where $V_1$ and $V_2$ are the volumes at $T$ and 0 K, respectively. $P$ and $Q$ are the material constants, and $E$, the thermal energy expressible in terms of Debye specific heat function.

Fischmeister (1956) and Pathak and Pandya (1960) have confirmed the validity of equation (4.34) for high temperature thermal expansion of a number of halides. Fletcher (1957) has, however, pointed out that the equation is too insensitive for useful prediction of the thermal expansion behavior. Nevertheless, his alternative models do not agree with the experimental data. Morley (1969) separated the free energy of the crystal into two parts, static and vibrational and hence implying the equation of state obtained the nearest neighbor separation as a function of temperature. His predictions showed satisfactory agreement with the experimental data for potassium halides. Leibfried and Ludwing (1961) have also made similar predictions from the empirically fitted coupling parameters of potential energy.

4.5 EXPERIMENTAL DETAILS

4.5(a) SAMPLE PREPARATION

The prepared LiNbO$_3$ crystals with different compositions were cut along $a$- and $c$-axes (as discussed in chapter-III). 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 later polished very rapidly. The dimension of the crystals was 1.5x1x1x0.5 cm$^3$.

4.5(b) CONSTRUCTIONAL DETAILS

The heating assembly and the Newton's ring apparatus were designed and assembled to provide temperature variation as shown schematically in figure 4.3. This
laboratory made setup comprises (i) heating assembly and (ii) Newton’s ring apparatus. The details are as given below.

4.5(b1) HEATING ASSEMBLY

To ensure uniform heating of the sample under test, the heating assembly was fabricated by taking a rectangular block of a fire-brick of dimensions 5.5x11.5x2 cm³

Fig. 4.3: Schematic representation of assembly to measure thermal expansion coefficient of solid samples.

Fig. 4.4: Clay fire-brick

Fig. 4.5: Grove in brick of dimensions (4x1 x 3) cm³
respectively, was machined. This disc was fixed into the block described above by using three screws at an angle of 120° to each other (Fig. 4.6). The heating assembly was then mounted on a triangular base, made up of asbestos sheet, provided with three screws of length 10 cm (Fig. 4.7). The temperature gradient within the sample = 0.5°C-mm⁻¹ may be neglected since it is lower than the instrumental constant.

4.5(b2) Newton's Ring Assembly

Two wooden annular discs with inner diameter of 7.5 cm and outer diameter of 4 cm were procured. The planoconvex lens of 100 cm focal length was fixed in between the above mentioned wooden annular discs. The lower annular disc was fitted with three rectangular aluminum strips of diameter 4×1×0.1 cm³ at an angle of 120° to each other so that the planoconvex lens can be lowered or raised easily in the cavity as depicted in figure 4.7. Sodium vapor lamp was used as monochromatic source. Its beam was made parallel with the help of double convex lens by placing the source at its focal point. The parallel beam was allowed to fall on a plane glass plate (dimensions 4x2.5x1 cm³) held inclined at an angle of 45° to the incident beam. The light thus reflected from the glass plate falls on the planoconvex lens, below which the sample under
investigation was placed as shown in figure 4.3. The tip of a pre-calibrated Chromel–Alumel thermocouple was kept in the close vicinity of the sample to record its actual temperature. The emf of the thermocouple was measured using digital voltmeter having high input impedance <10 MΩ.

4.5(c) PRINCIPLE

Let \( d \) be the thickness of air film enclosed by the lower surface of planoconvex lens and upper surface of sample. The path difference between the rays reflected from the upper surface of the sample and the lower surface of the planoconvex lens for normal incidence, \( \Delta \), is given by:

\[
\Delta = 2d = \frac{2n\lambda}{2} \quad \text{for dark fringe} \quad (4.35)
\]

and

\[
\Delta = 2d = \frac{(2n+1)\lambda}{2} \quad \text{for bright fringe} \quad (4.36)
\]

where \( n \) and \( \lambda \) are the order of band and the wavelength of light (sodium) used, respectively. The increase in temperature of the sample gives rise to the decrease in air film thickness chiefly due to thermal expansion of former. Let \( d_1 \) be the thickness of air film at temperature \( T_1 \). So for the dark fringe

\[
2d_1 = n\lambda. \quad (4.37)
\]

Let \( d_2 \) be the thickness of the air film when the temperature was increased from \( T_1 \) to \( T_2 \) that shifts the order of fringe from \( n \) to \( (n + x) \). Now the condition for dark fringe is,

\[
2d_2 = (n + x)\lambda. \quad (4.38)
\]

From equations (4.37) and (4.38), one can obtain
\[2(d_2 - d_1) = \lambda[n + x - n]
\]
\[= x \cdot \lambda
\]
\[\therefore (d_2 - d_1) = \frac{x \lambda}{2}.
\]

(4.39)

The change in the thickness is due to the variation in the temperature. Hence, the thermal expansion coefficient \(\alpha\) is given by

\[\alpha = \frac{1}{l} \frac{\Delta d}{\Delta T}.
\]

(4.40)

Substitution of \((d_2 - d_1)\) values from equation (4.39) leads to

\[\alpha = \frac{1}{l} \frac{d_2 - d_1}{T_2 - T_1} = \frac{x \lambda}{2l(T_2 - T_1)}
\]

(4.41)

where \(l\) is the thickness of the sample, \(x = 1, 2, 3, \ldots\)

4.5(d) METHODOLOGY

The sample was kept on the metal plate with its reflecting surface facing the lens. The leveling screws were adjusted to regulate the required thickness of the air film formed between the curved surface of the plano-convex lens and reflecting surface of the sample. The shape of the air film produced in radial was of increasing thickness in all directions from the center of lens. The monochromatic rays from the source were reflected downwards due to the glass plate held inclined at an angle of 45°, and thus, the rays fall at the normal incidence on the plano-convex lens. The rays travel without deviation from the upper surface of the lens. The rays get partially reflected and refracted from the lower curved surface of the lens. The transmitted/refracted rays
through the lens that fall on the reflecting surface of the sample get reflected back. The interference is produced between the rays reflected from the upper surface of the sample and from the lower surface of the lens due to additional path difference. Thus, depending upon the path difference, the dark or bright fringes appear (Eqs. 4.35 and 4.36). These fringes were viewed with a high power, calibrated microscope placed above the glass plate. Cross wires of graduated microscope are adjusted over any one of the bright fringes of which the order is treated to be zero.

The temperature of the brass plate (in turn the sample) was increased up to a set temperature by allowing a pre-calibrated current through the heater with the help of a dimmerstat. The sample expansion during heating causes a change in thickness of the air film that in turn changes the path difference of reflected rays. Concurrently, the order of Newton’s fringes shifts. The reverse process (thermal contraction) takes place during cooling cycle. Thus, the number of fringes shifted across the crosswires of microscope was recorded at different temperatures while heating and cooling cycles.

A well-polished rectangular slab of silicon single crystal with dimensions 0.4x0.4x0.09 cm\(^3\) (prepared carefully) was used to calibrate/standardize the above discussed experimental setup. Reproducibility of the data was confirmed by repeating experiments.

4.6 RESULTS AND DISCUSSION

Figure 4.8 depicts the variation of sample thickness, caused by thermal expansion, with temperature for silicon crystal. The value of \( \alpha = 2.39 \times 10^{-6}/^\circ \text{C} \) obtained following linear regression is in a very close agreement with reported one (2.3\( \times 10^{-5}/^\circ \text{C} \)) by Lovell et al (1979). This result ensures appreciably good precision of the experimentation.
The variation of thermal expansion coefficients along $a$- and $c$-axes as a parametric function of $(\text{Li/Nb})_c$ ratio is depicted in figure 4.9. The coefficients $\alpha_a$ and $\alpha_c$, in general, are seen to be decreasing with increase in $(\text{Li/Nb})_c$ ratio. Particularly, expansion along the $a$-axis is larger than that of along the $c$-axis. Furthermore, the
The curves of Figure 4.9 indicate relatively a steeper decrease in α₀ vis-a-vis α₆ with non-stoichiometry. It is worth mentioning here that, the values of α₀ and α₆ for congruent composition (Table 4.3) are in close agreement with those obtained from x-ray investigations (Abrahams et al, 1966). A small deviation in the values of α₀ (Table 4.3) is attributed to the difference in losses due to evaporation during the crystal growth. It is worth mentioning here that in the present case the LN crystals were grown from the slow cooling of the melt where the soaking period of the melt was of 12 h. The thermal expansion coefficient for other compositions are given in Table 4.4.

**Table 4.3:** A comparison of thermal expansion co-efficient along a and c-axes of the LiNbO₃ crystals with (Li/Nb)ₘ = 1 of present study with earlier reporting.

<table>
<thead>
<tr>
<th>Composition (Li/Nb)ₘ</th>
<th>Along a-axis x10⁶/°C</th>
<th>Along c-axis x10⁶/°C</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.000</td>
<td>15.482</td>
<td>6.012</td>
<td>Present study</td>
</tr>
<tr>
<td>1.000</td>
<td>16.700</td>
<td>2.000</td>
<td>Abrahams et al (1966)</td>
</tr>
<tr>
<td>1.000</td>
<td>16.596</td>
<td>3.498</td>
<td>Smolenskii et al (1966)</td>
</tr>
<tr>
<td>1.000</td>
<td>15.000</td>
<td>7.500</td>
<td>Kim &amp; Smith (1969)</td>
</tr>
<tr>
<td>1.00</td>
<td>15.400</td>
<td>7.500</td>
<td>Smith &amp; Welsh (1971)</td>
</tr>
<tr>
<td>1.000</td>
<td>15.000</td>
<td>7.500</td>
<td>Sugii et al (1976)</td>
</tr>
<tr>
<td>1.000</td>
<td>14.000</td>
<td>4.000</td>
<td>INSPEC (1989)</td>
</tr>
</tbody>
</table>

**Table 4.4:** Thermal expansion coefficients along a- and c-axes of the LiNbO₃ crystals with different crystal compositions.

<table>
<thead>
<tr>
<th>(Li/Nb)ₖₙ</th>
<th>Along a-axis x10⁶/°C</th>
<th>Along c-axis x10⁶/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.948</td>
<td>14.862</td>
<td>6.012</td>
</tr>
<tr>
<td>0.954</td>
<td>15.482</td>
<td>6.544</td>
</tr>
<tr>
<td>0.969</td>
<td>15.846</td>
<td>7.012</td>
</tr>
<tr>
<td>0.980</td>
<td>16.012</td>
<td>7.362</td>
</tr>
</tbody>
</table>
The LiNbO₃ being rhombohedral, with symmetric point group 3m and space group R̅3c, two coefficients of thermal expansion are expected viz. (i) \( \alpha_x \), describing the longitudinal effect in \( x \)-\( y \) plane, i.e. along \( a \)-axis and (ii) \( \alpha_z \), describing the longitudinal effect perpendicular to \( x \)-\( y \) plane, i.e. along \( c \)-axis. Thus, the observed experimental results (difference in \( \alpha_x \) and \( \alpha_z \)) are in good agreement. Abrahams et al (1966) have also shown a difference in linear thermal expansion coefficients along \( a \)- and \( c \)-axes for lithium niobate single crystals. Zheludev (1971) has reported that the elastic force constant varies with temperature only because of the change in distance between the ions, which could be explained on the basis of Cochran’s theory of ferroelectric transitions applied to LiNbO₃. In the present case, Nb⁵⁺ substitution leads to expansion in lattice thereby causing variation in elastic force constant. Concurrently, the thermal expansion coefficient varies commensurately with Li/Nb ratio.

The Li⁺ and Nb⁵⁺ in LiNbO₃ single crystal occupy special position 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 is .....Nb Li ø Nb Li ø .... The tilt of octahedra, 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 increasing tendency of octahedral tilt with increasing temperature, obviously, leads to higher thermal expansion coefficient along \( a \)-axis (table 4.3) than along \( c \)-axis.

Smolenskii et al (1966) as well as Kim and Smith (1969) reported that the thermal expansion is directly proportional to the change in lattice spacing due to the variation in temperature. The variation of lattice cell constant with temperature shown in figure 4.10. They using equation (4.42) have evaluated thermal expansion coefficients (up to 2nd order).
\[ \frac{\Delta l}{l_R} = \alpha(T - T_R) + \beta(T - T_R)^2 \]  \hspace{1cm} (4.42)

where, \( T_R \) and \( T \) are reference the temperature (25 °C) and the temperature under consideration, respectively. \( l_R \) is length of crystal at \( T_R \). Figure 4.10 suggests that the LiNbO\(_3\) single crystal expands more in \( a \) direction compared to along \( c \)-axis. Beyond 600 °C, the expansion along \( c \)-axis decreases while along \( a \)-axis, it increases (Abrahams et al, 1966).

Since the temperature range of the present investigation is restricted to 300 °C, within this range a linear variation in thermal expansion is justified, and it obeys the equation (4.42) up to first order, i.e. it can be represented by

\[ \frac{\Delta l}{l_R} = \alpha(T - T_R). \]  \hspace{1cm} (4.43)

![Graph showing the variation of lattice constants with temperature](image.png)

Fig. 4.10: Variation of the \( a_H \) and \( c_H \) - lattice constants of LiNbO\(_3\) as a function of temperature (Abrahams et al, 1966).
However, it may follow second order equation (Eq. 4.42) if the experiments would be carried out up to 950 °C. Due to limitations of experimental facility, it was not taken up.

Megaw (1968) has analyzed the data related to thermal expansion on the basis of structural distortion of niobates. As discussed earlier, the LiNbO$_3$ structure is characterized by Nb–filled octahedral forming a corner linked framework. Structural peculiarities are the tilting of the octahedra about their mean triad axis and the displacement of niobium ions in the direction of the triad. The Li$^+$ ions are supposed to play a minor role in the expansion of lattice. By careful analysis of the movement of ions with temperature, and using the data of Abrahams et al (1966), Megaw (1968) has made the following statements:

(i) The nearly regular thermal expansion of $a$, edge of the unit cell is mainly due to the tilting of octahedra; the change in the size of octahedra plays a minor role in that direction.

(ii) The change in edge length of 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 of crystals is dependent on the rise or fall of a scalar quantity; temperature.

(iv) Coefficients of thermal expansion of the crystal for all systems except for cubic are dependent on the direction because of anisotropy.

(v) Change in the edge of unit cell is more along the $a$-axis than the $c$-axis.

All above facts satisfactorily explain the higher value of $\alpha_c$ than $\alpha_a$ (table 4.4) in all the crystals under investigation.
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