Effect of stoichiometry on the thermal expansion coefficients of lithium niobate single crystals

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MS received 2 March 1998; revised 20 August 1998

Abstract. The chemical analysis of LiNbO_3 single crystals, with different melt compositions $(\text{Li/Nb})_m = 0.945, 1.0, 1.1$ and 1.2 , grown by slow cooling technique, reveals a remarkable difference in solid and melt compositions. The thermal expansion coefficients along a and c axes, determined by using Newton's ring experiment, are found to increase anisotropically with increase in $(\text{Li/Nb})_m$ ratio. The variation in thermal expansion coefficient with increase in the $(\text{Li/Nb})_m$ ratio is discussed in the light of defect chemistry i.e. the partial replacement of Li^+ by excess Nb^{5+} creates additional cation vacancies to attain the electro-neutrality in the crystal.

Keywords. Single crystal; thermal expansion; non-stoichiometry; defects; octahedra.

1. Introduction

Ferroelectric LiNbO_3 , hereafter abbreviated as LN, is one of the most exciting materials in having a large electromechanical coupling constant, extremely small acoustic losses, optical transparency over a wide range of wavelength, and a very high Curie temperature (1210°C). It has a number of technological applications viz. second harmonic generations (SHG), Q-switch, parametric oscillator, laser modulators and transducer (Boyd *et al* 1964; Kaminov and Turner 1966; Geusic *et al* 1968; Chen 1969).

The LN crystal at room temperature has rhombohedral structure with point group $3m^*$ and space group $R3c$ (Abrahams *et al* 1966). It melts incongruently. Its structure and physical properties are dependent on the ratio of $\text{Li}:\text{Nb}$ (Rauber 1978). Also, doping of it with other cations drastically alters its physical properties.

Several defect models proposed to account for the deviation in Li/Nb or metal/oxygen stoichiometry (Reisman and Holtzberg 1958; Shapiro *et al* 1964; Nassau *et al* 1966; Ohmachi *et al* 1967; Carruthers *et al* 1979; Singh and Deshmukh 1976; Singh and Tikkar 1986) have revealed that the defect concentration has a significant role to play beyond the congruent composition. Ballman and Gernand (1966) have suggested two major types of defects viz. oxygen vacancies and interstitial ions along with two electrons in one vacancy i.e. F_2 centres in LN single crystal. Later, Lerner *et al* (1968)

introduced a concept of native atom in cationic sublattice on the basis of the following three assumptions: (i) niobium ions substituting to Li sites, (ii) lithium vacancies and (iii) interstitial niobium ions. According to him the first one is the most preferred one. On the other hand, Peterson and Carnevale (1972) have promoted the model with Li-vacancies. Nassau and Lines (1975) had suggested stacking fault model, which was well accepted earlier. However, recently a cation substitution model, proposed by Zotov *et al* (1994), describes, on the basis of fully occupied Nb-sites and Li-site vacancies a best average structure which is substantiated by experimental evidences (combined neutron and X-ray diffraction).

While the dependence of properties such as dielectric, electrical conductivity, refractive indices and phase matching temperatures on stoichiometry of LN crystals have been studied extensively (Chung *et al* 1981; Volk 1984; Singh 1988), the investigation on its role in thermal expansion coefficients has been restricted only to the composition with $(\text{Li/Nb})_m = 1$ (Abrahams *et al* 1966; Kim and Smith 1969; Smith and Welsh 1971). According to Abrahams *et al* (1966), the thermal expansion coefficient data is useful in revealing structural disorders. Further, a systematic study of the dependence of thermal expansion coefficients with the variation in the stoichiometry would be of importance due to its direct bearing on elastic and piezoelectric properties.

In the present paper, we report the thermal expansion coefficients (using indigenously developed experimental set up) along a and c axes on technologically important

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high-tech LN crystals with different melt compositions and grown by slow cooling of the melt.

2. Experimental

Lithium niobate single crystals, with four different melt compositions $(\text{Li/Nb})_m = 0.945, 1.0, 1.1$ and 1.2 , were grown by slow cooling (Deshmukh and Singh 1972). The starting materials Li_2CO_3 and Nb_2O_5 were procured from Fluka AG, Germany. These were mixed in the above-mentioned stoichiometric proportion, ground and sintered for 12 h at 900°C in a platinum crucible. The temperature was steadily raised at the rate of 40°C/h to 1300°C which is well above the melting point (1253°C). After the melt had been kept at this temperature for 12 h, it was cooled down at the rate of 5°C/h . At 1250°C , a seed crystal of predetermined orientation was introduced in the melt and the slow rate of cooling maintained till it reached 1100°C , which is below the eutectic temperature (1160°C). The crystals thus obtained were annealed in atmospheric air at 1100°C for 12 h, and subsequently the temperature was allowed to fall at a faster rate of 50°C/h . The prepared crystals of LN were finally oriented by optical method and their faces were ground and polished to normal to the crystallographic a and c axes. The irregular shaped crystals were polished mechanically, and etched in one part of HF acid and two parts of HNO_3 at boiling point of about 110°C . The disturbed surfaces were then polished very rapidly. The crystals thus obtained were colourless, clear and transparent, with dimensions $1.5 \times 1 \times 0.5 \text{ cm}^3$. The solid (final) compositions of each crystal $(\text{Li/Nb})_c$ were estimated by chemical analysis (atomic absorption spectroscopy, plane photometry) at the Institute of Chemistry, University of Uppsala, Sweden.

X-ray diffraction (XRD) scans were recorded on powder of crushed and sieved single crystals with the help of PW 1700 X-ray powder diffractometer using $\text{CuK}\alpha$ radiation at the scanning rate of $2\theta = 2.4^\circ/\text{min}$.

Thermal expansion coefficients along a and c axes of LN single crystals were determined by a home made Newton's ring assembly designed especially to give variation in temperature. Other than a heating assembly, part-8 of figure 1, which comprises of a brass disc of 2.5 and 3 cm diameter and thickness, respectively and is fitted on top of the rectangular fire brick block grooved precisely to fit a strip heater of dimension $4 \times 1 \times 0.2 \text{ cm}^3$ in flat position on the top, the rest of the assembly was the usual Newton's ring assembly. The crystal was placed on the metal plate with its reflecting surface facing towards the lens.

During the measurements, at each set temperature, the crystal was allowed to attain thermal equilibrium for a dwell time of 900 s. The temperature was measured with an accuracy of $\pm 0.5^\circ\text{C}$ using pre-calibrated standard

Chromel–Alumel thermocouple. The temperature gradient within the sample may be neglected, since it is less than 0.5°C/mm , i.e. the instrumentation constant.

2.1 Principle

The thickness of the air film, enclosed by the lower surface of lens and upper surfaces of the crystal introduces the path difference between the rays reflected from these surfaces, in turn the interference. The air film thickness d for dark ring (due to destructive interference) is:

$$2d = 2n\lambda/2, \quad (1)$$

and d' for bright ring (due to constructive interference) is:

$$2d' = (2n + 1)\lambda/2. \quad (2)$$

Let d_1 be the air film thickness at T_1 , thereby satisfying the condition for constructive/destructive interference, when the Newton's ring under consideration is bright/dark. The successive appearances of bright/dark ring are related with the change in air film thickness d_2 as a result of thermal expansion of the crystal. Thus

Figure 1. Newton's ring assembly for determination of thermal expansion coefficient.

$$\Delta d = d_1 - d_2 = x\lambda/2, \quad (3)$$

where, x is the number of times bright/dark ring appears, d_2 the air film thickness at temperature, T_2 and λ the wavelength of light used. Accuracy in the measurement of change in the air film thickness, in turn its expansion, is $\lambda/2$. The thermal expansion coefficient α is given by

$$\alpha = \frac{\Delta d}{l\Delta T},$$

$$= \frac{x\lambda}{2l(T_2 - T_1)}, \quad (4)$$

where l is the thickness of the specimen.

Since we have used sodium vapour lamp, theoretical precision of the thermal expansion measurement is 294.5 nm. The number of rings shifting across the cross wire was counted as a parametric function of temperature while heating and cooling, so as to determine the thermal expansion coefficients of the LN crystals, using the expression given in (4).

2.2 Calibration

A well-polished rectangular slab of silicon (single crystal) with dimensions $0.4 \times 0.4 \times 0.09$ cm³ (prepared carefully) was used to calibrate/standardize the experimental setup. Figure 2 depicts the variation of sample thickness with temperature. The value of α ($2.39 \times 10^{-6}/^\circ\text{C}$) thus obtained following regression agrees with $2.3 \times 10^{-6}/^\circ\text{C}$, as reported by Lovell *et al* (1979).

3. Results and discussion

Figure 3 displays the diffractogram of LN crystal with $(\text{Li/Nb})_m = 1.01$. All the experimental lines agree with the standard JCPDS data corresponding to LN, thereby indicating the absence of impurity precipitation. Single

Figure 2. Calibration curve (expansion (Δd)/number of rings vs temperature (t)); hollow circles $\rightarrow$ experimental data points; continuous line $\rightarrow$ after regression.

Figure 3. X-ray powder diffraction pattern of LiNbO_3 .

crystal nature of each sample was confirmed by taking Laue pattern.

The chemical compositions of the crystal as determined by its chemical analysis are compared with the melt composition (table 1). Except for 48.5Li₂O : 51.5Nb₂O₅, the crystal compositions of almost all the samples were observed to be different from that of the melt composition. Similar results have also been reported by Polgar *et al* (1979). The deviation in the crystal composition (Li/Nb)_c from the melt (Li/Nb)_m, in general, is chiefly linked with the relative losses of Li₂O and Nb₂O₅ individually and/or both during the crystal growth. Particularly, for higher content of Li₂O in melt composition, its losses increase whereas, for lower content of Li₂O in the melt composition, Nb₂O₅ losses dominate. At a critical composition (48.5Li₂O : 51.5Nb₂O₅), possibly Li₂O and Nb₂O losses become quantitatively comparable. Thus, in the crystalline samples of many compounds nonstoichiometry is noticed, which is not so well understood from their phase diagrams.

LN is a nonstoichiometric compound and it forms a continuous solid solution Li₂O–Nb₂O₅ in the Nb rich side (47–50 mol% Li₂O). Lithium losses *vis-à-vis* increase in Nb⁵⁺ content lead to formation of solid solution. Since the ionic sizes of Li⁺ (0.67 Å) and Nb⁵⁺ (0.70 Å) are comparable, partial substitution of the latter ion at lithium regular sites (Nb_{Li}^{••••}) is preferred rather than at interstitial sites (Nb_i^{••••}). Such partial substitution creates additional

Li⁺ vacancies in the vicinity of Nb_{Li}^{••••} so as to achieve the charge neutrality according to the formula,

i.e.,

where, Li_{Li}, Nb_{Nb} and O_O represent lithium, niobium and oxygen atoms at their regular sites, respectively; Nb_{Li}^{••••} denotes Nb ion with four unshared electrons at lithium regular site and □ is the vacancy. Similarly in Li₂O rich side, Nb-vacancies would be expected according to the relation

The decrease in density of the LN crystal (table 1) with the decrease in Nb content rules out the charge compensation mechanism via oxygen vacancies. Holms and Minford (1987) have also unambiguously rejected the oxygen vacancy mechanism on the basis of accurate density (ρ) measurements. Lerner *et al* (1968), on the basis of results obtained towards density of LN (increase in ρ with Li₂O losses), have proposed that unit cells of LN are lost in proper stoichiometric ratio, as the Li₂O content decreases according to reaction (5).

Table 1. Melt and crystal compositions, %Li⁺ vacancy and density of LN single crystal with different Li/Nb ratio.

Starting composition (Li ₂ O/Nb ₂ O ₅)	Melt composition (Li/Nb) _m	Crystal composition (Li/Nb) _c	Actual composition (Li ₂ O/Nb ₂ O ₅)	Li ⁺ vacancy (%)	Density (g/cm ³)
48.6/51.4	0.945	0.948	48.68/51.32	4.96	4.61
50/50	1.000	0.954	48.83/51.17	4.39	4.55
52.4/47.6	1.100	0.969	49.22/50.78	2.39	4.48
54.6/45.4	1.200	0.980	49.5/50.5	1.88	4.45

Table 2. Comparison of thermal expansion coefficients α_a and α_c for different (Li/Nb) ratio.

Composition (Li/Nb) _m	α _a (°C ⁻¹)	α _c (°C ⁻¹)	Reference
0.945	14.862 × 10 ⁻⁶	6.544 × 10 ⁻⁶	Present study
1.000	15.482 × 10 ⁻⁶	6.012 × 10 ⁻⁶	Present study
1.100	15.846 × 10 ⁻⁶	7.012 × 10 ⁻⁶	Present study
1.200	16.012 × 10 ⁻⁶	7.362 × 10 ⁻⁶	Present study
1.000	16.700 × 10 ⁻⁶	2.000 × 10 ⁻⁶	Abrahams <i>et al</i> (1966)
1.000	15.000 × 10 ⁻⁶	7.500 × 10 ⁻⁶	Kim and Smith (1969)
1.000	15.400 × 10 ⁻⁶	7.500 × 10 ⁻⁶	Smith and Welsh (1971)

α_a → thermal expansion coefficient along *a* axis;

α_c → thermal expansion coefficient along *c* axis.

Above results and discussion allow to represent general cation-substituted LN (nonstoichiometric) crystals by

where, m_1 and n_1 are the Li and Nb occupancy at Li site, m_2 and n_2 are the occupancies at the ideally empty octahedral sites and m_3 , n_3 are the corresponding occupancies at the regular Nb sites. Equation (5) describes not only the Li/Nb vacancy models, but also the Li-Nb antisite defects ($n_1 = m_3$), and Li-split ($m_2 = 0.0$) proposed initially by Shiozaki and Mitsui (1963). Although Lerner *et al* (1968) have considered antisite defects (Li-Nb) as very probable, a meticulous investigation by Zotov *et al* (1994), combining neutron and X-ray data refinement, could not detect Li on Nb sites. Also, Li^+ at vacant octahedron has not been detected (Zotov *et al* 1994). The vacancy concentration obtained by taking all the above facts into consideration indicates commensurable increase with increasing Nb_2O_5 content (table 1). In nut shell, the lithium vacancy describes the best average structure of LN crystals under investigation.

The LN crystal being rhombohedral, with symmetric point group $3m$ and space group $R3c$, two coefficients of thermal expansion are expected viz. (i) α_a , describing the longitudinal effect in X-Y plane i.e. along the a axis and (ii) α_c , describing the longitudinal effect perpendicular to X-Y plane i.e. along the c axis. The experimental thermal expansion coefficients along the a and c axes for different melt compositions, in general, are observed to increase with the increase in the Li/Nb ratio (table 2). Particularly, expansion along the a axis is larger than along the c axis, indicating an anisotropy. Furthermore, the data given in table 2 and figure 4 (a continuous line is only a guide) indicates relatively a steeper increase in α_a compared to α_c with non-stoichiometry. A comparison of the present values of α_a and α_c with earlier reported values for congruent composition (table 2) reveals a close agreement between the two. However, an observed small deviation in the values of α_c is attributed to the difference in evaporation losses during the crystal growth (variation in techniques).

Megaw (1968) during experiments on thermal expansion has made the following important observations: (i) the nearly regular thermal expansion of the a edge of a unit cell is mainly due to tilting of octahedra; the change in size of octahedra plays a minor role in that direction, (ii) the change in edge length of the octahedra is responsible for the change in thermal expansion parameter, as the displacement of Nb decreases with rise in temperature as does the edge length s , (iii) expansion or contraction in crystals is dependent on the rise or fall of a scalar quantity, temperature, (iv) coefficient of

Figure 4. Variation of α_a and α_c with change in Li/Nb stoichiometry.

thermal expansion of a crystal for all systems, except cubic, is dependent on the direction because of anisotropy, and (v) change in edge of a unit cell is more along the a axis than the c axis.

The Li^+ and Nb^{5+} in LN single crystal occupy special positions on the 3-fold axis such that 2/3 of the octahedral sites (oxygen atom at the corners) are occupied by them. Additionally, the cation sequence along the 3-fold axis isNb Li $\square$ Nb Li $\square$ The octahedral tilt, oriented with pair of opposite forces perpendicular to triad axes, displaces the Nb ions in the direction of triad. Actual displacement, however, depends on the (Li/Nb) ratio and temperature. The increase in non-stoichiometry causes an increase in octahedral tilt. This in turn, increases the thermal expansion coefficient along a axis. This explains the observed increase in α_a with the increase in Li/Nb ratio (table 2).

4. Conclusion

The nonstoichiometry in LN single crystals introduces Li^+ vacancies in its regular sites, which alters the dynamic and static disorder and can best be explained by experimentally determined values of thermal expansion coefficients.

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