Observation of Pendellösung Fringes in a Melt-grown Lithium Niobate Single Crystal

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The crystal perfection of a Czochralski-grown lithium niobate single crystal was investigated by the X-ray topographic technique. Pendellösung fringes as well as dislocations were observed in the crystal grown from the congruent melt in the [00.1] direction. The fringes, which have been interpreted using the dynamical theory of X-ray diffraction, indicate that such a boule is high in crystal quality.

A lithium niobate crystal, which is rhombohedral with hexagonal lattice constants $a_h = 5.14829$, $c_h = 13.8631$ Å and space group $R3c(C_6^h)$, at room temperature (Abrahams, Reddy & Bernstein, 1966), can be easily grown from a melt by the Czochralski method. In general, melt-grown single crystals contain considerable lattice strain and more lattice imperfections than those grown by the solution and the hydrothermal methods, in which crystal growth proceeds under nearly thermal-equilibrium conditions. Compared to melt-grown Ge and Si crystals, complex oxide ferroelectrics, such as LiNbO$_3$, are far less nearly perfect because of their complex compositions and structures, ferroelectric domain structures and anisotropy of crystal properties (Sugii, Iwasaki, Miyazawa & Niizeki, 1973). Observation of Pendellösung fringes is one of the useful tools for evaluating crystal quality, and it has been successfully used for several oxide crystals, such as Verneuil-grown MgO (Lang & Miles, 1965) and flux-grown Al$_2$O$_3$ (Belt, 1966) and BeO (Austerman, Newkirk & Smith, 1965; Chikawa & Austerman, 1968) crystals. This communication reports the observation of Pendellösung fringes as well as various types of lattice imperfection in a LiNbO$_3$ single crystal grown from the melt by the Czochralski method.

The crystal boule, ~40 mm long and 20 mm in diameter, was grown from the congruent melt [Li$_2$O/Nb$_2$O$_5$ = 0.942 in mole ratio (Lerner, Legras & Dumas, 1968)]. It was pulled along the [00.1] axis (hexagonal indices are used throughout this paper) at 5 mm h$^{-1}$ with a seed rotation of 45 r.p.m. In the initial stage of the pulling process, the ‘necking down’ technique (Dash, 1959) was applied to eliminate the propagation of dislocations and other defects from the seed crystal into the growing crystal. After the growth run, the crystal was cooled at a rate of 50°C h$^{-1}$ down to room temperature. As a specimen for X-ray topography, a (00.1) plate was cut out from the crystal boule by a diamond wheel, then ground with fine carborundum powder, and finally etched in a boiling mixture of two parts HF and one part HNO$_3$ to remove the surface layers mechanically damaged by grinding. The (00.1) plate was shaped as a thin wedge-shaped plate with the wedge angle of 3° of arc. The thickness of its edge, which was parallel to (2T.0) planes, was about 40 μm. The X-ray topographs were taken with a conventional Lang camera and Mo Kα$_1$ radiation (absorption coefficient of LiNbO$_3$ is about 5.18 mm$^{-1}$). The apparent focal size of the X-ray source was about 40×40 μm$^2$.

Figs. 1 and 2 show the topographs taken with the 30.0 and the 11.0 reflexions respectively. It was found that the rim, of the specimen (indicated as A in the figures), which corresponds to a part of the surface of the as-grown crystal boule has very poor crystallographic quality. A number of dislocations are seen to originate from the V-shaped growth ridge (indicated as B in the figures) (Niizeki, Yamada & Toyoda, 1967). These two kinds of lattice imperfections, those at A and dislocations near B, were considered to originate from the thermal stress resulting from the high temperature gradient around the crystal boule, during both growing and cooling processes. As for the dislocations in the central part of the specimen, whose density is about $10^4$ lines cm$^{-2}$, the image of dislocations running along [01.0] direction (indicated as C in the Figures) had higher contrast in Fig. 1 than in Fig. 2. On the other hand, the image of dislocations running along the [10.0] direction (indicated as D in the Figures) had slightly higher contrast in Fig. 2 than in Fig. 1. The image formation from dislocation lines depends generally on the relation between the diffraction vector g.
and the Burgers vector \( \mathbf{b} \), i.e. a necessary condition for no contrast of dislocation lines is \( \mathbf{g} \cdot \mathbf{b} = 0 \), and that for the strongest contrast is \( \mathbf{g} \cdot \mathbf{b} = 1 \). Therefore, the dislocations along the \( C \) and \( D \) directions in the Figures contain a larger edge component than screw component. Some of them are seen to polygonize into dislocation bundles, which are closely related to the formation of subgrain boundaries. Point-like defects are also seen in the central parts of the figures, but their origin has not yet been clarified.

Light and dark bands on the upper parts of the Figures are the ‘Pendellösung fringes’ of the 2nd, 3rd and 4th orders for \( \mathbf{g} = 30.0 \), and those of the 1st to 5th orders for \( \mathbf{g} = 11.0 \). According to Kato (1969), the spacing of Pendellösung fringes \( A_g \) for a specimen with a wedge angle of \( \delta \), is given by the formula:

\[
A_g = \frac{A_g^c \Phi_g}{\mathbf{g} \cdot \mathbf{g}}
\]

where \( A_g^c \) is the extinction distance for the \( \mathbf{g} \) reflexion and is inversely proportional to the absolute value of the structure factor, i.e. \( |F_g| \), and \( \Phi_g^c \) is a geometric factor. The geometric factor can be approximated by \( 1/\delta \) for the specimen with a small wedge angle \( \delta \) in the symmetrical Laue geometry. The measured values of \( A_g^c \) were 0.48±0.03 mm for \( \mathbf{g} = 30.0 \) and 0.71±0.03 mm for \( \mathbf{g} = 11.0 \). These are in good agreement with the calculated values of 0.458 and 0.735 mm using the observed structure factors of \( F_{30.0} = 217.0 \) and \( F_{11.0} = 151.2 \) (Abrahams et al., 1966) respectively. Since Pendellösung fringes arising from the variation of crystal thickness were observed in this specimen, it was found that the crystal, except for the rim, was of very high quality from the standpoint of the X-ray diffraction.

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References