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Defect Structure Dependence on Composition in Lithium Niobate

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Abstract

The lattice constants of stoichiometric $LiNbO_3$ and congruent [$Li_2O:Nb_2O_5 = 48{\cdot}45:51{\cdot}55$] composition lithium niobate at 298 K are $a = 5{\cdot}14739\,(8)$, $c = 13{\cdot}85614\,(9)$ [$a = 5{\cdot}15052\,(6)$, $c = 13{\cdot}86496\,(3)$] Å for Cr $K\alpha_1 = 2{\cdot}28970$ Å in space group $R3c$ with $V = 317{\cdot}941\,[318{\cdot}513]$ Å^3, $M_r = 147{\cdot}846\,[148{\cdot}551]$, $D_m = 4{\cdot}635\,(5)\,[4{\cdot}648\,(5)]$, $D_x = 4{\cdot}6327\,[4{\cdot}646]$ Mg m^{-3} for $Z = 6$, $F(000) = 408\,[409{\cdot}89]$, $\mu = 5{\cdot}116\,[5{\cdot}165]$ mm^{-1}. All reflections in the reciprocal-lattice spheres of both compositions with $(\sin\theta)/\lambda \le 1{\cdot}1$ Å^{-1} were measured, with 746 [769] symmetry independent $F_m^2 > 3\sigma F_m^2$. Final $R(F) = 0{\cdot}0117\,[0{\cdot}0121]$. No atomic disorder was detected in stoichiometric $LiNbO_3$ but 6% Li is missing from all Li sites in the congruent composition. Each missing Li^+ ion is replaced by an Nb^{5+} ion, with compensating vacancies at the Nb site maintaining charge neutrality, as given by the formula $[Li_{1-5x}Nb_{5x}]Nb_{1-4x}O_3$ with $x = 0{\cdot}0118\,(7)$ in the congruent composition. The stability range of the nonstoichiometric composition corresponds to $0 \le x \le 0{\cdot}02$. Lithium vapor-phase equilibration of congruent material at 1373 K or higher temperature is postulated to involve: Nb-ion migration from Li to Nb sites by about 3·1 Å through an octahedral face of O atoms followed by Li atoms filling the resulting vacancies; an exchange between the remaining Nb at Li sites with other Li atoms; and formation of an oriented overgrowth of additional unit cells. The Nb-ion displacement of 0·2768 [0·2701] Å along the polar axis from the mid-position between O-atom planes allows the Curie temperature to be predicted as 1532 [1459] K; the experimental Curie temperature is 1471 [1402] K. Anharmonic thermal vibrations were detected only in the congruent composition.

Introduction

The properties and applications of lithium niobate have been widely studied, resulting in the publication of more than three thousand papers on this material since 1967 and over one thousand since 1980. A detailed review of the physics and chemistry of lithium niobate has been given by Räuber (1978), whose two hundred or more references provide ready access to the literature. The high level of interest in lithium niobate, originating in its combination of useful dielectric, elastic and optoelectronic properties together with the ready growth of large high-quality single crystals from the melt, has recently increased even further as its electrooptic-device use has led to optical switching speeds as fast as 50 ps. In consequence, high-speed switches, modulators, waveguide arrays, multiplexers, filters and polarization converters have been built based on lithium niobate. Stoichiometric lithium niobate melts incongruently. The congruent melting temperature of 1513 K corresponds to the formula $Li_{0{\cdot}946}NbO_{2{\cdot}973}$ (Carruthers, Peterson, Grasso & Bridenbaugh, 1971). Many physical properties are dependent, some with considerable sensitivity, on the Li : Nb ratio as well as on the precise oxidation state of the crystal. An easily measured and strongly composition-dependent property is the Curie temperature of this ferroelectric crystal. Gallagher & O'Bryan (1985) report $T_c = 1471$ (2) K for $LiNbO_3$ and 1402 (2) K for $Li_{0{\cdot}946}NbO_{2{\cdot}973}$, with a range of ±0·007 Li from this nominal congruent composition. A smaller, but still significant, dependence on composition has been found both for the lattice constants and the density by Lerner, Legras & Dumas (1968). Measurements made on crystals with composition-dependent properties clearly have larger variances than those estimated only from the experimental

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uncertainties if the composition has not been well characterized. The general results of the present study may hence be relevant to other materials with detectable departures from stoichiometry. The structural dependence of lithium niobate on composition has been speculated upon by Lerner *et al.* (1968), Nassau & Lines (1970) and others, but has not previously been investigated directly. In the present study the structure of two well characterized crystals, corresponding to the stoichiometric and congruent-melting compositions, has been exhaustively examined and the defect structure determined in relation to some structure-sensitive physical properties.

Sample preparation and characterization

Colorless transparent plates of lithium niobate with dimensions 30 × 10 × 1 mm and oriented normal either to the hexagonal *a*-, [11.0]- or polar *c*-axis were cut from large poled single-crystal boules, grown by Crystal Technology, Palo Alto, CA, from the congruent melt at 48·6 mol% Li_2O by the Czochralski technique. The Curie temperature T_c of a *c*-axis congruent composition plate was determined by differential thermal analysis (DTA) to be 1414·7 K, corresponding to 48·50 mol% Li_2O or the formula $Li_{0\cdot942}NbO_{2\cdot971}$, based on the equation $T_c = 9368\cdot4 - 369\cdot05C + 4\cdot228C^2$ (K) where C is the mol% Li_2O present (O'Bryan, Gallagher & Brandle, 1985). This plate is subsequently referred to as 'congruent' lithium niobate. A second congruent composition plate with [11.0] orientation was assumed to have identical T_c. Two additional plates with composition corresponding to 48·61% Li_2O, in (10.0) and (00.1) orientations, were converted to the stoichiometric composition by lithium vapor-phase equilibration over a period of about 800 h at 1373 K (O'Bryan, Holmes & Kim, 1984). The lithiated composition was determined dilatometrically, by measurement of T_c as 1470 K, to be stoichiometric by H. M. O'Bryan on a small fragment of the *c*-axis plate and use of the preceding equation. The (10.0) plate was assumed to have identical composition. The *c*-axis plate is described hereunder as 'stoichiometric' lithium niobate.

All four plates were further characterized by measurement of the corresponding lattice constant in a Bond (1960) diffractometer. The plates were etched in a fluorine plasma to remove cold-work damage caused by cutting and polishing. The angular and intensity coordinates of the 30.0, 33.0 or 00.12 reflection profiles were measured at four points on either side of each peak around half-maximum-peak height. Each point was measured sequentially three times and the midpoint on the chord at half-peak height was taken as the reflecting position. The crystal and counter were then rotated to allow the profile on the negative side of the direct beam to be similarly measured. Each complete set of measurements was made at five points along the length of each plate, with about 2 mm between points. The linewidths of the 30.0, 33.0 and 00.12 profiles ranged between 85 and 635 arc″. The resulting *a*- or *c*-lattice constant at each point on a plate, corrected to 298 K by the expansion coefficients for well characterized material (Gallagher & O'Bryan, 1985), was based on $\lambda(\mathrm{Cr}\ K\alpha_1) = 2\cdot28970$ Å (*International Tables for X-ray Crystallography*, 1974) for the 30.0 and 00.12 and $\lambda(\mathrm{Cu}\ K\alpha_1) = 1\cdot540598$ Å (Deslattes & Henins, 1973) for the 33.0 reflections. The standard deviation in each lattice-constant measurement was estimated by three methods: an internal estimate based on differences among replications, an external estimate based on the difference between the midpoint at half height and the centroid of the profile, and a third estimate based on differences among the final lattice-constant magnitudes assuming crystalline homogeneity. The resulting lattice constants, given in Table 1, show a variation on the order of 10^{-5} or less across the four samples.

The lattice constants were also determined on a CAD-4 diffractometer, using a ground stoichiometric [congruent] sphere (see following section). A group of 25 reflections with $22\cdot2 \le \theta \le 45\cdot7°$ was measured on both crystals with Mo $K\alpha$ radiation [$\lambda(K\alpha_{1,2}) = 0\cdot709319, 0\cdot713609$ Å (Deslattes & Henins, 1973)] from a graphite monochromator. Values of $2\theta(hkl) = \omega(hkl) - \omega(\overline{hkl})$, with $\omega(\overline{hkl})$ determined at negative 2θ angle in the bisecting mode, were used to obtain the lattice constants at 298 K in Table 1 by the method of least squares. The largest deviate between the CAD-4 and the Bond-method lattice constants is 2·7, hence the e.s.d.'s of the former are most likely underestimated by a factor of two or more. The internal and external estimates of error in the Bond measurements bracket the third estimate obtained from the spread in each value. Since the external estimate contains an unknown factor (the centroid gives a reasonable but unexplored measure of the systematic error due to asymmetry in the profile), the third estimate is taken for this paper but increased by the arbitrary factor $\sqrt{2}$. The lattice constants in Table 1, measured on four different crystals, may be compared with those measured by Abrahams, Marsh, Brandle & O'Bryan (1985) on a single specimen of congruent composition, before and after lithiation.

It is notable that both *a*- and *c*-lattice constants increase significantly, by 0·061–0·064%, as the crystal composition changes from stoichiometric to congruent, see Table 1. If a linear relationship holds between lattice constant and composition, the Bond measurement method would provide a convenient way to determine the composition at room temperature. The density of a stoichiometric plate (about 2·5 g) and a congruent plate (about 1·5 g) were measured by a hydrostatic method as 4·635 (5)

Table 1. *Lithium niobate lattice constants at* 298 K *by Bond and CAD-*4 *methods*

	Bond method				
	a-axis			*c*-xis	
Position on plate	Stoichiometric σ(int)σ(ext)	Congruent σ(int)σ(ext)	Position on plate	Stoichiometric σ(int)σ(ext)	Congruent σ(int)σ(ext)
1	5·147335 (2) (103) Å	5·150513 (15) (150) Å	1	13·856144 (15) (231) Å	13·864938 (17) (279) Å
2	5·147447 (14) (43)	5·150578 (32) (178)	2	13·857066 (6) (298)	13·864970 (13) (238)
3	5·147431 (3) (100)	5·150488 (12) (112)	3	13·856086 (32) (185)	13·864993 (31) (282)
4	5·147410 (7) (103)	5·150476 (17) (72)	4	13·856150 (23) (205)	13·864953 (7) (235)
5	5·147332 (4) (56)	5·150561 (38) (148)	5	13·856238 (9) (172)	13·864952 (21) (220)
Av.	5·147391 (54)*	5·150523 (45)*	Av.	13·856137 (67)*	13·864961 (21)*
	CAD-4 method				
	5·1496 (8)	5·1483 (10)		13·8539 (16)	13·8654 (16)

* Each e.s.d. in the average lattice constant at 298 K has been increased by $\sqrt{2}$, see text.

[4·648 (5)] Mg m^{-3}, compared with calculated densities of 4·6327 [4·646] Mg m^{-3}. The calculated congruent density is dependent on the defect formula. Higher accuracy measurements on a single massive block of lithium niobate are planned.

Structural measurements

A spherical crystal was ground from the stoichiometric [congruent] plate of lithium niobate (see preceding section) with radius 0·0896 (16) [0·1422 (13)] mm and mounted in random orientation on a CAD-4 diffractometer. All reflections having $-h+k+l=3n$, within a full reciprocal-lattice sphere of radius $(\sin\theta)/\lambda \leq 1{\cdot}1$ Å^{-1} and corresponding to $-11\leq h\leq 11$, $-10\leq k\leq 11$, $-29\leq l\leq 30$ [$-11\leq h\leq 11$, $-11\leq k\leq 11$, $-30\leq l\leq 30$], were measured at 295 K under the control of a PDP 11/24-8e minicomputer. Intensity measurements were made by the θ, 2θ step-scan technique with $\Delta 2\theta = 0{\cdot}85° + 0{\cdot}35° \tan\theta$. A total of 4011 [4201] measured reflections resulted in 784 [785] averaged and deposited independent values.* With six symmetry-equivalent reflections in a form, $R_{\rm int} = \sum |F(hkl) - \langle F(hkl)\rangle| / \sum F(hkl) = 0{\cdot}0096$ [0·0085] for all reflections, excluding magnitudes less than 3σ based only on counting statistics. Ten [eight] standard reflections, well distributed throughout reciprocal space, were measured at 6 h intervals: a small linear decline in their intensities was detected and corrected by $I_t = I_o(1 - 0{\cdot}0001170t)$ [$I_o(1 - 0{\cdot}00006801t)$]. Total exposure time $t = 178$ [151] h. The average internal agreement factor for each standard is 0·0085 [0·0058] before correction, 0·0072 [0·0050] afterward. The absorption coefficient of 5·116 [5·165] mm^{-1} resulted in maximum, minimum transmission factors of 53·35 [38·71], 51·01 [34·64]%. Application of Lorentz, polarization and absorption corrections gave F_m.

The variance in F_m^2 ($\sigma^2 F_m^2$) was taken as the larger of V_1 or V_2, where V_1 is the variance due to counting statistics, absorption, attenuation factor and variation in the standards, and V_2 is calculated from the differences within each equivalent form. The 38 [16] magnitudes less than $3\sigma F_m^2$ were excluded from subsequent analysis: none differed by more than 1·5 e.s.d. from F_c^2. A total of 746 [769] observed structure amplitudes thereupon resulted. The reciprocal of $\sigma^2 F_m^2$ gave the least-squares weight in each observation.

Stoichiometric crystal structure

The atomic coordinates and isotropic thermal parameters of Abrahams, Reddy & Bernstein (1966) refined rapidly, based on anisotropic thermal parameters and F_m^2 magnitudes, to $R(F) = 0{\cdot}0399$, $wR(F) = 0{\cdot}0492$ and $S = 5{\cdot}305$. All indicator values hereafter are based on F_m, for refinement based on F_m^2. Evidence for extinction was striking, with 20 large-magnitude low-angle $F_m^2 \ll F_c^2$. Inclusion of a correction term for primary extinction reduced the indicators to $R = 0{\cdot}0166$, $wR = 0{\cdot}0390$ and $S = 2{\cdot}065$, based on the Becker & Coppens (1974) formalism. Correction for secondary extinction alone was less successful but for equal spherulite radii (r) in the primary and secondary extinction and a mosaic spread parameter g, $R = 0{\cdot}0130$, $wR = 0{\cdot}0151$ and $S = 1{\cdot}637$.

The possibility that the atomic thermal vibrations might have an anharmonic component was investigated, with due allowance made for the symmetry restrictions in space group $R3c$ on atoms occupying the Li and Nb sites, using a combined Gram-Charlier, Edgeworth expansion for the probability density function with polar tensors to sixth rank in a locally modified version of the *ORXFLS*4 (Busing, Martin & Levy, 1973) least-squares program. The resulting improvement in wR is without significance at the 0·005 level.

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* Tables of measured and calculated structure factors corresponding to the coordinates in Table 2 for stoichiometric and congruent lithium niobate, also the full set of position and thermal parameters to sixth rank for the congruent composition, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42517 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic coordinates* ($\times10^5$) *and anisotropic thermal displacements* ($\times10^5$ Å^2) *for stoichiometric* (*upper*) *and congruent* (*lower*) *lithium niobate at* 295 K.

The temperature factor expression used is exp $[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Li	0	0	27 872 (65)	1132 (172)	1132	1755 (230)	566	0	0
	0	0	27 909 (53)	2558 (157)	2558	3092 (223)	1279	0	0
Nb	0	0	0	361 (5)	361	323 (4)	181	0	0
	0	0	0	448 (5)	448	359 (5)	224	0	0
O	4757 (12)	34 328 (13)	6336 (8)	674 (17)	540 (14)	673 (10)	297 (16)	−102 (16)	−203 (11)
	4790 (12)	34 299 (12)	6385 (9)	777 (17)	593 (13)	761 (10)	339 (15)	−134 (15)	−228 (10)

The possibility of anisotropy in crystal extinction was also investigated. Least-squares refinement of a model with isotropic extinction and simple harmonic anisotropic temperature factors, based on 3779 unaveraged $F_m^2>3\sigma F_m^2$, led to $R=0\cdot0151$, $wR=0\cdot0182$, $S=2\cdot542$. Inclusion of anisotropy in the model spherulite radius (r) and/or mosaic distribution (g) did not lead to significantly lower indicators, hence it is concluded that anisotropy is absent in the extinction process.

The electron density difference corresponding to the best model with simple harmonic thermal motion was found to have a maximum height of 0·84 eÅ^{-3} at the Nb site, with 0·50 eÅ^{-3} at the O site. The corresponding map based only on $F(hkl)$ with $(\sin\theta)/\lambda\geq0\cdot5$Å^{-1} for which $R=0\cdot0116$, $wR=0\cdot0136$, $S=1\cdot465$ and m (the number of observations) = 670 contained fewer features, with maximum height at the Nb site of 0·17 eÅ^{-3} and 0·19 eÅ^{-3} at the O site. The e.s.d. in electron density in both maps was close to 0·1 eÅ^{-3}. The improvement both in indicator values and in difference electron density thus obtained could be due to elimination of error associated either with inadequate description of the bonding electrons in the model, which would primarily affect only low-angle data, or with residual error in the extinction correction which is generally also largest in the strongest low-angle data.

A series of least-squares refinements followed by calculation of the electron density difference was made in which all terms were eliminated with extinction correction factor (in F_c^2) less than 0·85, 0·75 and 0·65, corresponding to $m=656$, 708 and 722 respectively. The resulting indicators were $R=0\cdot0123$, 0·0117, 0·0123; $wR=0\cdot0143$, 0·0141, 0·0146; and $S=1\cdot530$, 1·523, 1·584 respectively and corresponded to maxima (minima) in the difference maps of 0·19, 0·25, 0·34 (−0·20, −0·22, −0·30) eÅ^{-3}, with largest residuals near atomic sites of 0·05, 0·15, 0·26 eÅ^{-3}. The best fit between model and largest number of observations is hence obtained by giving zero weight to the 38F_m^2 for which the Becker & Coppens (1974) extinction correction is less than 0·75. The resulting atomic coordinates and anisotropic thermal factors, given in Table 2,* do not differ significantly from those obtained excluding the 90 F_m^2 with extinction-correction factors less than 0·85, nor from those with low-angle data excluded. In the final refinement cycle the maximum ratio $\Delta/\sigma=10^{-4}$: for all 784 $F_m>0$, $R=0\cdot0134$, $wR=0\cdot0159$, $S=1\cdot681$. The structural sense was examined by refining the best model above with its 708 $F^2(hkl)$ replaced by $F^2(\overline{hkl})$, which gave $R=0\cdot0131$, $wR=0\cdot0162$, $S=1\cdot748$: the resulting ratio $wR(hkl)/wR(\overline{hkl})=1\cdot149$ confirms the polarity as given by the atomic coordinates in Table 2 and the deposited list of structure factors, since the Hamilton (1965) ratio $\mathcal{R}_{1,690,0\cdot005}=1\cdot0059$. The relation between atomic arrangement and macroscopic dipoles in $LiNbO_3$ was previously determined by Abrahams, Reddy & Bernstein (1966). Atomic scattering factors for Li^+, Nb and $O^{\frac{1}{3}-}$, together with values of f' and f'', were taken (or interpolated) from *International Tables for X-ray Crystallography* (1974).

Congruent crystal structure

The atomic coordinates and isotropic thermal factors of Abrahams, Reddy & Bernstein (1966) were again taken as initial values in refining the congruent composition structural parameters, based on 769 F_m^2. Least-squares refinement with anisotropic thermal parameters led to $R=0\cdot0623$, $wR=0\cdot0857$, $S=10\cdot924$, with numerous large-magnitude F_m^2 notably smaller than the calculated values. Variation of the Becker & Coppens (1974) spherulite radii and mosaic-spread parameters sharply improved the agreement, with $R=0\cdot0123$, $wR=0\cdot0191$, $S=2\cdot445$. The small resulting magnitudes of the Li^+-ion thermal vibration amplitudes, with r.m.s. value of 0·080 Å, and a residual density of 0·85 eÅ^{-3} near the Li^+ site in the difference Fourier series indicated the possible presence of Nb at the Li^+ site.

The likelihood that the Li^+ site contains detectable Nb was investigated by assuming the experimental formula for congruent lithium niobate $Li_{0\cdot942}NbO_{2\cdot971}$ (see above) under the constraint of overall charge neutrality. Assignment of identical anisotropic thermal parameters to Nb at both the Nb and Li sites (see Table 2) led to wide oscillatory parameter shifts, whereas assignment of the Li^+ thermal parameters to Nb at the Li^+ site gave rapid convergence at $R=0\cdot0121$, $wR=0\cdot0163$, $S=2\cdot079$ for all 769 F_m^2. Com-

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* See deposition footnote.

parison with the ordered model gives wR(ordered)/wR(disordered) = 0·0191/0·0163 = 1·1718, for the addition of a single new variable. The Hamilton (1965) ratio $\mathscr{R}_{1,751,0\cdot005} = 1\cdot0054$, hence the improvement in fit is significant at the 0·005 level.

The occupancy of the Li and Nb sites was further investigated. Simultaneous variation of both Li and Nb occupancy at the Li site leads to a singular matrix, hence the restriction imposed of conforming to the experimental formula was lifted by fixing the Li occupancy at several values and refining the Nb occupancy at that site (while maintaining one Nb per formula together with the nonintegral O occupancy that gave charge neutrality), then fixing the Nb occupancy at the Li site and refining the Li occupancy there. A shallow minimum at $wR = 0\cdot01622$ corresponded to an Li-site occupancy of 95·0 (9·3) atom% Li and 5·9 (6) atom% Nb. The resulting nonstoichiometric formula $Li_{0\cdot941}NbO_{2\cdot970}$ cannot be distinguished from $Li_{0\cdot950}Nb_{1\cdot010}O_3$ by diffraction analysis, unless absolute measurements are made with an accuracy of about $\frac{1}{4}$% or better. However, six of the former formulas per congruent unit cell give a calculated density of 4·597 Mg m^{-3}, whereas the latter formula corresponds to $D_x = 4\cdot642$ Mg m^{-3} and is in significantly closer agreement with the experimental density 4·648 (5) Mg m^{-3}. An integral number of O atoms with a nonintegral number of Li and Nb atoms hence most closely represents the formula of congruent lithium niobate, with six such formulas in the unit cell.

The distribution of both Li and Nb atoms was thereupon varied under the constraint of a fully occupied O site and overall charge neutrality, which resulted in an Li-site occupancy of 87·3 (8·7) atom% Li and 6·8 (6) atom% Nb and an Nb-site occupancy of 95·8 (7) atom% Nb (and 4·2% vacancies), with $R = 0\cdot0121$, $wR = 0\cdot01622$, $S = 2\cdot074$ for the 769 $F_m > 3\sigma F_m$. These results correspond to the formula $[Li_{1-5x}Nb_{5x}]Nb_{1-4x}O_3$ with $x \simeq 0\cdot0120$, which was taken as the basis for the final set of least-squares refinements in which the single parameter x replaced the two independent occupancy factors: essentially identical final refinement indicators resulted, with $x = 0\cdot0118$ (7) and all other parameter values in Tables 2 and 3 from this model identical (within 0·1σ) to those obtained with the preceding defect models in their final refinement cycles.* The maximum ratio $\Delta/\sigma = 1\cdot3 \times 10^{-4}$ in the final refinement cycle, with corresponding residual electron density in the final difference Fourier synthesis of −0·23 eÅ^{-3} at the Nb and −0·73 eÅ^{-3} at the Li site, largest residual density along the Nb–O bond of 0·22 eÅ^{-3} and $\Delta\rho_{max} = 0\cdot70$, $\Delta\rho_{min} = -1\cdot30$ eÅ^{-3}. For all 785 $F_m > 0$, $R = 0\cdot0123$, $wR = 0\cdot0163$, $S = 2\cdot058$.

Table 3. *Defect structure site occupancy and extinction parameters for stoichiometric (upper) and congruent (lower) lithium niobate*

Nonstoichiometric lithium niobate may be represented by the formula $[Li_{1-5x}Nb_{5x}]Nb_{1-4x}O_3$: in the congruent composition, $x = 0\cdot0118$ (7) (see text).

Site	Occupancy (% atom)	
Li	100 Li	0 Nb
	94·1 (3) Li	5·9 (3) Nb
Nb	0 Li	100Nb
	0Li*	95·3 (3) Nb
O	100 O	—
	100 O	
Isotropic extinction		
	r(μm)	$g \times 10^{-4}$
	6·0 (3)	0·09 (3)
	9·5 (2)	0·05 (1)

* Assumed, see text.

The exclusion of large extinction-correction terms from the congruent compositon least-squares refinement results in significant parameter shifts, unlike the stoichiometric composition case. Elimination of 11 terms with extinction corrections in F_c^2 less than 0·40, for example, gave $R = 0\cdot0108$, $wR = 0\cdot0142$, $S = 1\cdot799$ but with some parameters that differ as much as 3·9σ from the values in Table 2. Model sensitivity to systematic exclusion without evidence for bias in any term suggests that the most objective results are obtained with all 769 F_m^2, as given by the model in Tables 2 and 3, which is hence taken as most characteristic of congruent lithium niobate.* Finally, the polarity given by the coordinates in Table 2 was examined by refining the model with all $F^2(hkl)$ replaced by their Friedel pairs $[F^2(\overline{hkl})]$, as in the preceding section. The resulting values of $R = 0\cdot0144$, $wR = 0\cdot01825$, $S = 2\cdot338$ confirm the polarity sense, since $wR(hkl)/wR(\overline{hkl}) = 1\cdot125$.

Anharmonicity in the thermal vibrations of this defect structure was investigated by including all thermal-motion tensors to sixth rank in the model, with probability density function given by a combined Gram-Charlier, Edgeworth expansion. Symmetry restrictions in $R3c$ on the contravariant and covariant coefficients for tensors to fourth rank are given in *International Tables for X-ray Crystallography* (1974), those to fifth and sixth rank were determined for this study.* O was the only atom for which the higher-order coefficients refined successfully: of the total 74 such coefficients, $\gamma(333)$, $\gamma(113)$, $\gamma(223)$, $\gamma(123)$, $\varepsilon(11333)$ and $\varepsilon(12333)$ were greater than 6 e.s.d. 12 others were 2 e.s.d. or larger, of which only one was a ζ coefficient. With final indicators of $R = 0\cdot0109$, $wR = 0\cdot0138$, $S = 1\cdot854$ for all 769 F_m^2, the experimental ratio wR(simple harmonic)/wR(anharmonic) = 0·0162/0·0138 = 1·174 compared with the

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* See deposition footnote.

* See deposition footnote.

Hamilton (1965) ratio $\mathcal{R}_{74,677,0\cdot005} = 1\cdot076$, hence the improvement is significant at the 0·005 level. The anharmonic model resulted in a z coordinate for the O atom that differed by as much as 10 joint-e.s.d.'s from that of the harmonic model: the other O-atom parameters also differed widely with e.s.d.'s for the anharmonic model that were as much as an order of magnitude larger than for the harmonic model. The corresponding $\Delta\rho_{\max} = 0\cdot62$, $\Delta\rho_{\min} = -1\cdot09$ e Å^{-3} in the difference Fourier synthesis. It may hence be concluded that the thermal vibrations in congruent lithium niobate are indeed anharmonic but that the atomic positions are defined more precisely on the basis of least-squares refinement with a harmonic vibrational model.

Table 4. *Bond lengths and angles in stoichiometric (upper) and congruent (lower) lithium niobate*

Nb—O*	1·8762 (7) Å		2·1296 (9) Å	
	1·8787 (7)		2·1264 (8)	
O—Nb—O†	99·88 (4)°	79·76 (4)°	88·58 (1)°	165·63 (6)°
	99·61 (4)	79·97 (4)	88·67 (1)	165·98 (6)
Li—O*	2·050 (3) Å		2·271 (7) Å	
	2·053 (3)		2·274 (5)	
O—Li—O†	109·7 (2)°	73·9 (2)°	80·71 (9)°	152·5 (4)°
	109·8 (2)	73·9 (2)	80·64 (8)	152·4 (3)

* Each cation—O distance is given twice more by the threefold axis.

† The angle values are in the sequence: both O atoms at z (see Table 2), both at $z-\frac{1}{6}$, at z and $z-\frac{1}{6}$, at z and $z-\frac{1}{6}$.

Lithium niobate defect structure and composition dependence

The nominal congruent composition of 48·45 mol% Li_2O and 51·55 mol% Nb_2O_5 (O'Bryan *et al.*, 1985) at which single crystals of lithium niobate grow from the melt with uniform composition necessarily corresponds to a defect structure, for which several models have been proposed. Lerner *et al.* (1968) suggested the formation of antisite defects, in which Nb^{5+} resides on some Li^+ sites: charge compensation thereby requires four accompanying Li vacancies (V'_{Li}), assuming all O sites are occupied, to give the formula $Li^+_{(1-5x)}(V'_{Li})_{4x}(Nb^{5+}_{Li})_x Nb^{5+}O^{2-}_3$. A partial stacking fault model was proposed by Nassau & Lines (1970) in which groups of cations along the polar axis form out of normal sequence. Räuber (1978) pointed out that detection of Nb on a 'wrong' site by X-ray diffraction methods would fail because the concentration of Nb at such a site is probably less than 1%. Peterson & Carnevale (1972) reported two types of ^{93}Nb NMR signals in congruent crystals: the intensity of the second line is about 6% that of the normal line. Smyth (1983) agrees with Peterson & Carnevale that this intensity is too high for 1% Nb at the Li site but suggests that it could correspond to a 6% cation stacking fault disorder of the Nassau & Lines (1970) type, due to the formation of line segments with the ilmenite ($FeTiO_3$) cation sequence: he proposes an Nb excess defect model, with $Nb^{\cdot\cdot\cdot\cdot}_{Li}$ most likely. Bollmann (1983) proposes both Li^+ and O^{2-} vacancies, with stacking faults having a role of only minor importance. Sweeney & Halliburton (1983) have postulated O vacancies containing either one or two electrons in partially reduced lithium niobate to explain their optical absorption measurements.

The final results of the X-ray diffraction analysis (Table 3) correspond to an Li-site occupancy in the congruent composition of 94·1 (3) Li, 5·9 (3) Nb atom% and an Nb-site occupancy of 95·3 (3)% Nb. Each missing Li^+ ion in the structure is hence replaced by an Nb^{5+} ion, leaving corresponding (Schottky) vacancies at the original Nb site as represented by the nonstoichiometric formula $[Li_{1-5x}Nb_{5x}]Nb_{1-4x}O_3$ (see also previous section). On the basis of O'Bryan *et al.*'s (1985) results, the phase field for nonstoichiometric lithium niobate is given by $0 \le x \le 0\cdot02$, with $x = 0\cdot0118$ (7) at the congruent composition. It may be noted that the diffraction data, by contrast, show no significant Nb at the Li site and hence no Li at the Nb site in stoichiometric $LiNbO_3$.

The environments of the Li and Nb sites at room temperature are comparable. Both sites occupy distorted octahedra as shown in Fig. 1, with cation–O distances and angles as in Table 4. The Li octahedron is clearly much larger than the Nb octahedron at room temperature and hence can readily accommodate an Nb ion. The temperature factors of Nb at the Li site in congruent lithium niobate are essentially identical to those of Li, *i.e.* considerably larger than those of Nb at the Nb site, as expected from occupying a larger octahedron. Lithium vapor-phase equilibration hence requires Nb ions at the Li site to migrate to the Nb site at the equilibration temperature of 1373 K in the congruent composition through a

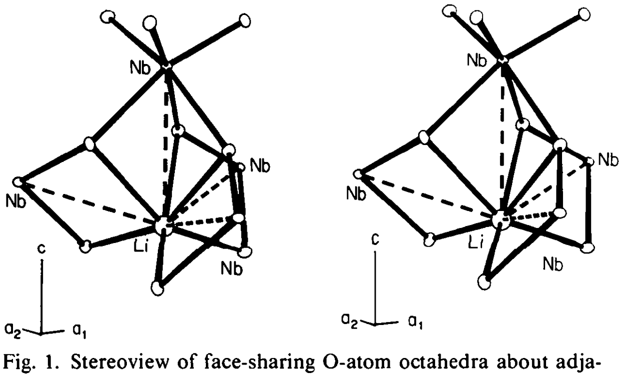

Fig. 1. Stereoview of face-sharing O-atom octahedra about adjacent Nb and Li atoms. The thermal ellipsoids outlined represent 50% probability. In stoichiometric $LiNbO_3$, the dashed line parallel to the polar axis represents a 3·064 (8) Å separation at 295 K. Three next-nearest Nb to Li atoms are also shown with dashed lines representing 3·068 (2) Å contacts. The right-handed hexagonal crystal axes are indicated. The dashed lines also represent possible cation migration paths in lithium vapor-phase equilibration, see text.

minimum distance at 295 K of 3·064 (8) Å along the polar axis, or through 3·068 (2) Å along a direction more nearly normal to this axis as indicated by the three equivalent dashed lines in Fig. 1. Both kinds of short Li–Nb contact are largely metallic in nature (see also Abrahams, Reddy & Bernstein, 1966). The first passes through an octahedral face of O atoms with O–O distances of 2·733 (1) Å: the second crosses an octahedral edge with O–O distance of 2·8046 (3) Å.

The process of lithium equilibration in a congruent composition lithium niobate crystal at 1373 K or higher temperature may be postulated to consist of four stages. In the first, Li^+ ions entering unit cells at the crystal exterior cause Nb atoms at the Li site to become less stable than those at the Nb site, resulting in migration to the Nb site of $4x$ Nb atoms per $[\mathrm{Li}_{1-5x}\mathrm{Nb}_{5x}]\mathrm{Nb}_{1-4x}\mathrm{O}_3$ formula. Migration can take place along the short path connecting adjacent octahedra (see Fig. 1), or along paths connecting next-nearest octahedra. The path parallel to the polar axis, see Fig. 1, requires passage through a potential corresponding to a minimum metal–O distance of 1·578 Å at 295 K whereas the edge-crossing path has a minimum metal–O distance of 1·402 Å. Although increased thermal amplitudes of vibration at the vapor-phase equilibration temperature effectively increase both minimum distances, the potential associated with the former path appears to be lower than the latter. The high-temperature experiments of Abrahams, Levinstein & Reddy (1966) show that the migration path lengths do not vary within experimental error over the temperature range 297–1273 K. In the second stage, vacancies produced at the Li site become occupied by entering Li atoms, causing the first stage to be repeated throughout the crystal interior. In the third stage, the remaining x Nb atom at the Li site exchanges with an Li atom situated at an Li site in another unit cell that likely is closer to the crystal exterior. Such a high-temperature exchange is known to be energetically favorable in view of the congruent composition defect structure. Continuation of the exchange process results in all Li sites finally becoming 100% occupied by Li atoms. In the fourth stage, the excess $x\mathrm{Nb}^{5+}$ ions reach the crystal surfaces to form an oriented overgrowth of LiNbO_3 unit cells in the oxidizing $\mathrm{Li}_2\mathrm{O}$ environment. Following first-stage initiation, it may be expected that all four stages will proceed together.

The composition of congruent lithium niobate $[\mathrm{Li}_{0\cdot94}\mathrm{Nb}_{0\cdot060}]\mathrm{Nb}_{0\cdot952}\mathrm{O}_3$ implies that one Nb atom in approximately every three unit cells occupies an Li site, leaving a corresponding Nb site vacant. A unit cell with vacant Nb site and with all other sites occupied experiences a net −5 charge, one with vacant Nb site but with Nb at the Li site experiences a net −1 charge, and a cell with both sites occupied by Nb a net +4 charge. Each combination necessarily occurs, but the diffraction experiment becomes sensitive to a pattern among the defects only if these are ordered. An additional defect to which the experiment is not sensitive would be a minor occupancy of the Nb site by Li. A direct result of these defects, however, is a weaker atomic interaction in the partially covalent Nb–O bond. Table 4 shows such an effect, with a slight but significant increase in the short Nb–O distance from 1·8762 (7) Å in stoichiometric to 1·8787 (7) Å in congruent lithium niobate. By contrast, the largely ionic Li–O separation is unaffected by substitution at the Li site.

Table 5. *Composition, site occupancy, predicted Curie temperature and* Nb-*atom displacement in lithium niobate*

$\mathrm{Li}_2\mathrm{O}$ mol%	Li(Li)*	Li(Nb)*	Nb(Nb)*	O(O)*	T_c(K)	Δz†
50	1	0	1	3	1486	0·277 Å
49·5	0·983	0·017	0·986	3	1460	0·275
49	0·967	0·033	0·974	3	1436	0·273
48·5	0·951	0·049	0·961	3	1416	0·271
48	0·935	0·065	0·948	3	1395	0·269
47·5	0·919	0·081	0·935	3	1378	0·267
47	0·904	0·096	0·923	3	1363	0·266

* $A(B)$ gives the B-atom occupancy at the A-atom site.

† Based upon $\Delta z = [T_c/1\cdot93\times10^4]^{1/2}$ Å, see text.

Curie-temperature dependence on defect structure

The formula of nonstoichiometric lithium niobate given in the preceding section, together with the value $x = 0\cdot0118\ (7)$ at the congruent composition and the O'Bryan *et al.* (1985) relationship between Curie temperature and growth composition, leads to the occupancy of each atomic site and corresponding Curie temperature as given in Table 5. It is notable that replacement of 9·6 atom% of the Li-site occupancy by Nb atoms, for a crystal composition of $[\mathrm{Li}_{0\cdot904}\mathrm{Nb}_{0\cdot096}]\mathrm{Nb}_{0\cdot923}\mathrm{O}_3$, causes a reduction of over 120 K in Curie temperature.

The Curie temperature may also be predicted, both in stoichiometric and in congruent lithium niobate, by means of the atomic displacement of the Nb atoms at room temperature from the midpoint between adjacent planes of O atoms normal to the polar axis, using the relationship of Abrahams, Kurtz & Jamieson (1968). The displacements of 0·2768 and 0·2701 Å respectively correspond to the predicted $T_c = 1532$ and 1459 K, compared with experimental values of 1471 and 1402 K. In view of the simplifications leading to the original relationship $T_c = (2\cdot00 \pm 0\cdot09) \times 10^4 (\Delta z)^2$ K, both absolute magnitudes and the difference between predicted Curie temperatures are regarded as satisfactory. The relationship may conversely be used to predict the displacement of Nb as a function of composition, using the modified value of $1\cdot93 \times 10^4$ for the average force constant-to-Boltzmann constant ratio, as in Table 5.

Thermal vibration dependence on defect structure

Comparison of the anisotropic thermal factors of stoichiometric and congruent $LiNbO_3$, given in Table 2, shows the latter values to be significantly larger than the former. In addition, the vibrations in the congruent composition have an appreciable anharmonic character due, at least in part, to the Schottky and substitutional defects present. The r.m.s. components of thermal displacement along the principal axes are: Li 0·106 (6), 0·106 (6), 0·133 (9); Nb 0·057 (1), 0·060 (4), 0·060 (4); O 0·063 (1), 0·083 (1), 0·091 (1) Å for stoichiometric and Li 0·160 (5), 0·160 (5), 0·176 (6); Nb 0·060 (1), 0·067 (1), 0·067 (1); O 0·065 (1), 0·088 (1), 0·096 (1) Å for congruent material. The corresponding radial r.m.s. displacements for stoichiometric [congruent] compositions are: 0·115 (12)[0·165 (9)] Å for Li, 0·059 (2)[0·064 (4)] Å for Nb and 0·079 (2)[0·083 (2)] Å for O. These displacements may be compared with the corresponding magnitudes of 0·109 (17), 0·079 (1) and 0·074 (2) Å found by X-ray diffraction on a crystal of uncharacterized composition (Abrahams, Reddy & Bernstein, 1966) and the 0·141 (10), 0·084 (4) and 0·101 (3) Å values found by neutron diffraction on another crystal of unknown composition (Abrahams, Hamilton & Reddy, 1966) at room temperature. The displacements suggest the former crystal was closer to stoichiometric, the latter to congruent composition.

An overall temperature factor B for a further lithium niobate crystal of unknown composition has recently been reported by Krec, Steiner, Pongratz & Skalicky (1984) as 0·33 (8) or 0·37 (8) Å^2, depending on the approximations made and corresponding to overall radial r.m.s. displacements of 0·065 (7), 0·068 (7) Å respectively. Fujimoto (1982) has reported $\bar{u}$(Li) = 0·094 (8), $\bar{u}$(Nb) = 0·067 (8) and $\bar{u}$(O) = 0·085 (7) Å in another crystal of uncharacterized composition. The latter values do not differ significantly from the r.m.s. radial displacements found in the present study for stoichiometric $LiNbO_3$. The e.s.d.'s of all composition-dependent parameters determined on uncharacterized samples are expected to be too small by unknown factors.

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