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Flux growth of perovskite-type $RAlO_3$ single crystals

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Abstract

Single crystals of $RAlO_3$ (R = La–Lu) were successfully obtained at atmospheric pressure by a flux method using KF. According to the R element, solute was prepared by three different processes. Single crystals of $RAlO_3$ (R = Ce, Pr and Tb) were grown in He atmosphere to prevent oxidation, and others were grown in air. Single crystals are transparent cubes. In the case of the growth experiment of $NdAlO_3$, the solute was prepared from alcoholates and it was very smoothly dissolved in the KF flux. As a result, crystals of $NdAlO_3$ were grown up to 300–600 μm in size compared with 30–60 μm for other phases. Single crystals of $LuAlO_3$ were successfully obtained for the first time by this flux method at ambient pressure in air. $RAlO_3$ for R = La, Pr and Nd shows trigonal symmetry with a rhombohedral lattice, and $CeAlO_3$ crystallizes in tetragonal symmetry. Others show orthorhombic symmetry. The lattice distortion from an ideal cubic perovskite structure is smaller in the aluminates of rare earth elements with lower atomic numbers in each structure group.

Keywords: Single crystals; Crystal growth; Crystal structure; Perovskite; $RAlO_3$ (R = La–Lu)

1. Introduction

Rare earth aluminates $RAlO_3$ have been studied from a single-crystal growth point of view [1–4]. In particular, it is hard to obtain single crystals of $RAlO_3$ (R = Ce, Pr and Tb) because of the difficulty in controlling the valency of R to 3+. These three elements generally tend to take a higher valency than 3+. Thus, there are few studies on the synthesis of these aluminates [4]. However, many studies on the synthesis of $RAlO_3$ (R = Dy–Tm) have been performed. The synthesis of $RAlO_3$ (R = Dy–Tm) at atmospheric pressure yielded mixed phases of perovskite-type and garnet-type structures [5,6]. Garton and Wanklyn reported the synthesis of single crystals of $RAlO_3$ (R = Dy–Yb) using an equimolar mixture of R_2O_3 and Al_2O_3, and PbO as flux, at a cooling rate of 50°C h^{-1} from 1260°C [7]. However, the products synthesized for $TmAlO_3$ and $YbAlO_3$ were not single phases but a mixture of perovskite-type and garnet-type phases, while perovskite-type $LuAlO_3$ could not be synthesized under these conditions. More recently, Dernier and Maines reported the synthesis of single phases of perovskite-type $RAlO_3$ (R = Dy–Lu) using equimolar mixtures of aluminium and rare earth oxides and NaOH as flux at 32.5 kbar and 1200°C for 4 h [5].

The purpose of the present work is to synthesize single crystals of rare earth orthoaluminates $RAlO_3$ and to characterize their crystal structures. We succeeded in obtaining single crystals of $RAlO_3$ (R = La–Lu except Pm) by a high-temperature solution growth method (flux method) with careful preparation of the solute for each R-element and by control of the growth conditions. Our attention for the synthesis is especially focussed on the following points:

(1) To synthesize $RAlO_3$ for Ce, Pr and Tb by making the valence of rare earth elements 3+.

(2) To synthesize perovskite-type $RAlO_3$ (R = Dy–Lu) at atmospheric pressure and at lower temperature than in former experiments.

2. Experiments

2.1. Sample preparations

Single crystals were synthesized by the solution

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growth method using KF (m.p. = 860°C, b.p. = 1505°C, $d_{20} = 2.481$ g cm^{-3}) as a solvent (flux reagent).

Solutes were prepared in three different ways depending on the rare earth elements. The process of sample preparation is shown in Table 1 together with several growth conditions.

2.1.1. *R = Ce, Pr and Tb*

These three elements generally tend to take a higher valency than 3+. Therefore, the synthesis of $RAlO_3$ for R = Ce, Pr and Tb was made by paying attention to keep the valency of the rare earth elements 3+. In the case of R = Ce, the conversion temperature from CeO_2 to Ce_2O_3 was first carefully examined, because most reagents of commercial Ce_2O_3 are actually composed of a mixture of CeO_2 and Ce_2O_3. In order to do this, the reagent CeO_2 was heated in He atmosphere by a high-frequency (h.f.) furnace at different temperatures using a graphite crucible, and the products were identified by X-ray powder diffraction method; as a result, the optimum conversion temperature (1600°C) was obtained. Then, polycrystalline $CeAlO_3$ was obtained from the mixture of CeO_2 (99.99%) and α-Al_2O_3 (99.99%) with molar ratio of 2:1 by a sintering method using a graphite crucible at the above optimum temperature. The products obtained were used as a solute for the flux growth experiment. The synthesis of $RAlO_3$ for R = Pr and Tb was performed with the oxide mixtures at the same temperature and atmospheric conditions as $CeAlO_3$.

2.1.2. *R = La, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb and Lu*

In these cases, rare earth oxides R_2O_3 (99.99%) and α-Al_2O_3 (99.99%) were mixed well, and the mixtures were directly used as a solute for the flux growth experiment.

2.1.3. *R = Nd*

In the flux growth method it is very important for the solute to dissolve easily in the flux [8–10]. Metal-alcoholates of Nd and Al were used for the synthesis of $NdAlO_3$ in order to obtain a solute. Nd-tri-i-propoxide and aluminium-tri-i-propoxide in a weighed molar ratio of 1:1 were dissolved in the ethanol and they were hydrolysed using distilled water. The gelled mass was heated up to 700°C in air, and the resultant low-calcined matter with highly dispersed atoms of Nd and Al was used as a solute for the flux growth experiment.

The solute mentioned above and solvent (KF) were mixed in a weight ratio range of 1:9–3:7. The mixture was placed in a platinum crucible 40 mm in diameter and 40 mm in depth. The crucible was set in an electric furnace and was heated up to 1010°C, which is 150°C higher than the melting point of KF, and the temperature was maintained for 8 days to obtain a denser solution by evaporation of the flux; the temperature was then decreased to room temperature. A purified He gas stream of 200 ml min^{-1} was applied while doing heat treatment for the growth of R = Ce, Pr and Tb.

Grown single crystals were separated from the solidified materials by dissolving KF in warm water. The growth procedure for $RAlO_3$ single crystals is shown in Table 2.

2.2. *Characterization*

The obtained products were first examined by X-ray powder diffraction and it was confirmed that they belonged to perovskite-type structure. The crystals were also observed by optical and scanning electron microscopes. Chemical compositions were examined by an electron probe energy dispersive (EDS) analysis.

Table 1
Conditions of crystal growth experiments for $RAlO_3$ (R = La–Lu except Pm)

R	Solute	Solvent (flux)	Temperature (°C)	Atmosphere
Ce, Pr and Tb	Polycrystalline $RAlO_3$ synthesized by sintering method, controlling R valency to 3+ using rare earth oxide and α-Al_2O_3 as raw materials	KF	1010	He
La, Sm, Eu, Gd, Dy, Ho, Er, Tm Yb and Lu	Mixture of rare earth oxide and α-Al_2O_3	KF	1010	Air
Nd	Polycrystalline $NdAlO_3$ derived from $Nd(OCH_3)_3$ and $Al(OCH_3)_3$	KF	1010	Air

Table 2
Growth procedure of $RAlO_3$ (R = La–Lu except Pm) single crystals by the flux method using KF as a flux

Solute ↘ ↙ Solvent
↓
Heat in Pt crucible, by electric furnace
↓
Keep at 1010°C for 8 days (flux evaporation)
↓
Furnace cool
↓
Solidified mass ($RAlO_3$ single crystals + KF)
↓
Dissolve KF in warm water
↓
Single crystals of $RAlO_3$

3. Results and discussion

As a result, single crystals of $RAlO_3$ (R = La–Lu except Pm) were successfully obtained at atmospheric pressure by the flux method. KF acted as a good solvent for the growth of these aluminates. By DTA-TGA measurement, it was confirmed that polycrystalline $CeAlO_3$ used as solute decomposed into CeO_2 and α-Al_2O_3 above 1000°C in air. Therefore inert atmosphere is obviously needed for the synthesis of its single crystals. Thus, $CeAlO_3$ can be synthesized only in inert atmosphere [11–14]. $PrAlO_3$ and $TbAlO_3$ were also successfully synthesized in He atmosphere. However, $RAlO_3$ except R = Ce, Pr and Tb can be synthesized in air. An SEM image of $CeAlO_3$ single crystals using the KF flux is shown in Fig. 1. The single crystals are pale yellow, transparent cubes with 30–60 μm edges.

In the case of R = Nd, the solute was specially derived from alcoholates, that is, by calcination of a sol which is a mixture of Nd- and Al-hydro-oxides obtained by co-precipitation. Calcination was performed at 700°C. The solute obtained contains highly dispersed Nd and Al. The solvation of this solute to the KF solvent proceeded very smoothly. Thus, the dissolved matter as an origin of numerous nucleation was effectively minimized. As a result, the crystals obtained are 300–600 μm in size, much larger than for other $RAlO_3$ products. Single crystals of $NdAlO_3$ are shown in Fig. 2. The crystals obtained are violet transparent cubes. The colour indicates that the valency of Nd is 3+.

It has been reported that $LuAlO_3$ is difficult to synthesize not only as single crystals but also as polycrystals. That is, the synthetic condition of the perovskite-type aluminate for $LuAlO_3$ is limited because of too small an ionic radius of Lu^{3+} compared with other R^{3+} elements. However, single crystals of $LuAlO_3$ were successfully grown in this work for the first time in air without high pressure conditions, as reported by Dernier and Maines [5]. The $LuAlO_3$ single crystals obtained are shown in Fig. 3. Most of the single crystals of $LuAlO_3$ are colourless, transparent and cubic, but some of them are pale red. These crystal sizes are 30–60 μm.

Fine twinned textures are observed by optical microscopy in most of the single crystals of $RAlO_3$. These twinned textures are considered to be formed at the cooling process by a phase transition from higher to room temperature structures with higher and lower symmetries, respectively. Geller and Bala [15] and Forrat et al. [16] also reported the existence of twined textures in some of rare earth aluminates by the single-crystal diffraction method. The systematic

Fig. 1. Single crystals of $CeAlO_3$ extracted from the KF flux.

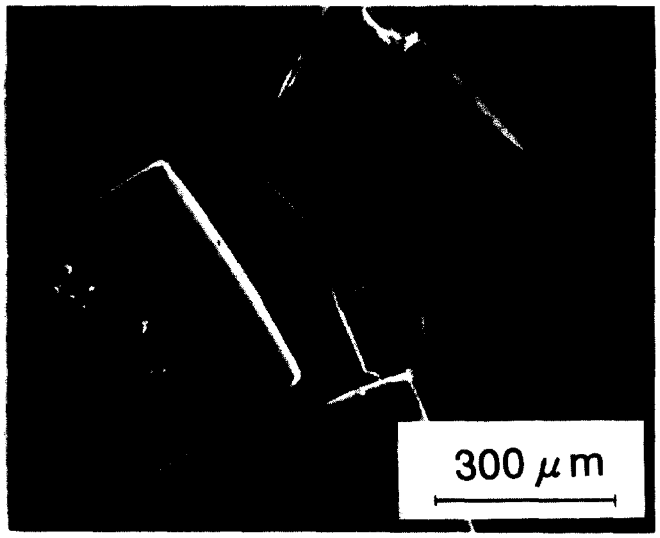

Fig. 2. Single crystals of $NdAlO_3$ extracted from the KF flux.

Table 3
Morphology, size and colour of $RAlO_3$ (R = La–Lu except Pm) single crystals extracted from the KF flux

$RAlO_3$	Morphology	Axial length (μm)	Colour
$LaAlO_3$	Cubic	30–60	Colourless
$CeAlO_3$	Cubic	30–60	Pale yellow
$PrAlO_3$	Cubic	30–60	Pale green
$NdAlO_3$	Cubic	300–600	Violet
$SmAlO_3$	Cubic	30–60	Pale yellow
$EuAlO_3$	Cubic	30–60	Pink
$GdAlO_3$	Cubic	30–60	Colourless
$TbAlO_3$	Cubic	30–60	Pale yellow
$DyAlO_3$	Cubic	30–60	Pale orange
$HoAlO_3$	Cubic	30–60	Colourless
$ErAlO_3$	Cubic	30–60	Pink
$TmAlO_3$	Cubic	30–60	Colourless
$YbAlO_3$	Cubic	30–60	Colourless
$LuAlO_3$	Cubic	30–60	Colourless or pale red

studies of their structures at room and elevated temperature will be an interesting problem in order to understand the mechanism of phase transitions.

The morphology, size and colour of the $RAlO_3$ (R = La–Lu except Pm) single crystals are listed in Table 3. No evidence of incorporation of K, F and Pt from the flux and the crucible in the $RAlO_3$ single crystals was observed by EDS analysis.

It was confirmed that each rare earth aluminate of La through Tm is a single phase and the structures of all specimens are based on a perovskite-type structure. In the case of $YbAlO_3$ and $LuAlO_3$, a garnet-type phase is also observed in addition to the perovskite-type phase. Well-developed facets of the $RAlO_3$ single crystals are {100}. As a result, three types diffraction pattern were observed throughout the perovskite-type phases from La to Lu aluminates.

$LaAlO_3$, $PrAlO_3$ and $NdAlO_3$ are confirmed to belong to the same lattice type and they are successfully indexed on the basis of the rhombohedral lattice. The diffraction peaks of $RAlO_3$ for Sm through Lu can be indexed on the basis of the orthorhombic lattice as reported by Dernier and Maines [5]. The lattice volumes of the orthorhombic and rhombohedral lattices are four and two times that of the ideal primitive cubic lattice, respectively. $CeAlO_3$ has somewhat different characteristics on the diffraction pattern from other $RAlO_3$ phases. It can be indexed on the basis of neither orthorhombic nor rhombohedral lattices, but can be indexed on the basis of the tetragonal lattice [13,17]. The deformation from the ideal cubic lattice of the perovskite-type structure is very small. However, the actual structure of $CeAlO_3$ seems to be more complicated because very weak extra diffraction spots were observed by single-crystal X-ray diffraction using synchrotron radiation (SR, BL-10A/Photon Fac-

Table 4
The lattice constants and cell volumes of $RAlO_3$ (R = La–Lu except Pm) single crystals extracted from the KF flux

Compounds	a-axis (Å)	b-axis (Å)	c-axis (Å)	α (°)	Cell volume (Å)	Volume[a] (Å^3)
$LaAlO_3$	5.353(2)			60.12(2)	108.8(1)	54.4
$CeAlO_3$	3.763(1)	3.763(1)	3.792(1)		53.687(5)	53.69
$PrAlO_3$	5.308(1)			60.29(1)	106.41(1)	53.2
$NdAlO_3$	5.289(1)			60.39(1)	105.5(1)	52.75
$SmAlO_3$	5.286(1)	7.475(1)	5.286(1)		208.87(1)	52.21
$EuAlO_3$	5.269(1)	7.456(1)	5.291(1)		207.89(6)	51.97
$GdAlO_3$	5.253(1)	7.441(1)	5.299(1)		207.11(5)	51.78
$TbAlO_3$	5.226(1)	7.417(2)	5.304(1)		205.60(8)	51.40
$DyAlO_3$	5.206(1)	7.392(1)	5.318(1)		204.67(4)	51.17
$HoAlO_3$	5.183(2)	7.370(3)	5.318(2)		203.2(1)	50.80
$ErAlO_3$	5.163(1)	7.354(1)	5.328(1)		202.31(5)	50.58
$TmAlO_3$	5.145(2)	7.325(3)	5.323(3)		200.61(1)	50.15
$YbAlO_3$	5.123(1)	7.303(2)	5.327(2)		199.33(9)	49.83
$LuAlO_3$	5.107(5)	7.298(7)	5.330(5)		198.65(5)	49.66

[a] Cell volume corresponding to the ideal cubic lattice.

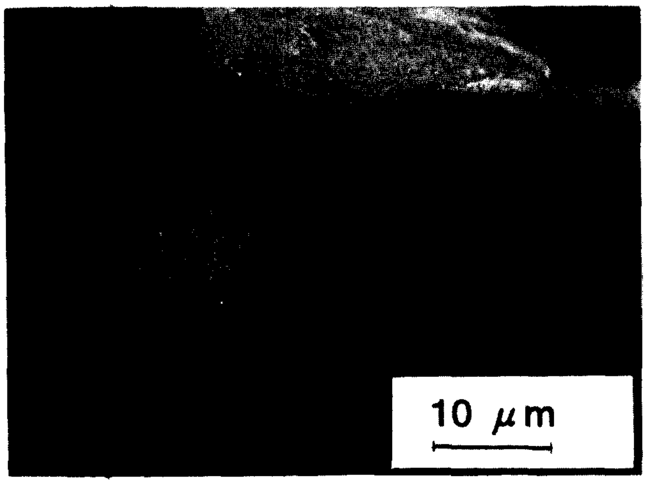

Fig. 3. Single crystals of $LuAlO_3$ extracted from the KF flux.

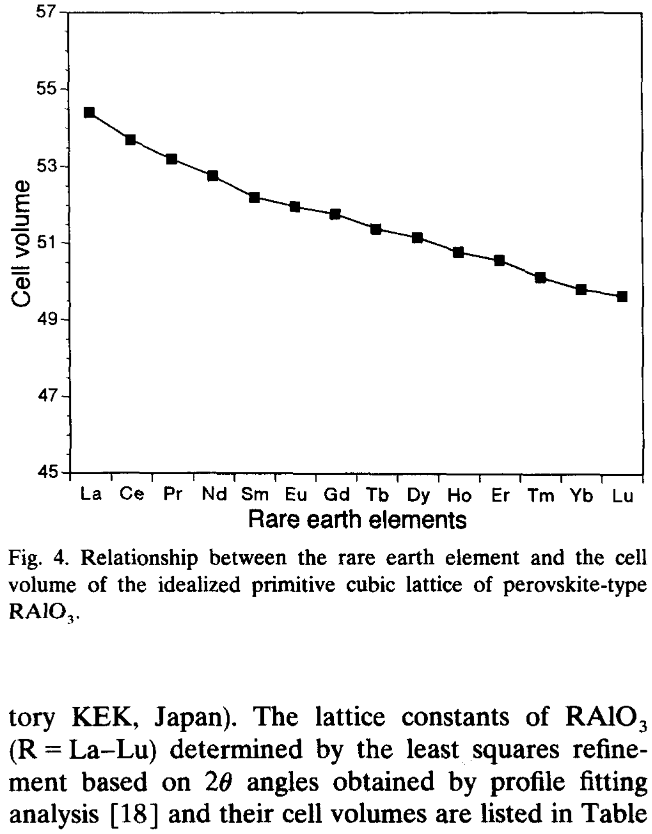

Fig. 4. Relationship between the rare earth element and the cell volume of the idealized primitive cubic lattice of perovskite-type $RAlO_3$.

tory KEK, Japan). The lattice constants of $RAlO_3$ ($R = La–Lu$) determined by the least squares refinement based on 2θ angles obtained by profile fitting analysis [18] and their cell volumes are listed in Table 4. As the atomic number of rare earth elements gets larger, that is, the ionic radius is smaller, the cell volume of $RAlO_3$ becomes smaller. The cell volume corresponding to the ideal primitive cubic lattice of the perovskite-type structure is plotted against the atomic numbers of R elements in Fig. 4. One can see that they decrease linearly from La to Lu. It is of interest to note that the distortion of the rhombohedral unit cell becomes larger from $LaAlO_3$ to $NdAlO_3$, that is, the angle α becomes larger. The degree of distortion from an ideal cubic lattice to the orthorhombic lattice is also larger for $RAlO_3$ with larger atomic number of R from $SmAlO_3$ to $LuAlO_3$.

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