Chapter 3

Ultrasonic investigation on elastic properties and phase transition in Lithium Sodium Sulphate crystal

This chapter describes in detail the synthesis of Lithium sodium sulphate single crystal (LSS), purification, crystal growth, identification of the morphology of the grown crystal and preparation of the specimen. All the six independent elastic stiffness constants, compliance constants and Poisson’s ratios of LSS are reported. The surface plots for phase velocity, slowness, Young’s modulus and linear compressibility for this crystal are also presented. The discrepancy in the structure of β-LSS crystal that was raised by NMR studies has been resolved the measurement of elastic constants. Investigation on the temperature variation of elastic constants of LSS, above room temperature using ultrasonics has been carried out. Ultrasonic technique is a very sensitive and precise tool for probing the phase transition in a crystal. The investigation of phase transition in this crystal by the Differential Scanning Calorimetric measurements at a very slow heating rate is also presented.
3.1 Introduction

Fast ion conductors or solid electrolytes at the present are of interest due to their potential use in new types of batteries (so called solid state batteries) and fuel cell for power sources applications. They have latent applications mainly in ion selective electrodes, capacitors, gas sensors, high temperature heating elements etc. The possible application of solid ionic materials for batteries have recently been reviewed \[3.7\]. In this context, considerable effort is being made to develop good Li\(^+\) ion based solid electrolyte. The family of mixed binary sulphate of the LiM\(\text{SO}_4\) type (where M = Na\(^+\), Ag\(^+\), NH\(_4\)\(^+\)) possesses interesting electrical properties.

Lithium sodium sulphate (LSS) is an interesting crystal for which quite a number of investigations have been made. It exhibits piezo-electric and pyro-electric property and do not have ferroelectric property. It is also non-centro symmetric. The structure of this phase is trigonal with space group P31c with lattice parameters \(a = b = 7.627\) Å and \(c = 9.8579\) Å \[3.1\] and \[3.5\]. There are six molecules per unit cell. The high temperature phase of Lithium sodium sulphate has been described as a plastic phase (\(\alpha\)-Li\(\text{NaSO}_4\)) with conductivity 1000 times that of \(\beta\)-Li\(\text{NaSO}_4\). The phase transition occurs at 518 °C from trigonal to b.c.c with 159 KJ/Kg latent heat of transformation and the salt melts at 615 °C.

Three crystallographically different sulphate groups are situated on two different three-fold axes. The lithium and sodium ions are surrounded by irregular arrangement of four and eight oxygen atoms respectively. The
polyhedron formed by oxygen atoms about the alkaline metal ions is not regular. The distorted tetrahedron about the Li$^+$ ion appears to be shortened along one of the three two fold axes of the tetrahedron. The polyhedron about the sodium ion is more complex, resembling a distorted Archimedean antiprism [3.5].

NMR studies by Junke and Mali [3.8] revealed inconsistencies between NMR data and the accepted X-ray diffraction data of LSS [3.1 and 3.5]. They found 12 rather than six different Electric field gradient (EFG) tensors, which fall into two sets with six tensors each. The two sets transform into each other by a mirror plane perpendicular to the trigonal axis not present in the P31c space group. They argued that there are 12 sodium and consequently also 12 lithium sites per unit cell. Hence they argued that the structure has to be modified.

Graneli et al. reported a reinvestigation of the structure of LSS by high-resolution neutron powder diffraction [3.2]. This investigation accounted for a small deviation from the original trigonal structure, which was not significant. No systematic differences in the average interatomic distances were found between the X-ray and Neutron measurements except for the distances between the sulphur atom and the 'wing' oxygens, which are somewhat larger in the neutron measurement. However they suggested that additional experiments are needed to resolve the apparent contradiction with the NMR results.

There have been several temperature dependent studies on LSS which are connected with different physical properties of the crystal. Most of the interest on this crystal is related to unusual electrical properties, temperature dependent ionic conductivity, frequency, temperature dependence of dielectric constant, temperature dependence of spin lattice relaxation, EPR spectra, Raman spectra, Specific heat, DSC, IR, ESR spectra and temperature dependence of heat content, NMR studies, lattice parameters, DTA and Pyro-luminescence etc. There is only one reported phase transition in LSS at 518°C from trigonal to b.c.c structure. No strong phase transition was reported above room temperature region. But certain weak phase transitions have been proposed in some investigations. A brief review of the previous studies are given below.
Kanashira et al. [3.9] have reported the temperature dependence of the spin lattice relaxation time for Li in a single crystal of LiNaSO₄ over the temperature range of 450 K-770 K. The result can be explained by a mechanism involving vacancy diffusion. The activation energy for the doping of Li⁺ and Na⁺ vacancies have been estimated. In addition, ionic conductivity has been measured as a function of frequency and activation energy. The ionic diffusion in the extrinsic region is estimated as 1.59 eV.

EPR spectra of paramagnetic centers of SO₄²⁻ SO₃⁻ and CrO₄³⁻ were used by Walplak et al. [3.5] to probe into the local dynamics of LSS crystal in the range 100K-500K. EPR spectra of above-mentioned center show a series of anomalies above room temperature range indicating high mobility of L⁺ ions in Jahn Teller glass.

Raman spectra of external mode in LSS have been measured by Teeters and Frech [3.14] in the range 12K-1000K. It exhibits single phase transition in the interval. LSS has a low frequency mode at 63cm⁻¹ that appears to soften with temperature and seems to be related to sulphate rotational motion. The failure to observe any external mode in LSS at temperatures above the phase transition suggested that the sulphate ions do not remain in fixed orientationally disordered position at temperatures above the phase transition.

The temperature dependence of specific heat at constant pressure has been measured by Hamed et al. [3.28] for LSS at different gamma radiation doses with external bias electric field in the temperature range 800K-900K. A non linear dependence of transition temperature Tₐ and remarkable change in the thermodynamic parameters were observed due to the effect of both electric field and gamma radiation. The effect of gamma radiation doses on the phase transition in LSS crystal was explained to be due to an internal bias field, Eₐ, originating from the interaction of polar defects with the order parameter of the host lattice. Polishchuk et al. [3.30] studied the temperature dependence of the heat content of the highly conducting solid electrolyte LSS and the anomalous high entropy of the β→α transformation attributed to positional disordering at the
transition point of the cationic lattice consisting of Li and Na ions owing to the excess of accessible sites and also to orientation disordering of the $\text{SO}_4^{2-}$ groups.

The conductivity of quenched LSS was measured by Rama Rao et al. [3.17] in the temperature range 30°C-300°C. They also studied the DSC, IR, and ESR spectra, which provide thermodynamic and microscopic support for the role of the anion disorder. An endothermic and broad exothermic peak at 344°C were interpreted as due to first order phase transition from hexagonal to bcc phase. The endothermic peak at 344°C was attributed to structural relaxation, while the one at 388°C was proposed as a phase transition from hexagonal structure.

The a.c. electrical conductivity studied by Gundusharma et al. [3.18] on LSS incorporating $\text{SiO}_4^{4-}$ as guest ion in $\text{SO}_4^{2-}$ sub lattice shows convincingly that the main rotation 'cogwheel or paddle wheel' mechanism does not contribute to the high mobility of $\text{Li}^+$ in LSS. The enhanced conductivity at higher frequency suggests relaxation effect and rigid network effect in the anion sub lattice.

Seeco et al. [3.19] have reported the a.c conductivity in LSS incorporating $\text{WO}_4$, $\text{MoO}_4$, Rb, and K. In all the case except K, an increase in cation conductivity was observed. The higher cation conductivity is attributed to lattice expansion or incorporation of ion vacancies by guest ion presence and structural transformation. The results are interpreted by them in terms of a percolation type transport mechanism and cannot be due to more disordered low temperature structure during subsequent thermal treatment. The temperature 488°C is shown to represent phase transition of metastable component. The conductivity studies proved that at high temperature the transport in LSS could not be due to formation and migration of $\text{Na}^+$ ions. The temperature dependence study of IR spectra showed the disappearance of bands at 528°C. IR spectra of LSS showed the evidence of freezing of static sulphate disorder by way of broadening $\nu_3$ mode.

Temperature variation of $\beta$-$\text{Li}_2\text{N}_2\text{SO}_4$ has been investigated by Mellander et al. [3.22] for crystal orientation parallel to a- and c- axes using complex
impedance spectroscopy in the temperature range 25°C-518°C. For ionic transport along the c- axis direction, the ionic conductivity is only slightly larger than for the transport in a- direction perpendicular to c- axis.

Bagdassarov et al. [3,44] carried out the pressure and temperature dependence of electrical impedance as a function of frequency in LSS over a range 400°C-800°C and under a pressure of 5, 10 and 20 kbar. They reported that LSS undergoes a displacive first order phase transition from trigonal to b.c.c at 578°C at a pressure 5 kbar and 641 °C at 10 kbar and 764 °C at 20 kbar.

Prabhaharan et al. [3,12] studied in detail X-ray, DSC, complex a.c impedance and d.c. conductivity. DSC studies reported that addition of LSS/LiCl solid solution affects the high conducting phase transition in LSS. Two very minor kinks with peak temperatures at 368 °C and 392 °C were observed for LSS.

Variation of lattice parameter with temperature was studied by Venudhar et al. [3,6]. They reported that due to the strong covalent link between the S-O and lithium, the expansion coefficients along the c- direction are expected to be smaller than those along a- direction. Both the parameter a- and c- increase nonlinearly with increasing temperature and the relative increase in the c- parameter is found to be smaller than that for a.

High temperature NMR study of LSS conducted by Massiot et al. [3,7] enables a better description of the high temperature phase transition of LSS. At this transition they proposed a double resonance mechanism between cation jumps and SO₄ rotations.

DTA and Thermo- Luminescence (TL) studies were conducted on gamma radiated LSS crystals doped with Tl by Kassem et al. [3,10]. They found that with increase of radiation dose, Tc was found to increase sharply to a maximum followed by a slow decrease.

Pyro- Electric Luminescence (PEL) has been observed by Sahare et al. [3,3] for LSS doped with Eu. Possibility of a new phase transition was suggested
in the range 92°C-117°C. Two spikes are observed. One during heating and the other during cooling cycle. PEL has often been observed near ferroelectric phase transition temperature. Hence they proposed a phase transition from pyroelectric to non-pyroelectric phase in the range 92°C-117°C, i.e., around 92°C. No other investigation proposed such a low temperature phase transition for LSS. Hence the observation has much importance.

Given above is a fairly complete review of the previous temperature variation studies on LSS.

To solve the structural inconsistency suggested by NMR studies [3.8], the investigation of elastic properties by ultrasonic technique has been preferred. Also the elastic properties of this crystal were not reported so far. In trigonal type I structure there were only six elastic constants C_{11} = C_{22}, C_{33}, C_{44} = C_{55}, C_{12}, C_{13}, C_{14}. By measuring the elastic constants of LSS, the structural discrepancy has been resolved and is discussed in detail in Section 3.3.1.

Even though several studies like XRD, neutron diffraction, electrical conductivity, optical, TL, PEL, Raman, NMR, EPR, Pressure induced phase transition etc. [3.1-3.3] were carried out, the elastic properties of this crystal and temperature variation of elastic constants are never reported so far. The measurement of the elastic stiffness constants and the investigation on the temperature variation of elastic constants of LSS, above room temperature using ultrasonics are reported for the first time. The enthusiasm for this investigation was the suspected weak phase transition in this crystal suggested by the Pyro-luminescence studies [3.3]. Since ultrasonic is a very sensitive tool, it is ideally suited for studying weak phase transition.
3.2 Experimental technique

3.2.1 Sample preparation

Large single crystals of size (28 × 15 × 15) mm³ have been grown from supersaturated aqueous solution by slow evaporation technique. The solution has been prepared by dissolving equimolecular fraction of Li₂CO₃, and NaHSO₄·H₂O in double distilled water.

\[ \text{Li}_2\text{CO}_3 + \text{NaHSO}_4\cdot\text{H}_2\text{O} \rightarrow 2 \text{LiNaSO}_4 + \text{CO}_2 + \text{H}_2\text{O} \]

The aqueous solution had some unknown brownish residue and was filtered several times. Similar kind of residue was also observed by Graneli et.al [3.2]. Several authors [3.2,3.22,3.23] reported the growth of LSS at 50°C. Mendes-Filho et.al [3.46] reported the growth of the crystal at 35°C resulting in hydrated LSS (LSSW). Hence in order to study the variation of growth property with temperature, I have tried to grow the crystal at six different temperatures. The details of the growth technique have been discussed in the Section 2.2. The photograph of the crystal grown is depicted in Figure 3.1. Ultrasonic experiments need big and defect free crystals. PEO method can be efficiently and precisely performed if big samples are available. The optical quality of the crystal can be enhanced by re-crystallization from the solution for several times, and with the usage of double distilled water. Temperature of the bath is kept constant by using an efficient temperature controller having 0.5°C stability. The morphology of the crystal is shown in Figure 3.2. The Figure is made with the help of the computer programme ‘Shape’. The natural faces of the sample have been identified using the technique [3.39] discussed in Section 2.2.3. The measured interfacial angles and the computed stereographic projection of the crystal planes are compared and given in Table 3.2. The stereographic net of the crystal about a- and c- axes are depicted in the Figures [3.3(a), 3.3(b)]. It is made with the help of the computer programme ‘Jcrystal’ by giving the values of lattice parameters, crystal system and space group of the crystal.
3.2.2 Density measurements

The density of the material is measured by Archimedes' principle by finding the loss of weight of the solid in liquid. Carbon tetrachloride is used in this measurement. The density of CC\textsubscript{4} is 1.57 gm/cc. The error in the density measurement can be decreased by using bulk sample and liquid of density nearly equal to that of solid. In the elastic stiffness constant measurements density has a vital role. Densities of lithium sodium sulphate crystals grown at 35, 40, 42, 44, 46, and 50\degree C are listed in the Table 3.1. The densities of LSS grown at 42, 44, 46 and 50\degree C are almost same.

<table>
<thead>
<tr>
<th>Temperature [\degree C]</th>
<th>Measured Density gm/cc</th>
<th>Reported Density gm/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>2.0151</td>
<td>2.007</td>
</tr>
<tr>
<td>42</td>
<td>2.5897</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>2.5801</td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>2.6009</td>
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</tr>
<tr>
<td>50</td>
<td>2.5995</td>
<td>2.536</td>
</tr>
</tbody>
</table>
Table 3.2 Comparison of the interfacial angles of LSS crystal (50°C grown) computed and measured

<table>
<thead>
<tr>
<th>Crystal faces</th>
<th>Interfacial angles between faces of the crystal</th>
<th>Computed</th>
<th>Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>100-101</td>
<td></td>
<td>142.85</td>
<td>143</td>
</tr>
<tr>
<td>100-110</td>
<td></td>
<td>142.85</td>
<td>143</td>
</tr>
<tr>
<td>001-011</td>
<td></td>
<td>75.26</td>
<td>75</td>
</tr>
<tr>
<td>001-101</td>
<td></td>
<td>75.26</td>
<td>75</td>
</tr>
<tr>
<td>001-110</td>
<td></td>
<td>75.26</td>
<td>75</td>
</tr>
<tr>
<td>010-120</td>
<td></td>
<td>130.6</td>
<td>130</td>
</tr>
<tr>
<td>010-011</td>
<td></td>
<td>130.6</td>
<td>130</td>
</tr>
<tr>
<td>101-111</td>
<td></td>
<td>130.6</td>
<td>130</td>
</tr>
<tr>
<td>010-110</td>
<td></td>
<td>130.6</td>
<td>130</td>
</tr>
<tr>
<td>110-210</td>
<td></td>
<td>151.75</td>
<td>151</td>
</tr>
<tr>
<td>101-101</td>
<td></td>
<td>151.75</td>
<td>151</td>
</tr>
<tr>
<td>111-111</td>
<td></td>
<td>151.75</td>
<td>151</td>
</tr>
</tbody>
</table>
3.2.3 Powder X ray diffraction of LSS

Powder X-ray diffraction pattern of LSS grown at 35, 40, 42 and 50°C were recorded with a Rigaku DMAX diffractometer using Cu-Kα radiation monochromatised with a graphite crystal and are shown in Figures 3.5(a)-3.5(d).

Crystal cutting and polishing

Bulk samples have been cut using a slow speed diamond wheel saw so as to have propagation direction along a- and c-axes. For a trigonal crystal the z-axis gives pure mode. In addition to this there are pure mode axes in the base plane, perpendicular to any of the three mirror planes and there are additional pure mode axes lying in the mirror planes. With these two axes, five of the C's can be determined. To obtain the sixth elastic constant one has to propagate the wave along the m3 plane at 45° to the z-axis and y-axis. The cuttings are made very accurately and the mis-orientation in cutting is less than 1°. The thickness of the sample crystals along the measurement direction are in the range 0.8-1.2 cm. The samples are well polished by using water paper of grade 1500 and Cerium oxide powder. This enables one to get proper bonding of transducer.
Figure 3.1 Photograph of Lithium Sodium Sulphate Crystals grown at 35, 40, 42, 45, 47, & 50°C

Figure 3.2 Morphology of Lithium Sodium Sulphate Crystals grown at 50°C
Figure 3.3 (a) Stereographic projection of LSS about a-axis
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Fig. 3.3(b) Stereographic projection of LSS about c-axis
Solubility curve

Figure 3.4 indicates the solubility curve of the LSS in water at different temperatures and one can see that temperature coefficient of solubility of LSS is positive, but rather small. This implies that the best method to grow crystals of big size is the slow evaporation technique.

*Figure 3.4 Solubility of lithium sodium sulphate crystal*
Figure 3.5(a) XRD of LSS grown at 50°C

Figure 3.5(b) XRD of LSS grown at 35°C
Figure 3.5 (c) XRD of LSS grown at 42°C

Figure 3.5(d) XRD of LSS grown at 40°C
3.3 Results and discussions

3.3.1 Structure change of LSS with growth temperature

Lithium sodium sulphate crystals are grown at six different temperatures from the mother solution containing equimolar fraction of Li$_2$CO$_3$ and NaHSO$_4$·H$_2$O using slow evaporation technique. The interesting point to be noted about the growth of this crystal is that the morphologies and densities of crystal grown at 40°C, 42°C, 44°C, 46°C and 50°C are almost same, while crystal grown at 35°C shows entirely different morphology and different density. The photograph of these crystals has been depicted in Figure 3.1. The crystals are heated slowly in a sealed crucible carefully up to 120°C. The crystal grown at 35°C was the only one to lose optical transparency. The colour of the crystal changed to white, which may be due to the presence of water, and subsequently it became hard.

![FTIR spectrum of LSS grown at 35°C](image)

*Figure 3.6 FTIR spectrum of LSS grown at 35°C*
The presence of water molecule was again confirmed by taking the FTIR of this salt (Figure 3.6). The stretching of OH group near 3431 cm$^{-1}$ is found in LSS grown at 35°C. This stretching mode has confirmed the presence of water of crystallization in the sample. The powder X-ray diffraction pattern of LSS crystals grown at 35, 40, 42 and 50°C have been taken and are shown in Figures [3.5(a)-3.5(d)]. The position of intensity peaks and indexing of hkl planes are same for crystals grown at 40, 42 and 50°C and different for that grown at 35°C. It is obvious from XRD that crystals grown at 35 and 50°C are different in structure. The XRD patterns are compared with JCPDS file [3.45]. The densities of the material grown at different temperatures are depicted in the Table 3.1 and it is found that measured density and reported density of the crystal grown at 35°C are the same [3.46]. Also the densities of the crystal grown at 40, 42, 45 and 50°C are almost same and are nearly equal to the reported density of the crystal grown at 50°C [3.1]. The natural faces of the crystal have been identified by measuring the interfacial angles of the crystal and by stereographic net [Figures 3.3(a)-3.3(b)], as discussed in Section 2.2.3.

The velocities of longitudinal and transverse waves of frequency 10MHz propagating along different crystallographic directions of the crystals grown at 35, 42 and 50°C have been measured accurately by Pulse Echo Overlap method (PEO) using a MATEC ultrasonic system [model 7700]. Traveling plane waves are introduced into the medium by piezo electric transducer. The travel time is the reciprocal of RF, which is adjusted during the measurements. This can be measured accurately from a frequency counter. The method uses a repetition rate 100 to 1000 times slower, thereby, allowing the echo train to leak out by attenuation before another input is applied. The input is synchronized with the RF, which is divided (by 100 to 1000) to generate the repetition rate. Echoes may be selected by intensification of the CRO electron beam, so that other echoes may be disregarded. The first and second echoes are intensified and the RF is set at the reciprocal of one round trip travel time, when the pairs of echoes get overlapped, if the echoes are in the phase matched condition. The accuracy of this measurement is of the order of $10^{-5}$. Eight different mode velocity measurements
can be measured along specified directions. Silicone grease is found to be a good bonding medium to fix the transducer onto the crystal surface and to admit ultrasonic wave pulse generated by it into the crystal medium.

The McSkimin Δt criterion [3.37-3.33] has been applied to correct for the phase lag introduced by the bonding medium on the RF echoes. The technique enables one to measure the ultrasonic transit time in the sample to an accuracy of a few parts per million. Taking into account the uncertainties in measuring the length and various other experimental limitations, an absolute accuracy better than 0.3% is obtained in velocity measurements.

3.3.2 Elastic stiffness constant measurement

LSS can be categorized in the type-1 Trigonal class with six independent elastic stiffness constants. They are \( C_{11} = C_{22}, C_{33}, C_{44} = C_{55}, C_{12}, C_{13}, C_{14} \) and \( C_{66} = \frac{1}{2} (C_{11} - C_{12}) \). The constants \( C_{11} = C_{33} \) and \( C_{33} \) have been determined directly from longitudinal velocity; the constants \( C_{44} = C_{55} \) can be determined from transverse velocity with the help of Chrisoffel Equation [3.41]. Eight-velocity measurements help one to measure 7 elastic constants. The ultrasonic velocities in these crystals in specified direction are listed in Table 3.3. Thus Elastic constants, Compliance constants and Poisson's ratios of LSS grown at 35, 42 and 50 °C are listed in Tables (3.4-3.6). The constants \( C_{12}, C_{13}, C_{14}, C_{66} \) are obtained from the combination of other elastic constants with cross checks.

\[
C_{11} > C_{12}; \quad (C_{11} + C_{12})C_{33} > 2C_{11}^2; \\
(C_{11} - C_{12})C_{44} > 2C_{14}^2
\]  

(3.1)

The off diagonal constants are determined from the Equations (3.2-3.4) and it is discussed in detail in Section 1.2.3. They are given by

\[
C_{14} = \sqrt{\frac{1}{2} \left[ 2\rho v_1^2 - (C_{66} + C_{44}) \right]^2 - (C_{66} - C_{44})^2}^{\frac{1}{2}}
\]  

(3.2)

\[
C_{12} = C_{11} + 2C_{44} - 2(\rho v_1^2 + \rho v_2^2).
\]  

(3.3)
where

\[ C_{11} n_1^2 + C_{44} n_4^2 = a \]
\[ C_{66} n_1^2 + C_{44} n_3^2 = b \]
\[ C_{44} n_1^2 + C_{33} n_3^2 = c \]
\[ (C_{15} + C_{44}) n_1 n_3 = n \]
\[ 2C_{44} n_1 n_3 = l \]
\[ \rho v^2 = m \]

where \( n_1 = 1/\sqrt{2}, \) \( n_3 = 1/\sqrt{2} \) and

\[ a + b + c = A \]
\[ ab + bc + ac - l^2 = B \]
\[ abc - cl^2 = C \]
\[ (a - b - 2l) = D \]

where \( n_3 = \cos \theta \) \( n_1 = \sin \theta \) and \( \theta \) is measured from c axis and is \( \theta = 45^\circ \). The diagonal elements can be measured with an accuracy of 0.2% and off-diagonal elastic constants are measured to an accuracy of 1%. 
Table 3.3  Velocity of ultrasonic modes in LSS at 300K. LT, QT and QT represent longitudinal, transverse, quasi-longitudinal and quasi-transverse modes respectively. The relations between mode velocities and elastic constants are also given.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Direction of propagation</th>
<th>Direction of polarisation</th>
<th>Measured mode velocity (m/s)</th>
<th>Mode velocity-elastic constant relation</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>[100]</td>
<td>[100]</td>
<td>(V_1 = 5112 \pm 5)</td>
<td>(C_{11} = C_{22} = \rho V_1^2)</td>
</tr>
<tr>
<td>T</td>
<td>[100]</td>
<td>[001]</td>
<td>(V_2 = 2796 \pm 3)</td>
<td>(C_{14} = f_{ab'}(V_2))</td>
</tr>
<tr>
<td>T</td>
<td>[100]</td>
<td>[010]</td>
<td>(V_3 = 3203 \pm 3)</td>
<td>(C_{12} = f_{ab}(V_2, V_3))</td>
</tr>
<tr>
<td>L</td>
<td>[001]</td>
<td>[001]</td>
<td>(V_5 = 6762 \pm 6)</td>
<td>(C_{33} = \rho V_5^2)</td>
</tr>
<tr>
<td>T</td>
<td>[001]</td>
<td>[100]</td>
<td>(V_6 = 3219 \pm 3)</td>
<td>(C_{44} = C_{33} = \rho V_5^2)</td>
</tr>
<tr>
<td>QL</td>
<td>[Along mirror plane 45° to C axes]</td>
<td>QL</td>
<td>(V_7 = 6031 \pm 6)</td>
<td>(C_{13} = f_{ae}(V_6))</td>
</tr>
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</table>

Table 3.4  Elastic stiffness constants, compliance constants and Poisson’s ratios of LSS at 300K

<table>
<thead>
<tr>
<th>Sl.No</th>
<th>Elastic stiffness constant (GPa)</th>
<th>Compliance constant ((\times 10^{-11} \text{N}^2\text{m}^2))</th>
<th>Poisson’s ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(C_{11} = 67.94 \pm 0.09)</td>
<td>(S_{11} = 0.259)</td>
<td>(\nu_{12} = 0.39)</td>
</tr>
<tr>
<td>2</td>
<td>(C_{33} = 118.8 \pm 0.09)</td>
<td>(S_{33} = 0.128)</td>
<td>(\nu_{23} = 0.39)</td>
</tr>
<tr>
<td>3</td>
<td>(C_{44} = C_{55} = 26.9 \pm 0.02)</td>
<td>(S_{44} = S_{55} = 0.536)</td>
<td>(\nu_{13} = 0.461)</td>
</tr>
<tr>
<td>4</td>
<td>(C_{66} = 26.67 \pm 0.03)</td>
<td>(S_{66} = 0.721)</td>
<td>(\nu_{31} = 0.228)</td>
</tr>
<tr>
<td>5</td>
<td>(C_{12} = 27.85 \pm 0.3)</td>
<td>(S_{12} = -0.101)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>(C_{13} = 44.12 \pm 0.5)</td>
<td>(S_{13} = -0.059)</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>(C_{14} = 12.89 \pm 0.12)</td>
<td>(S_{14} = -0.172)</td>
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</tbody>
</table>
Table 3.5  Elastic stiffness constants, compliance constants and Poisson’s ratios of LSS grown at 42 °C

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Elastic stiffness constant (GPa)</th>
<th>Compliance constant ( \times 10^{-10} \text{N}^{-1} \text{m}^2 )</th>
<th>Poisson’s ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( C_{11} = C_{22} = 63.2 \pm 0.09 )</td>
<td>( S_{11} = 0.29 )</td>
<td>( \nu_{12} = 0.2862 )</td>
</tr>
<tr>
<td>2</td>
<td>( C_{33} = 81.9 \pm 0.09 )</td>
<td>( S_{33} = 0.228 )</td>
<td>( \nu_{23} = 0.2862 )</td>
</tr>
<tr>
<td>3</td>
<td>( C_{44} = C_{55} = 27.8 \pm 0.02 )</td>
<td>( S_{44} = S_{55} = 0.49 )</td>
<td>( \nu_{13} = 0.4605 )</td>
</tr>
<tr>
<td>4</td>
<td>( C_{66} = 18.26 \pm 0.03 )</td>
<td>( S_{66} = 0.743 )</td>
<td>( \nu_{11} = 0.362 )</td>
</tr>
<tr>
<td>5</td>
<td>( C_{12} = 26.72 \pm 0.3 )</td>
<td>( S_{12} = -0.083 )</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>( C_{13} = 41.3 \pm 0.5 )</td>
<td>( S_{13} = -0.0105 )</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>( C_{14} = 11.67 \pm 0.12 )</td>
<td>( S_{14} = -0.156 )</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.6  Comparison of elastic constants and ultrasonic velocities of LSS grown at 50, 35, and 42 °C

<table>
<thead>
<tr>
<th>( C_{ij} )</th>
<th>Elastic constant of crystals grown at</th>
<th>Velocity through crystal grown at</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>50°C</td>
<td>35°C</td>
</tr>
<tr>
<td>( C_{11} = C_{22} )</td>
<td>67.9±0.09</td>
<td>45.84±0.09</td>
</tr>
<tr>
<td>( C_{33} )</td>
<td>118.8±0.09</td>
<td>46.60±0.09</td>
</tr>
<tr>
<td>( C_{44} = C_{55} )</td>
<td>26.94±0.02</td>
<td>12.21±0.02</td>
</tr>
<tr>
<td>( C_{12} )</td>
<td>27.85±0.3</td>
<td>15.3±0.3</td>
</tr>
<tr>
<td>( C_{13} )</td>
<td>44.12±0.5</td>
<td>2.54±0.5</td>
</tr>
<tr>
<td>( C_{14} )</td>
<td>12.89±0.12</td>
<td>0.648±0.12</td>
</tr>
</tbody>
</table>
3.3.3 Surface plots of Phase velocity, Slowness, Young’s modulus and Linear compressibility

The anisotropy of elastic wave propagation in this crystal can be made clear by drawing the phase velocity surface plots in the a-b and a-c planes following a well known procedure [3.40,3.42]. Figure 3.7(a) shows surface plots of phase velocity in the quasi-longitudinal mode in the y-z plane with higher velocity of propagation and Figure 3.7(b) shows that for the quasi-shear [QS] mode in the y-z plane.

The Equation for phase velocity is derived and discussed in Section 1.2 and in the y-z plane it is given by

\[ \rho v_0^2 = C_{66}n_2^2 + C_{44}n_3^2 + 2C_{56}n_2n_3 \] (3.6)

\[ 2\rho v_1^2 = (C_{11}n_2^2 + C_{44}n_3^2 + C_{44}) + \]
\[ [(C_{11}n_2^2 + C_{44}n_3^2 + C_{44})^2 - 4 \]
\[ (C_{11}n_2^2 + C_{44}n_3^2)(C_{44}n_2^2 + C_{44}n_3^2) - (C_{13} + C_{44})^2n_2^2n_3^2 \] \[ \] \[ ]^{1/2} \]
\[ 2\rho v_2^2 = (C_{11}n_2^2 + C_{44}n_3^2 + C_{44}) - \]
\[ [(C_{11}n_2^2 + C_{33}n_3^2 + C_{44})^2 - 4 \]
\[ (C_{11}n_2^2 + C_{44}n_3^2)(C_{44}n_2^2 + C_{44}n_3^2) - (C_{13} + C_{44})^2n_2^2n_3^2 \] \[ \] \[ ]^{1/2} \]

A greater insight into the elastic anisotropy of a crystal is obtained by plotting the inverse phase velocity (slowness) surfaces. In general, in an anisotropic crystal, the energy of propagation in the direction of phase velocity is not collinear. Slowness surface also provides a better pictorial representation of elastic anisotropy in a crystal. Figure 3.8 represents the surface plots of slowness of the longitudinal mode in the y-z plane.

The velocity surface plots are insufficient to describe the anisotropy of the elastic properties of a crystal completely. Surface plots of Young’s modulus are
very important in this regard. The Young's modulus $E$ in this direction of unit vector $\mathbf{n}$ for a trigonal crystal is given by [3.40]

$$E^{-1} = [1 - n_2^2] S_{11} + S_{31} n_1^4 + [2S_{12} + S_{66}] n_2^2 + n_3^2 [1 - n_3^2] [2S_{11} + S_{44}] + 2n_2n_3 [3n_2^2 - n_2^2] S_{11}$$

(3.7)

The cross sections of Young's moduli surfaces are plotted in the $x$-$y$, $x$-$z$ and $y$-$z$ planes. They are shown in Figures 3.9(a-c).

The linear compressibility of a trigonal crystal [3.40] in matrix form can be written as

$$\beta = [S_{11} + S_{12} + S_{33}] - [S_{11} + S_{12} - S_{13} - S_{33}] n_3^2$$

(3.8)

The linear compressibility plots of LSS crystal in the $x$-$y$, $x$-$z$ and $y$-$z$ planes have been plotted. The plots are as shown in Figure 3.10. The volume compressibility $S_{nkk}$ is an invariant parameter for a crystal. For a trigonal crystal, in matrix notation, it is given by [3.40],

$$S_{nkk} = S_{nkk} = S_{33} + 2[S_{11} + S_{12} + 2S_{13}]$$

(3.9)

where $S_{ij}$'s are the corresponding compliance constants.

The Poisson's ratios have been evaluated and the corresponding Equations are derived and discussed in Section 1.3. The Equation for Poisson's ratio along $a$- and $c$- axes are given by

$$\nu_{21} = -\varepsilon_{22} / \varepsilon_{11} = -S_{2211} / S_{1111} = -S_{21} / S_{11}$$

$$\nu_{31} = -\varepsilon_{33} / \varepsilon_{11} = -S_{3311} / S_{1111} = -S_{31} / S_{11}$$

$$\nu_{12} = -\varepsilon_{11} / \varepsilon_{22} = -S_{12} / S_{22}$$

$$\nu_{13} = -\varepsilon_{11} / \varepsilon_{33} = -S_{13} / S_{33}$$

(3.10)
Figure 3.7(a) Surface plots of phase velocity in the quasi longitudinal mode in the y-z plane

Figure 3.7(b) Surface plots of phase velocity in the quasi-transverse mode in the y-z plane
Figure 3.8 Surface plots of slowness in the longitudinal mode in the y-z plane

Figure 3.9(a) Surface plot of Young's moduli in the x-y plane
Figure 3.9(b) Surface plot of Young's moduli in the y-z plane

Figure 3.9(c) Surface plot of Young's moduli in the x-z plane
The bulk modulus and volume compressibility of LSS are given in the Table 3.7

**Table 3.7 Bulk modulus and volume compressibility of LSS**

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Bulk Modulus K (GPa)</th>
<th>Vol. Compressibility $S_{\text{lkk}} (10^{10})$ N$^{-1}$m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSS</td>
<td>45.045</td>
<td>0.222</td>
</tr>
</tbody>
</table>

3.3.4 The temperature variation of elastic constants

The temperature variations of the velocity of longitudinal and shear waves propagating along various directions in the crystal are measured between 300 - 410 K by keeping the sample mounted on a suitable holder, in a temperature controlled chamber. The details of the experimental set up have been described in Section 2.2. The changes in velocity with temperature have been measured by adjusting carefully the CW oscillator frequency of the PEO system keeping the selected RF echoes in the phase-matched condition. The elastic constants $C_{11}$, $C_{33}$, $C_{44}$ and $C_{12}$ have been subjected to temperature variation study and they are
depicted in the Figures (3.11 and 3.12). The precision of this measurement of velocity is of the order of $10^{-5}$. The rate of temperature change in all the measurements is in the range of 0.5K to 1K per minute.

[a] Elastic anomaly near 320K and 350K

In the temperature variation study of LSS the elastic constant $C_{12}$ shows an anomaly near 350K. The value of the elastic stiffness constant $C_{12}$ decreases very sharply at around 350K. The transverse constant $C_{44}$ exhibits an anomaly near 310K and 320K. A rise in the value of elastic constant $C_{44}$ after 320K and 355K. The longitudinal constants $C_{11}$ and $C_{33}$ show no significant anomaly. For all constants a change of slope was observed at around 310K.

![Graph showing temperature variation of elastic constants $C_{12}$ and $C_{44}$ of LSS](image)

*Figure 3.11 Temperature variation of elastic constants $C_{12}$ and $C_{44}$ of LSS.*
Figure 3.12 Temperature variation of elastic constants $C_{11}$ and $C_{33}$ of LSS

These anomalies in the behavior may be due to the weak phase transition for this crystal at 320K and 350K.

3.3.5 Investigation of phase transition using DSC

The thermal changes associated with this crystal have been assessed by the method of Differential Scanning Calorimetry (DSC) based on ASTM E-537-98 using DSC-2920, TA Instruments Inc. Thermal changes have been observed in the range 30°C-100°C at a heating rate of 10/min. The DSC scan of the crystal is depicted in Figure 3.13.
Annealed samples are used for this study. DSC data shows a weak anomaly around 310K and ultrasonic study shows the anomaly at 320K. The energy associated with this transition at 310K is 0.2375 J/g. Both these studies show a shift in temperature of 10K and no anomaly was observed in DSC at 355K. This may be due to the fact that the thermal changes associated with this transition are not appreciable. Ultrasonic technique, being a sensitive tool, able to detect these weak anomalies.

3.4 Conclusions

The inconsistency about the structure of LSS raised by NMR studies has been resolved by the elastic property study. Six elastic stiffness constants have been measured for this crystal. Hence the symmetry of the crystal is confirmed as trigonal. If it exhibits hexagonal symmetry it should have five elastic constants and hence the elastic constant \( C_{14} \) should be zero. But from this study it is found that for LSS \( C_{14} \neq 0 \). Hence it is confirmed that the crystal belongs to trigonal symmetry. Temperature variation study of the elastic constant \( C_{12} \) has shown weak anomalies around 350K. The constant \( C_{44} \) showed elastic anomalies 310K and 355K. This may lead to a weak phase transition at those temperatures. The present DSC study conducted at very slow heating rate of 1K/min also exhibits...
minor anomalies around 310K and does not show any anomalies around 360K. The weak elastic anomalies around 360K may be a supporting evidence to Pyro-Electric Luminescence (PEL) studies [3.3], which have suggested the possibility of a weak phase transition from pyro-electric to non pyro-electric phase around 365K. The reason for the nature of this transition needs more investigation.
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