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DOMAIN STRUCTURES OF $LiNbO_3$ CRYSTALS GROWN BY A FLOATING ZONE TECHNIQUE

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$LiNbO_3$ single crystals were grown from the congruently melting composition by a floating zone technique. It was confirmed by etching that the single domain crystals were produced without applying any external electric field. When annealed above the Curie temperature, antiparallel domain appeared in the form of annual rings.

Single crystals of $LiNbO_3$ were first grown from a LiF flux by Matthias and Remeika, and the ferroelectric properties were further investigated.[1,2] This material was also grown from the melt by a Czochralski technique by Ballman.[3] The $LiNbO_3$ crystal, however, contains ferroelectric multidomains. Generally the single domain production has been achieved by the application of an electric field either during or after growth.[2] Much attention has been denoted to the floating zone (FZ) technique, in that high purity single crystals of refractory materials can be grown without using a crucible. This paper reports on the FZ growth and domain structures of $LiNbO_3$ single crystals.

The sintered feed rods for FZ growth were prepared from Li_2CO_3 (Kanto Kagaku, 99%) and Nb_2O_5 (Mitsuwa Kagaku, 99.9%). These were mixed in the congruently melting composition of 48.6 mol% $Li_2O \cdot 51.4$ mol% Nb_2O_5.[4] The mixture was pressed into rods hydrostatically and then sintered at 1100 °C for 3 h. The apparatus for crystal growth was of an infrared radiation convergence type,[5] and an 1.5 kW halogen lamp was used as the radiation source. A Czochralski grown crystal of $LiNbO_3$ was cut in desired size and orientation, and the small bars were used as the seed for the FZ growth. The atmosphere of the growth region was 1 atm dry-air through a liquid nitrogen trap.

It was difficult to melt the feed rods with this apparatus. Because the $LiNbO_3$ solid has a low light-absorption coefficient and can hardly be heated by the radiation of the halogen lamp. So a light-absorber consisted of black refractory ring was placed around the molten zone. The absorber was first heated by the radiation of the halogen lamp, and the heat from the absorber made it possible for the rod of $LiNbO_3$ to melt.

The pedestal method, one of the modified FZ methods, was also used in this work. In this method, the seed crystal is mounted on the upper shaft whereas the feed rod on the lower shaft. Then the crystal is pulled up from the melt. In short, the pedestal method is the very reverse to the usual FZ method in the arrangement of seed crystal and feed rod. Table 1 shows the growth conditions of $LiNbO_3$ by the pedestal method.

The usual FZ method was also used for comparison. In this case, the single crystal grown by the pedestal method was used as the feed rod, in addition to the sintered feed rod. Single crystals were grown along the c-axis at the rate of 6 mm/h.

In order to observe ferroelectric domain structures, the grown crystals were cut perpendicular to the c-axis. The c-faces were then polished with a diamond paste and further etched by a solution of one part of HF and two parts of HNO_3 at about 90 °C for 30 min.

When the sintered feed rods were used, the boules grown by the usual FZ method were always found to be polycrystalline. But single crystals were grown by the pedestal method. In the use of single-crystal feed rod prepared by the pedestal method, however, single crystals were grown by the usual FZ method. The reason is considered as follows: In the case of usual FZ method, some particles of $LiNbO_3$ drop down from the sintered feed rod through the melt and then cling on the growing crystal. The particles grow to form variously oriented grains in the crystal.

Figure 1 shows a $LiNbO_3$ crystal grown by the pedestal method, and the growth direction is parallel to the c-axis. This crystal has large holes in the central part and contains a few cracks. These holes probably originate from pores in the sintered feed rod. In the usual FZ method, no hole was observed in the crystal grown from the single-crystal feed rod, but some cracks occured in it.

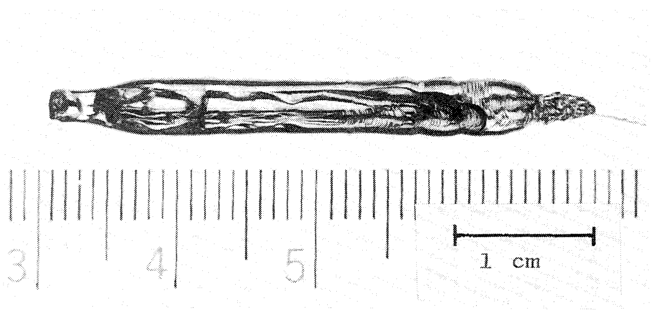

Fig. 1. $LiNbO_3$ crystal grown by the pedestal method, where the growth direction is parallel to the c-axis.

The ferroelectric domains of these crystals were examined by the etching method. Figures 2-6 show the etched c-faces observed

Table 1. Growth conditions of $LiNbO_3$ by the pedestal method

Growth rate (pull up rate of the crystal)		12-24 mm/h
Feed rate (push up rate of the feed rod)		6-12 mm/h
Rotation speed	Upper shaft	10 rpm
	Lower shaft	10 rpm
	(rotated in opposite direction)	
Feed rod diameter		6-8.5 mm
Grown crystal diameter		4-5.5 mm
Growth direction	along the c-axis or a-axis	

under a metallurgical microscope. The crystal grown along the c-axis by the pedestal method was sliced perpendicular to the growth axis. Both the c-faces of the slice are shown in Figs. 2 and 3. In the case of $LiNbO_3$ crystal, the negative side of the c-face is etched fast and etch pits appear, but the positive side is hardly etched.[6)] Therefore, most of the c-face shown in Fig. 2 consists of the positive surface, whereas Fig. 3 shows the negative surface. It can be further concluded that a large domain occupies most of the crystal. A number of small domains which have a polarity opposite to the large domain, are observed only near the edge and central hole of the crystal. The small domains near the edge of the crystal are particularly shown in Fig. 4. In the case of usual FZ method, such small domains existed only near the edge of the crystal. This crystal has no central hole, and small domains were not observed in the central part. Consequently such small domains are considered to appear in the terminal part of

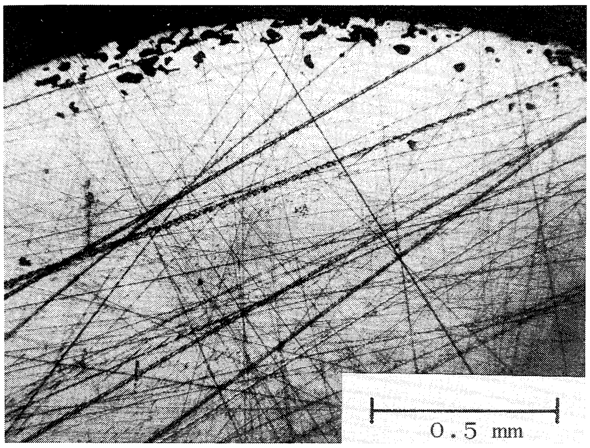

Fig. 2. Etched positive c-face of the $LiNbO_3$ crystal grown along the c-axis.

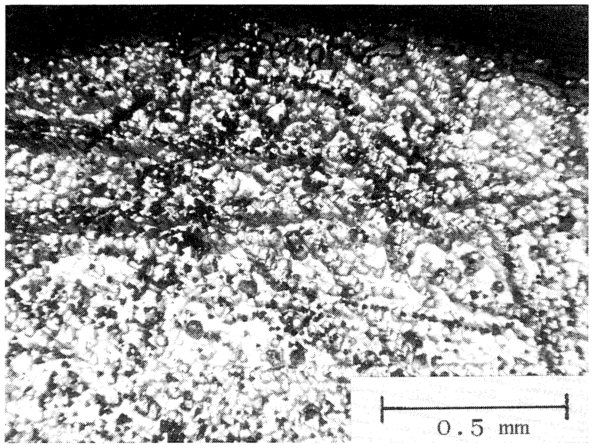

Fig. 3. Etched negative c-face of the $LiNbO_3$ crystal grown along the c-axis.

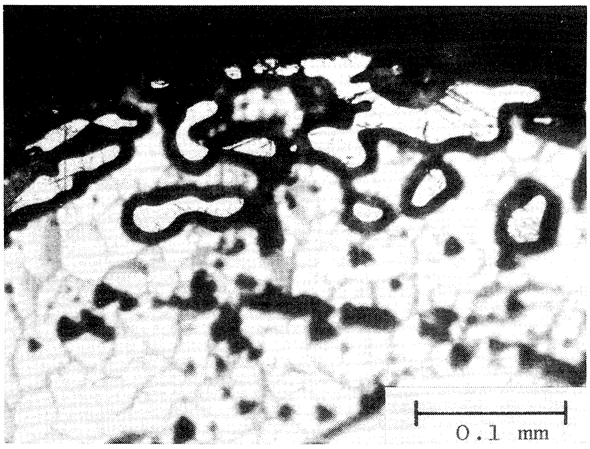

Fig. 4. Small domains near the edge of the crystal (in Fig. 3).

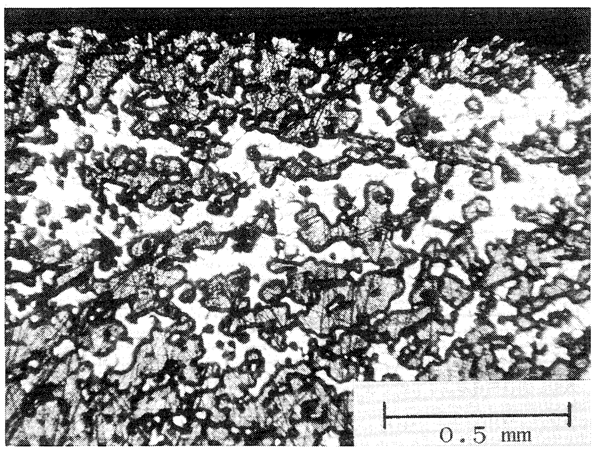

Fig. 5. Domain structure of the $LiNbO_3$ crystal grown along the a-axis.

the crystal.

Figure 5 shows the etched c-face of a $LiNbO_3$ crystal grown along the a-axis. In this case positive and negative domains are randomly distributed. Thus the appearance of single domain was found to depend on the growth direction of single crystal. This may be related with the fact that $LiNbO_3$ is polar only in the c-axis.

A slice cut from the same crystal as that shown in Figs. 2 and 3 was annealed at 1230 °C for 30 min. The annealing temperature is by 20 °C higher than the Curie temperature. Then the slice was polished and etched. As shown in Fig. 6, antiparallel domains appeared in the shape of concentric annual rings. It is evident that the antiparallel domains come from the single domain owing to the annealing. It follows that the antiparallel domain structure has lower electrostatic energy than the single domain one. Nevertheless, it should be noted that the $LiNbO_3$ crystal grown along the c-axis was poled without appling any external electric field, as seen in Figs. 2 and 3. The reason for this phenomenon is not known.

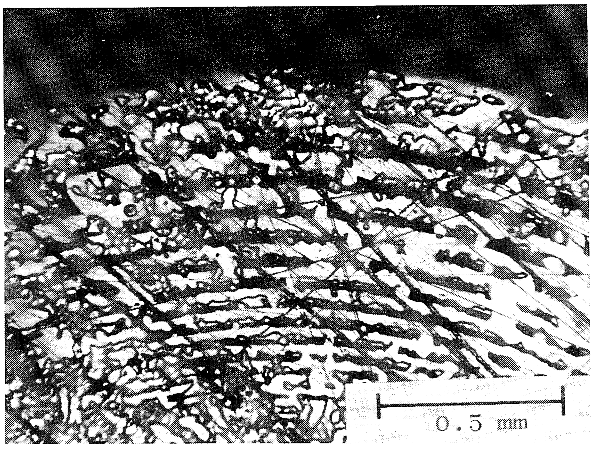

Fig. 6. Domain structure of the c-axis grown crystal of $LiNbO_3$ after annealing.

In conclusion, we have grown $LiNbO_3$ crystals from the melt of congruently melting composition by the FZ method. In the pedestal method, the single crystals were grown from the sintered feed rods. In the usual FZ method, the single crystals were not grown from the sintered feed rods, but were grown from the single-crystal feed rods. In addition, the as-grown crystals were found to have a large single domain without applying any external electric field.

References

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