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The Crystal Structure of Lanthanum Hexaaluminate

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The least-square refinement of lanthanum hexaaluminate ($La_{0.827}Al_{11.9}O_{19.09}$) was accomplished using single crystal X-ray diffraction data. The result of the final anisotropic refinement, corresponding to an R-value of 0.039, revealed the structure of a magnetoplumbite type. In the structure interstitial Al ions were found, which were probably formed by a Frenkel defect mechanism. These interstitial Al ions are proposed to be situated in pairs making a bridge between spinel blocks, and to cause Al and La defects in the intermediate layer ($z \simeq 0.25$). The nonstoichiometry of lanthanum hexaaluminate is attributed to these defects.

Introduction

The hexaaluminates containing mono-, di-, or trivalent cations have either the β-alumina or the magnetoplumbite structure. Among them are nonstoichiometric compounds, so the cause of nonstoichiometry has been one of the interesting problems besides the problem of the structure type.

Extensive investigations of the structures of the hexaaluminates with monovalent cations such as Na, K, Ag, etc. have been accomplished by several researchers (*1–3*) and the interstitialcy mechanism for charge compensation or nonstoichiometry has been proposed (*4, 5*). The structures of the hexaaluminates containing divalent cations, such as Ca, Sr, and Ba, have been refined using X-ray single crystal diffraction data (*6–8*). However, the structural knowledge of hexaaluminates with large trivalent cations (La, Ce, Nd, etc.) is very limited. In the phase investigation of the system La_2O_3–Al_2O_3, the "β-alumina-type compound" ($La_2O_3 \cdot 11Al_2O_3$) was first recognized by Roth and Hasko (*9*). Stevels and Verstegen (*10*) considered lanthanum hexaaluminate to have the magnetoplumbite structure and, later, mainly based on luminescence data Stevels (*11*) constructed the structure model in which excess oxygen enters into the BR (Beevers–Ross) site instead of a large cation to form 6-coordinated interstitial Al. On the other hand, using powder diffraction and fluorescence data, Dexpert-Ghys *et al.* (*12*) proposed that this compound was composed of β-alumina-type and magnetoplumbite-type unit cells, the ratio of which depended on the composition. A refinement using single crystal X-ray diffraction data was accomplished, for the first time, by Kahn *et al.* (*13*) on the structure of $LaMgAl_{11}O_{19}$. The result showed this Mg-substituted hexaaluminate to be of the magnetoplumbite structure. As Mg^{2+} ions are substituted for Al^{3+} ions to attain neutrality in the case of $LaMgAl_{11}O_{19}$, the problem of nonstoi-

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chiometry or charge compensation for the nondoped hexaaluminates that contain trivalent cations still remains unsolved.

The present paper reports the crystal structure determination of nonsubstituted lanthanum hexaaluminate using X-ray single crystal diffraction data and presents a possible structure model explaining the nonstoichiometry of this compound.

Experimental

The single crystal was grown by the FZ (floating zone) method using a xenon arc lamp as the heat source. The growth rate was 1.5 mm/hr and nitrogen was used as the atmosphere during growth. The molar ratio Al/La of the grown crystal was revealed to be always near 13.6 by the electron probe microanalyzer (EPMA) even if the starting material was of composition Al_2O_3/La_2O_3 = 11.0, so the composition with the molar ratio of 13.6 was used as starting material. The grown boule was 3–4 mm in diameter and 15 mm in length. It was, for the most part, clear and transparent, but still contained small amounts of inclusions besides large and tiny cracks. From clear part of the boule several specimens were taken, which were examined by Laue and precession methods. The space group was determined to be $P6_3/mmc$ and superstructure reflections were not detected. A crystal measuring approximately 0.09 × 0.06 × 0.04 mm was used for data collection on an automatic four circle diffractometer (Rigaku Denki Co.) with graphite-monochromatized Mo$K\alpha$ radiation. Reflections hkl, $h \geq k \geq 0$, and $l \geq 0$, were measured to a maximum 2θ of 115°. A set of three standard reflections (107), (220) and (00 · 10) was measured every 100 reflections. The linear absorption coefficient for the specimen was $\mu = 43.6$ cm^{-1}. Absorption correction was after Busing and Levy (*14*). After Lorenz polarization and absorption corrections, the intensities of 290 non-zero unique reflections were obtained. The scattering factors for the neutral atoms were taken from the *International Tables for X-Ray Crystallography* (Vol. 4). The least-square refinement was carried out using the modified RSFLS-4 program (UNICS) which was originally written by Sakurai *et al.* (*15*) and Fourier synthesis was accomplished with RSSFR-5 program (UNICS) written by Sakurai (*16*). The lattice parameters were refined using 20 2θ-data collected on the four-circle diffractometer. The type I isotropic correction was applied for the secondary-extinction correction after Becker and Coppens (*17*). The nomenclature of the sites in the mirror plane is after that of Peters *et al.* (*1*). The crystallographic data are shown in Table I, in which the density of the specimen was determined by the method of Archimedes. The molar ratio Al/La was determined by means of EPMA using Al_2O_3 and LaB_6 as the standard material.

A list of the observed and calculated structure factors is available from the authors.

Chemical Formula

The result of EPMA showed that the molar ratio Al/La of the grown crystal was about 13.6. However, even with the composition of Al_2O_3/La_2O_3 = 13.6 as the starting materials, the grown boules still contained a small amount of $LaAlO_3$ inclusions. The inclusion-free part was se-

TABLE I

CRYSTALLOGRAPHIC DATA

Formula	$La_{0.827}Al_{11.9}O_{19.09}$
Symmetry	Hexagonal
Space group	$P6_3/mmc$
$a = 5.561(2)$ Å	
$c = 22.07(1)$ Å	
$V = 591.0(4)$ Å^3	
$Z = 2$	
$D_{obs} = 4.17$ g cm^{-3}	

lected and examined by the wet chemical analysis (chelatometry titration method). As a result, Al/La molar ratio of 14.4 was obtained. The result of EPMA may be less reliable probably due to inappropriate condition of measurement and/or of standard materials. From data of density, wet chemical analysis, and cell volume, the chemical formula of lanthanum hexaaluminate was deduced to be $La_{0.827}Al_{11.9}O_{19.09}$ as shown in Table I.

Refinement

At first, Fourier and difference Fourier syntheses, which corresponded to an R-value, $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, of 0.286, were carried out using the positional parameters of $LaMgAl_{11}O_{19}$ (*13*). It was revealed that the structure of lanthanum hexaaluminate was essentially of a magnetoplumbite type and that the occupation factors of La at the 2*d* site ($\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{4}$) and Al at the 2*b* site (0, 0, $\frac{1}{4}$) were less than unity for each site as can be supposed from the chemical formula. The refinement using general isotropic temperature factor, the occupancy of La (at 2*d*) and Al (at 2*b*), and the positional parameters as variable parameters yielded an R-value of 0.169. The difference electron map at this stage indicated a slight displacement of the La ion from the three-fold axis (2*d* site) to the 6*h* site. When the La ion was split in the 6*h* site in the refinement, the R-value dropped to 0.118. However, electron density difference was still observed around the large cation site in the difference Fourier section at $z = \frac{1}{4}$. This is probably because La ions are distributed among various sites around the BR site. So, in the next step, La was placed at the 2*d* site in addition to the 6*h* site and the refinement was tried again. The resulting R-value was 0.093. When introducing individual isotropic temperature factors, the refinement converged at $R = 0.079$ and $wR = (\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2)^{1/2} = 0.096$, with unit weight. The result showed the isotropic temperature factor of Al(5) at the 2*b* site increased anomalously to 2.2 as compared to 0.08–0.36 for the other Al ions. The difference Fourier sections corresponding to $R = 0.093$ indicated an elongated electron density from the 2*b* site in the *c*-direction. From these features we assumed Al(5) was moved off the mirror plane into 4*e* sites (0, 0, $\frac{1}{4} + \alpha$) and split with 50% occupancy for each site. After the refinement with Al(5) at the 4*e* site gave an R-value of 0.071 and a reasonable isotropic temperature factor of 0.57 for Al(5). Further refinement introducing individual isotropic temperature factors and secondary extinction corrections gave $R = 0.049$ and $wR = 0.053$, with unit weight. The difference Fourier maps at this stage still indicated a small amount of additional electron density (about 2 e Å^{-3}) at (x, $2x$, 0.19) and (x, $2x$, 0.18) sections with $x = 0.83$, which we attributed to interstitial Al, as was found in other hexaaluminates having a β-alumina structure (*4*, *5*, *8*). The refinement incorporating interstitial Al as Al(6) yielded an R-value of 0.043 ($wR = 0.045$) when individual isotropic temperature factors were used. Here the common temperature factor of 0.47 was used for Al(6) and this temperature factor was fixed during the refinement. In addition, the occupancy of Al(1) was varied. At this stage all occupation factors were varied with the other parameters being fixed. However, the occupation factors of all sites including oxygen sites showed no sign of reduction. Anisotropic refinements, except the temperature factor of Al(6), converged quickly to give a final R-value of 0.039 ($wR = 0.042$). The final difference synthesis showed random peaks and depressions not exceeding the largest amplitude of ±1.0 e Å^{-3}. The g-value for the secondary extinction correction was $5.1(6) \times 10^3$. The final values of the positional parameters are shown in Table II. The interatomic distances and bond angles

TABLE II

The 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
La(1)	2(d)	0.98(21)	$\frac{2}{3}$	$\frac{1}{4}$	64(51)	$\beta 11$	23(5)	0	
La(2)	6(h)	0.69(21)	0.718(7)	$\frac{1}{4}$	100(48)	115(139)	37(10)	0	
Al(1)	12(k)	11.0(2)	0.8310(4)	0.10772(8)	47(8)	50(11)	18(3)	−11(26)	
Al(2)	4(f)	4	$\frac{1}{3}$	0.0271(2)	59(11)	$\beta 11$	17(5)	0	
Al(3)	4(f)	4	$\frac{1}{3}$	0.1899(2)	52(11)	$\beta 11$	16(5)	0	
Al(4)	2(a)	2	0	0	34(14)	$\beta 11$	14(7)	0	
Al(5)	4(e)	1.70(7)	0	0.2389(4)	58(29)	$\beta 11$	51(21)	0	
Al(6)	12(k)	0.58(8)	0.839(7)	0.186(2)					0.47
O(1)	12(k)	12	0.1561(7)	0.0518(2)	86(17)	49(25)	26(5)	39(45)	
O(2)	12(k)	12	0.5023(7)	0.1501(2)	51(15)	69(22)	20(5)	53(44)	
O(3)	4(f)	4	$\frac{2}{3}$	0.0553(4)	57(26)	$\beta 11$	47(14)	0	
O(4)	4(e)	4	0	0.1481(4)	29(23)	$\beta 11$	36(14)	0	
O(5)	6(h)	6	0.178(1)	$\frac{1}{4}$	116(26)	126(46)	22(8)	0	

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

TABLE III

Interatomic Distances

	Number of bonds	Distance (Å)
Octahedral coordination		
Al(1)–O(1)	2	1.996(6)
–O(2)	2	1.839(6)
–O(3)	1	1.960(6)
–O(4)	1	1.856(6)
Al(3)–O(2)	3	1.850(7)
–O(5)	3	2.000(8)
Al(4)–O(1)	6	1.889(6)
Tetrahedral coordination		
Al(2)–O(1)	3	1.792(7)
–O(3)	1	1.819(10)
Polyhedron 5-coordinated		
Al(5)–O(4)	1	2.004(13)
–O(4)′	1	2.494(13)
–O(5)	3	1.732(10)
Al(6)–O(2)	2	1.81(4)
–O(4)	1	1.76(2)
–O(5)	2	2.16(4)
Polyhedron 12-coordinated		
La(1)–O(2)	6	2.714(5)
–O(5)	6	2.783(8)

are presented in Tables III and IV, respectively.

Discussion

The refined parameters of lanthanum hexaaluminate correspond to a magnetoplumbite structure. Dexpert-Ghys *et al.* (*12*) considered the structure to be made up of a mixture of β-alumina-like and magnetoplumbite-like unit cells, the ratio of which depends on the composition. In the present study, difference Fourier maps at various stages did not give any indications of the additional electron density at the 2*c* site ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{4}$) which could be expected if there were β-alumina-like cells. The final synthesis showed a difference electron density of about -0.5 e Å^{-3} at the 2*c* site. Thus, there is no possibility for β-alumina-like cells to exist in the present specimen.

An interesting feature in the refined structure is the coordination of the Al(5) ions. For other hexaaluminates with

TABLE IV

Bond Angles

	Bond angles (°)
Octahedral coordination	
O(1)-Al(1) -O(1)′	81.43(37)
O(1)-Al(1) -O(2)	90.97(29)
O(1)-Al(1) -O(3)	89.41(25)
O(1)-Al(1) -O(4)	84.95(28)
O(2)-Al(1) -O(3)	87.30(31)
O(2)-Al(1) -O(4)	97.64(25)
O(2)-Al(3) -O(2)′	99.30(25)
O(2)-Al(3) -O(5)	89.19(30)
O(5)-Al(3) -O(5)′	80.79(31)
O(1)-Al(4) -O(1)′	87.16(24)
O(1)-Al(4) -O(1)″	92.84(24)
Tetrahedral coordination	
O(1)-Al(2) -O(1)′	111.17(19)
O(1)-Al(2) -O(3)	107.71(20)
Polyhedron 5-coordinated	
O(5)-Al(5) -O(4)	98.13(29)
O(5)-Al(5)′-O(4)	81.87(29)
O(5)-Al(5) -O(5)′	118.03(14)
O(2)-Al(6) -O(4)	102.4(20)
O(2)-Al(6) -O(5)	85.4(16)
O(4)-Al(6) -O(5)	91.6(10)

magnetoplumbite structure, this Al ion is known to be situated at the 2*b*(0, 0, $\frac{1}{4}$) site and 5-coordinated. In the course of the refinement, the isotropic temperature factor of Al(5) at the 2*b* site became anomalously large, as mentioned in the preceeding section. The difference Fourier map at that stage also indicated an elongated electron density in the *c*-direction. When Al(5) is split into 4*e* sites (0, 0, 0.24) with 50% occupation for each, the *R*-value dropped significantly in the subsequent refinements, finally giving a value of $z = 0.240$ with a reasonable isotropic temperature factor of 0.57. Accordingly, we assumed that Al(5) was split and placed Al(5) into 4*e* sites in the subsequent refinements. Al(5) can thus be considered as "distorted 4-coordinated." In addition to the above described treatment, a refinement was tried on the assumption that the Al ions were distributed among the 4*e* and 2*b* sites. The occupation ratio Al(4*e*)/Al(2*b*) of 4.0 was obtained as the result. This model was not, however, adopted in the further refinement because no improvement of the *R*-value could be seen. In other hexaaluminates of magnetoplumbite type, strong anisotropy of Al(5) was observed (6).

One of the interesting problems on lanthanum hexaaluminate is the cause of nonstoichiometry or its charge compensation mechanism. As La and Al ions have the same +3 charge, the occupation factor of La and Al ions cannot be fixed, *a priori*. Thus, a structure model must be sought to explain the nonstoichiometric nature of the composition. In the structure of barium β-alumina (*8*), part of Al(1) was supposed to be migrated in a pair to form interstitial Al ions which were bridged by an interstitial oxygen in a mirror plane. Similar interstitial Al ions could be detected in lanthanum hexaaluminate. The difference Fourier map corresponding to an *R*-value of 0.049 showed a small amount of excess electron density as described in the preceding section. To assure that an interstitial Al ion is formed by the same Frenkel defect mechanism as was found in barium β-alumina, the occupation factors of all Al ions including interstitial Al were varied with the scale factor being fixed. As a result only the occupation factor of Al(1) decreased beyond the e.s.d. When incorporating interstitial Al as Al(6) with occupancy of Al(1) varied, a significant reduction of the *R*-value could be observed and, when taking errors into account, the defect of Al(1) could be said to be near to the number of Al(6) in a unit cell. Accordingly it was postulated that interstitial Al ions were migrated from Al(1) according to Frenkel defect mechanism. To examine whether there are other defects, we varied all occupation factors with fixing the other parameters, but no reduction of occupancy was observed. So, we supposed that interstitial Al ions are the clue to un-

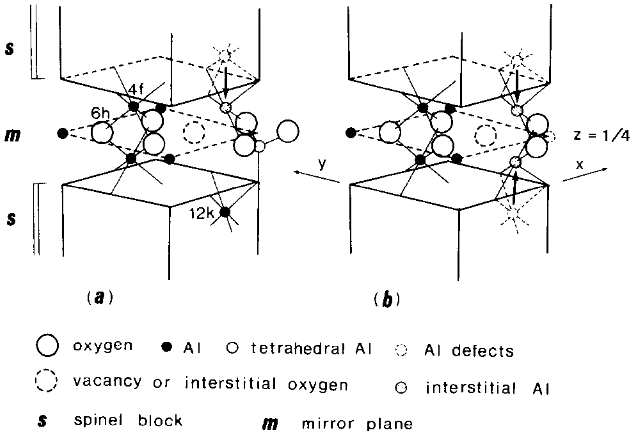

FIG. 1. Two possible types of interrelation between interstitial Al ions in lanthanum hexaaluminate. (a) Type 1: interstitial Al ions are formed singly and bonded to Al tetrahedra. (b) Type 2: interstitial Al ions due to Frenkel defects occur in a pair to bridge the spinel blocks. The bold arrows indicate the shift of Al ions and the large cation site is vacant or filled with an interstitial oxygen.

derstand the nonstoichiometry of lanthanum hexaaluminate.

For the coordination of interstitial Al, there seem to be two possibilities. First, defect of La takes place to avoid cation–cation interaction between La and interstitial Al(6) (about 2.1 Å) and the large cation site (BR site) becomes vacant. In this case interstitial Al square piramid is formed (Fig. 1). Defect structure of this type is referred to as "vacancy model" in the present paper. Second, interstitial oxygen is situated at the BR site instead of a La ion and interstitial Al octahedron is formed. This model resembles that of Stevels (*11*). We refer to this model as the "*i*O model." As the existence of interstitial O cannot be determined directly by X-ray diffraction method owing to the very large difference in the scattering power between La and oxygen, both models are to be considered in the following discussion.

Besides the coordination of interstitial Al, we assumed two types of interstitial Al—interstitial Al relation depending on whether interstitial Al ions are migrated in a pair or not as shown in Fig. 1. According to type 1 (Fig. 1a), interstitial Al ions are formed singly and an interstitial Al polyhedron (Al octahedron in "*i*O model," and Al square piramid in "vacancy model") shares an edge with an Al(5) tetrahedron. In this case, for charge compensation, the defects of Al(5) are only randomly distributed among the Al(5) ions which do not share edges with interstitial Al polyhedra. On the other hand, interstitial Al ions in a pair form the bridge between two spinel blocks in type 2 (Fig. 1b). In this case Al(5) site in the vicinity of interstitial Al ions would be vacant because an Al(5) tetrahedron would avoid sharing a face with an Al(6) polyhedron. Consequently simultaneous defects of La and Al(5) would occur by a pairwise migration of interstitial Al. The result of refinement shows that the number of La per unit cell is almost equal to that of Al(5), and that the number of Al(6) per unit cell is twice that of the La defects. These can be better explained by the interstitial Al formation of type 2, so we have chosen the type 2 structure, in which interstitial Al exist in a pair, for the subsequent considerations, though more evidences would be needed to confirm this defect model.

As discussed above, interstitial Al(6) ions

TABLE V

COMPARISON OF THE SITE OCCUPANCY AND FORMULA

	The number of atoms per unit cell				Al/La (mole)	Chemical formula
	La	Al(1)	Al(5)	Al(6)		
Result of refinement	1.67	11.0(2)	1.70(7)	0.58(8)	13.9(4)	$La_{0.835}Al_{11.64}O_{19.0}$[a]
"Vacancy model"	1.667	11.333	1.667	0.667	14.2	$La_{0.833}Al_{11.833}O_{19.0}$
"*i*O model"	1.750	11.500	1.750	0.500	13.6	$La_{0.875}Al_{11.875}O_{19.125}$
Chemical analysis					14.4	$La_{0.827}Al_{11.9}O_{19.09}$

[a] Charge balance is not attained.

cannot coexist with La and Al(5) in the same mirror plane of a single unit cell. On the basis of these considerations, we assumed two types of half unit cell having a spinel block and a mirror plane as the main constituent of lanthanum hexaaluminate, as shown in Figs. 2a and b: One contains a La ion and has the composition of "$LaAl_{12}O_{19}$" with charge +1; (a) the other contains, for "vacancy model," La and Al(5) defects due to interstitial Al(6), with composition of "$Al_{11}O_{19}$" having charge −5, and (b) for "*i*O model," the other contains an interstitial oxygen in addition, with composition of "$OAl_{11}O_{19}$" having charge −7. In "vacancy model," the ratio of the half unit cells should be 5 to 1 in order to attain the charge balance and the resulting chemical formula would be $La_{0.833}Al_{11.833}O_{19.0}$, where the molar ratio of Al/La is 14.2. On the other hand, in "*i*O model," the ratio should be 7 to 1 and $La_{0.875}Al_{11.875}O_{19.125}$, where Al/La = 13.57, can be obtained as the formula. The chemical formulas and the number of atoms in a unit cell at La, Al(1), Al(5), and Al(6) sites for two models are presented in Table V together with the result of the final refinement for comparison. In conclusion, because the results of refinement and chemical analysis are more consistent with the "vacancy model" than the "*i*O model," we adopt the structure model based on the "vacancy model" for explaining the nonstoichiometry of lanthanum hexaaluminate.

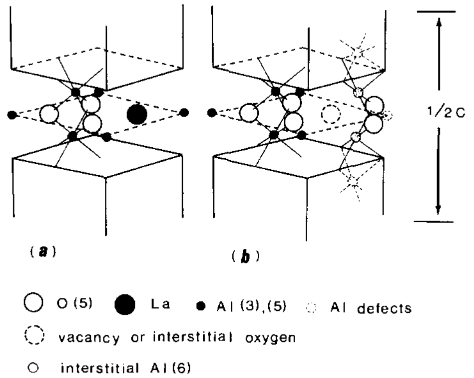

FIG. 2. Two kinds of half unit cell supposed to constitute lanthanum hexaaluminate. (a) Half unit cell containing a large cation La^{3+} in the mirror plane. (b) Half unit cell containing interstitial Al ions. In this case, the large cation site is vacant or filled with an interstitial O ion.

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