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BRIEF COMMUNICATION

The Crystal Structure of Neodymium Hexaaluminate

N. IYI, Z. INOUE, AND S. KIMURA

National Institute for Researches in Inorganic Materials, Namiki 1-1, Sakura-mura, Niihari-gun, Ibaraki, 305, Japan

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While the existence of the "β-alumina-type compound" containing a trivalent rare-earth element has been recognized for elements with large ionic radii such as La, Ce^{3+}, and Pr, such a phase is unknown for the elements with small ionic radii as Gd, Tb, and Yb. (*1, 2*) However, for elements of intermediate ionic size, e.g., Nd, Sm, and Eu^{3+}, the existence of such a phase is uncertain (*2*).

We have conducted preliminary studies on the solidification of melts with the composition $Ln_2O_3 \cdot 11Al_2O_3$ (Ln = La, Nd, Sm, and Eu) in the FZ (floating zone) apparatus. In the solidified specimens, a "β-alumina-type" phase was detected for Ln = La, Nd, but not for Ln = Sm, Eu when using the X-ray powder diffraction method. We, presume, then, that Nd-hexAl_2O_3 (neodymium hexaaluminate) is the hexaaluminate containing the smallest rare-earth ion.

Recently, we reported La-hexAl_2O_3 ($La_{0.827}Al_{11.9}O_{19.09}$) (*3*) to have a magnetoplumbite structure with Frenkel defects of Al ions. The present study compares Nd-hexAl_2O_3 with the hexaaluminate containing the larger rare-earth ion La^{+3} by using single-crystal X-ray structure data.

Experimental and Results

Before conducting the single-crystal growth, we first explored the melting nature of Nd-hexAl_2O_3. A molten zone with composition of $Nd_2O_3 \cdot 11Al_2O_3$ was formed between sintered rods in the FZ apparatus with a xenon arc lamp as the heat source (Nichiden Kikai Co.), and a boule was pulled gradually according to the SCFZ method (*4*). A longitudinal section of the solidified specimen was examined by electron probe microanalysis (EPMA) and revealed successive segregation of Al_2O_3, Nd-hexAl_2O_3, and eutectic lamellae composed of Nd-hexAl_2O_3 and $NdAlO_3$, which indicates the incongruent melting nature of Nd-hexAl_2O_3.

The single-crystal growth of Nd-hex Al_2O_3 by the FZ method was not very successful. The boule still contained small amount of Al_2O_3 and $NdAlO_3$ besides the single-crystal grains of Nd-hexAl_2O_3. The molar ratio of Al/Nd in the clear crystalline part (pale purple) was determined by EPMA to be 13.3 (±0.3). Several specimens from these boules were examined by Laue and precession methods. The structure belongs to the hexagonal space group

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TABLE I

POSITIONAL AND THERMAL PARAMETERS[a]

	Position	Number per unit cell	x	z	$\beta_{11} \times 10^4$	$\beta_{22} \times 10^4$	$\beta_{33} \times 10^5$	$\beta_{23} \times 10^5$	B
Nd(1)	2(*d*)	1.02(5)	$\frac{2}{3}$	$\frac{1}{4}$	86(16)	β11	28(2)	0	
Nd(2)	6(*h*)	0.63(5)	0.728(2)	$\frac{1}{4}$	47(20)	128(54)	15(4)	0	
Al(1)	12(*k*)	11.1(1)	0.8311(3)	0.10808(6)	30(6)	14(8)	18(2)	6(17)	
Al(2)	4(*f*)	4	$\frac{1}{3}$	0.0268(1)	33(7)	β11	14(3)	0	
Al(3)	4(*f*)	4	$\frac{1}{3}$	0.1902(1)	33(8)	β11	11(3)	0	
Al(4)	2(*a*)	2	0	0	37(11)	β11	13(5)	0	
Al(5)	4(*e*)	1.62(6)	0	0.2396(4)	56(24)	β11	45(15)	0	
Al(6)	12(*k*)	0.70(7)	0.847(5)	0.185(1)					0.51
O(1)	12(*k*)	12	0.1559(6)	0.0523(2)	59(12)	60(18)	31(4)	−25(31)	
O(2)	12(*k*)	12	0.5046(6)	0.1507(2)	36(11)	29(16)	24(4)	−3(30)	
O(3)	4(*f*)	4	$\frac{2}{3}$	0.0548(3)	31(15)	β11	21(7)	0	
O(4)	4(*e*)	4	0	0.1488(3)	22(16)	β11	30(9)	0	
O(5)	6(*h*)	6	0.1809(9)	$\frac{1}{4}$	158(23)	48(31)	31(6)	0	

[a] The thermal parameters are of the form: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2kh\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. $\beta_{12} = \frac{1}{2}\beta_{22}$; $\beta_{13} = \frac{1}{2}\beta_{23}$

$P6_3/mmc$. The electron diffraction patterns showed no sign of superstructure. Using a 0.11 × 0.07 × 0.07-mm crystal, intensity data were collected on an automatic four-circle diffractometer (Rigaku Denki Co.) using graphite monochromatized Mo$K\alpha$ radiation. The final set of 422 non-zero independent reflections below $2\theta = 115°$ were corrected for Lorenz polarization and absorption effects. The atomic scattering factors were taken from the International Table for X-Ray Crystallography (Vol. 4). For the least-square refinement, the modified RSFLS-4 (UNICS) (*5*), and for Fourier synthesis RSSFR-5 (UNICS) (*6*) was applied. The lattice parameters were a = 5.553(2) Å, c = 21.990(7) Å. The structural refinement was almost the same as that of La-hexAl_2O_3 (*3*). The refinement without an extinction correction met with failure. When an isotropic type I secondary extinction correction (*7*) was applied, the anisotropic refinement was successful, yielding $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.046$ and $wR = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2} = 0.058$, where $w = 1.0$. As anisotropy of corrections was observed, the anisotropic refinement incorporating a constrained anisotropic correction (*8*) was accomplished to give a final R-value of 0.044 ($wR = 0.047$). The difference Fourier synthesis at this stage is practically featureless with a minimum of $-1.4\ e\ Å^{-3}$ at (0, 0, 0.03). The other peaks or depressions are below $1.0\ e\ Å^{-3}$ in amplitude. Final parameters are given in Table I.

Discussion

The final parameters correspond to a magnetoplumbite structure as in the case of La-hexAl_2O_3. Furthermore, the interstitial Al ion as described in La-hexAl_2O_3 was also detected in difference Fourier sections at (x, $2x$, z) with $x = 0.83$, $z = 0.18$, and 0.19, and was assigned as Al(6) in the refinement. In our previous paper (*3*), the structure of La-hexAl_2O_3 was assumed to be mainly made up of two types of half unit cell with dimension $\frac{1}{2}c$; one has a La ion and contains no defects, the other has an interstitial Al(6) migrated from Al(1), a vacancy at the Beevers-Ross site ($\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{4}$) instead of a La

TABLE II

COMPARISON OF THE OCCUPANCY

Atom	Position	Number per unit cell	
		La-hexAl_2O_3	Nd-hexAl_2O_3
M(1)	2(*d*)	0.98(21)	1.02(5)
M(2)	6(*h*)	0.69(21)	0.63(5)
Al(1)	12(*k*)	11.0(2)	11.1(1)
Al(5)	4(*e*)	1.70(7)	1.62(6)
Al(6)	12(*k*)	0.58(8)	0.70(7)

ion, and a defect of Al(5) at the 4*e* site. The former has the composition of "$LaAl_{12}O_{19}$," and the latter "$Al_{11}O_{19}$." These nonneutral half cells were supposed to cause the nonstoichiometry of La-hex Al_2O_3. As shown in Table II, the occupancy of Nd-hexAl_2O_3 is quite similar to that of La-hexAl_2O_3, which leads to the conclusion that the nonstoichiometry in Nd-hex Al_2O_3 is the same as La-hexAl_2O_3.

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