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Twinning structure of $LaGaO_3$ grown by the Czochralski method

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Crystals of lanthanum gallate were grown by the Czochralski method and their quality was tested by microscopic observation in polarized light. This material is used as a substratum for the epitaxial growth of high T_c films of YBCO, particularly for certain high-frequency device applications. Two types of twins were observed and the difference in their temperature behaviour is discussed. The best quality single crystals (practically without twins) were obtained with the ⟨1 0 1⟩ and ⟨1 0 0⟩ seeds.

1. Introduction

Lanthanum orthogallate, $LaGaO_3$, belongs to the group of perovskites, and contains double oxides of trivalent ions, La_2O_3 and Ga_2O_3 [1–3]. $LaGaO_3$ has orthorhombic structure with lattice constants $a = 0.5487$ nm, $b = 0.520$ nm, $c = 0.7752$ nm [4] at room temperature. The lattice constants given by several authors show small differences and the average values given by Sandrom *et al.* [5] are $a = 0.5519$ nm, $b = 0.5494$ nm and $c = 0.7777$ nm. These discrepancies in the lattice constants can be caused by the observed twinning structure.

Mizuno *et al.* [6] reported the phase diagram for the La_2O_3–Ga_2O_3 system and the data show that $LaGaO_3$ melts congruently at 1715 °C. Small crystals of lanthanum gallates were produced from a PbO flux [7] and from a mixture of PbO–PbF_2–PbO_2–MoO_3–B_2O_3 [8], and the mixed lanthanides, gallates and aluminates were grown from Pb and PbF_2 flux [9, 10].

It should be mentioned that from the known orthogallates, $LnGaO_3$ (Ln = La–Gd), only $LaGaO_3$ [6, 11] and $NdGaO_3$ [11] melt congruently, and the Czochralski technique was used to grow single-crystal $NdGaO_3$ [11, 12] and $LaGaO_3$ [5, 13–15].

$LaGaO_3$, as well as $NdGaO_3$ single crystals, are promising new substrates for thin layers of high-temperature superconductors, which have less lattice mismatch, good thermal expansion and a lower dielectric constant, $\varepsilon = 25$, than other materials used ($SrTiO_3$, MgO). However, $LaGaO_3$ changes its crystal structure at about 140 °C and above 830 °C, and the lamellar structure is observed. $NdGaO_3$ shows no such phase changes from room temperature to 1000 °C [12, 16].

The recent investigation of O'Bryan *et al.* [17] shows that $LaGaO_3$ has first-order orthorhombic-to-rombohedral transition at 145 °C and second-order transition at 1180 °C.

To improve the crystal quality, to reduce the number of twins and to suppress the lamellar structure, $LaGaO_3$ single crystals were grown by the Czochralski technique using seeds with different orientations at the optimal conditions for crystal growth.

2. Crystal growth

The main difficulty in growing good single crystals of lanthanum gallate is the tendency to twinning. Factors which can influence the twinning structure and quality of this material grown by the Czochralski method are:

(a) the purity and stoichiometry of its starting materials;
(b) crystal growth conditions, such as pulling rate and rotation rate influencing the shape of the crystal–liquid interface;
(c) orientation of the seed.

Single crystals of lanthanum gallates were grown from a molten charge by the Czochralski technique using r.f. induction heating. Crystals were grown in a nitrogen atmosphere with an oxygen concentration of about 1%. The melt was a stoichiometric composition of La_2O_3 and Ga_2O_3 (with 2% excess Ga_2O_3) all at 99.999% purity. Immediately prior to preparation of a charge, the reagents were dried at 1100 °C for a period of 10 h. Single crystals of diameter 17.5 mm were grown from a 36 mm diameter iridium crucible. The pulling rate was 4 mm h^{-1} and the rotation rate was changed to investigate the crystal–melt interface. It was found that the twinning–lamella phenomenon depends on seed orientation and the habit of the crystal interface. The crystallization processes on ⟨1 1 0⟩, ⟨1 0 1⟩, ⟨1 0 0⟩, ⟨1 1 2⟩ and ⟨0 0 1⟩ seeds were performed.

Crystals were cut into platelets and polished slices were tested by microscopic observation in polarized light. We found the best quality single crystals were obtained with the ⟨1 0 1⟩ and ⟨1 0 0⟩ seeds. Also, a much smaller number of defects were observed in crystals grown with a convex crystal–melt interface. For crystals pulled on ⟨1 0 0⟩ and ⟨1 0 1⟩ seeds, virtually no twins and only (1 1 2) lamellae were observed.

3. Twinning in orthorhombic structure

The orthorhombic crystal structure of lanthanum gallate is very close to the ideal perovskite structure and its lattice constants satisfied conditions: $a \simeq b$ and $a^2 + b^2 \simeq c^2$. Therefore, some crystallographic directions (e.g. $\langle 1\,1\,0 \rangle$ and $\langle 0\,0\,1 \rangle$ or $\langle 1\,0\,0 \rangle$, $\langle 0\,1\,0 \rangle$ and $\langle 1\,1\,2 \rangle$) are quasi-equivalent (they are also hardly distinguished by X-ray diffraction). Consequently, the tendency toward twinning occurs during crystal growth.

There are two main types of twin in this material. One of them is connected with a variety of orientations of the orthorhombic c-axis. There are three possible spatial orientations of this axis in the frame of the ideal perovskite structure, as shown in Fig. 1. In this case the boundary between twins is a (1 1 2)-type plane and the crystal structure is transformed as a mirror reflection in this plane. As a result, the $\langle 1\,0\,0 \rangle$ or $\langle 0\,0\,1 \rangle$ directions change into their quasi-equivalent $\langle 1\,1\,2 \rangle$ or $\langle 1\,1\,0 \rangle$ directions, respectively.

The second type of twin, connected with the spatial orientation of a and b orthorhombic axes, is shown in Fig. 2. In this case, the boundary between twins is a (1 1 0)-type plane and by a mirror reflection in this plane the $\langle 1\,0\,0 \rangle$ and $\langle 0\,1\,0 \rangle$ directions interchange with each other. Twins of this type vanish at temperatures above 418 K due to first-order transition from orthorhombic ($a \neq b$) to rhombohedral ($a = b$) structure.

It should be noted that both types of twin described above are characteristic for orthorhombic structure and cannot be described in the frame of ideal perovskite lattice approximation. Therefore, identification of twins in orthogallates by X-ray topography is very difficult [13, 14]. A simple optical method of investigation of twinning structure applied to $LaGaO_3$ crystals is described below.

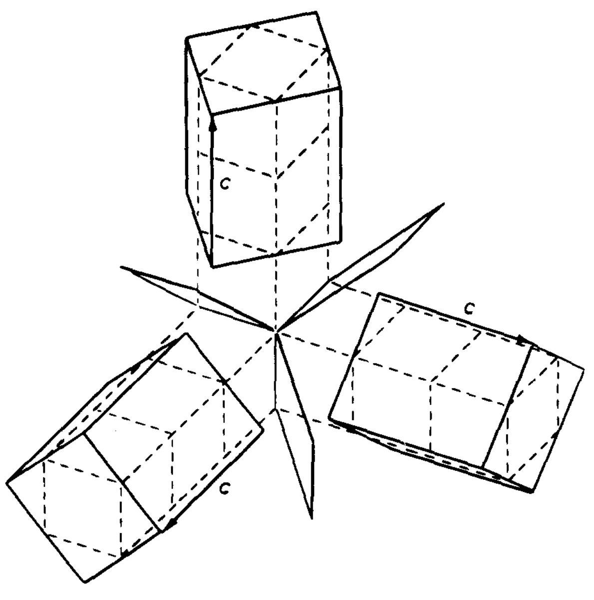

Figure 1 First type of twinning structure with (1 1 2) boundary planes. Three possible positions of the orthorhombic cell (——) in the frame of the perovskite structure (– – –).

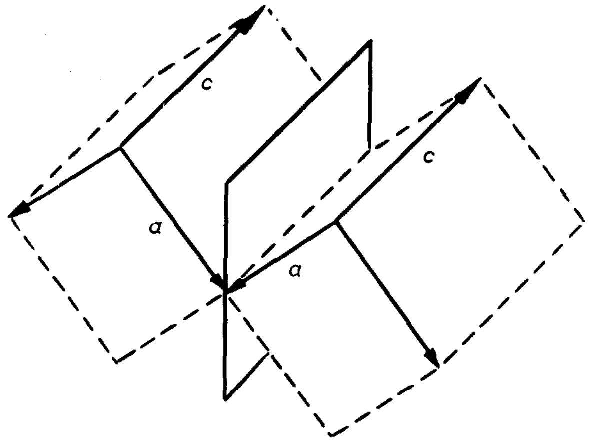

Figure 2 Second type of twinning structure with a (1 1 0) boundary plane.

4. Observation of twins

$LaGaO_3$ is transparent in visible light and, as in other orthorhombic crystals, shows biaxial optical birefringence. The three main axes of the ellipsoid of optical diffraction index are oriented parallel to the base directions $\langle 1\,0\,0 \rangle$, $\langle 0\,1\,0 \rangle$ and $\langle 0\,0\,1 \rangle$. If the crystal slice is placed between two crossed polarizers, the transmitted light is extinguished when one of the base directions, laid in the slice plane, is parallel (or perpendicular) to the plane of polarization. Thus part of the crystal with different contrast observed in the polarized light corresponds to volume twins. As an example, a slice in the (1 1 2) plane is shown in Fig. 3. Two photographs were taken at different orientations of the sample between crossed polarizers (shown by a cross). This twin structure is connected with rearrangement of the c-axis (first type described above). Twin boundaries of (1 1 2)-type are oriented perpendicular to the plane of the platelet.

The coexistence of all three possible orientations of the first type of twin is shown in Fig. 4. In the upper-left corner, the $\langle 1\,0\,0 \rangle$ direction is perpendicular to the plane of the photograph, while in the rest of the sample, two different twins, similarly oriented as on the previous picture (see Fig. 3), are visible. This structure strictly corresponds to theoretical predictions shown in Fig. 1.

Other defects visible on the photographs as bright stripes have the form of thin lamellae inclined to the platelet surface. Most of them have (1 1 2) orientation. These lamellae are glide-planes or other two-dimensional imperfections of crystal structure, and they can vanish after annealing above the structural transition temperature (145 °C). This suggests that some of these lamellae may be connected with two-dimensional twins of the second type. On the other hand, the polished surface of the platelet becomes rough, with a step-like form, after annealing showing glide-type distortion of the crystal. Fig. 5 shows a typical pattern of (1 1 2) lamellae observed on a (1 0 0) platelet. All lamellae in this photograph are inclined to the surface. In

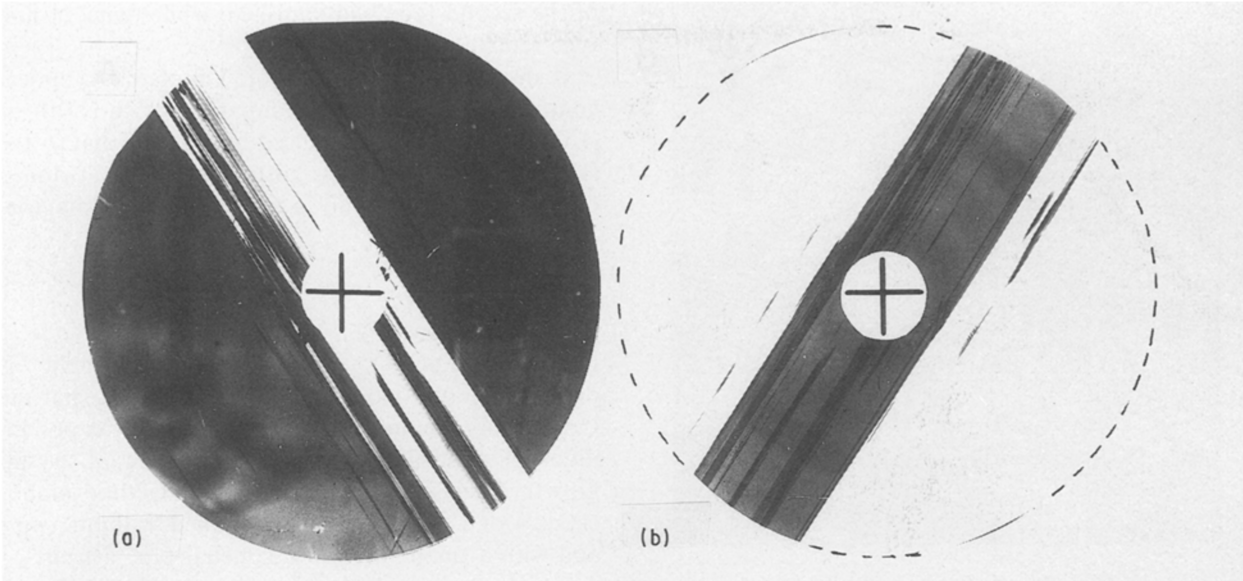

Figure 3 Twins on a platelet cut from the crystal grown in the ⟨1 1 2⟩ direction. (a, b) Two different positions of the sample with respect to the crossed polarizers (+). Sample diameter 16 mm. Negative picture.

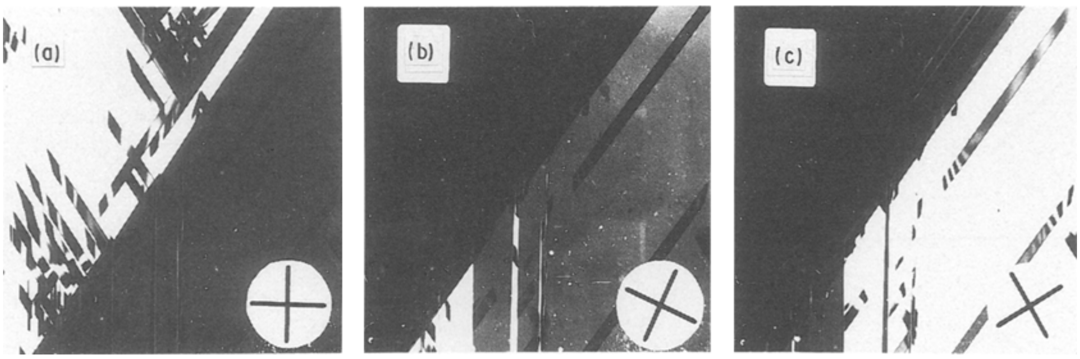

Figure 4 (a–c) Three different orientations of the first type of twin visible at three positions of crossed polarizers (+). 10 mm × 10 mm slice cut from twinned crystal grown on a ⟨1 0 0⟩ seed. Negative picture.

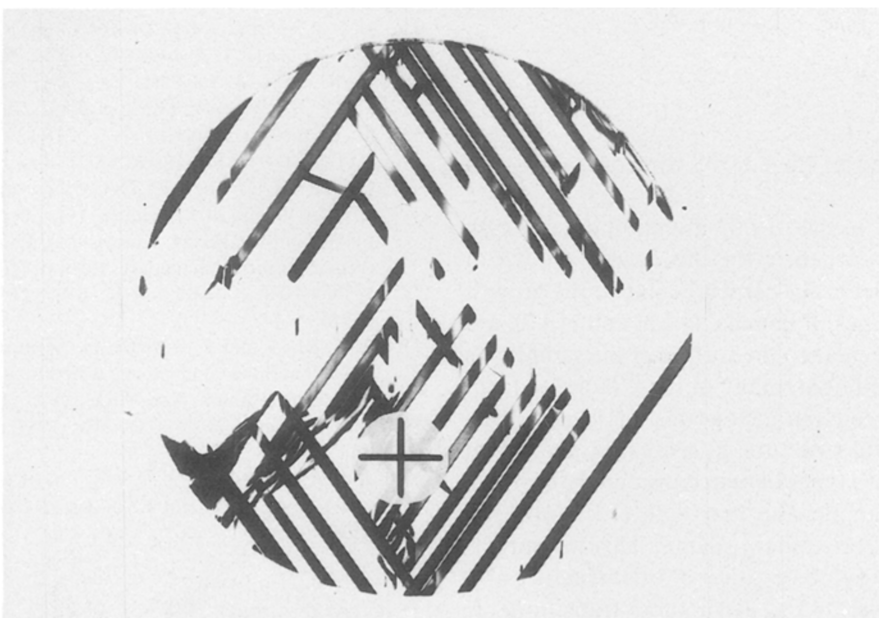

Figure 5 Lamellar pattern on a twin-free platelet of 16 mm diameter, cut from a crystal pulled in the ⟨1 0 0⟩ direction. Negative picture.

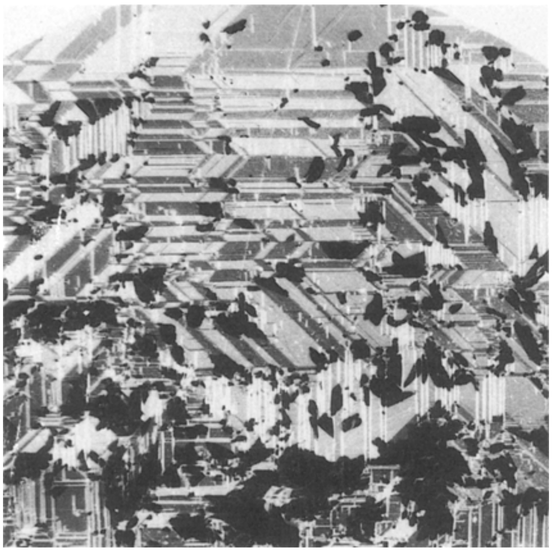

Figure 6 Coexistence of first and second type twins observed on the (1 1 0) plane. 10 mm × 10 mm slice cut from a crystal pulled in the ⟨1 1 0⟩ direction. Negative picture.

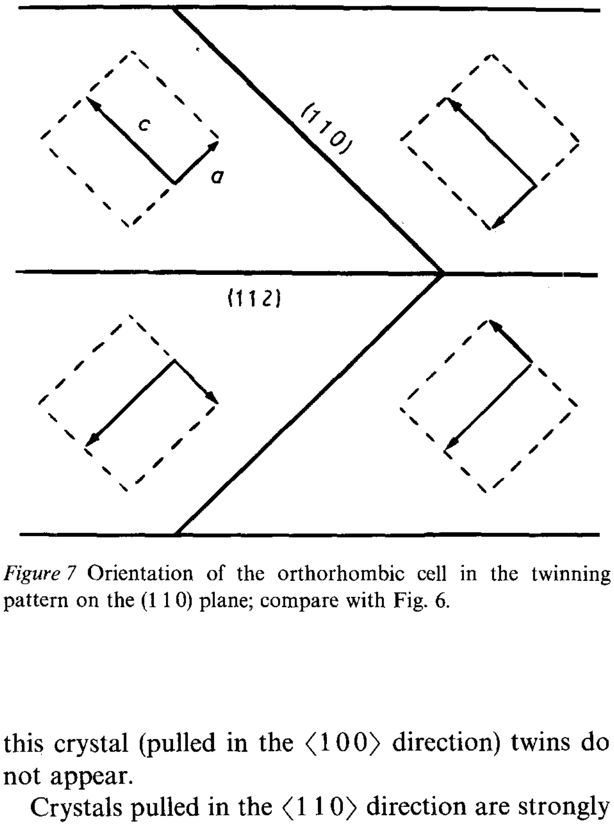

Figure 7 Orientation of the orthorhombic cell in the twinning pattern on the (1 1 0) plane; compare with Fig. 6.

this crystal (pulled in the ⟨1 0 0⟩ direction) twins do not appear.

Crystals pulled in the ⟨1 1 0⟩ direction are strongly twinned. Typical structure for this case is shown in Fig. 6. This platelet is cut perpendicular to the growth direction. Two types of lamella, (1 1 2) and (1 1 0), are oriented perpendicular to the surface of the sample. As visible in polarized light, many of these lamellae form boundaries between parallelograms of various orientations of crystal structure, as schematically shown in Fig. 7. Thus both types of twin considered above are formed in this sample; the first with (1 1 2) and the second with (1 1 0) boundary planes. This interpretation is confirmed by observation of this structure at a temperature above 145 °C (structural transition). It was found, that in the high-temperature phase, twins of the second type had vanished, while twins of first type remained.

It should be noted that on (1 1 0) platelets, optical contrast is very poor in comparison with (1 0 0) or (1 1 2) platelets. This is caused by the fact that in the (1 1 0) plane the angular distortion of the twinned crystal structure is only about 1° for this material [13, 14].

5. Conclusion

Growth of $LaGaO_3$ crystals with good quality is difficult due to a tendency towards twinning, but the Czochralski method is promising, due to the possibilities of controlling various parameters of crystal growth. It was found that using this method monocrystals of $LaGaO_3$ can be obtained without twins and with a small amount of lamellar-type defects.

Simple optical observation in polarized light is a very convenient method of investigation of twinning structure in pseudoperovskite crystals and was successfully used for detection of two types of twin appearing in $LaGaO_3$.

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