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Dislocations in yttrium orthoaluminate single crystals

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The dislocations present in single crystals of yttrium orthoaluminate grown by the Czochralski technique have been studied by means of etch pits and electron microscopy. They are shown to be predominantly edge in character with Burgers vectors which are principally *a* [1 0 0] and *b* [0 1 0]. In most instances, the dislocations form simple tilt boundaries. A few dislocations of a more random nature occur in association with twin boundaries. Dislocation formation is shown to be a characteristic of *c*-axis growth related to stresses caused by the anisotropic contraction of the material; *b*-axis crystals can be grown in a dislocation-free form.

1. Introduction

In anisotropic single crystals such as the orthorhombic perovskite, yttrium orthoaluminate ($YAlO_3$), the presence of dislocation low-angle boundaries can locally tilt the crystal lattice and thereby, present changes in refractive index to a light beam passing through the crystal. Changes of this type are obviously undesirable when the material is used in optical applications such as laser devices. The use of $YAlO_3$ as a laser host lattice incorporating Nd^{3+} and other rare-earth ions is widely reported [1–2].

The present study has investigated the distribution, character and origin of the dislocations found in Czochralski grown single crystals of $YAlO_3$ using etching techniques and high voltage electron microscopy. Some comment is made upon methods for controlling the dislocation density in this material and upon the sources of stress causing dislocation generation.

2. Experimental details

All crystals used in this study were grown by the Czochralski technique using apparatus and growth conditions specified fully in an earlier paper [3]. Both *b*-axis and *c*-axis crystals were examined.

The crystal sections required for etching studies were prepared by using a slow speed diamond saw to obtain slices, approximately 0.5 mm thick, which were mechanically polished through successively finer grades of diamond abrasive down to the 0.25 μm grade. Subsequent chemical etching using orthophosphoric acid at a temperature of 380° C for periods up to 1 h showed that the work damage produced by mechanical lapping was not readily removed. An additional stage of polishing using a colloidal silica suspension (Syton) produced little further improvement. A number of potentially useful compounds were found to be ineffective as chemical polishing agents. These were molten sodium molybdate, potassium dichromate, vanadium pentoxide and mixtures of lead fluoride with lead oxide. However, molten lead oxide alone (PbO) proved to be a very suitable chemical polishing agent for removing all traces of work damage when the crystal slice was immersed for a period of 15 to 20 min at a temperature within the range 910 to 930° C. Subsequent etching in phosphoric acid, as described above, produced characteristic dislocation etch pits. Any residual PbO on the specimen surface was removed with dilute nitric acid prior to etching.

Specimens for electron microscopy were prepared by ion-beam machining from 100 μm thick slices, cut as described above and polished to a Syton finish. The specimens were examined in an

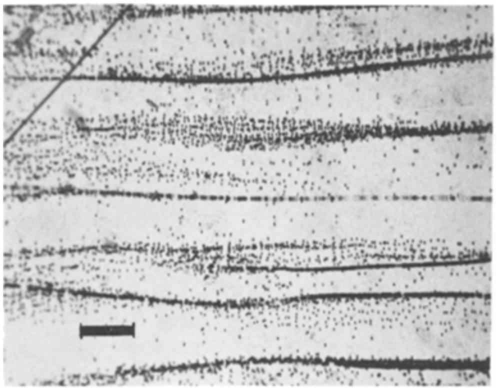

Figure 1 Dislocation etch pits lying in bands approximately parallel to [1 0 0] on a (0 0 1) surface of a *c*-axis crystal. (Bar marker = 0.2 mm.)

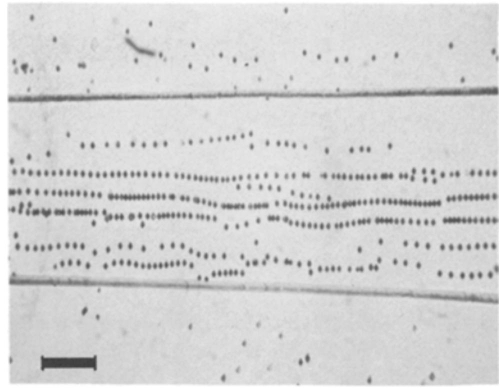

Figure 2 Dislocation etch pits delineating simple tilt boundaries on a (0 0 1) surface of a *c*-axis crystal. (Bar marker = 0.1 mm.)

AEI high voltage electron microscope (HVEM) at an accelerating voltage of 1 MeV. This voltage obviates the need to place a carbon layer on the specimen surface for the elimination of charging effects and also increases the penetration so that thicker samples can be used and the handling difficulties associated with brittle samples considerably diminished.

3. Results

3.1. Etching

The only crystal surface on which etch pits could be produced was the (0 0 1) plane in crystals with their growth axis parallel to the *c*-direction. No etching effects were obtained on (1 0 0) and (0 1 0) surfaces cut from *c*-axis crystals or on any of the low index surfaces (0 1 0), (1 0 0) and (0 0 1) in *b*-axis crystals. A typical etched (0 0 1) surface from a *c*-axis crystal (Fig. 1), shows etch pits aligned in bands which are generally parallel to [1 0 0] and [0 1 0] directions, principally the former. The bands of pits are typical of dislocations produced by slip; a greater density of pits occurs near to the crystal circumference than the crystal centre. The slight wavy appearance and splitting of some of the bands can be attributed to partial polygonization occurring by climb during the crystal growth cycle in which the cooling rate is slow enough (1 to 2° C min^{-1}) for some annealing to occur. In the central parts of some crystals, where the cooling rate will be lower than at the crystal edge, polygonization is further advanced, leading to the formation of distinct lines of pits corresponding to the dislocation low-angle boundaries of Fig. 2.

Etch pits also form along the twin boundaries formed in *c*-axis crystals [3]. These boundaries correspond to [1 1 0] and [1 $\bar{1}$ 0] directions and a typical example is given in Fig. 3. This figure also shows that the major axis of the etch pit changes direction from [1 0 0] to [0 1 0] across a twin boundary and confirms that the twin boundaries separate the crystal into blocks in which *a* in any given block is parallel to *b* in adjacent blocks and vice versa. This behaviour is similar to that observed during the formation of a twinned orthorhombic structure from a tetragonal phase in single crystal barium sodium niobate [4]. In $YAlO_3$, the similarity between the *a* and *b* dimensions of the unit cell ($a = 5.179$ Å, $b = 5.329$ Å) means that the change from *b* to *a* and *a* to *b* across a twin boundary can be accommodated by a lattice rotation of only 1.7°, which is consistent with the small number of dislocation etch pits usually observed along a twin boundary.

Figure 3 Dislocation etch pits in the vicinity of a twin on a (0 0 1) surface of a *c*-axis crystal. The twin boundaries are parallel to [1 1 0]. (Bar marker = 0.1 mm.)

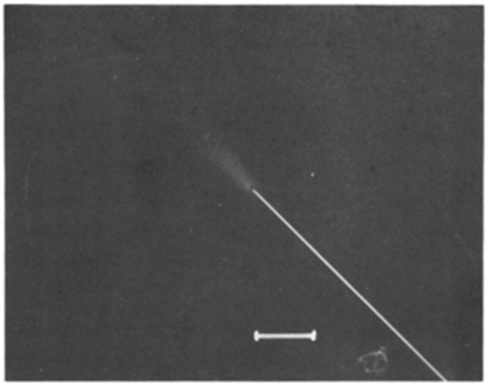

Figure 4 A dislocation etch pit and associated strain field at the tip of a twin lying parallel to [1 $\bar{1}$ 0] on a (0 0 1) surface of a *c*-axis crystal. Viewed between crossed polars. (Bar marker = 0.1 mm.)

Earlier work [3] has shown that twins parallel to [1 $\bar{1}$ 0] can intersect the predominant [1 1 0] twins and contribute to crystal cracking. However, in many instances the [1 $\bar{1}$ 0] twins terminate within the crystal without intersecting the conjugate twins. At the point of termination, a single dislocation etch pit can be produced; this can be seen in Fig. 4 together with a stress field at the tip of the twin.

3.2. Electron microscopy

In order to test the validity of the results obtained

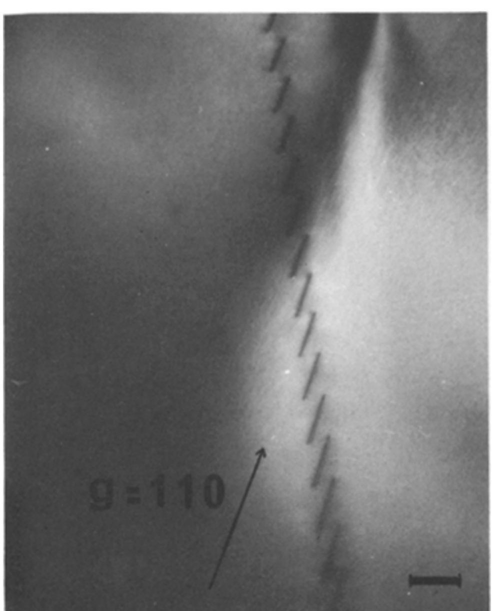

Figure 5 An electron micrograph of a typical dislocation low-angle tilt boundary in a *c*-axis crystal. (Bar marker = 0.2 μm.)

from etch pit studies, electron microscopy was used to determine the distribution and Burgers vectors of the dislocations produced in as-grown crystals. The Burgers vector analysis was performed using standard $\mathbf{g}\cdot\boldsymbol{b} = 0$ invisibility criteria; this analysis is subject to a slight ambiguity in the present case because it is not possible to differentiate clearly between (1 0 0) and (0 1 0) reflections using electron diffraction due to the small difference in the *a* and *b* unit cell dimensions. However, this ambiguity is removed by the etching studies where orientation can be unambiguously determined by conoscopic techniques.

In agreement with the etch pit data, electron microscopy has shown that *b*-axis crystals can be grown in a dislocation-free form whereas the *c*-axis crystals contain two main areas of dislocation substructure; these are either associated with low-angle tilt boundaries or are in close proximity to twin interfaces.

Random dislocations were observed in specimens cut from *c*-axis crystals but most of the dislocations were in low angle tilt boundaries as shown in Fig. 5. These boundaries were of two types defining the (1 0 0) and (0 1 0) planes. One type was observed frequently, the other occasionally, but because of the ambiguity discussed above, the indices cannot be uniquely ascribed to a particular boundary. The dislocations forming both types of boundary were determined to lie with their cores along the [0 0 1] direction with respective Burgers vectors of [1 0 0] and [0 1 0]. Since these dislocations are edge in character, the angle of tilt can be calculated from their measured separation and has always been found to be $<1^\circ$.

The only other area of appreciable dislocation density in *c*-axis crystals was in the region of the twin interfaces. In such areas, several different types of dislocation occur and, as can be seen from Fig. 6, these dislocations lie along varied directions. Burgers vector analysis showed the presence of dislocations having $\boldsymbol{b} = [0\,1\,0]$, [1 0 0] and [1 1 0] but the majority corresponded to $\boldsymbol{b} = [0\,1\,0]$ and [1 0 0].

4. Discussion

The dislocations lying in bands are consistent with edge dislocations generated by slip, principally on (0 1 0) planes in a [1 0 0] direction and to a lesser extent on (1 0 0) planes in a [0 1 0] direction, under the influence of an intrinsic stress. Some of these dislocations form simple tilt boundaries by

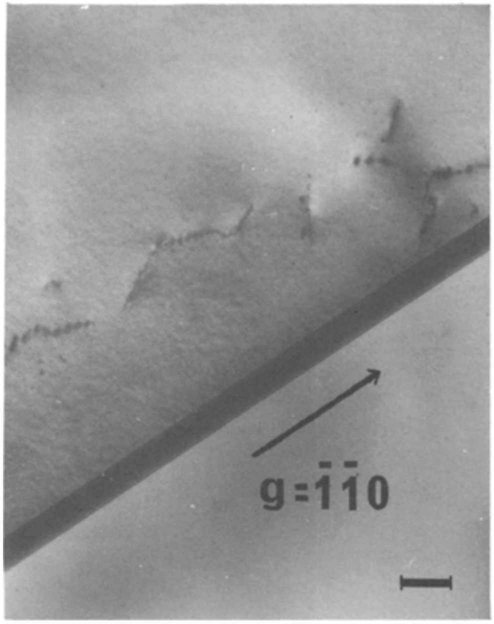

Figure 6 An electron micrograph of the dislocations observed near a twin boundary in a c-axis crystal. (Bar marker $= 0.2\,\mu$m.)

polygonization during the period in which the crystal grows and cools to room temperature. The observations made in etching studies are fully confirmed by electron microscopy.

The slip directions correspond to the shortest lattice translations, [1 0 0] and [0 1 0], necessary to produce structural identity in the orthorhombic $YAlO_3$ structure [5]. The predominance of the [1 0 0] system agrees with the a-dimension of the unit cell being slightly shorter than b.

The major sources of stress in Czochralski-grown $YAlO_3$ single crystals have already been identified by the present authors [3] as a radial hoop stress caused by differential cooling between the crystal surface and centre and stresses arising from anisotropic contraction during crystal cooling. The difference in behaviour between c-axis and b-axis crystals observed here suggests that stress from the latter source predominates for the ensuing reasons. The slip systems in c-axis crystals are orientated so that the resolved shear stress from a radially acting hoop stress can be a maximum on either of the observed systems. In b-axis crystals, the (1 0 0) [0 1 0] system is rotated by $90°$ out of the radial plane and would be inoperative but the (0 1 0) [1 0 0] system remains in the radial plane and should be activated. Radial hoop stress considerations cannot, therefore, fully explain the experimental observations because no evidence of dislocations or slip is found in b-axis crystals. In contrast, stresses arising from anisotropic contraction are a minimum in the radial plane during b-axis growth and a maximum in that plane for c-axis growth because the greatest anisotropy of the expansion coefficient is along the b-direction [3]. Thus, in the absence of pronounced hoop stresses, anisotropic contractional stresses could activate the observed slip systems during c-axis growth. However, because of the similarity between the a and c expansion characteristics, such stresses would be small for b-axis growth and therefore unlikely to operate an available slip system, which is precisely the experimental observation. Any hoop stresses generated would of course add to the level of stress and assist the activation of slip systems. On this hypothesis, the hoop stresses present during the growth of $YAlO_3$ are significantly less important than supposed previously [3].

The observation of dislocations in close proximity to twins can be attributed to the relief of stresses generated during twin formation provided that the stress in the twinning direction is sufficiently large to cause both twinning and dislocation production. This view is supported by the detection of a stress field at the twin tip. Hitherto insufficient evidence was available to distinguish between hoop stresses and anisotropic contractional stresses as the prime cause of twin generation [3]. The additional evidence given here suggests that the latter stresses are the major cause of twinning as well as dislocation production.

5. Conclusions

Earlier work by the present authors showed that twinning and cracking can be controlled in the Czochralski growth of $YAlO_3$ single crystals by using the b-direction as the crystal growth axis. The present work clearly demonstrates that the same axis can also be used to control the dislocation density of this material. The relative importance of stresses caused by the anisotropic contraction of the material and radial hoop stresses has also been established.

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References

1. M. J. WEBER, M. BASS, K. ADRINGA, R. R. MONCHAM and E. COMPERCHIO, *Appl. Phys. Letters* **15** (1969) 342.
2. M. J. WEBER, *J. Appl. Phys.* **44** (1973) 4058.
3. B. COCKAYNE, B. LENT, J. S. ABELL and I. R. HARRIS, *J. Mater. Sci.* **8** (1973) 871.
4. A. W. VERE, J. G. PLANT, B. COCKAYNE, K. G. BARRACLOUGH and I. R. HARRIS, *ibid* **4** (1969) 1075.
5. R. W. G. WYCKOFF, "Crystal Structures", Vol. 2 (Wiley, New York, 1964) p. 409.

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