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the extraordinary index is dependent on the lithium ion vacancy concentration; decreasing the vacancy concentration by adding excess Li_2O to the melt decreases the value of n_e and correspondingly increases the birefringence, $n_o - n_e$.

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CURIE TEMPERATURE, BIREFRINGENCE, AND PHASE-MATCHING TEMPERATURE VARIATIONS IN LiNbO_3 AS A FUNCTION OF MELT STOICHIOMETRY

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The Curie temperature, birefringence, and phase-matching temperature of LiNbO_3 are shown to vary with the stoichiometry of the melt from which the crystals are pulled. The range of melt stoichiometry, indexed by the Li/Nb mole ratio, was varied from 1.20 to 0.80. This Li/Nb variation changes the Curie temperature, refractive index for the extraordinary ray, and the phase-matching temperature by 120°C, .03, and 320°C respectively. The relevance of these changes are discussed in terms of the susceptibility of LiNbO_3 to index inhomogeneities.

Lithium niobate has been the subject of a large number of investigations recently because of its interesting optical, acoustic, and piezoelectric properties. Recent studies have revealed differences in properties between crystals.

The Curie temperature of $1210 \pm 10^\circ\text{C}$, reported by Nassau, et al.,¹ was obtained by observing the temperature at which a single-domain sample returned to the multidomain state. Pankratz and King,² from heat capacity measurements, found the second order transition at $1177 \pm 15^\circ\text{C}$. Smolenski et al.³ found T_c at 1140°C and further showed that only $\epsilon_{||}$ undergoes a dielectric anomaly, while Shapiro et al.⁴ found T_c at 1210°C and stated that both dielectric constants ($\epsilon_{||}$ and ϵ_{\perp}) show anomalies. Thus, we find a variance not only in the value of T_c but in the dielectric constant behavior as well.

Furthermore, it has been reported that the phase-matching temperature, (T_{pm}), for difference mixing between 0.5145μ and 1.1526μ has varied from $+80^\circ\text{C}$ to -52°C for various crystals.⁵

A recent study by Ballman et al.,⁶ which showed

that the Curie temperature and birefringence of LiTaO_3 were both linear functions of melt stoichiometry, suggested that stoichiometry variations existed in LiNbO_3 , since the phase-matching temperature is functionally related to the birefringence.

In view of these observations, a study was initiated of the Curie temperature, birefringence, and phase-matching temperature as a function of melt stoichiometry. The results of this investigation are here reported.

Crystals were pulled by the Czochralski technique. A detailed description of the growth of LiNbO_3 is given by Nassau et al.¹ The mole ratio of Li/Nb in the melt was varied from 0.80 to 1.20 by addition of Nb_2O_5 or Li_2CO_3 to stoichiometric LiNbO_3 . Dielectric constants were measured at 1 kHz as a function of temperature on a General Radio (type 1673-A) capacitance bridge. The birefringence was determined both with prisms and quartz compensators at 6328 \AA .

A typical plot of dielectric constant vs temperature, in the region of the Curie point, is shown in

Fig. 1 for a sample pulled from a stoichiometric melt. The Curie temperature was found to vary from a maximum of 1190°C for the highest Li composition to 1070°C for the sample pulled from the melt richest in Nb. Figure 2 shows the variation of Curie temperature with melt stoichiometry. Our results agree well with those of Smolenski both in the case of the Curie temperature and the fact that we were also unable to observe a dielectric anomaly normal to the c axis. It is possible that Shapiro's samples were misoriented since she reports dielectric anomalies both \parallel and \perp to the 3-fold axis. With regard to the higher values of T_c reported by others, their samples may have been rich in Li or they may have contained an impurity. (The samples used by Nassau et al. were pulled from a melt doped with 0.05 wt. % molybdenum oxide.)

The phase-matching temperature, T_{pm} , for 1.08 μ and 1.15 μ laser beams are also shown in Fig. 2 as a function of melt stoichiometry. The higher the lithium content of the melt, the higher the phase-matching temperature obtained.

The birefringence as a function of melt stoichiometry was also determined and is shown in Fig. 3. The changing birefringence, $.09 > \Delta n > .07$, is

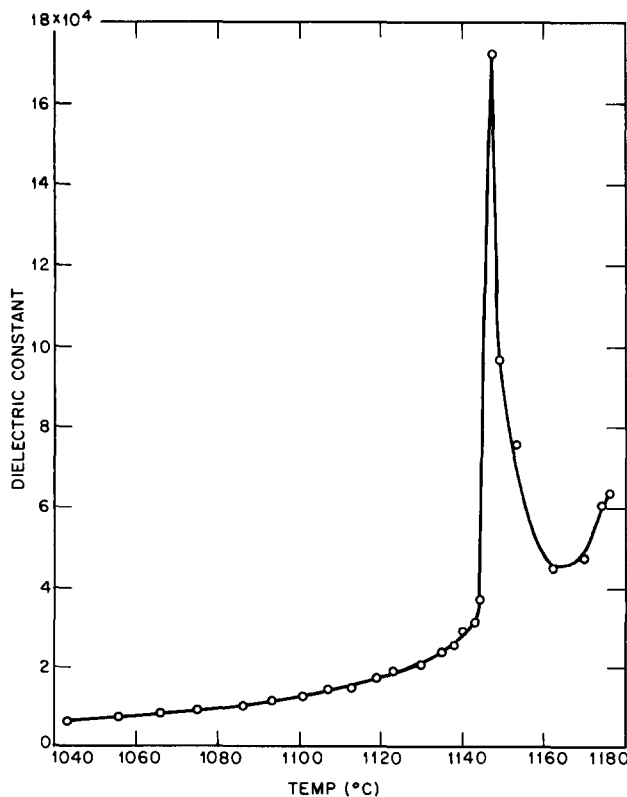


Fig. 1. Dielectric constant parallel to the 3-fold axis as a function of temperature.

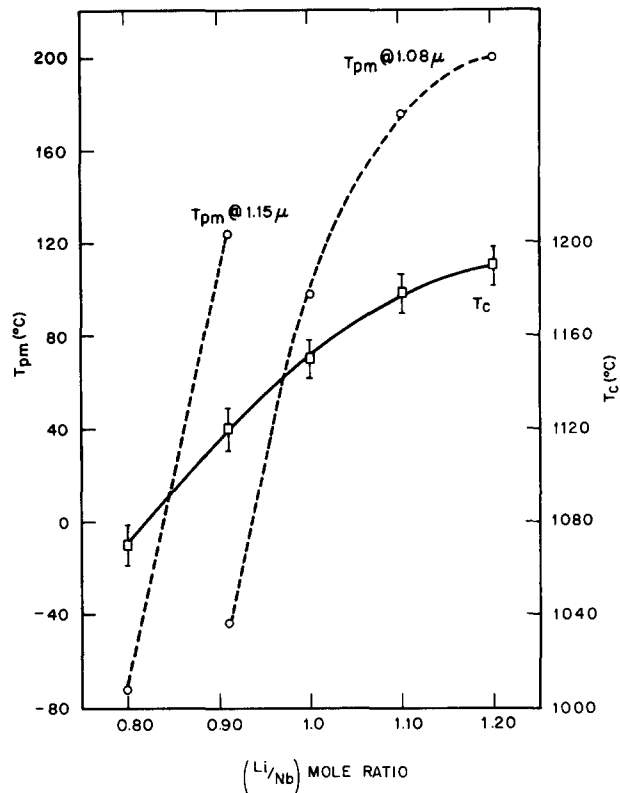


Fig. 2. Curie Temperature, T_c , and phase-matching temperature, T_{pm} , vs melt stoichiometry.

shown to be entirely due to the change in the extraordinary ray.

Analytical determinations of Li and Nb in both the crystal and melt samples indicate that even though the Li/Nb ratios in the melts ranged from 1.20 to 0.80, the corresponding ratios in the crystals pulled from the melts are of the order 1.04 to 0.96. This is in agreement with the further observation that no measurable change in the lattice parameters was detected.

The variations in phase-matching temperature, T_{pm} , can be related to R , the (Li/Nb) mole ratio in the melt as follows. For phase matching normal to the optic axis, the birefringence B defined as $n_2^o - n_2^e$ is equal to the dispersion D defined as $n_2^o - n_1^o$, where n^o and n^e refer to ordinary and extraordinary indices of refraction, and the subscripts 1 and 2 refer to fundamental and harmonic, respectively; that is, $B - D = 0$. If we change $B - D$ by changing R by ΔR , we must compensate with a change in the phase-matching temperature ΔT so as to keep $B - D = 0$. Thus

$$\frac{\partial(B - D)}{\partial T} \Delta T = - \frac{\partial(B - D)}{\partial R} \Delta R.$$

If we make the assumption that only the birefringence B changes with melt stoichiometry (i.e., $\partial D/\partial R = 0$), we find from the measured slopes of Figs. 2 and 3 around $R = 1$ (for $\Delta R = 0.1$) $\Delta B = 0.0072$, and $\Delta T_{pm} = 122^\circ\text{C}$)

$$\frac{\partial(B-D)}{\partial T} = -\frac{0.0072}{122^\circ\text{C}} = -5.9 \times 10^{-5} \text{ }^\circ\text{C}^{-1}.$$

This compares well with the value $\partial(B-D)/\partial T = -5.7 \times 10^{-5} \text{ }^\circ\text{C}^{-1}$ found by Miller, Boyd, and Savage⁷ on another crystal by a different technique. Thus, the assumption that $\partial D/\partial R = 0$ near $R = 1.0$ seems well justified.

If $\partial B/\partial R$ is linear, we would expect T_{pm} to vary linearly with R if $\partial D/\partial R = 0$ over the range of R investigated. Figure 2 shows significant curvature for $R > 1$. For $R > 1$ this may be attributed to an increasing value of $\partial D/\partial R$. Beyond $R = 1.1$, however, the departure from linearity of B vs R must also be considered. Furthermore, it is possible that the Li/Nb ratio in the crystal itself has reached a saturation value even though the melt ratio is increased.

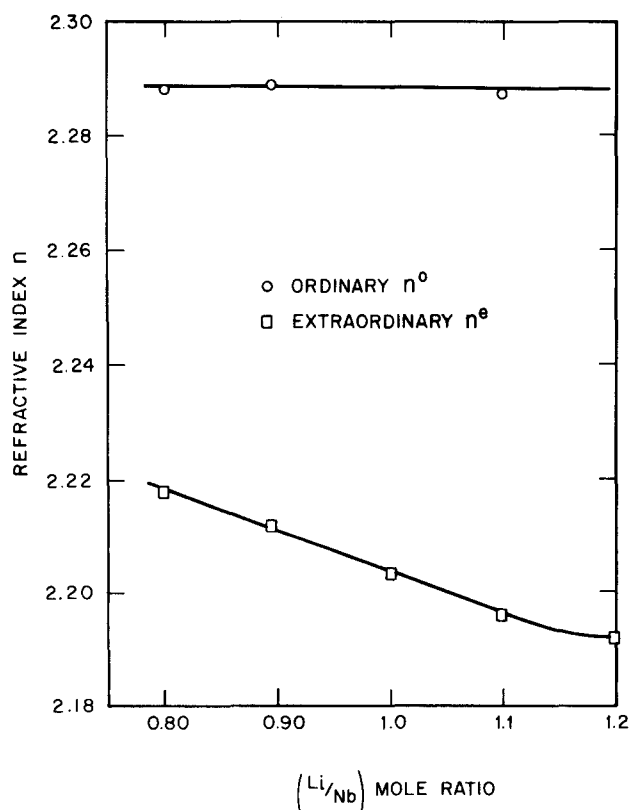


Fig. 3. Refractive index at 6328 Å vs melt stoichiometry.

These results are particularly important because of the susceptibility of LiNbO_3 to index inhomogeneities produced by the laser beam reported previously by Ashkin et al.⁸ The use of LiNbO_3 for parameter amplification and efficient harmonic generation has been restricted because of the index inhomogeneity produced by the light. Above approximately 170°C the index inhomogeneity relaxes faster than it is created. Thus if the phase-matching temperature is higher than 170°C , the index inhomogeneity relaxes faster than it is created. Hence, if the phase-matching temperature is higher than 170°C , the problem of refractive index inhomogeneities can be circumvented and the crystals will then be useful for nonlinear devices. By varying the melt composition, the range of wavelengths that can be phase matched above 170°C is significantly broadened. This makes LiNbO_3 a more versatile material than previously realized. Furthermore, this work suggests that investigation of the effects of adding other impurities to LiNbO_3 would be fruitful. It should be noted that thus far none of the variations in stoichiometry have resulted in significant reduction of the damageability of these crystals at room temperature.

We have shown that the Curie temperature, the birefringence, and the phase-matching temperature of LiNbO_3 all vary drastically with melt stoichiometry. It is probable that the electro-optic, acoustic, piezoelectric and nonlinear properties are also functions of stoichiometry and studies are continuing to determine these functional relationships.

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