REFRACTIVE INDICES OF LITHIUM NIOBATE

D.S. SMITH and H.D. RICCIUS
Division of Physics, National Research Council of Canada, Ottawa, Ontario, Canada

and

R.P. EDWIN
Division of Mechanical and Optical Metrology, National Physical Laboratory, Teddington, Middlesex, UK

Received 8 March 1976

The refractive indices and optical birefringence of congruently grown lithium niobate ($LiNbO_3$) have been measured at 0.633 μm and 3.39 μm in the temperature range 20° to 600°C.

For the successful use of lithium niobate in nonlinear optical experiments, as for instance second-harmonic generation, optical mixing and parametric conversion, a knowledge of this uniaxial crystal's refractive indices as a function of wavelength and temperature is necessary. Recently, Nelson and Mikulayak [1] reported measurements of the refractive indices of congruently grown lithium niobate at 24.5°C accurate to ±0.0002 over the wavelength range 0.404 63 to 3.051 48 μm. Crystals grown from a congruent composition melt [2] are significantly less susceptible to birefringence variations which reduce the useful phase-match lengths of $LiNbO_3$ crystals.

During the course of measuring the wavelength of the 3.39 μm radiation of a CH_4 stabilized laser [3] by mixing the infrared laser radiation with 0.633 μm laser radiation in $LiNbO_3$ an interest developed for predicting the phase-matching temperatures for these mixing processes. In this letter, we present a study of the spectral and temperature dependence of the refractive index of lithium niobate crystals grown from a congruent composition melt.

The principal refractive indices of congruently grown $LiNbO_3$ which is optically uniaxial were obtained for several wavelengths in order to confirm the measurements of Nelson and Mikulyak of Bell Labs. and extend the data to include the wavelength 3.39 μm for which index values were not previously obtained. A prism was cut in the form of a truncated Littrow prism with apex angle nominally 18° and polished faces of dimensions 38 mm by 23 mm from a single crystal boule grown by Union Carbide Corporation. The optic axis was arranged to be parallel to the line of intersection of the planes defining the two polished faces, and one of the polished faces was coated with an opaque aluminium film. This geometry allowed the ordinary and extraordinary indices at 20.0 ± 0.1°C to be measured on the infrared refractometer [4] at the NPL. The refractometer was primarily designed for operation in the wavelength range 8 μm to 14 μm and uses a calibrated monochromator to define wavelength. In this experiment a mercury spectral source was used to produce radiation of 0.435 and 0.546 μm, a He–Ne laser for 0.633 μm and the monochromator for 1.15 and 3.39 μm. The results with the spectral sources are estimated with 95% confidence to be accurate to ±0.000 05 in index, the main uncertainty being inherent in the measurement of the angle of refraction, and the uncertainty for the results at 1.15 and 3.39 μm is estimated to be ±0.0002, due mainly to the uncertainty associated with the wavelength setting of the monochromator. In table 1 our results are tabulated together with the corresponding results of Nelson and Mikulyak obtained at temperature 24.5°C. Their results have been corrected to 20.0°C in a separate

Table 1
Absolute refractive indices for congruently melting $LiNbO_3$

λ (μm)	Polarisation	Present results (20.0°C)	Results of Nelson and Mikulyak (20.0°C)	(24.5°C)
0.43584	o	2.39276	2.3926	2.3928
	e	2.29278	2.2928	2.2932
0.54608	o	2.31657	2.3164	2.3165
	e	2.22816	2.2282	2.2285
0.63282	o	2.28647	2.2866	2.2866
	e	2.20240	2.2026	2.2028
1.1523	o	2.2273	2.2272	2.2272
	e	2.1515	2.1515	2.1517
3.3913	o	2.1451	-	-
	e	2.0822	-	-

Accuracy of first three wavelengths ± 0.00005, ± 0.0002 for the last two.

column using temperature coefficients for a stoichiometric melt obtained by Boyd, Bond and Carter [5] so that the two sets of results can be directly compared. The results are in excellent agreement and within the respective uncertainties.

It was noted during interferometric examination of the prism for homogeneity that the sample was more inhomogeneous for the e ray radiation and was most marked at shorter wavelengths. The only satisfactory explanation we have of this observation is that the crystal axis wanders slightly within the nominal single crystal as observed in other crystals e.g. ruby laser rods [6].

The indices were fitted to modified Sellmeier equations and gave:

$$n_o^2 = 4.9048 - \frac{0.11768}{0.04750 - \lambda^2} - 0.027169\,\lambda^2$$
$$n_e^2 = 4.5820 - \frac{0.099169}{0.044432 - \lambda^2} - 0.021950\,\lambda^2 , \quad (1)$$

where n_o and n_e are the ordinary and extraordinary absolute refractive indices and λ is the wavelength in μm.

The temperature dependence of the refractive index has been obtained by using the end faces of the crystal as interferometer reflectors. Interference maxima are found from the relation

$$2n\,d(T) = N(T)\,\lambda , \quad (2)$$

where $d(T)$ is the length of the crystal parallel to the light beam and $N(T)$ is the order of interference. The change of the temperature from T_0 to T causes a change of the interference order from $N(T_0)$ to $N(T)$. The change of the refractive index with tepmerature was thereby measured by passing plane polarized radiation from a He–Ne laser, operating at either 0.633 or 3.39 μm, through a $LiNbO_3$ crystal with the c axis perpendicular to the light path. The crystal was in an oven in which an atmosphere of pure oxygen was maintained in order to prevent dissociation of oxygen from the compound at high temperatures. As the temperature was increased the variation in intensity due to the refractive index change for that polarization permitted counting the fringes directly; the plane of polarization was rotated with appropriate λ/2 plates to obtain the e and o polarizations, and the emergent radiation was passed through a polarizer to suppress unwanted radiation and focussed onto a photo diode.

The refractive index as a function of temperature is given by

$$n = \frac{\lambda}{2}\,\frac{a_0 + a_1 T + a_2 T^2 + a_3 T^3 + a_4 T^4}{d_{25}[1 + \alpha(T-25) + \beta(T-25)^2]} , \quad (3)$$

where the length of the crystal is represented by the

Table 2
The polynomial coefficients for the least squares fit of the experimental data

	0.633×10^{-4} cm			3.39×10^{-4} cm		
	o-ray	e-ray	birefringence	o-ray	e-ray	birefringence
d_1	$1.898\,802 \times 10^{-6}$	$1.714\,651 \times 10^{-5}$	$-5.051\,392 \times 10^{-4}$	$1.302\,416 \times 10^{-7}$	$1.384\,239 \times 10^{-5}$	$-3.897\,207 \times 10^{-4}$
d_2	$1.814\,362 \times 10^{-8}$	$5.330\,995 \times 10^{-8}$	$-6.389\,624 \times 10^{-7}$	$1.031\,300 \times 10^{-8}$	$4.564\,947 \times 10^{-8}$	$-1.336\,837 \times 10^{-6}$
d_3	$-2.545\,860 \times 10^{-11}$	$-7.023\,143 \times 10^{-11}$	$1.642\,823 \times 10^{-10}$	$-1.316\,482 \times 10^{-11}$	$-5.744\,349 \times 10^{-11}$	$1.567\,855 \times 10^{-9}$
d_4	$1.851\,642 \times 10^{-14}$	$5.590\,826 \times 10^{-14}$	$-2.891\,326 \times 10^{-13}$	$8.880\,433 \times 10^{-15}$	$4.912\,069 \times 10^{-14}$	$-1.236\,676 \times 10^{-12}$
n_o	2.286 363	2.201 587		2.145 088	2.081 587	
B_o			0.084 798			0.063 501

polynomial expansion in terms of the temperature deviation from the reference temperature of 25°C. The thermal expansion coefficients α and β in the a–b crystallographic plane are 1.54×10^{-5} and 5.3×10^{-9}, respectively [8]. The length of the crystal at 20°C was measured with a travelling microscope as 3.988 cm. The number of fringes counted for each wavelength and polarization were fitted by a least squares technique to a fourth order polynomial expansion in temperature. It was found that a third order polynomial expansion was not sufficient.

Eq. (3) can be rewritten as

$$n = n_0(1 + d_1T + d_2T^2 + d_3T^3 + d_4T^4)\,, \qquad (4)$$

where n_0 is the refractive index at 0°C. The polynomial coefficients for the least squares fit are listed in table 2.

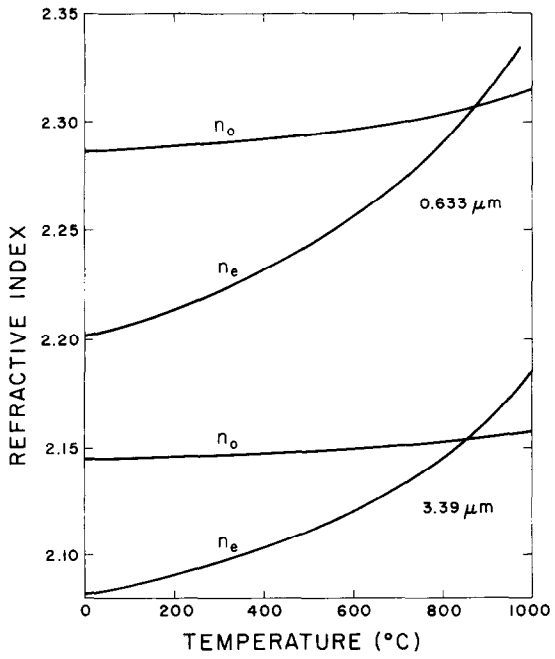

Fig. 1. Temperature dependence of the refractive index of congruently grown $LiNbO_3$ for two He–Ne laser wavelengths.

The temperature dependence of the refractive indices obtained by the method described is shown in fig. 1. The temperature variation of the extraordinary refractive index is quite large, particularly at higher temperatures. It should also be noted that for congruently grown lithium niobate the temperature coefficient dn/dT of the ordinary refractive index no longer becomes negative [5] at longer wavelengths, and the temperature dependence of the refractive indices reported for stoichiometrically grown lithium niobate [7] is slightly smaller than for congruently grown $LiNbO_3$. For comparison, the optical birefringence of the crystal was measured at 0.633 and 3.39 μm from room temperature up to 600°C. In this measurement the optic axis of the crystal was set at 45° to the plane of polarization of the incoming radiation, and the emerging radiation passed through a crossed polarizer. The results obtained agree to within 5 parts in 10^4 with the birefringence determined directly from the measured refractive indices.

From these data the phase-matching temperature

to generate the 0.778 μm difference frequency radiation from 3.39 μm and 0.633 μm He–Ne laser radiation using type I phase matching in $LiNbO_3$ is calculated to be 499 ± 1°C. Apparatus to observe the difference frequency was assembled and a search instituted for it, but it was not found in the temperature range 400 to 600°C. The rate of temperature scan was 10°C per hour, and it was verified that the sum frequency was easily seen at 422°C as predicted. No absorption of light through the crystal, due either to colour centres or line absorption, was found anywhere around 778 nm nor are irregularities seen either in the refractive indices or in the non-linear coefficient [9] in the temperature range investigated. Furthermore, there is no irregularity in the x-ray measurements of thermal expansion [8]. The only report of an irregularity of which we are aware of is that of Ismailzade [10] who saw a phase change in polycrystalline stoichiometric $LiNbO_3$ at 585°C. Warner et al. [11], however found, no optical evidence of this.

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