

X-Ray Diffraction Study of the Decomposition Process Occurring in Single Crystals of the K_2NiF_4 -Type Aluminate $LaCaAlO_4$

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The results of an X-ray diffraction study of the decomposition process occurring in the K_2NiF_4 -type aluminate $LaCaAlO_4$ are reported. The experimental data concern two small single crystals heated for 1 and 10 h at 1200°C, respectively. As a final result, the presence of $LaAlO_3$ perovskite and CaO is unambiguously observed. After 1 h of heating, several intermediate phases can be identified as small-size $LaAlO_3$ -like microprecipitates. Well-defined orientation phenomena with respect to the matrix $LaCaAlO_4$ are evidenced for these phases and for CaO as well. On the basis of the variation of the perovskite cell volume of the intermediate phases, the decomposition process is tentatively modeled. In this respect, a tetragonal phase is considered as the precursor of $LaAlO_3$ perovskite. © 1997 Academic Press

INTRODUCTION

$LaCaAlO_4$ is a member of the series of $A^{3+}A^{2+}AlO_4$ aluminates (for example, $A^{3+} = La, Nd, Y$; $A^{2+} = Ca, Sr$) whose structure belongs to the K_2NiF_4 type of the A_2BO_4 oxides (Fig. 1), i.e., the 1/1 intergrowth of ABO_3 perovskite (P) and AO rock-salt (RS) type layers (1–4). Some of these compounds are of particular interest due to their dielectric properties at microwave frequencies (e.g., $NdCaAlO_4$ (5)) and, above all, their use as substrates for the epitaxial growth of high- T_c thin films (e.g., $LaSrAlO_4$ and $NdCaAlO_4$ (6–8)). Under these conditions, it is of importance to learn more about the thermal stability of these aluminates. Recently, the metastability of $LaCaAlO_4$ was reported (9). When a sintered powder was heated for more than 10 h at 1400°C in air, the perovskite-type parent phase $LaAlO_3$ was unambiguously identified from X-ray powder diffractograms. This specific behavior of $LaCaAlO_4$ — $YCaAlO_4$ and $LaSrAlO_4$ are stable at 1400°C—was discussed in terms of an enhancement of the crystal chemical constraints in the K_2NiF_4 -type structure, owing to the simultaneous presence of La^{3+} and Ca^{2+} in the (RS) layer (9).

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The ability to obtain single crystals of $LaCaAlO_4$ brings the opportunity to investigate the decomposition process from more informative X-ray diffraction data. We herein report the experimental data obtained from the X-ray diffraction of small single crystals of $LaCaAlO_4$ heated for 1 or 10 h at 1200°C in air. On the basis of the knowledge of the orientation relationships between the phases that are present, namely CaO, $LaAlO_3$, and $LaCaAlO_4$, a tentative modeling of the decomposition process is proposed.

EXPERIMENTAL

A bulky single crystal of $LaCaAlO_4$ with a good development of a (001) face was obtained at the Institute of Silicates Chemistry of the Russian Academy of Sciences by using the zone melting technique (10). It was cleaved into small single species of thickness less than 1 mm. Two crystals—one with a (100) face and another with a surface development close to (110) (called C1 and C2)—were heated in alumina containers at 1200°C in air for 10 and 1 h, respectively. After heating, the surface of the crystals became brownish. Such a phenomenon does not seem to be an intrinsic optical property of $LaCaAlO_4$; it is more likely to give an indication of the occurrence of the crystal chemical process that results in the progressive decomposition of the crystal. A further cleavage gave evidence of the development of such a process from the surface to the inner part. Moreover, the thickness of the decomposed layer showed a dependence on the heating time.

The X-ray diffraction investigation was carried out in terms of a rotating crystal experiment along the [100] direction for C1 and [001] for C2. The diffraction patterns were obtained from a (001) face and the (110) surface, respectively, to avoid a strong absorption in the bulk.

RESULTS AND DISCUSSION

In Fig. 2, one can see a 10° oscillation pattern of $LaCaAlO_4$ after heating for 1 h at 1200°C (C2 crystal

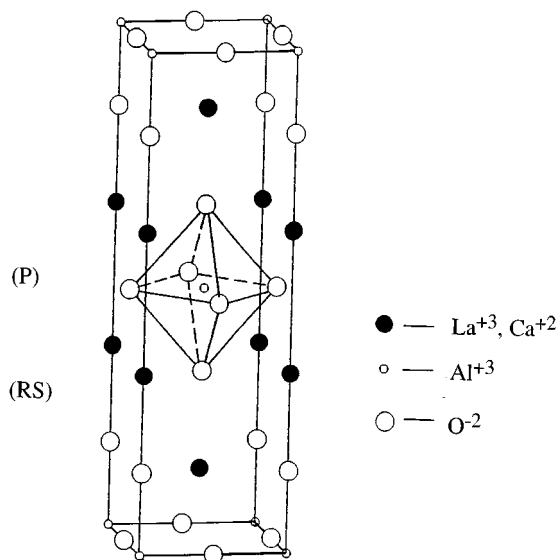


FIG. 1. K₂NiF₄-type structure of LaCaAlO₄: (P), perovskite layer; (RS), rock-salt layer.

(Fig. 2a)) and fragments of 10° oscillation patterns after heating for 10 h at 1200°C (C1 crystal (Fig. 2b–d)). The observed spots are ascribed to three systems of reflections, namely that of LaCaAlO₄, LaAlO₃, and CaO, as reported in Table 1. In addition, satellite spots as fragments of Debye–Scherrer rings accompany some strong reflections of

LaAlO₃ at low angles. The preferential distribution of some reflections along layered lines is the likely consequence of the existence of orientation relationships between the precipitates and the matrix, i.e., CaO and LaAlO₃ with LaCaAlO₄.

The matrix reflections are well defined and look like those given by a bulk scattering, i.e., the single crystal of LaCaAlO₄. The *a* parameter along the rotation axis is found to be close to 3.72 Å, in agreement with the powder data (9). Besides these reflections, the existence of a partial powder diffraction diagram gives evidence of the presence of some LaCaAlO₄ phase which is spread on the surface. The understanding of such a phenomenon, as connected to the decomposition process, is not so clear.

The reflections due to CaO appear only for the C1 crystal, as points of the reciprocal lattice which are more diffuse than those of LaCaAlO₄ and somewhat spread along the Ewald sphere (Fig. 2d). They have no well-defined form, as a consequence of a likely isometrical characteristic of the precipitation. Considering the distribution of these points in the reciprocal space of LaCaAlO₄ allows one to point to two different sets of nonequivalent orientations of CaO. These reflections, as belonging to the reciprocal lattice of CaO, correspond to the following values of the rotation axis parameters: 4.80, 3.39, and 2.40 Å. Clearly, the first and last values are consistent with the same orientation of CaO, the so-called [CaO]_I orientation, with [100] as the rotation axis; the second value, i.e., 3.39 Å, with [110] as the rotation axis, corresponds to the [CaO]_{II} orientation.

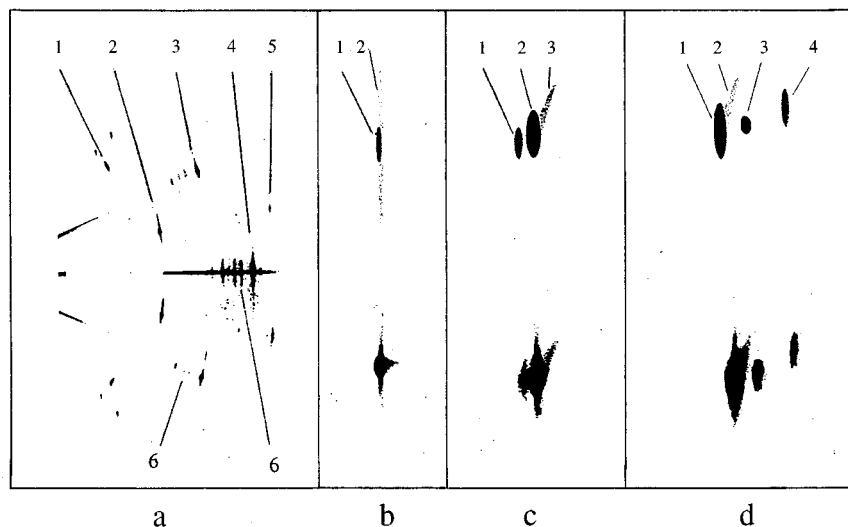


FIG. 2. Fragments of oscillation X-ray diffraction patterns and corresponding schemata obtained for LaCaAlO₄ single crystals heated at 1200°C. (a) C2 heated for 1 h: (1 and 4) 111 and 220 reflections for parallel orientation of LaAlO₃ precipitates; (2, 3, and 5) 200, 211, and 300 reflections for “twin” orientation of LaAlO₃ precipitates; (6) fragments of Debye rings for P₂ precipitates. (b) C1 heated for 10 h: (1) 100 reflection of LaAlO₃; (2) vertical rodlike diffuse scattering of P_T precipitates. (c) C1 heated for 10 h: (1) diffuse satellite of P₁ precipitates; (2) 112 reflection of LaAlO₃; (3) diffusion streak of P_T precipitates. (d) C1 heated for 10 h: (1) 113 reflection of LaAlO₃ precipitates; (2) diffusion streak of P_T precipitates; (3) 110 reflection of LaCaAlO₄; (4) 224 reflection of [CaO]_{II} precipitate.

TABLE 1
Crystallographic Data of the Phases Resulting from the Decomposition Process of LaCaAlO_4 : C1 and C2 Crystals Heated at 1200°C

Type of phase	Diffusion effect (i–vii in text)	Crystallographic cell, parameters (Å)	Form and size (Å)	Crystal C1 or C2 ^a
LaCaAlO_4 (matrix)		Tetragonal $a = 3.72$; $c = 12.33$	Isometric > 1000	C1 and C2
CaO		Cubic $a = 4.80$	Isometric ^b 70–150	C1
LaAlO_3	i	Cubic $a = 3.79$	Isometric < 1000	C1 and C2
LaAlO_3	ii	Cubic $a = 3.79$	Isometric > 1000	C1 and C2
LaAlO_3	iii, iv	Cubic $a = 3.79$	Isometric ^b 70–150	C1, C2
P_1 phase	v	Cubic $a = 3.87$	Isometric ^b 70–150	C1
P_T phase	vi	Tetragonal $a = 3.79$; $c = 3.72$	disklike ^b Thickness < 30	C1 and C2
P_2 phases	vii	not solved $a = 3.95$; 4.03	Isometric > 1000	C2

^aC1, heated for 10 h; C2, heated for 1 h.

^bOrientation with respect to the matrix; see text.

Visual estimation of the intensities of these reflections does not enable one to find a preferential orientation of the precipitates. The geometrical analysis of all the points of the reciprocal space of the matrix LaCaAlO_4 results in the set of orientation relationships between the matrix and the precipitates reported in Table 2 and pictured in Fig. 3. The absence of reflections due to CaO for the C2 crystal after 1 h of heating at 1200°C is understandable if one takes into account the small thickness of the decomposed layer.

The LaAlO_3 -like Phases

In the vicinity of the points of the reciprocal space of LaAlO_3 , rather complex diffusion effects appear. The existence of some of them is dependent on the crystal habit plane and the heating time. Seven distinct types can be

considered:

(i) Some fragments of powder diffraction rings are related to microprecipitates of LaAlO_3 that are randomly oriented with respect to the matrix.

(ii) On these diffraction rings are superimposed some discrete reflections originating from larger precipitates of LaAlO_3 and showing also no coherent orientation with respect to the matrix.

(iii) Some strongly textured precipitates of LaAlO_3 show a well-defined and parallel orientation with respect to the

TABLE 2
Orientation Relationships between the Matrix and $[\text{CaO}]_I$, $[\text{CaO}]_{II}$, and LaAlO_3 Precipitates

LaCaAlO_4	$[\text{CaO}]_I$	$[\text{CaO}]_{II}$	LaAlO_3
[100]	[100]	[110]	[100]
[010]	[010]	[110]	[010]
[001]	[001]	[001]	[001]

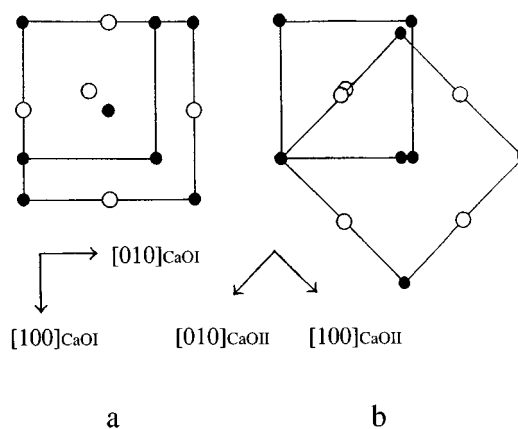


FIG. 3. Two lattice orientations of CaO precipitates with respect to the (001) plane of LaCaAlO_4 : (a) $[\text{CaO}]_I$; (b) $[\text{CaO}]_{II}$.

matrix LaCaAlO₄ (Fig. 2a, 1 and 4; Table 1). The value 3.79 Å is found for the a parameter of the rotation axis. The indexation of all the reflections is performed by using a cubic unit cell (space group $Pm\bar{3}m$). No evidence of any distortion, as previously reported for LaAlO₃ (11), can be found from these data. In such a case, the increase of the width of the reflections on the scattering angle can be used to evaluate the size of these microdomains as being in the range 70–150 Å.

(iv) This diffraction effect, which is due to another kind of textured precipitate of LaAlO₃, originates only in the C2 crystal, i.e., after 1 h of heating at 1200°C (Fig. 2a, 2, 3, and 5). The orientation relationships are not based on important crystallographic directions for both the LaAlO₃ and LaCaAlO₄ lattices. The mutual orientation of these precipitates and the matrix looks like a twin one, namely the (111) twinning plane for LaAlO₃.

(v) Regarding the C1 crystal only, some satellite spots looking like that reported as **iii** are observed along the direction of central vectors of the reciprocal lattice of LaAlO₃, close to the 100, 110, 200, and 112 reflections (Fig. 2c, 1 and 2) and toward the lower angles. The very small number of such reflections—only four—prevents one from obtaining significant information about the structure–composition relationship for this phase, the so-called P₁ phase (Table 1). At best, one can suppose this phase to be a cubic one with $a = 3.87$ Å, a value somewhat larger than $a = 3.79$ Å for LaAlO₃, and to contain elements lighter than La, i.e., Ca as deduced from the orientation of the spots toward the low angles.

(vi) This type of diffraction information is found again close to some points of the reciprocal lattice of LaAlO₃; it is very interesting as regards the problem of the decomposition of LaCaAlO₄ because it occurs in both the C1 and C2 crystals; it is ascribed to the so-called P_T phase (Table 1). It can be well imaged for the C1 crystal—i.e., after 10 h of heating at 1200°C—as rodlike diffusion streaks crossing the 100, 112, and 113 reflections of LaAlO₃ (Fig. 2b, 2; 2c, 3; and Fig. 2d, 2), which are parallel to the [100] rotation axis of LaCaAlO₄. The diffusion streak that crosses the 100 reflection is rather narrow: its length is close to one third of the a^* parameter of LaAlO₃ and its intensity decreases regularly and without any modulation, from the center to the edges. The streaks that are located nearby the 112 and 113 reflections are shorter, more diffuse, and less intense. From Fig. 2c, 3 and Fig. 2d, 2, they look like diffusion streaks that are orientated along the H_{\parallel} reciprocal lattice vector—a vector parallel to the rotation axis—toward the high angles. Consequently, the middle part of such streaks is visible on the first layer of the diffraction pattern of LaCaAlO₄. Owing to the tetragonal symmetry of the crystal, another orientation of the streaks, namely [010], is possible: under the present experimental conditions it was never observed, except for a slight “horizontal” diffusion streak from the 100

reflection (Fig. 2b). The existence of such kind of diffuse scattering usually is connected with the presence of metastable phases at the early stages of the decomposition process, for example in supersaturated solid solutions such as Al–Cu alloys: some small platelike Cu-enriched precipitates are identified in terms of Guinier–Preston zones and the so-called Θ' and Θ'' phases (12). A rather similar phenomenon takes place in our experiments: there is evidence of disklike precipitates of a new metastable phase, the LaAlO₃-like P_T phase. Its thickness does not exceed 10 times the unit cell constant of LaAlO₃; as to the in-plane direction, there is no limitation of the size. On the basis of the aforementioned data, one can tentatively propose the following for the tetragonal P_T phase: $a_{P_T} \approx a_{LaAlO_3}$ (i.e., 3.79 Å) and $c_{P_T} \approx a_{LaCaAlO_4}$ (i.e., 3.72 Å). Similar information can be deduced from the same diffraction effect obtained after 1 h heating at 1200°C (C2 crystal), except as regards the orientation of the disklike precipitates of the P_T phase: the diffusion streaks are perpendicular to the [100] axis of the matrix; i.e., the disklike precipitates are parallel to the perovskite layers in LaCaAlO₄ instead of being perpendicular, as for the C1 crystal.

(vii) For the C2 crystal only, close to the reflections of LaAlO₃ observed with both the parallel and the “twin” orientation, there exist rather small coupled fragments of diffraction rings (Fig. 2a, 6). The four main pairs of reflections can be ascribed to 110, 200, 112, and 220 for a perovskite cubic cell. Owing to such scarce information, it is difficult to propose an unambiguous explanation for these diffraction data; i.e., one cannot decide whether this is the signature of a tetragonally distorted perovskite or that of two slightly different cubic perovskites. In any case, for such so-called P₂ phases, the values of the a_p -type parameters are close to 3.95 and 4.03 Å, respectively. The value 4.03 Å is likely to take into account the elongation of the (P) octahedral layer in the intergrowth structure of LaCaAlO₄, which results in apical Al–O distances close to 2.03 Å and consequently, a corresponding value of a_p equal to 4.06 Å (9).

All of the foregoing diffraction effects reported for the various LaAlO₃-like phases are preserved during the first 2 months after the crystals are heated, if they are stored at room temperature in ambient air. Still, there is a progressive weakening of the effects reported as **iii**, **iv**, **v**, **vi**, and **vii**, namely that one which concerns the small textured precipitates of LaAlO₃, the P₂ phases, and CaO as well. After 5 months, all these effects have disappeared and only the powder diffraction rings due to the randomly orientated “microcrystals” of LaCaAlO₄ and LaAlO₃ are visible.

Tentative Modeling of the Decomposition Process

The main result obtained beyond the complexity of the diffraction phenomena that are observed is the evidence of

LaAlO₃ and CaO to be in any case the final products of the decomposition processes of LaCaAlO₄. As these processes already occur rather significantly after 1 h at 1200°C, the metastability of the intergrowth structure of LaCaAlO₄ is well settled. The absence of the typical reflections of CaO in the X-ray patterns, after 5 months for the C1 crystal and only several days for the C2 crystal, is due to the chemical reaction of the small precipitates of CaO with the ambient moisture. As an important result, the knowledge of the orientation relationships of the final products of the decomposition processes with respect to the matrix was reached: LaAlO₃ shows a parallel orientation with the matrix, as CaO shows two distinct orientations, one being parallel with the matrix, the other diagonal, with [110] as the rotation axis.

On the basis of the present results, namely the identification of various intermediate perovskite phases all related to LaAlO₃, a unique pathway to decompose LaCaAlO₄ cannot be proposed. It is very likely that the occurrence of several decomposition processes takes into account at least a time and temperature dependence and, to some extent, the quality and the habits of the crystal under consideration. In the following, a model is proposed that considers the parallel orientation of the LaAlO₃-like precipitates with respect to the matrix and because of this, is assumed to be the most significant.

As useful information to model the decomposition of LaCaAlO₄, one can take into account the crystallographic data concerning the cells of the LaAlO₃-like perovskite phases obtained from the X-ray diffraction study, in terms of the volume of a cubic unit cell: $V_p = a_p^3$. These data are reported in Table 3 together with the value V_{LaAlO_3} deduced from the analysis of the (P)/(RS) intergrowth structure of LaCaAlO₄. This value is significantly larger than that of LaAlO₃—5.7% more: this is rather unusual, as in the similar intergrowth-type $A^3+A^2+AlO_4$ aluminates the excess volume of LaAlO₃ is <1%. Under these conditions, the decomposition process of LaCaAlO₄ can be tentatively understood in three stages:

- first, the formation of the P₂ phases, at the very first time of the process, followed by that of P₁—P₁ is not

observed after 1 h at 1200°C. The P₂ phases are highly unstable, as imaged by their large excess volume with respect to LaAlO₃—14 to 20%. This is the likely consequence of conditions of formation, at the very early stage, which are fully out of equilibrium. P₁ gives a more realistic picture of a LaAlO₃-like phase, as it still exists after 10 h at 1200°C and, moreover, its excess volume is moderately increased with respect to that coming from the (P)/(RS) intergrowth of LaCaAlO₄—7% instead of 5.7%.

- second, the coming out of the P_T phase (vi in the diffraction effects) as disklike microprecipitates which originate from both P₁ and P₂. P_T seems to be rather close to LaAlO₃. Its slight negative excess volume with respect to LaAlO₃ (1.6%) can be understood in the following way: the constraint due to the coherent “growing” of P_T with LaAlO₃ is responsible for a tetragonal cell with $c_{P_T} \approx a_{\text{LaCaAlO}_4} \approx 3.72 \text{ \AA}$ —i.e., a value smaller than that of “pure” LaAlO₃ ($a_p \approx 3.79 \text{ \AA}$)—and consequently induces a lowering of the cell volume. Such a P_T phase is rather metastable. The thickness of the disklike microprecipitates is small—30 Å at best—and one can see in P_T the precursor phase of LaAlO₃ perovskite.

- third, the formation of LaAlO₃ in terms of microprecipitates with a random orientation or not with respect to the matrix is ensured in a simple way: as soon as the disklike precipitates of P_T reach some critical size, they transform into LaAlO₃. The crystallographic data concerning such a LaAlO₃ phase point to the absence of any distortion and qualify it as an actual cubic perovskite.

CONCLUSION

The decomposition process of LaCaAlO₄ as studied from X-ray single-crystal diffraction is effective at 1200°C. Its kinetics is fast since after 1 h rather large precipitates of LaAlO₃ perovskite are identified. They are randomly oriented with respect to the matrix. The very first intermediate phases to appear are highly unstable, as deduced from the large excess volume of their perovskite cell in comparison with that of LaAlO₃. Further, more realistic models of the final product of the decomposition take place. They show well-defined orientation phenomena with respect to the matrix and their size is small: this is particularly the case for the tetragonal perovskite phase, whose thickness of the disklike microprecipitates, even after 10 h at 1200°C, remains very small. Because of this, such a P_T phase is assumed to be the precursor of LaAlO₃ perovskite.

Work in progress is focusing on the early stage of the decomposition process, i.e., the orientation phenomena that appear for some textured precipitates of LaAlO₃ after 1 h at 1200°C, in terms of a twinning with the matrix. This seems of importance to gain an understanding of the

TABLE 3

Volume of the Perovskite Cubic Unit Cell V_p (Å)³ of the LaAlO₃-like Phases Obtained during the Decomposition Process of LaCaAlO₄ at 1200°C

Phases	P in (P/RS) ^a	P ₂	P ₁	P _T ^b	LaAlO ₃
V_p	57.3	61.6 → 65.4	58.4	53.3	54.2

^a $V_p = V_{(P/RS)} - V_{(RS)} = V_{\text{LaCaAlO}_4} - V_{\text{CaO}}$.

^bP_T coming from P₁.

lanthanum–calcium demixing that occurs in the (P)/(RS) intergrowth structure of LaCaAlO₄.

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