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Crystallographic Study of Lanthanum Aluminate by Convergent-Beam Electron Diffraction

BY C. Y. YANG, Z. R. HUANG AND W. H. YANG

Institute of Physics, Chinese Academy of Sciences, PO Box 603, *Beijing* 100080, *People's Republic of China*

AND Y. Q. ZHOU AND K. K. FUNG

Institute of Physics, Chinese Academy of Sciences, PO Box 603, *Beijing* 100080, *People's Republic of China, and Beijing Laboratory of Electron Microscopy, Chinese Academy of Sciences, PO Box* 2724, *Beijing* 100080, *People's Republic of China*

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Abstract

The space group of a well annealed $LaAlO_3$ crystal, determined by convergent-beam electron diffraction, is $Fm\bar{3}c$. Lower-symmetry monoclinic and triclinic phases have also been observed in not so well annealed and as-grown crystals. The cubic structure with $Fm\bar{3}c$ symmetry arises from a side-doubling transformation of the cubic perovskite structure due to the tilting of oxygen octahedra. Lower-symmetry phases are associated with the distortion of the cubic lattice due to oxygen deficiency or strain in the crystal. The previously reported $R\bar{3}c$ space group is probably due to the coexistence of the cubic phase and a lower-symmetry phase in the same crystal.

1. Introduction

Lanthanum aluminate ($LaAlO_3$) has recently attracted attention because of its use as a substrate for the epitaxic growth of high-temperature superconducting oxide (Zhang *et al.*, 1990). The structure of $LaAlO_3$, determined by optical microscopy and X-ray diffraction, has been reported to be rhombohedral with space group $R\bar{3}m$ (Geller & Bala, 1956). Subsequently, space group $R\bar{3}c$ was reported (Derighetti, Drumheller, Laves, Müller & Waldner, 1965). In the course of a routine study of the structure of $LaAlO_3$ by convergent-beam electron diffraction (Steeds, 1979; Buxton, Eades, Steeds & Rackham, 1976), a fourfold zone axis which is inconsistent with the reported rhombohedral symmetry was found (Yang, Huang, Yang, Li, Zhou & Fung, 1990). A systematic study was then started. It has been found that the structure of $LaAlO_3$ is cubic, with lattice parameter twice that of its high-temperature perovskite phase and space group $Fm\bar{3}c$. Referring to the X-ray powder diffraction data of $LaAlO_3$ as reported by Geller & Bala (1956), we have found that no splitting of reflections has actually been observed. The rhombohedral structure was deduced by excluding the cubic structure on the basis of optical microscopy examination and by analogy with $PrAlO_3$. In fact, the X-ray powder reflections of $LaAlO_3$ can be indexed with a cubic cell. The results of a transmission electron microscopy study of $LaAlO_3$ is reported in this paper.

2. Experimental

Single crystals of $LaAlO_3$ were grown by the Czochralski method at a temperature of about 2370 K at the Institute of Physics, Chinese Academy of Sciences. Subsequently, the $LaAlO_3$ crystals were annealed under controlled conditions. Three kinds of crystals, as-grown, short-annealed and long-annealed, have been studied. Thin sections cut from the crystals were mechanically thinned and polished to about 50 μm thick before being ion milled to electron transparency for examination in a Philips EM 420 and a Philips EM 430 transmission electron microscope. Convergent-beam electron diffraction (CBED) provides three-dimensional diffraction information from local regions probed by the convergent electron beam (about 50 nm). Diffraction from the third dimension parallel to the electron beam is in the form of fine higher-order Laue zone (HOLZ) lines in the diffraction discs. Zone-axis CBED clearly shows the crystal symmetry. It is now firmly established that CBED is an accurate and reliable method for the determination of crystal symmetry.

3. Transmission electron microscopy results

The microstructure of a short-annealed $LaAlO_3$ crystal is shown in Fig. 1. Regions of high and low intensity are clearly visible when the $\bar{2}20$ reflection is excited. CBED from the respective regions shows that the symmetry of the high-intensity region is cubic while that of the low-intensity region is of lower symmetry. Heating a low-intensity region with a focused probe changes it to high intensity and its symmetry becomes cubic. Thus there are two phases in the short-annealed crystal. In as-grown crystals, the lower-symmetry phase has not been observed while this phase is occasionally observed in the long-annealed crystals. Selected-area electron diffraction

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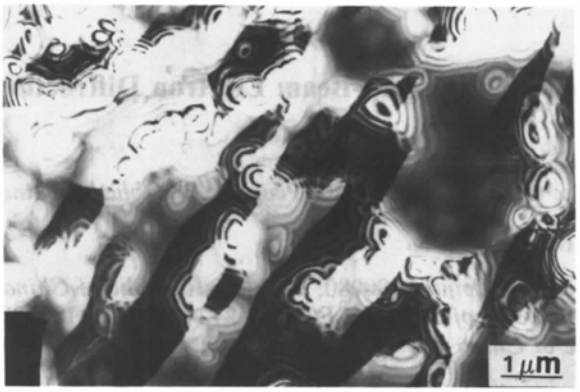

Fig. 1. Microstructure of a short-annealed $LaAlO_3$ crystal, the high- and low-intensity regions correspond to the cubic and monoclinic phases.

patterns from the major zone axes of a stereographic triangle of the cubic phase is shown in Fig. 2. The crystal lattice is consistent with that of a face-centred-cubic lattice. The lattice parameter $a = 0{\cdot}753$ nm, which is twice the cubic perovskite lattice parameter. CBED from the as-grown crystal gives patterns with imperfect $4mm$ [001] symmetry. Intense diffuse scattering is also evident in the corresponding selected-area diffraction patterns. CBED patterns of the cubic phase in the two annealed crystals are similar. CBED patterns of the [001] and [111] zone axes are shown in Fig. 3. Figs. 3(a) and (b) are obtained from a short-annealed crystal while Figs. 3(c) and (d) are obtained from a long-annealed crystal. The whole-pattern symmetry of the [001] zone axis is $4mm$ (Fig. 3a). The symmetry of the (220) dark-field pattern in which HOLZ lines are visible is $2mm$ (Fig. 3b). This

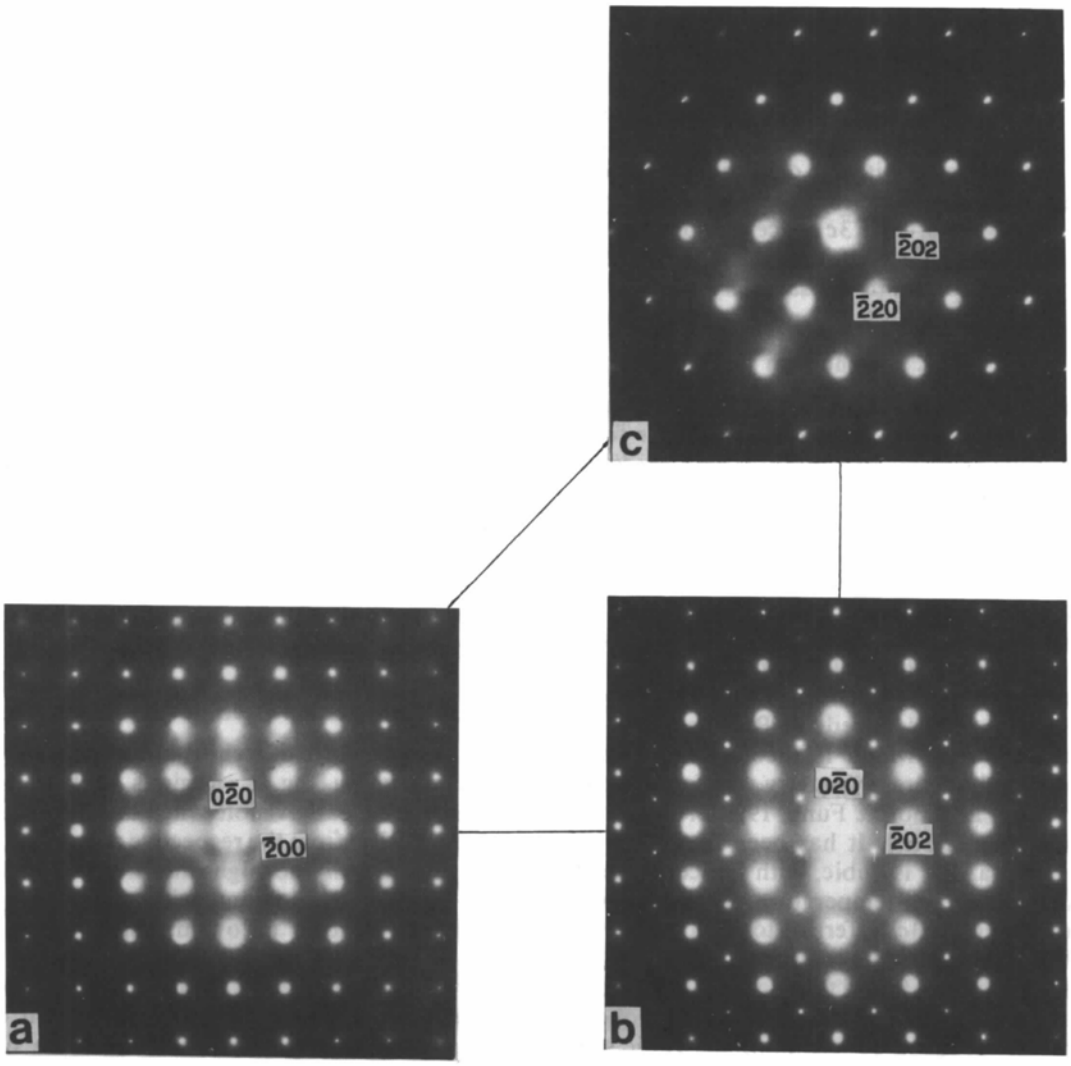

Fig. 2. Electron diffraction patterns of the cubic phase of $LaAlO_3$. (a) [001]; (b) [101]; and (c) [111] zone axes.

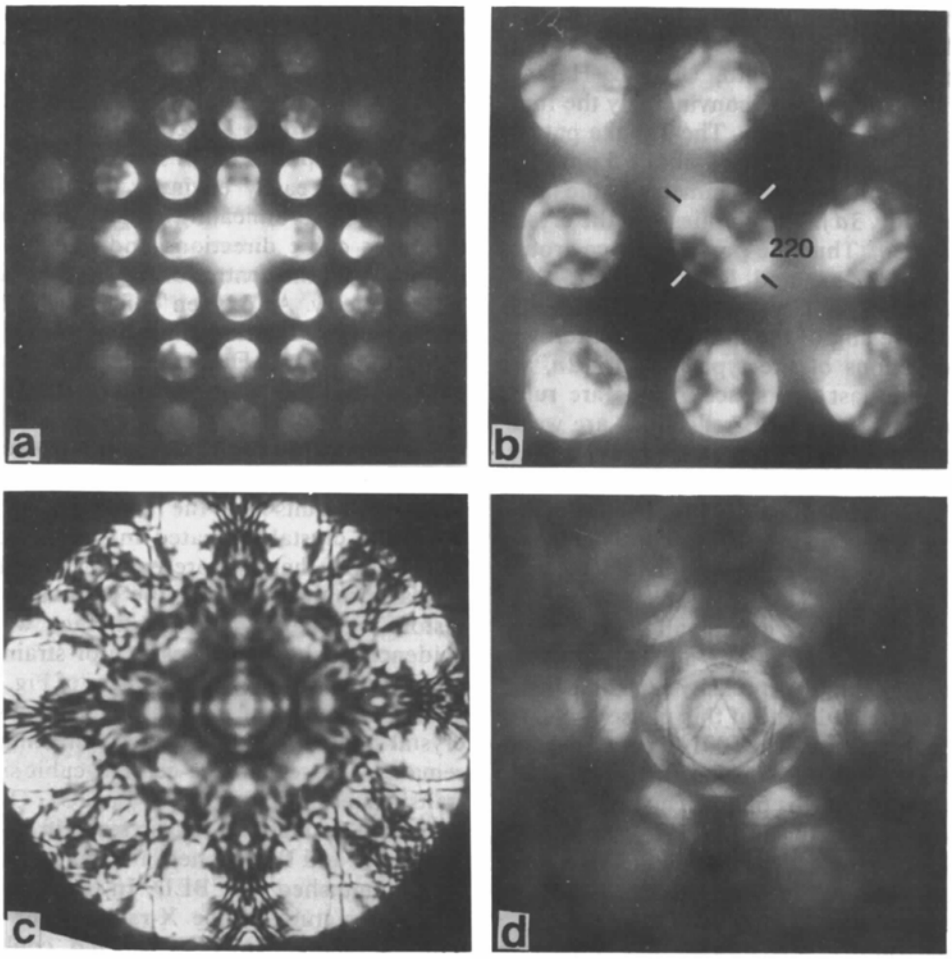

Fig. 3. CBED patterns of the cubic phase of $LaAlO_3$. (*a*) [001] zone axis showing 4*mm* symmetry; (*b*) the associated (220) dark-field pattern showing 2*mm* symmetry; (*c*) [001] large-angle bright-field Tanaka pattern; and (*d*) [111] zone axis showing 3*m* symmetry.

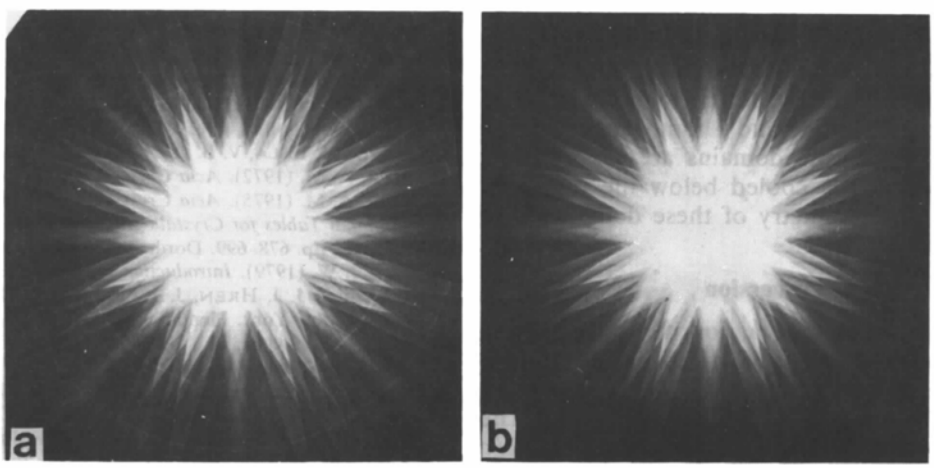

Fig. 4. [001] CBED patterns of (*a*) the $Fm\bar{3}c$ cubic phase and (*b*) the high-temperature perovskite $LaAlO_3$ showing 4*mm* symmetry. The HOLZ reflections disappear in (*b*).

means that the diffraction group is $4mm1_R$ (Buxton *et al.*, 1976). The [001] bright-field large-angle CBED Tanaka patterns (Tanaka, Saito, Ueno & Harada, 1980) in Fig. 3(*c*) shows quite convincingly the four-fold symmetry of the [001] axis. The Tanaka pattern has been taken from a region of about 5 μm. The bright-field and whole-pattern symmetry of the [111] zone axis is $3m$ (Fig. 3*d*). This implies that the crystal point group is $m3m$. Thus the possible space groups are $Fm\bar{3}m$, $Fm\bar{3}c$, $Fd\bar{3}m$ and $Fd\bar{3}c$ (nos. 225–228) (*International Tables for Crystallography*, 1983). It is clear from the indexing of the diffraction patterns in Fig. 2 that reflections of the type $h00$, $h=2n$, are present so that the last two space groups are ruled out. Note that the 111 and 313 reflections are weak, but the 222 reflections are strong in the [101] diffraction pattern (Fig. 2). Indeed, very weak 313 reflections were noted by Geller & Bala (1956). The reflection conditions hhl, $h, l=2n$ (even), are consistent only with the space group $Fm\bar{3}c$ (*International Tables for Crystallography*, 1983). Thus the space group of $LaAlO_3$ is $Fm\bar{3}c$. This space group will degenerate to $R\bar{3}c$ when slightly distorted along a [111] direction.

The symmetry of the low-intensity phase in Fig. 1 has not been determined yet but this phase is clearly related to the cubic phase. The [001] axes of the two phases are parallel but only the mirror in the [220] direction is preserved in this phase. The highest symmetry observed is m. In addition to the lower-symmetry phase, ferroelastic domains are also present. The larger ferroelastic domains can easily be observed by optical microscopy.

The specimen transforms to simple cubic perovskite when heated to about 720 K in the transmission electron microscope. This is shown in Fig. 4. The HOLZ reflections disappear, but the $4mm$ symmetry is unchanged. The first HOLZ ring in the room-temperature phase of $LaAlO_3$ corresponds to a lattice repeat of $2a_p$, where a_p is the perovskite lattice parameter. This periodicity vanishes in the high-temperature perovskite phase. Reflections corresponding to a_p are too weak to be visible above 720 K. The lower-symmetry phase and ferroelastic domains disappear at the transition and a homogeneous image is obtained. Ferroelastic domains are again visible when the specimen is cooled below the transition temperature. The symmetry of these domains is of course $Fm\bar{3}c$.

4. Discussion

The side-doubling transformation due to the tilting of oxygen octahedra in perovskite has been considered in detail by Glazer (1972, 1975). There are four types of lattice centring in three-tilt systems. The possible space groups for F centring are $R\bar{3}c$, $I2/a$ and $F\bar{1}$ (tilt systems nos. 14, 13 and 12). The $Fm\bar{3}c$ space group deduced above for $LaAlO_3$ corresponds to $R\bar{3}c$ with $\alpha=\beta=\gamma=90°$ (or equivalently the rhombohedral angle = 60°). It is clear that the perfection of crystal symmetry is dependent on the annealing conditions. Note that the symmetry of the low-intensity phase in Fig. 1 is consistent with tilt system no. 13, space group $I2/a$. Furthermore, the as-grown crystal corresponds to tilt system no. 12, space group $F\bar{1}$. We can easily envisage that the deficiency of oxygen before annealing results in unequal tilts in the three cubic directions and the displacement of cations from the centres of the octahedra resulting in $F\bar{1}$ symmetry. As oxygen deficiency is reduced and finally removed during annealing, higher crystal symmetries $I2/a$ and $Fm\bar{3}c$ result. This is supported by the fact that the colour of the crystal is changed by annealing. However, when the specimen is heated in the high vacuum of the electron microscope, oxygen is not readily available. It is likely that the cubic symmetry results from the removal of residual strains when the crystal is heated in the microscope. It is well known that the presence of strain lowers the crystal symmetry so that the removal of strain will restore the high symmetry. In fact, we have some evidence to show the presence of strain in the low-intensity and low-symmetry phase of Fig. 1. A detailed study of the role of oxygen deficiency and strain on crystal symmetry would be an interesting problem. It remains to be seen if face-centred-cubic side-doubling transformation is unique to $LaAlO_3$. Of course, the same transformation can also result in $R\bar{3}c$ symmetry. The cubic and rhombohedral symmetries can readily be distinguished by CBED. In the determination of crystal structure by the X-ray powder method, the splitting of reflections, if observed, could arise from the cubic $Fm\bar{3}c$ phase and a closely related lower-symmetry phase if the crystals are not properly annealed. In view of the results we have obtained, it is well worthwhile to initiate a systematic study of the breaking of symmetry due to the tilting of octahedra in perovskites by TEM.

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