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Annual Report
GROWTH OF HIGH PHASE-MATCH TEMPERATURE
 LiNbO_3 SINGLE CRYSTALS

for period ending March 15, 1978

P.O. # 6253903

CMR-78-13

CENTER FOR MATERIALS RESEARCH

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Introduction

While congruently grown, low phase-match temperature (T_{pm}) LiNbO_3 single crystals have been successfully used in many low power nonlinear optics device applications; the material property requirements become quite different and more stringent when used in high power device applications. One requirement is that the material should phase-match at a temperature $\geq 180^\circ\text{C}$ to avoid optically induced refractive index damage. Secondly, the material should be optically homogeneous to allow for optimum efficiency in second harmonic generation (SHG). The main purpose of the current program is to develop techniques for the growth of single crystal LiNbO_3 with the desired properties. In Phase I of the program, efforts were made to find a melt composition along with a set of growth parameters which would lead to the growth of high T_{pm} LiNbO_3 crystals with high optical perfection. In Phase II, the program involved the following objectives: (1) To optimize and confirm the melt composition from which LiNbO_3 crystal with $T_{pm} \geq 180^\circ\text{C}$ can be grown; (2) To refine and improve the parameters and techniques used for the growth of these crystals whereby both size and optical homogeneity can be obtained reproducibly; and (3) To provide high T_{pm} , high quality, and reasonable size crystals for evaluation.

Crystal Growth

High phase-match temperature LiNbO_3 single crystals are being grown by the Czochralski technique with equipment as described previously⁽¹⁾ (see also Fig. 1). During Phase I of the program, it was found that high T_{pm} crystals can be grown from Li_2O rich melt doped with MgO . While the effect of MgO appeared to saturate at 1.0 mole %, increased Li_2O in the melt almost linearly increased T_{pm} (Fig. 2). Optical homogeneity was attained by growth with a planar interface through the use of slow pull rate

and fast rotation rate together with a set of suitable temperature gradients.

As of the end of Phase I and the interim report period (September 30, 1978), crystal #515 was grown in the c-axis direction from the melt composition of .54 Li_2O /.46 Nb_2O_5 and 1.0 mole % MgO with a pull rate of 1.6 mm/hr and a crystal rotation rate of 50 rpm. The planar growth interface of this crystal (Fig. 3) has yielded a high degree of crystal perfection. This was indeed the case as shown by the second harmonic vs. temperature measurement (Fig. 4). It shows that a phase-match temperature $>180^\circ\text{C}$ was achieved, together with a single narrow peak ($\Delta T = 0.5^\circ\text{C}$) as measured normally. However, T_{pm} at the top of the crystal was still only 181°C . Since the top was below 180°C and there was a large temperature difference between it and the bottom of the boule, some modifications to the growth conditions were indicated. But the immediate goal was to duplicate and confirm the result of #515 by additional growth runs. Major efforts were made along this line.

To duplicate the melt composition, the charge was replenished with proper amounts of Li_2CO_3 , Nb_2O_5 , and MgO as calculated by the use of appropriate distribution coefficients for Li_2O and MgO (.3 and 1.3 respectively). Four growth runs were made from this charge without success due to diameter control or twinning problems. It was suspected that either the crucible was distorted causing a change in temperature gradient or the melt was contaminated. For this reason, a fresh melt was made for the subsequent run. As a result, crystal #528 was a successful duplication of #515 in both diameter control and interface shape (Fig. 3). Again the second harmonic vs. temperature curve (Fig. 5) shows the crystal to possess a high degree of optical quality, together with a phase-match temperature of 201.5°C . This growth experiment confirmed that high T_{pm} , good quality crystals can be obtained; but the explanation for the increase in T_{pm} from 184° to 201.5°C requires further analysis.

However, as shown by the difficulty encountered in poling, and since the crystal is grown from a highly noncongruent melt, it appears that some improvement is still needed along the line of structural quality.

References

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3. D. W. Carruthers, C. E. Peterson, P. M. Bridenbaugh, and M. Grasso, J. Appl. Phys. 42 1846 (1971).
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Fig. 1. LiNbO_3 Crystal Growing Furnace

1. Alumina Pull Rod	8. Alumina Plate
2. After-Heater	9. RF coil
3. TC signal to Aux. Controller	10. Alumina tubes
4. Pt Seed Holder	11. Firebricks
5. LiNbO_3 crystal	12. Sapphire Rod-Radiation Pyrometer
6. LiNbO_3 melt	13. Temp. signal to main controller
7. Pt crucible	

Figure 2. T_{pm} vs. X_{Li_2O} and C_{MgO} in the melt.

Figure 3. Photographs of high T_{pm} $LiNbO_3$ crystals. Note in particular the solid-liquid interface shape at the bottom of the crystals.

#515

#528

(Actual size)

Figure 4a. SHG vs. Temperature Scan
(Sample from bottom of crystal)

Boule #515

 $x_{\text{Li}_2\text{O}} = 0.540$ $c_{\text{MgO}} = 1.0 \text{ mole } \%$

PR: 1.6 mm/hr

SR: 50 rpm

 $\lambda_f = 1.06 \mu$ $l = 10 \text{ mm}$ $E = 22\%$ $\Delta T = 0.5^\circ\text{C}$

Figure 4b. SHG vs. Temperature Scan
(Sample from top of crystal)

Figure 5a. SHG vs. Temperature Scan
(Sample from bottom of crystal)

Boule #528

 $x_{\text{Li}_2\text{O}} = 0.540$ $C_{\text{MgO}} = 1.0 \text{ mole } \%$

PR: 1.6 mm/hr

SR: 50 rpm

 $\lambda_f = 1.06 \mu$ $l = 10 \text{ mm}$ $E = (\text{not available})$ $\Delta T = 0.5^\circ\text{C}$

Figure 5b. SHG vs. Temperature Scan
(Sample from approximate middle of crystal)

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