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Mechanical Twinning and Crack Nucleation in Lithium Niobate

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Single-crystal, multidomain specimens of ferroelectric lithium meta-niobate have been plastically deformed by compression in the temperature range 1150 to 1250° C.

Subsequent examination of the specimens shows that deformation occurs by twinning on a $(10\bar{1}2)$ $[\bar{1}011]$ system. The nucleation of microcracks at twin-band intersections has been commonly observed and a nucleation mechanism, based on the observation that the ferroelectric polarity of the twin band is always opposite to that of the matrix, is proposed.

Measurements of the critical resolved shear stress for twinning afford a partial explanation of the observation that the crack-susceptibility of the material is greater in *a*-axis crystals than in those grown on the *c*-axis.

1. Introduction

Lithium meta-niobate, $LiNbO_3$ is now well established as a useful electro-optic material, particularly for second harmonic generation in laser systems [1, 2]. Despite this however, large, good-quality crystals of the material remain in scarce supply owing to its extremely low thermal shock resistance. As part of a programme to investigate the fracture characteristics of the material in more detail, a study has been made of the mechanical deformation of $LiNbO_3$ in the temperature range 1150 to 1250° C.

The crystal-structure of the material is reported to be rhombohedral [3], ($R3c$) and may therefore be indexed using a hexagonal unit cell. Abrahams *et al* [4], showed that the ferroelectric domain structure occurring below the Curie point at 1205° C resulted from the displacement of the lithium and niobium atoms in the structure with respect to the sheets of oxygen atoms on (0001) planes. This atomic model of the ferroelectric domain structure is used in the work reported below to explain the frequent observation of microcracks nucleated at twinband intersections in mechanically deformed $LiNbO_3$.

2. Experimental Techniques

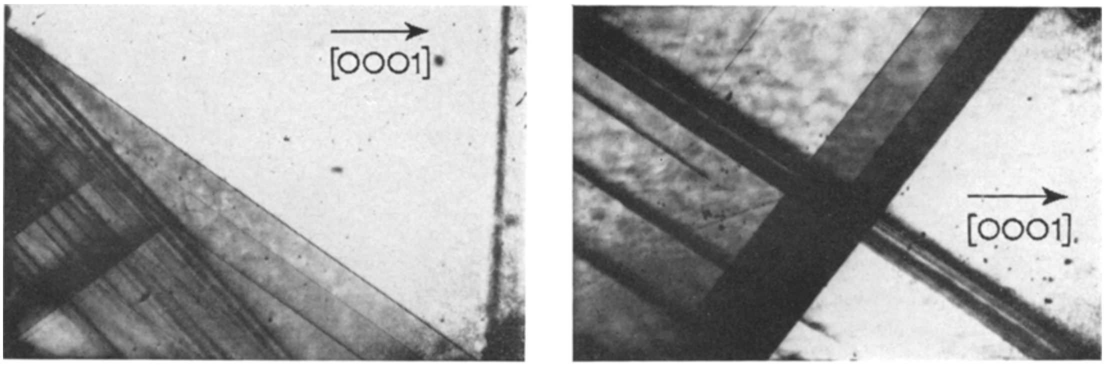
Single-crystal boules of stoichiometric $LiNbO_3$ were oriented using a Laue back-reflexion X-ray technique and were sectioned with a diamond saw to produce rectangular prisms 8 × 3 × 3 mm. These were compressed under uniaxial stress at selected temperatures in the range 1150 to 1250° C using an Instron Universal Testing Machine. Both [0001] and $[01\bar{1}0]$ directions were used as compression axes.

After compression, the specimens were removed from the machine and examined under an optical microscope for evidence of plastic deformation. Selected specimens were subsequently etched for 5 min in a hot solution of 5 g KHF_2 in 25 cm^3 conc HNO_3 in order to reveal the ferroelectric domain structure.

3. Results

Specimens of stoichiometric $LiNbO_3$ compressed along an [0001] axis showed no evidence of plastic deformation below 1160° C. Above this temperature, approximately 1% plastic deformation was observed prior to failure by brittle fracture. The yield stress of $LiNbO_3$ at 1160° C was found to be approximately 100 kg/cm^2. Tests performed at 1230° C revealed a slightly lower yield point of about 85 kg/cm^2 but little improvement in the ductility of the material. Failure occurred by brittle fracture at all temperatures within the range 1160 to 1245° C.

Subsequent optical examination of the $(0\bar{1}10)$



(a) (b)

Figure 1 Twin bands on orthogonal faces of a mechanically-deformed specimen of $LiNbO_3$ (× 44). (a) $(0\bar{1}10)$ face; (b) $(2\bar{1}\bar{1}0)$ face.

face (fig. 1a) of specimens compressed within this temperature range revealed broad deformation bands running through the crystal at an angle of 36° to the compression axis and a second set of finer bands making an angle of approximately 45 to 50° with the compression axis. The latter were confined to regions of the specimen directly below the compression plates and are undoubtedly due to the anomalous stress state in these regions. The broad bands were also visible on the $(2\bar{1}\bar{1}0)$ face (fig. 1b) and two-surface analyses and back-reflexion Laue patterns taken from the bands and the matrix indicated that these bands result from plastic deformation by twinning on a $(10\bar{1}2)$ $[\bar{1}011]$ system.

For specimens compressed along the *a*-axis, $[01\bar{1}0]$, the threshold temperature for macroscopic plastic deformation is about 20° C higher than for deformation of [0001] axis specimens. Moreover, although the same twinning system is operative, the yield stress observed during $[01\bar{1}0]$ axis compression is consistently lower than that for [0001] axis specimens compressed at the same temperature. The ductility of the material is extremely low even at temperatures approaching the melting point, and it appears that the onset of mechanical twinning and the nucleation of fracture are almost simultaneous, even for very low twin densities.

In both [0001] and $[01\bar{1}0]$ axis specimens the intersections of twin bands frequently act as nucleating sites for microcracks (fig. 2), lying on $\{0\bar{1}10\}$ planes. Fig. 2 also indicates the occurrence of secondary slip within the twinband. To study the microcracking in further detail, multidomain specimens were compressed at 1185° C. Crack nucleation was observed at most twin band intersections. Subsequent etching to reveal the ferroelectric domain structure showed that the twin bands are undeviated by changes in polarity in the matrix and further that the twin band is always of opposite polarity to that of the matrix in which it lies (fig. 3). Thus, in a positive domain matrix, the deformation band is deeply etched, characteristic of a negatively-polarised domain, whilst on entering a negatively-polarised region of the matrix the band is only lightly etched and crosses the heavily-etched matrix in the form of a low-relief ridge, suggesting that the band is a positive domain region.

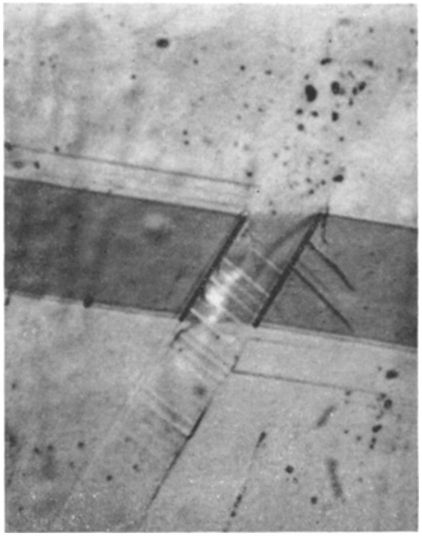
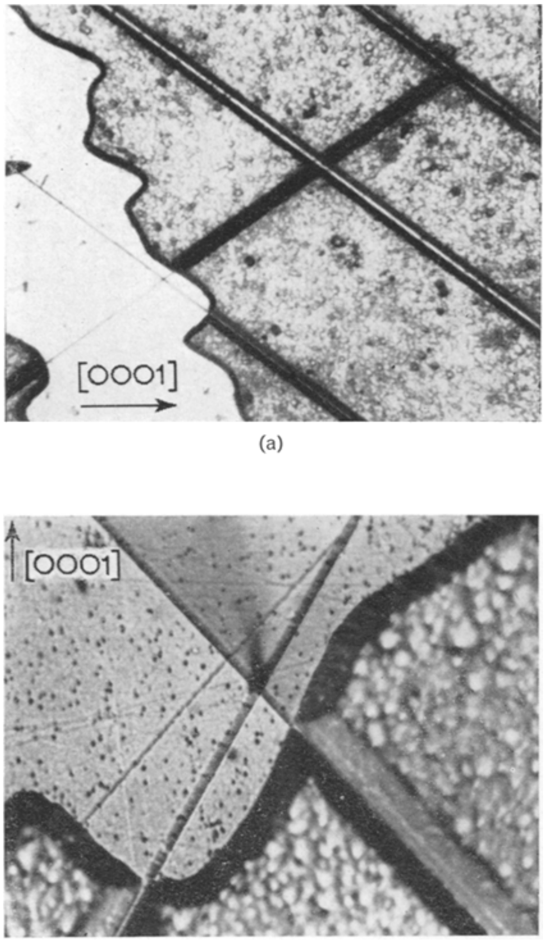


Figure 2 Secondary slip on the (0001) basal plane within a twin band (× 520).



(a)

(b)

Figure 3 Twin bands crossing a split-domain matrix. Etch: KHF_2/HNO_3. (a) × 88; (b) × 344.

4. Discussion of Results

The high yield stress and extremely low ductility in $LiNbO_3$ most probably result from the combined effects of a low density of "grown-in" dislocations and a high-lattice friction force. The high purity and high-lattice friction forces make dislocation nucleation and propagation difficult and plastic deformation, if any, occurs by twinning rather than by slip, especially when the few available slip systems are unfavourably oriented with respect to the deformation axis.

This is particularly so in hexagonal and rhombohedral materials in which slip is usually restricted to the (0001) basal plane. Such materials usually deform by twinning on a $(10\bar{1}2)$ $[\bar{1}011]$ system, i.e. a pyramidal plane. Thus, since lithium niobate is a rhombohedral material which may also be indexed as a pseudo-hexagonal structure, it is not surprising that deformation occurs by twinning on $(10\bar{1}2)$ $[\bar{1}011]$ and that the material is highly brittle, even at temperatures approaching its melting point.

As indicated in fig. 2 a small amount of plastic deformation occurs by secondary slip on (0001) planes within the twin bands, but the dislocation density is so low that it is unlikely that a substantial increase in ductility would be obtained by favourable orientation of the basal plane with respect to the compression axis.

The results obtained for compression along [0001] and those for compression along $[10\bar{1}0]$ indicate that the twin system is the same in each case. However, since the inclination to the compression axis is different in each case, the resolved shear stress on the twin plane is different for any given applied stress. The resolved shear stress τ is given by the equation

$$\tau = \sigma \cos \lambda \cos \phi$$

where σ is the applied stress and ϕ and λ are the angles of inclination of the normal to the twin plane and twin direction respectively to the compression axis. For compression along [0001]

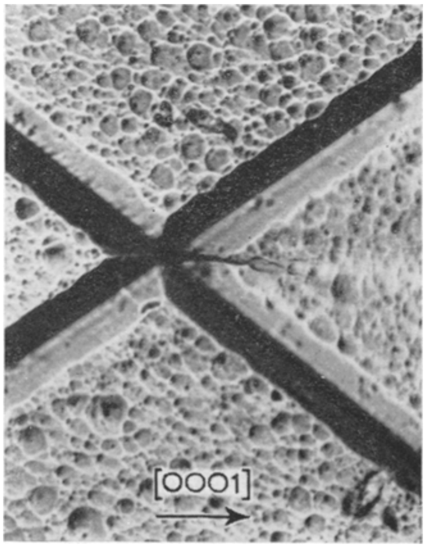
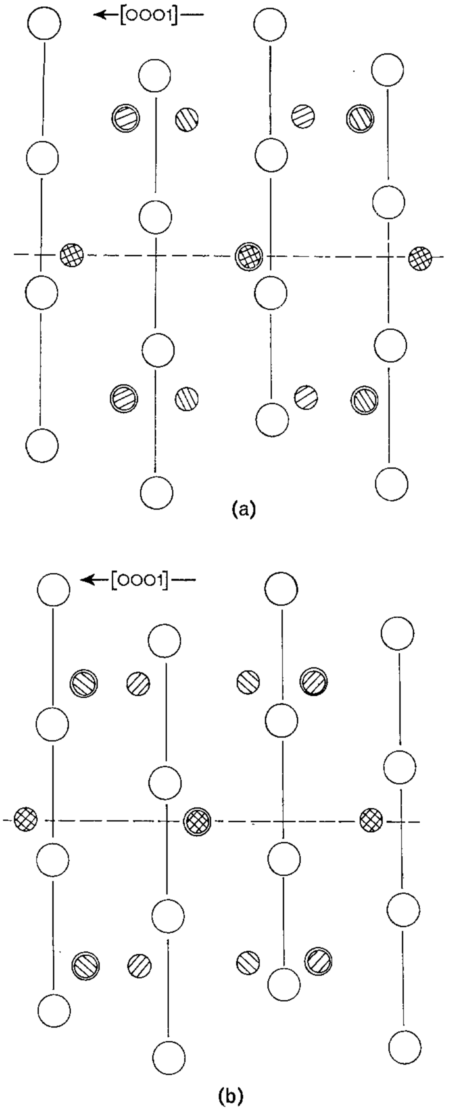


Figure 4 High-magnification micrograph showing the difference in etching rate between twin-band and matrix and the nucleation of fracture at a twin-band intersection.



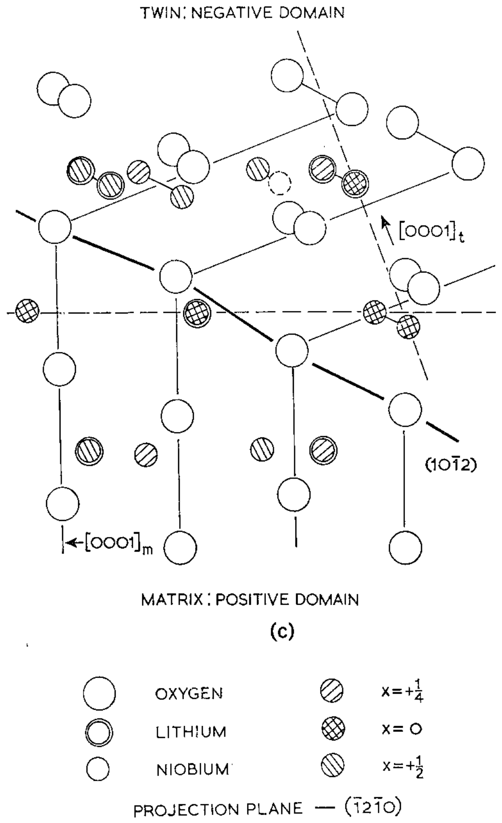


Figure 5 Atomic model of the ferroelectric domain structure of $LiNbO_3$ showing the displacement of lithium- and niobium-atoms with respect to the (0001) oxygen atom sheet. (a) "Positive" domain; (b) "negative" domain; (c) the change in polarity resulting from the reorientation of the atomic structure within the twin-band with respect to that of the matrix.

$\tau = 0.17\sigma$ while for $[01\bar{1}0]$ axis compression $\tau = 0.79\sigma$. Thus the critical resolved shear stress for twinning is achieved at a lower applied stress during $[01\bar{1}0]$ axis compression. Moreover, since $(1\bar{1}2)$ is also the observed fracture plane in as-grown $LiNbO_3$ the same argument may be applied in the case of the critical resolved shear stress for fracture, thus affording a possible explanation of the observation that *a*-axis crystals are more susceptible than *c*-axis crystals to brittle fracture during cooling after growth from the melt. In this case the assumptions made are that the internal stresses generated during cooling may be approximated to a uniaxial stress acting along the growth axis and that these are the same for both *a* and *c* growth axes provided that the external temperature gradient is the same in each case. The latter is not strictly true for $LiNbO_3$, in which *a*-axis contraction is greater than *c*-axis contraction under the same external temperature gradient within the pertinent temperature range [4]. The resulting internal stress is therefore greater along the *a*-axis than along the *c*-axis and the probability of fracture is correspondingly enhanced.

Although the predominant fracture plane in as-grown crystals is $(10\bar{1}2)$ cracking is also observed on $(0\bar{1}10)$ planes and in mechanically deformed specimens the latter are the predominant fracture planes. As illustrated in figs. 1, 3b and 4 $(0\bar{1}10)$ cracks are nucleated at the intersections of twin bands. The evidence of fig. 3 indicates that, irrespective of the polarity of the ferroelectric matrix, or changes in this polarity, the twin band is always of opposite polarity to that of the matrix and hence the intersection of two twin bands corresponds to the intersection of two ferroelectric domains of the same polarity. It is probable therefore that the electrostatic forces within this region are extremely high and that the intersection will therefore act as a crack-nucleation centre.

The reason for the reversal of polarity on twinning is evident from a consideration of Abraham's [3] model of the ferroelectric domain structure. Fig. 5 shows that the polarity of a domain is determined by the direction of the displacement of the lithium and niobium atoms with respect to the (0001) sheets of oxygen atoms. Fig. 5c shows the effect of shearing this structure about a $(10\bar{1}2)$ plane in a $[\bar{1}011]$ direction. In so doing the lithium and niobium atoms in the twinned region are moved through the sheet of oxygen atoms and the polarity of the twinned region is thus reversed with respect to that of the matrix. This mechanism operates, irrespective of the polarity of the matrix.

According to this hypothesis, crack nucleation at twin intersections should not occur during deformation at temperatures above the Curie point, but this postulation is difficult to verify since it is almost impossible to suppress subsequent cracking at temperatures below the Curie point during cooling to room temperature. It is significant however that specimens tested to failure above 1210° C fracture on $(10\bar{1}2)$ whereas those tested below this temperature fracture primarily on $(0\bar{1}10)$ planes.

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