (4b)</td>
</tr>
<tr>
<td></td>
<td>O/N2 (2a)</td>
</tr>
<tr>
<td></td>
<td>O/N3 (2a)</td>
</tr>
<tr>
<td>Gd/Ca2 (2a)</td>
<td>O/N1 (4b)</td>
</tr>
<tr>
<td></td>
<td>O/N2 (2a)</td>
</tr>
<tr>
<td></td>
<td>O/N3 (2a)</td>
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</table>
**Figure Captions**

Fig. 1 Crystal structures of $K_2NiF_4$-type oxynitrides: (a) $Nd_2AlO_3N$ ($I4/mm$) and (b) $Sr_2TaO_3N$ ($I4/mmm$).

Fig. 2 XRD patterns of products obtained from starting mixtures with AlN only as the aluminum source for $Gd_{1+x}Ca_{1-x}AlO_{4-x}N_x$ at $x = (a) 0$, (b) 0.05, (c) 0.1, (d) 0.15, (e) 0.20, (f) 0.25, and (g) 0.30. The product obtained for $x = 0$ ($GdCaAlO_4$, (a)) was prepared using $\gamma-Al_2O_3$ as the aluminum source. Diffraction lines marked with diamonds, triangles and circles indicate the $K_2NiF_4$-type $Gd_{1+x}Ca_{1-x}AlO_{4-x}N_x$, $Gd_2O_3$, and $CaAl_2O_4$ phases, respectively.

Fig. 3 Diffuse reflectance spectra of $Gd_{1+x}Ca_{1-x}AlO_{4-x}N_x$.

Fig. 4 Observed (+), calculated (solid line) and difference synchrotron XRD profiles for $K_2NiF_4$-type $Gd_{1.2}Ca_{0.8}AlO_{3.8}N_{0.2}$. Vertical bars indicate the positions of Bragg reflections.

Fig. 5 Atomic arrangement around Al and Gd/Ca sites in (a) $Gd_{1.2}Ca_{0.8}AlO_{3.8}N_{0.2}$
(I4/m) and (b) GdCaAlO$_4$ (I4/mmm). The schematic structure of GdCaAlO$_4$ was
drawn using the reported structural parameters [26].
Fig. 1 Crystal structures of K$_2$NiF$_4$-type oxynitrides: (a) Nd$_2$AlO$_3$N ($I4mm$) and (b) Sr$_2$TaO$_3$N ($I4/mmm$).
Fig. 2 XRD patterns of products obtained from starting mixtures with AlN only as the aluminum source for Gd$_{1+x}$Ca$_{1-x}$AlO$_{4-x}$N$_x$ at $x = (a) 0$, (b) 0.05, (c) 0.1, (d) 0.15, (e) 0.20, (f) 0.25, and (g) 0.30. The product obtained for $x = 0$ (GdCaAlO$_4$, (a)) was prepared using $\gamma$-Al$_2$O$_3$ as the aluminum source. Diffraction lines marked with diamonds, triangles and circles indicate the K$_2$NiF$_4$-type Gd$_{1+x}$Ca$_{1-x}$AlO$_{4-x}$N$_x$, Gd$_2$O$_3$, and CaAl$_2$O$_4$ phases, respectively.
Fig. 3 Diffuse reflectance spectra of Gd$_{1-x}$Ca$_{1-x}$AlO$_{4-x}$N$_x$. 
Fig. 4 Observed (+), calculated (solid line) and difference synchrotron XRD profiles for K$_2$NiF$_4$-type Gd$_{1.2}$Ca$_{0.8}$AlO$_{3.8}$N$_{0.2}$. Vertical bars indicate the positions of Bragg reflections.
Fig. 5 Atomic arrangement around Al and Gd/Ca sites in (a) Gd$_{1.2}$Ca$_{0.8}$AlO$_{3.8}$N$_{0.2}$ ($I4mm$) and (b) GdCaAlO$_4$ ($I4/mmm$). The schematic structure of GdCaAlO$_4$ was drawn using the reported structural parameters [26].