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The structure of $CeAlO_3$ by Rietveld refinement of X-ray powder diffraction data

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Abstract

The room temperature structure of perovskite $CeAlO_3$ has been reinvestigated by X-ray powder diffraction. The Rietveld refinement has confirmed the tetragonal symmetry; but revealed a super cell, $a = 5.32489(6)$ Å and $c = 7.58976(10)$ Å, with the space group $I4/mcm$. In $CeAlO_3$, the distortion from the ideal cubic perovskite is caused by the cooperative tilting of the AlO_6 octahedra around the primitive cubic $[001]_p$-axis.

Keywords: Perovskites; X-ray powder diffraction; Crystal structure

1. Introduction

Many distorted perovskites ABO_3 are due to the cooperative tilting of the BO_6 octahedra. This type of distortion mostly occurs when the ionic radii, r_A, r_B and r_O, do not fulfill the condition of the Goldsmith tolerance factor $t = 1 : t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$. Glazer [1,2] developed a description on the classification of the different tilting patterns in terms of component tilts around the four-fold pseudo-cubic axes, and obtained 23 corresponding space groups. Recently Howard and Stokes [3] undertook a group-theoretical analysis and found 15 possible structures, as derived from the cubic aristotype, under the similar conditions of tilting the rigid octahedra.

The orthoaluminates, $LnAlO_3$ (Ln = lanthanides and Y) have long been known to have the perovskite-like structure. The compounds with Ln = La, Pr and Nd are rhombohedral (space group $R\bar{3}c$, tilting ($a^-a^-a^-$) in Glazer's notation) at room temperature [4,5], whereas the orthorhombic $GdFeO_3$-type structure (space group $Pnma$, tilting ($a^+b^-b^-$)) is adopted by the members with Ln = Sm–Lu and Y [5–8].

Among the $LnAlO_3$ perovskites, the structure of $CeAlO_3$ appeared to be less well characterized. Zachariasen [9] noticed it as tetragonal, with the lattice parameters closely related to that of the simple cubic aristotype ($a = 3.768$ Å and $c = 3.795$ Å); but Kim [10] described it to be rhombohedral ($a = 5.327$ Å and $\alpha = 60.25°$), having the same structure as $LnAlO_3$ (Ln = La, Pr and Nd). Cuneyt-Tas et al. investigated the Ce_2O_3–Al_2O_3 system and found the primitive cell for $CeAlO_3$ ($a = 3.763$ Å and $c = 3.792$ Å) as well [11]. Tanaka et al. [12] have, from X-ray single crystal diffraction data, confirmed the primitive tetragonal cell ($a = 3.7669(9)$ Å and $c = 3.7967(7)$ Å), and reported the space group $P4/mmm$ for $CeAlO_3$. This space group belongs, however, to none of the known space groups derived from the tilting of the normally rigid octahedra [1–3]. Indeed, the authors have found unusually large anisotropic thermal parameters for the basal oxygen atoms and, to a less extend, for Ce atoms. Thus, these atoms were statistically split in more general positions characterized by small deviations from their ideal positions of the basic perovskite lattice.

There is continuous interest in the structural phase transitions in the $LnAlO_3$ perovskites [13]. For example, the rhombohedral distortion in $LnAlO_3$ (Ln = La, Pr and Nd) decreases with increasing temperature; only for Ln = La the structure transforms at 820 K to the simple

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cubic aristotype. Moreover, in the current three-way catalyst system, the ceramic monolith is covered with a high-surface-area γ-Al_2O_3 layer, which contains up to 30 wt% metal oxide additives, e.g. CeO_2 and La_2O_3 [14]. It is known that CeO_2 confers remarkable stability to the surface of γ-Al_2O_3 due to the formation of $CeAlO_3$ under reducing conditions operated in the catalyst system [15]. The recent investigation of the Ln_2O_3–Al_2O_3 systems, using combinatorial approach, has also proved the perovskite structure being efficient host lattice for luminescence [16], although the optimized phosphor compositions largely deviate from the perovskite stoichiometry. We, therefore, carried out an investigation of the crystal structure of $CeAlO_3$. In this communication, we report new result as was obtained from X-ray powder diffraction.

2. Experimental

Powder samples of $CeAlO_3$ were prepared from high purity CeO_2 (99.999%) and Al_2O_3 (99.99%) in a platinum crucible. The stoichiometric mixtures were intimately ground and heated in a diluted hydrogen flow (10% H_2 in N_2) at 1748 K for 15 h. After regrinding they were treated under the same conditions for additional 15 h, followed by furnace cooling to room temperature.

X-ray diffraction data were collected with a Philips PW1050 diffractometer using monochromatic Cu*Kα* radiation in the range $10° < 2\theta < 115°$ with the steps of 0.02° and 15 s counting time at each step. Structure calculations were performed by the Rietveld method using the Rietica computer program [17]. A polynomial function with six parameters was used to fit the background. The profiles have been fitted using a Pseudo-Voigt function with peak asymmetric correction.

3. Results

The X-ray diffraction pattern of $CeAlO_3$ at room temperature (Fig. 1) revealed a single phase and is dominated by the strong lines characteristic of a primitive perovskite cell, with subtle splitting of them. A few very weak additional lines, indicated by arrows in Fig. 1, at the 2θ-values of about 39.6°, 52.7° and 74.4°, respectively, were also visible (see also inset (a) in Fig. 1 for an enlarged section), which cannot be indexed with the primitive tetragonal cell [9,11,12]. Since all of the additional reflections can be accounted for in terms of the double unit cell with odd integer indices, it suggests the presence of the octahedral tilt with only antiphase (-) tilting of the adjacent octahedra. Considering the tilting being restricted around the principle axes of the primitive cubic cell, it leads to three possible space groups: $I4/mcm$ ($a^0a^0c^-$), $Imma$ ($a^0b^-b^-$) and $R\bar{3}c$ ($a^-a^-a^-$), of which $R\bar{3}c$ has been suggested previously [10]. Close examination of the splitting of some basic diffractions has, however, ruled out both $Imma$ and $R\bar{3}c$ space groups. For example, the basic (100) reflection is not allowed to split in $R\bar{3}c$, and it does in $CeAlO_3$ (see inset (b) in Fig. 1). On the other hand, the basic (222) reflection is expected to split in two in $Imma$; but it remains single, only $K\alpha_1$ and $K\alpha_2$ splitting being resolved. As all observed reflections could readily be indexed in a tetragonal cell with the cell parameters of $a = b \approx \sqrt{2}a_p$ and $c \approx 2a_p$, where a_p is the cell parameter of the primitive cubic perovskite, we modeled the structure of $CeAlO_3$ in the space group $I4/mcm$, as was recently reported for the perovskite $BaTbO_3$ [18].

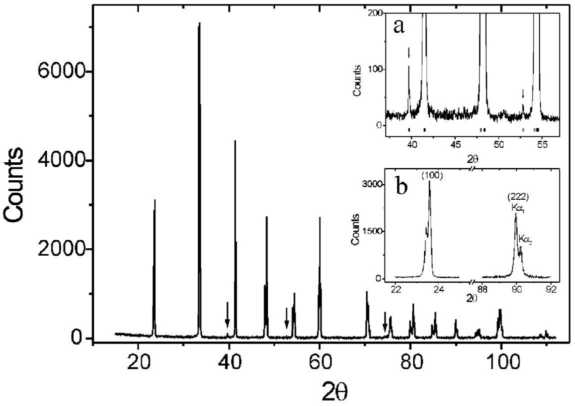

Fig. 1. X-ray diffraction pattern of $CeAlO_3$ at room temperature. Some visible superlattice reflections are indicated by arrows. Inset (a) is an enlarged section showing the first two supperlattice reflections. The tick marks below indicate the positions of allowed reflections of the supercell in the space group $I4/mcm$. Inset (b) shows the basic (100) and (222) reflections. The intensity of the (222) reflection has been multiplied by 5. The significance of their splitting is discussed in the text.

Rietveld refinement yielded satisfactory results. On convergence, the agreement factors are $R_{wp} = 18.48\%$ and $R_p = 12.68\%$ respectively with the Goodness-of-fit (S) of 1.76. The refined cell parameters are $a = 5.32489(6)$ Å and $c = 7.58976(10)$ Å. Table 1 lists the refined structural and thermal parameters. The plots of the observed and calculated profiles are shown in Fig. 2. Some selected interatomic distances are given in Table 2.

4. Discussion

In agreement with the observation of Tanaka et al. [12], the structure of $CeAlO_3$ at room temperature is indeed tetragonal; but it has a super cell instead of a primitive one. In a distorted ABO_3 perovskite, the intensity of super lattice reflections are solely determined by the shifts of the oxygen atoms away from their ideal positions, when there are no displacements of A and B

Table 1
Refined atomic positions and thermal parameters of $CeAlO_3$ in the space group $I4/mcm$

Atoms	Site	x	y	z	B (Å^2)
Ce	4*b*	0.5	0	0.25	0.54(2)
Al	4*c*	0	0	0	0.49(6)
O(1)	4*a*	0	0	0.25	1.1(2)
O(2)	8*h*	0.2777(8)	$x+0.5$	0	0.4(1)

$R_{wp} = 18.48\%$, $R_p = 12.68\%$, $S = 1.76$.

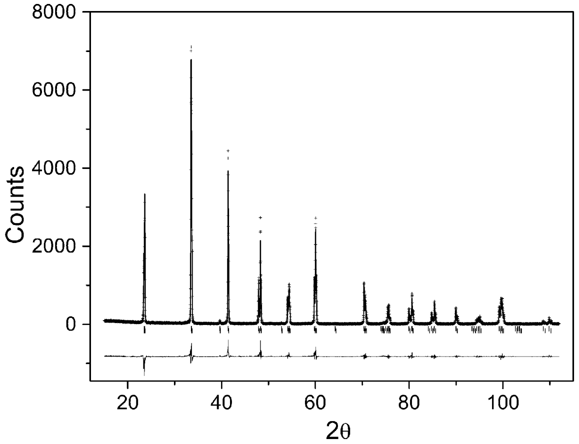

Fig. 2. Observed (crosses) and calculated (continuous line) profiles of $CeAlO_3$ in the space group $I4/mcm$. Tick marks. A difference curve ($I_{obs.} - I_{cal.}$) is shown at the bottom.

Table 2
Selected interatomic distances (Å)

Ce–O(1)	2.66245(3) × 4
Ce–O(2)	2.530(4) × 4
Ce–O(2)	2.824(5) × 4
Al–O(1)	1.89744(3) × 2
Al–O(2)	1.8942(7) × 4

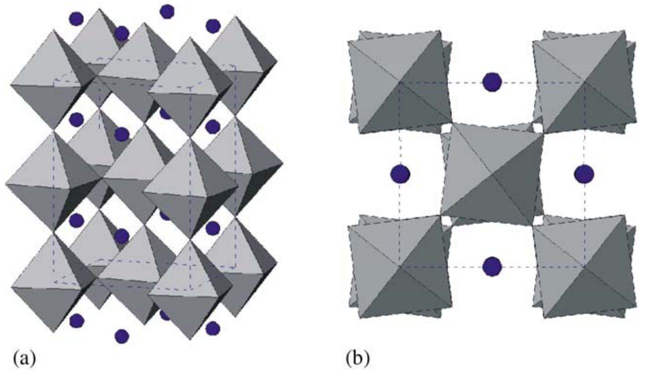

Fig. 3. (a) Schematic representation of the crystal structure of $CeAlO_3$ showing the AlO_6 octahedra and the Ce atoms. (b) A projected view of $CeAlO_3$ along the c-axis. The antiphase (-) tilting of the adjacent AlO_6 octahedral layers can be clearly seen.

cations. In the case that the perovskite contains heavy atoms, the super lattice reflections are usually extreme weak, and are, sometimes, difficult to be revealed by X-ray diffraction. Care should, therefore, be taken in determining the unit cell dimension. In fact, the space group that is used by Tanaka et al. in describing the crystal structure was apparently determined from only one procession photograph [12]. The observations of supperlattice diffractions that occur in the space group $I4/mcm$ depend, however, on the exact sections of the reciprocal lattice used. The failure of observing an enlarged cell of $CeAlO_3$ from the single crystal X-ray diffraction data may, therefore, be accidental. On the other hand, we noticed that a powder diffraction pattern of $CeAlO_3$ reported by the same group [19] is essentially the same as ours; the presence of the supperlattice diffractions is clearly visible. It is also interesting to note that the split model of Tanaka et al. [12] corresponds actually to the tilt system ($a^0a^0c^-$), if the basal oxygen atoms in the adjacent layers along the c-axis take one set of oppositely shifted values.

The space group $I4/mcm$ that was found for $CeAlO_3$, falls logically into the Glazer's classification of distorted perovskites due to the tilts of octahedra [1,2]. The same space group has also been found for $BaTbO_3$ [18], $SrTiO_3$ ($T < 110$ K) [20] and $SrZrO_3$ ($T > 1103$ K) [21]. In $CeAlO_3$, the AlO_6 octahedra are tilted around the pseudo-cubic c-axis with the tilting angle of about 6.3° (Fig. 3), resulting in three different Ce–O distances ranging from 2.530 to 2.824 Å (Table 1). The Al–O distances, with the averaged value of 1.8953 Å, are in good agreement with the sum of corresponding ionic radii [22] and those found in other LnAlO$_3$ (Ln = La (1.900 Å), Pr (1.895 Å) and Nd (1.893 Å)) perovskites [13]. The calculated effective valences of cations by using the formula and the bond valence parameters given by Brown et al. [23] and Brese et al. [24] are 3.10 and 3.09 for Al and Ce, respectively. These values are expected for the perovskite formula.

It is interesting to note that $CeAlO_3$, with the Ce^{3+} ionic radius in-between of its neighbor lanthanides, adopts different tilting pattern than $LaAlO_3$ and $PrAlO_3$. We notice, however, that the tolerance factor is either slightly larger ($t = 1.009$) or slightly smaller ($t = 0.994$) than the unity for $LaAlO_3$ and $PrAlO_3$, respectively. On the other hand, the tolerance factor for $CeAlO_3$ ($t = 1.001$) would be that expected for an ideal cubic perovskite; but it is tetragonal instead. Recently, Woodward [25] analyzed the energy stabilization as attributed to the Coulomb term in $R\bar{3}c$ with respect to the other tilt systems, and found that it decreases with decreasing the charge of A cation in the ABO_3 perovskites. This might reasonably explain why the rhombohedral distortion commonly occurs in the $A^{3+}B^{3+}O_3$-type perovskites but rarely observed in the

$A^{2+}B^{4+}O_3$-type perovskites. However, the present results clearly indicate the complexity of crystal structure in even apparently simple perovskites.

A related structural problem is found in $CeGaO_3$. This perovskite has, recently, been described by Shishido et al. [19,26] to have also the primitive tetragonal cell ($a = 3.873(1)$ Å and $c = 3.880(1)$ Å). In the light of the present investigation, the correctness of this unit cell seems highly questionable. As compared to $CeAlO_3$, the tolerance factor of $CeGaO_3$ ($t = 0.959$) deviates significantly from unity. It is rather unexpected that the tilting of the GaO_6 does not occur in $CeGaO_3$. In fact, a number of perovskite-like gallates, LnGaO$_3$ (Ln = La, Pr, Nd and Gd), are known [27–29], and they all adopt the space group *Pnma* corresponding to the tilt system ($a^+b^-b^-$). The powder diffraction patterns reported thus far [19,26] contain several phases; but a preliminary simulation shows that some of the weak lines are likely due to an enlarged cell of the dimension $a \approx b \approx \sqrt{2}a_p$ and $c \approx 2c_p$, where a_p and c_p are the lattice parameters given by Shishido et al. [19,26]. Consequently, the structure of $CeGaO_3$ necessitates further investigations.

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