Optical birefringence study of the ferroelectric phase transition in lithium niobate tantalate mixed crystals: $LiNb_{1-x}Ta_xO_3$

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Abstract
The optical birefringence of a complete solid-solution series of lithium niobate–tantalate crystals has been measured as a function of temperature. It is found that, irrespective of composition, the high-temperature paraelectric phase has a birefringence close to $+0.063$, suggesting that this value arises purely from the oxygen octahedra in the crystal structure. It is also observed that a small addition of lithium niobate to the tantalate produces a crystal that has zero birefringence at room temperature.

1. Introduction

$LiNbO_3$ (LN) is one of the most important crystals, being the equivalent in the field of optics, nonlinear optics and optoelectronics to silicon in electronics. LN single crystals have unique electro-optical, piezoelectric, photoelastic and nonlinear optical properties, and are strongly birefringent. LN is used in laser frequency doubling, nonlinear optics, Pockels cells, optical parametric oscillators, Q-switching devices for lasers, other acousto-optic devices, optical switches for gigahertz frequencies, etc. It is an excellent material for the manufacture of optical waveguides. It is used extensively in the Telecoms market, e.g. in mobile telephones and optical modulators, and is the material of choice for the manufacture of surface acoustic wave devices. In more recent applications it has been periodically poled in order to obtain enhanced second harmonic generation. $LiTaO_3$ (LT) has almost the same crystal structure but different physical properties and is sometimes used as a replacement for LN, particularly for shorter-wavelength applications, although it is true to say that LN is by far the more widely used of the two materials at present. Despite the extensive interest in LN and LT themselves, there has been no crystal structural study of the mixed crystals to date and relatively little investigation of their physical properties. This is a gross oversight, particularly given the existence of compositions with highly unusual

combinations of properties, such as the zero birefringence crystals identified here.

Both LN and LT are isomorphous and crystallize in the space group $R3c$ and have structures of the ilmenite type, which can be considered to be an extreme version of the perovskite family (Megaw 1968). The cations are displaced along the c-axis direction (on trigonal axes) while at the same time possessing alternating tilted octahedra (with reference to pseudocubic perovskite axes the Glazer (1972) tilt system is $a^-a^-a^-$). Unlike, normal perovskites, both Li and Nb/Ta cations lie within oxygen octahedra, although there is evidence from Boysen and Altorfer (1994) that the NbO_6 tilt angle changes towards a true perovskite value with temperature. There are indications too of disorder in the Li positions. The structures are polar and ferroelectric i.e. they possess a reversible spontaneous electric polarization, $\mathbf{P}_s$, by virtue of displacements of the Nb atoms relative to the oxygen framework. Both crystals undergo a high-temperature phase transition (LN: $1195 \pm 15\,°C$; LT: $608 \pm 83\,°C$) to a structure with space group $R\bar{3}c$ in which the Nb displacements disappear but the oxygen octahedral tilts remain, thus becoming non-polar and paraelectric. The large variations in Curie temperature for LT appear to arise from variation of the Li_2O concentration (Barns and Carruthers 1970). Crystal growth and domain properties have been extensively described, for instance by Nassau *et al* (1966a, 1966b) and very large, almost perfect, crystals are currently commercially available. Careful structural analyses of LN and LT were published

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mainly by Abrahams *et al* (1966a, 1966b, 1966c, 1967), with relatively more up to date investigations by Hsu *et al* (1997) and by Boysen and Altorfer (1994). A complicating, but no less interesting factor is that LN and LT crystals can be made with a considerable degree of non-stoichiometry with respect to the Li:metal ratio and this influences the properties Santoro *et al* (1982). Recently, Marshall *et al* (2007) have had success with the growth of LN on a patterned LT substrate by liquid phase epitaxy.

Elegant measurements of the temperature dependence of the principal refractive indices, n_e and n_o, and birefringences ($\Delta n = n_e - n_o$) of LN and LT, from room temperature to above the ferroelectric phase transitions, have been made by Miller and Savage (1966), using an interferometric technique at a wavelength of 632.8 nm. Smith *et al* (1976) also used similar methods to determine the refractive indices and birefringence of LiNbO$_3$ in the range RT—600 °C, at wavelengths of 633 nm and 3.39 μm. By fitting their data to 4th-order polynomials and extrapolating to higher temperatures they were able to conclude that this material changes its optic sign from negative to positive at about 900 °C. In this connection, we point out that the birefringence of stoichiometric LN is negative at room temperature; however in LT it can vary from being slightly positive to being slightly negative with increasing Li$_2$O concentration (Barns and Carruthers 1970), passing through zero birefringence for 49.9 mol% Li$_2$O.

Other measurements of the temperature dependence of the refractive indices of LN include those by Hobden and Warner (1966) and Warner *et al* (1966). The wavelength dependence of the refractive indices of this material has been measured by Boyd *et al* (1967) and by Nelson and Mikulyak (1974). In addition, the refractive indices (and consequently the birefringence) of LN have been demonstrated to increase linearly with pressure up to 7 kbar by Vedam and Davis (1968).

What is less well known, however, is that it is possible to grow single crystals over the whole solid-solution range from pure LN to LT. Crystal growth and density, dielectric behaviour and thermal expansion have been studied by Shimura and Fujino (1977). In addition, the lattice parameters have been measured as a function of composition and temperature (Sugii *et al* 1976). Shimura (1977) measured refractive indices as a function of composition, and showed that it is possible to grow a mixed crystal of zero birefringence at room temperature for $0.95 < x < 0.96$. Birefringence at all compositions was found to be independent of wavelength. Growth of thin films on LT substrates has also been demonstrated for waveguide applications (Kondo *et al* 1979). Xue *et al* (2000) and Xue and Kitamura (2002) calculated the dielectric properties of the mixed system. Calculations of the spontaneous polarizations for the mixed crystals were also published by Xue and Kitamura (2003a) as well as nonlinear optical properties (Xue and Kitamura 2003b). Using bond valence calculations (2005) they also examined the cation positions. Most recently, Zhang and Xue (2007) carried out bond energy calculations to predict the Curie temperatures in pure and doped crystals.

It is interesting to note that, despite the intense interest world-wide in LN and its properties, as far as we are aware there have been no experimental measurements made on the

Table 1. Composition of LiNb$_{1-x}$Ta$_x$O$_3$ Crystals, as determined by EPMA.

Nominal composition, x, of melt	Composition, x, of crystal
0.20	0.486(6)
0.40	0.669(9)
0.60	0.841(3)
0.80	0.929(2)

LN–LT system since 1979. In the present paper we show results of birefringence measurements versus temperature for mixed LN–LT crystals over the whole composition range.

2. Experimental details

The crystals of LiTa$_x$Nb$_{1-x}$O$_3$ were grown by the Czochralski method (Brown 1983). Although this system forms a complete solid-solution series (see e.g. Peterson *et al* 1974), there is a wide separation between the liquidus and solidus lines in the phase diagram and the melting point of LiTaO$_3$ is about 400 K higher than that of LiNbO$_3$. These factors result in the formation of crystals in which the composition varies as the crystal grows and which are considerably more Ta-rich than the melt. The composition of the samples used in the present experiments was determined by electron-probe microanalysis of pieces of the boule adjacent to the areas that were cut for the birefringence measurements. The results of these measurements are shown in table 1. The boules were oriented using back-reflection x-ray Laue photographs, and parallel-sided, polished plates, nominally about 0.5 mm thick, were then prepared, with the three-fold axis lying in the plane of the plate. Since the material is optically uniaxial, it was not necessary to place any other constraints on the orientation of the specimens and so no attempt was made to do so. For the two end-members of the solid-solution series, LN and LT, samples of commercially grown and oriented material were used.

The change in birefringence of the specimens as a function of temperature was determined by the 'rotating-analyser method', using the apparatus described by Wood and Glazer (1980). The light source was a He:Ne laser ($\lambda = 632.8$ nm) and the temperatures were measured by means of a chromel–alumel (type K) thermocouple. Data were collected as the specimens were heated, at heating rates of approximately 1 K min^{-1}. For the pure LN sample, it was necessary to make some minor modifications to the heating stage to enable it to reach the required temperature of about 1250 °C. The rotating-analyser apparatus measures the change in the optical retardation, $\Gamma = (\Delta n)t$, where Δn is the birefringence and t is the thickness of the specimen, as a function of some continuously-changing variable (in this case temperature). For the specimens used in the present study, the changes in Γ were very large (between 40λ and 90λ), thus allowing the variation of Γ with temperature to be determined simply from the temperatures of the maxima and minima of the periodic output signal from the rotating-analyser apparatus (these occur when $\Gamma = (2N + 1)\lambda/4$, where N is an integer, see figure 1).
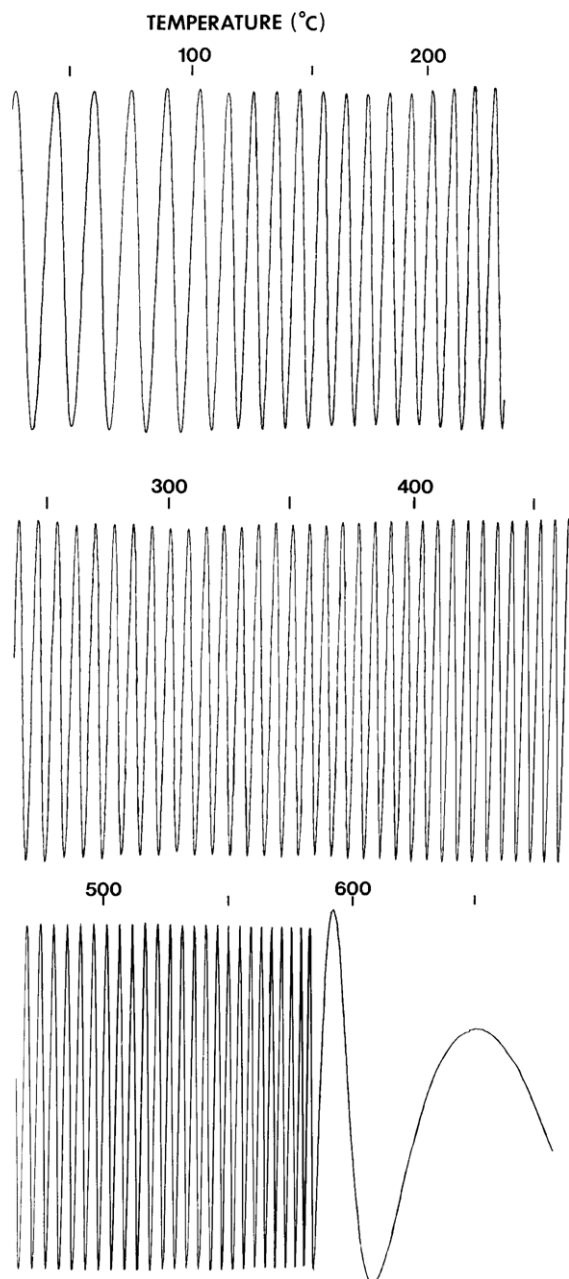
Figure 1. Signal output from rotating-analyser apparatus for LiTaO$_3$.

Figure 2. Temperature dependence of the birefringence $\Delta n = (n_e - n_o)$ of LiNb$_{1-x}$Ta$_x$O$_3$ crystals: from right to left $x = 0$, 0.492, 0.658, 0.841, 0.926 and 1. The horizontal dashed line marks $\Delta n = 0$.

The data recorded above 1175 °C were of poor quality and the interpretation of the trace above 1190 °C (i.e. the final three data points shown in figure 2) is somewhat speculative.

When used as described above, the rotating-analyser method can determine neither the absolute value of the birefringence nor whether Δn is increasing or decreasing. Some further observations at, or close to, room temperature were, therefore, made to establish these quantities. For pure LT, the optic sign at room temperature was found to be positive from a conoscopic figure and the birefringence at room temperature of the specimen used in the heating experiment was determined using an Ehringhaus compensator. For the solid solution with $x = 0.929$, it was also possible to use an Ehringhaus compensator to determine the birefringence at room temperature and the optic sign (positive) was inferred from the optically fast and slow directions of the plate and its known morphology. The remainder of the solid solutions were all found to be optically negative at room temperature, with optical retardations that were too high to allow the use of a compensating plate. Their birefringences were determined by polishing the edges of the specimens into wedges and then counting the interference fringes up the wedge, with the crystal viewed in white light between crossed polars. In the case of LiNbO$_3$, the specimen used in the heating experiment had melted and a value at room temperature of −0.08 was assumed for Δn, based on the results of Bergman *et al* (1968). The mixed crystals all showed a variation in Γ of about 1λ across the specimen, corresponding to a change in Δn of approximately +0.001. The most likely reason for this is a variation in Ta:Nb ratio but it is also possible that it arises from strain in the crystals or from deviations in the stoichiometry (Bergman *et al* 1968, Barns and Carruthers 1970). Table 2 shows the values determined for the birefringence at the positions of the lowest-temperature maxima/minima recorded during the rotating-

Since the change in Γ between adjacent maxima and minima is $\lambda/2$, it is a simple matter to construct the birefringence versus temperature curve, provided that the thickness of the specimen at room temperature and the thermal expansion coefficient of the material is known. In the present work we assumed that the linear thermal expansion coefficient, perpendicular to the three-fold axis, had a value of 2.136×10^{-5} K^{-1} for all compositions (Sugii *et al* 1976); the thickness of the crystals, at room temperature, was measured with a micrometre. Some difficulties were encountered with the LiNbO$_3$ specimen, as the temperatures required approached the limits of the heating stage and deposition of metal from the furnace windings on the windows led to a large reduction in the amplitude of the signal.
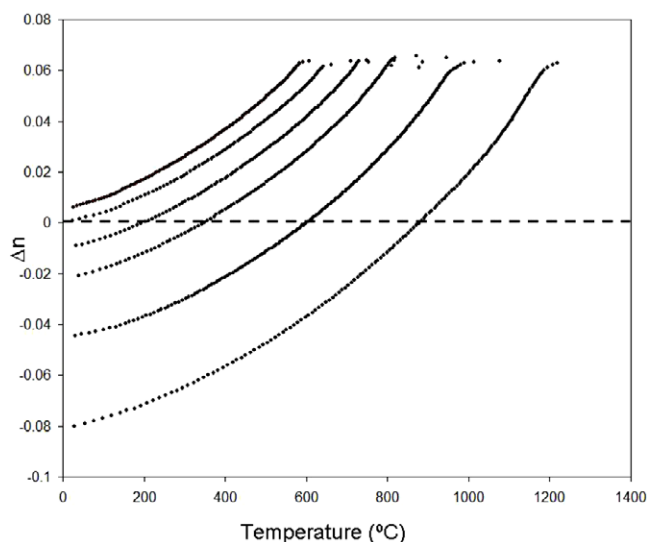
Table 2. Birefringence and transition temperatures of $LiNb_{1-x}Ta_xO_3$ crystals. (Note: For the purpose of this table Δn is defined as $(n_e - n_o)$.)

x	Δn[a]	T (°C)[a]	Δn (20 °C)[c]	T_c (°C)[d]
1	+0.0062	26.7	+0.0059	584
0.928	+0.0008	24.7	+0.0006	643
0.841	−0.0091	31.8	−0.0096	729
0.658	−0.0207	40.3	−0.0216	811
0.492	−0.0446	29.7	−0.0447	952
0	−0.08[b]	29.4	−0.0804	1185

[a] The values of Δn and T given in these columns correspond to those for the lowest-temperature data point from the rotating-analyser experiment. For the mixed crystals a variation in optical retardation corresponding to a change in Δn of about 0.001 was observed across the specimen.

[b] Value taken from Bergman *et al* (1968).

[c] Values at 20 °C estimated by extrapolation of birefringence curves (for details see text).

[d] Estimated temperature of ferroelectric phase transition (for details see text).

analyser experiments. The value for the Curie temperature (584 °C) and room-temperature birefringence (+0.006) of the pure LT sample is consistent with the crystal having 49.1 mol% Li_2O, according to the work of Barns and Carruthers (1970).

3. Results and discussion

Figure 1 shows the rotating-analyser output from the crystal of $LiTaO_3$. On heating, the fringes gradually become closer together showing that the increase in retardation (hence birefringence) accelerates with temperature; however at the phase transition we see a rapid decrease in the frequency of the fringes, indicating that the birefringence now changes much more slowly. The birefringence curves from the set of $LiTa_xNb_{1-x}O_3$ crystals are shown in figure 2. It can be seen that in all cases there is a large change in the slope of birefringence associated with the paraelectric–ferroelectric phase transition. The forms of the birefringence curves and the magnitudes of the changes in birefringence of the two end-members ($\approx$0.057 for $LiTaO_3$ and $\approx$0.143 for $LiNbO_3$) are very similar to those reported by Miller and Savage (1966). Since this phase transition is non-ferroelastic, involving a change in space group from $R3c$ to $R\bar{3}c$, there is no component of the spontaneous birefringence which falls to zero in the paraelectric phase; instead, the transition is between two optically uniaxial phases. In all cases the birefringence becomes more positive as the temperature increases. For the four most Nb-rich samples this involves a change in optic sign, from negative to positive, with increasing temperature, with the crystals, therefore, passing through a point at which they are accidentally optically isotropic. A similar result for $LiNbO_3$ has been reported by Smith *et al* (1976), who estimated that this material became accidentally isotropic when 879 °C $< T <$ 880 °C. This is in almost exact agreement with the results from our present work, in which we found that the isotropic point in $LiNbO_3$ occurred when 878 °C $< T <$ 884 °C. The value of the birefringence
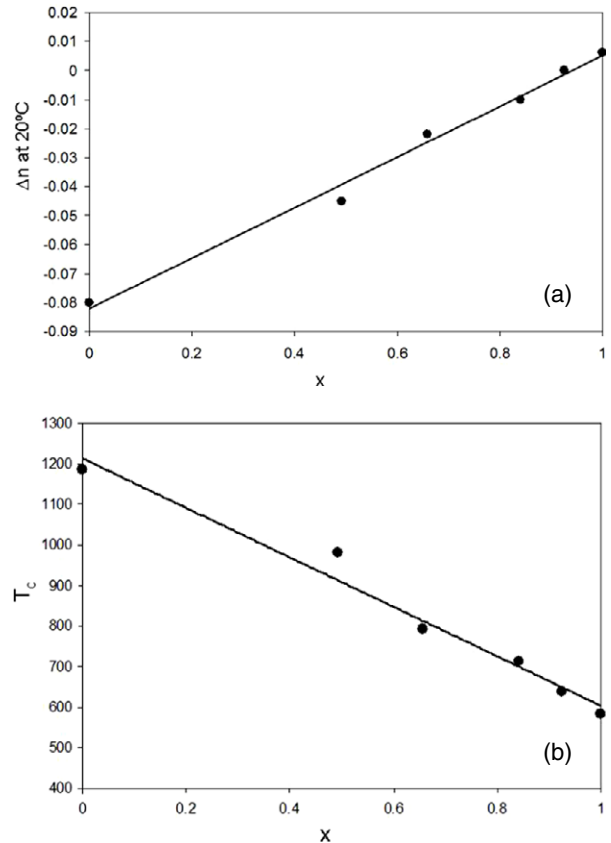
Figure 3. Variation of (a) estimated birefringence at 20 °C and (b) estimated ferroelectric transition temperature (°C) with composition, x, for $LiNb_{1-x}Ta_xO_3$ crystals. The straight lines shown are least-squares fits to the data. $\Delta n = 0.0873x - 0.0821$ with $R^2 = 0.9905$; $T_c = -609.55x + 1213.4$ with $R^2 = 0.9752$.

in the paraelectric phase is remarkably constant across the solid-solution series, lying in the range 0.062–0.064, for all compositions.

Shimura (1977) measured the wavelength dependence of the refractive indices of LNT crystals at 20 °C, concluding that a crystal with $0.95 < x < 0.96$ would be accidentally optically isotropic at this temperature and that the zero birefringence composition was fairly insensitive to the wavelength of the light. For comparison with Shimura's results, we estimated the birefringences at 20 °C in the present study by extrapolation of a second-order polynomial fitted to the five lowest-temperature data points; the results are shown in table 2 and figure 3. It can be seen that the birefringence at 20 °C shows a linear variation with composition, with the accidentally-isotropic point occurring at $x = 0.94$. A similar result for thin films of $LiTa_xNb_{1-x}O_3$ was obtained by Kondo *et al* (1979) who reported the accidentally-isotropic composition at about $x = 0.93$, for a wavelength of 632.8 nm.

Table 2 and figure 3 also show the estimated ferroelectric phase transition temperatures (T_c). Since the spontaneous birefringence does not fall to zero in the paraelectric phase, these values are somewhat subjective; the transition temperature was estimated as being that of the data point at which the birefringence curve showed an abrupt change in slope. The relationship between T_c and composition

Table 3. Quadratic fit for birefringence of LiNb$_{1-x}$Ta$_x$O$_3$ crystals.

x	Quadratic	R^2	T (°C) for $\Delta n = 0$
1	$1 \times 10^{-7}T^2 + 4 \times 10^{-5}T + 0.0049$	0.9999	873
0.926	$9 \times 10^{-8}T^2 + 3 \times 10^{-5}T - 0.00009$	0.9998	599
0.841	$9 \times 10^{-8}T^2 + 3 \times 10^{-5}T - 0.01$	0.9998	348
0.658	$9 \times 10^{-8}T^2 + 3 \times 10^{-5}T - 0.0213$	0.9995	206
0.492	$9 \times 10^{-8}T^2 + 2 \times 10^{-5}T - 0.0443$	0.9995	3
0	$8 \times 10^{-8}T^2 + 2 \times 10^{-5}T - 0.0785$	0.9992	—

appears to be closely linear, in agreement with the results of Shimura and Fujino (1977), who determined the Curie temperatures of LNT single crystals by dielectric constant measurements. In addition to changes in T_c arising from the Ta:Nb ratio, however, the Curie temperature is also a function of stoichiometry i.e. of the Li:(Ta/Nb) ratio; Barns and Carruthers (1970) and Carruthers *et al* (1971) reported variations of 80 °C and 120 °C for single crystals of LiTaO$_3$ and LiNbO$_3$ respectively (with wider ranges for ceramics). Table 3 shows that the birefringence in the polar phase can be fitted to a quadratic in temperature very precisely, from which the values of temperature at which the birefringence changes sign can be obtained.

The fact that all the birefringence values above T_c are nearly constant at a value of around 0.063 for all compositions can be explained in terms of the changes in crystal structures with temperature. On heating, the Nb/Ta displacements along **c** of the ferroelectric phase decrease until they become zero at T_c, whereupon the phase is paraelectric. However, the oxygen tilt system **a$^-$a$^-$a$^-$** is maintained. Boysen and Altorfer (1994) showed that the Nb/Ta displacement decreases with temperature while the NbO$_6$ tilt angle increases. At the same time the strain in this octahedron decreases towards zero at T_c, showing that the octahedron becomes regular. The constancy of Δn above T_c with composition therefore suggests that this value arises from the anisotropy caused by the oxygen tilts *alone* and that the Nb/TaO$_6$ tilt angle can no longer change significantly above T_c (no structural measurements have been made sufficiently far enough above T_c to demonstrate this to date). Thus the difference in birefringence from its maximum value of 0.063 below T_c is related mainly to the Nb/Ta displacement plus a contribution from the corresponding change in octahedral tilt angle.

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