Chapter IX

THERMALLY STIMULATED POLARIZATION AND DEPOLARIZATION
CURRENT STUDIES IN PURE AND DOPED NaNO₃ CRYSTALS

Abstract

Results of careful measurements of thermally stimulated polarization current (TSPC) and thermally stimulated depolarization current (TSDC) carried out in single crystals of pure and doped NaNO₃ crystals in the temperature range 80K to 350K are presented. Both TSPC and TSDC spectra show sharp peaks in doped NaNO₃ crystals in which the temperatures corresponding to the current maxima depend on the nature of the impurities added. The activation energies and pre-exponential factors for dipole relaxation process have been evaluated from the TSPC and TSDC results. The DSC spectrum obtained for pure NaNO₃ also supports the results obtained from the TSPC and TSDC measurements.
9.1 INTRODUCTION

Sodium nitrate crystallises in the rhombohedral subgroup of the trigonal system of space group $R\bar{3}c$ with two formula units of $\text{NaNO}_3$ per unit cell \([1-3]\). The nitrogen and sodium atoms lie on threefold axes and the three oxygen atoms of each nitrate group are arranged symmetrically about the nitrogen atoms in planes normal to the threefold axes as shown in figure 9.1a. Each oxygen atom lies on a twofold axis. Sodium nitrate has been extensively studied since the work of Kracek \([4]\) who first noticed the appearance of a gradual phase transformation. Kracek et al. \([5]\) observed marked changes in the intensities of the X-ray reflections from some of the planes on heating $\text{NaNO}_3$ above 488K. They attributed this to the rotation of the $\text{NO}_3^-$ ions about the trigonal axis. The investigations of Katelaar and Strijk \([6]\) also show that the transition is caused by internal rotation of the $\text{NO}_3$ groups in the crystal. They found that the probable mode of rotation is that about an axis through the $\text{N}$-atom and perpendicular to the plane of the $\text{NO}_3$ group. Later specific heat investigations \([7]\) confirmed the existence of a characteristic lambda curve with transformation beginning in the vicinity of 423K and reaching the lambda point at $T_c = 549K$, just below the melting point at 584K. This phase transition was shown to be of order-disorder type. It is the dynamics of the phase
Figure 9.1a. Crystal structure of NaNO₃ crystal.
transition, i.e., the change from a complete order to complete disorder of the crystal structure, spread over a wide temperature range of nearly 100K, that generates most of the interest in sodium nitrate.

Terauchi and Yamada [8] by X-ray scattering, studied the phase transition of sodium nitrate crystal associated with the ordering of the orientation of \( \text{NO}_3^- \) ions. They have analysed the results on a microscopic basis and have concluded that the pair interactions between \( \text{NO}_3^- \) ions play an important role during this phase transition process.

In addition, the lattice dynamics of NaNO\(_3\) has been investigated by neutron, Raman and infrared spectroscopy, mainly above room temperature in order to study the disorder phenomena related to the order-disorder phase transition. All the active lattice modes in sodium nitrate are known from the neutron scattering measurements of Logen et al. [9], Trevino et al. [10] and Lefebvre et al. [11]. Besides, the phonon dispersion curves of NaNO\(_3\), Lefebvre et al. [11] have also studied the temperature behaviour of some lattice modes from room temperature up to 563K. The effect of heating, upon the frequencies and dampings of the Raman active lattice modes were studied from 300 to 573K [12-15]. It may be mentioned in this context that Lettieri et al. [16] using Raman spectro-
scopy have observed a soft lattice mode in the pressure induced ferroelectric phase above 45 kbar at room temperature.

The electrical conductivity, dielectric constant and loss of this material have been thoroughly investigated by Ramasastry and Murti [17] and Ramasastry and Syamasundara Rao [18] in the temperature range 300 to 480K, whereas the low temperature studies on this material are due to Badr and Kamel [19]. They have measured the resistivity and dielectric constant of NaNO₃ in the temperature range -30 to -80°C and obtained some anomalous change at -30°C in the $\varepsilon$ vs T curve accompanied by a non-monotonous change in the resistivity plot. From the results they concluded that this anomalous change was due to the occurrence of a phase transition in the NaNO₃ crystals by the change in the nature of the vibrational mobility of the nitrate group which affects the temperature dependence of dielectric constant and resistivity. In this chapter we discuss the results obtained from TSPC and TSDC measurements made on single crystals of pure and doped NaNO₃ in the temperature range 80 to 350K. Detailed analysis of the TSPC and TSDC spectra have been made by studying their characteristics as a function of impurity concentration, poling field, poling temperature, poling time and heating rate.
9.2 EXPERIMENTAL DETAILS

Single crystals of pure and (Ba\(^{2+}\) and Sr\(^{2+}\)) doped NaNO\(_3\) crystals were grown from melt using Bridgemann's technique in open pyrex glass tubes. Samples of typical sizes 6x6x1 mm\(^3\) were prepared for TSPC and TSDC measurements after cleaving the grown samples along (100) faces. The thin film electrodes used were of evaporated aluminium (Difficulties were encountered with silver paint). The method of measurement of TSPC and TSDC and the experimental set up used have been already described in Chapter II. Thermally stimulated polarization current (TSPC) and thermally stimulated depolarization current (TSDC) were measured using Keithley model 617 Electrometer. The concentration of the impurities, in the specimens have been determined from the atomic absorption spectra obtained for the respective samples. The DSC spectrum of NaNO\(_3\) was taken using a Perkin-Elmer instrument (Delta Series Model DSC 7) in the temperature range 120 to 300K with a heating rate of 10°C/m.

9.3 EXPERIMENTAL RESULTS

9.3.1 TSPC and TSDC measurements in NaNO\(_3\) crystals

The TSPC measurements carried out in pure sodium nitrate by quenching the specimen to liquid nitrogen temperature and warming it with a biasing voltage of 200V (heating rate - 0.07K/sec) in the temperature range 80 to 350K give
a well defined current peak at 263K (denoted as B) as shown in figure 9.3a. The TSDC spectrum obtained by polarizing the specimen with a field of 2 KV/cm at 300K for a period of 2 minutes (heating rate 0.07K/sec) is shown in figure 9.3b. A sharp current peak is observed exactly at the same temperature where the TSPC peak is found to occur. The height of the TSPC peak is found to be large compared to that in the case of TSDC. It is also found that the height of the peaks increase slightly with the rate of heating.

9.3.2 TSPC measurements in doped NaNO₃ crystals

The TSPC spectra recorded for doped crystals for three different concentrations (250, 500 and 1000 ppm) of Ca²⁺ and Sr²⁺ impurities in the range 80 to 350K are shown in figures 9.3c and 9.3d. The spectra obtained for the two specimens by applying a biasing voltage of 200V (heating rate 0.07K/sec) show two distinct peaks of varying magnitudes. Let us denote these peaks as A and B in the increasing order of temperature. The temperature corresponding to the current maxima (T_m) for the peaks denoted by A are found to be 224.5K and 231K respectively for the Ca²⁺ and Sr²⁺ doped NaNO₃ crystals, whereas T_m for the peaks denoted by B is same as that for the current peak observed in the pure NaNO₃ crystals. Though the heights of the peaks A are found to increase in
Figure 9.3a. TSPC spectrum of pure NaNO₃ crystal.
Figure 9.36. TSDC spectrum of pure NaNO₃ crystal.
Figure 9.3c. TSPC spectra recorded for doped NaNO₃ crystals for various Ca²⁺ impurity concentrations.
Figure 9.3d. TSPC spectra recorded for doped NaNO₃ crystals for various Sr²⁺ impurity concentrations.
proportion to the concentration of impurity ions, the magnitudes of the current peaks B are unaffected by this process. The shape of the current peaks also depends on doping concentration. The activation energies (E) and pre-exponential factors (γ) obtained by making use of the log I vs T\(^{-1}\) plots for the peaks A for both Ca\(^{2+}\) and Sr\(^{2+}\) doped specimens of NaNO\(_3\) are shown in table 1.

Table 1

Values of various parameters obtained from TSPC spectra of doped NaNO\(_3\) crystals

<table>
<thead>
<tr>
<th>Sample</th>
<th>(T_m) (K)</th>
<th>E (eV)</th>
<th>(\gamma) (Sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNO(_3):Ca(^{2+}) 250 ppm</td>
<td>224.5</td>
<td>0.45</td>
<td>1.1x10(^{-8})</td>
</tr>
<tr>
<td>NaNO(_3):Sr(^{2+})</td>
<td>231.0</td>
<td>0.49</td>
<td>2.78x10(^{-9})</td>
</tr>
</tbody>
</table>

9.3.3 TSDC measurements in doped NaNO\(_3\) crystals

The TSDC spectra recorded for doped NaNO\(_3\) crystals for three different concentrations (250, 500 and 1000 ppm) of Ca\(^{2+}\) and Sr\(^{2+}\) impurities are shown in figures 9.3e and 9.3f. The spectra obtained by polarizing the specimen with
Figure 9.3e. TCCD spectra recorded for HgI₂ crystals for various Ca²⁺ impurity concentrations.
Figure 9.3f. TSDC spectra recorded for NaNO$_3$ crystals for various Sr$^{2+}$ impurity concentrations.
a field of 2KV/cm for two minutes of 300K (heating rate 0.07K/sec) show two distinct current peaks. It is observed that the temperature corresponding to the current maxima for peaks A and B in both the specimens are found to be exactly the same as that obtained from TSPC measurements. The magnitudes of the TSPC peaks are found to be larger than that TSDC counterparts. It has been observed that the height and shape of the TSPC peaks A are strongly dependent on the concentration of the impurities while peaks B are found to be independent of the impurities present in the sample. The activation energies and pre-exponential factors evaluated by making use of the log I vs $T^{-1}$ plots are shown in table 2.

**Table 2**

Values of various parameters obtained from TSDC spectra of doped NaNO$_3$ crystals

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_m$(K)</th>
<th>E(eV)</th>
<th>$\tau_e$(Sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaNO$_3$:Ca$^{2+}$ (250 ppm)</td>
<td>224.5</td>
<td>0.46</td>
<td>$6.5\times10^{-9}$</td>
</tr>
<tr>
<td>NaNO$_3$:Sr$^{2+}$ (250 ppm)</td>
<td>231.0</td>
<td>0.51</td>
<td>$9.8\times10^{-10}$</td>
</tr>
</tbody>
</table>
9.3.4 Effect of poling field

The nature of variation of TSDC peaks A for Ca\(^{2+}\) doped (250 ppm) NaNO\(_3\) as a function of poling field for fixed poling temperature and poling time is shown in figure 9.3g. The effect of poling field on the variation of TSDC peak A for Sr\(^{2+}\) doped (250 ppm) NaNO\(_3\) crystals is shown in figure 9.3h. In both these specimens the height and shape of the TSDC spectra are found to vary with the increase in poling field. The height of the peaks shows linear relation with the field as shown in the inset of figures 9.3g and 9.3h. The height and shape of peaks B in Ca\(^{2+}\) and Sr\(^{2+}\) doped specimens are found to be unaffected by change in poling field. We have thus found that the role of biasing voltage in determining the nature of variation of the current peaks A in the TSPC spectra is the same as that of poling field in the TSDC spectra of the doped NaNO\(_3\) crystals.

9.3.5 Effect of poling temperature

In order to study the effect of poling temperature on the nature of variation of the TSDC spectra, samples with fixed impurity concentration, poling field and poling time have been used. The effect of poling temperature on the nature of variation of peaks A in Ca\(^{2+}\) and Sr\(^{2+}\) doped specimens with impurity concentration 500 ppm, poling field 2KV/cm,
Figure 9.3g. Effect of poling field on the nature of variation of TSDC peak A in Ca\textsuperscript{2+} doped (250 ppm) NaNO\textsubscript{3} crystal. Inset shows the linear variation of the height of the current peak A.
Figure 9.3h. Effect of poling field on the nature of variation of the TSDC peak A in Sr\textsuperscript{2+} doped (250 ppm) NaN\textsubscript{3} crystal. Inset shows the linear variation of the peak height of the current peak A.
Figure 9.3i. Effect of poling temperature on the TSDC peak A in Ca$^{2+}$ doped (500 ppm) NaNO$_3$ crystal.
Figure 9.3j. Effect of poling temperature on the TSDC peak A in Sr$^{2+}$ doped (500 ppm) NaNO$_3$ crystal.
and poling time 5 minutes is shown in figures 9.3i and 9.3j. Since, no appreciable variation in the B peaks has been observed, they have not been shown in the figure. It should be noted that the height of the peaks A in both the specimens is found to decrease with poling temperature. It should also be noted that the effect of poling temperature is more predominant in samples with higher impurity concentration.

9.3.6 Effect of poling time

In order to study the effect of poling time on the TSDC spectra of doped specimens of NaNO₃, we made TSDC measurements on samples containing a fixed amount of impurity ions by varying poling time, while keeping the poling field and temperature constant. Figure 9.3k shows the variation of the current maxima as a function of poling time ranging from 1-10 minutes for the peak A in Ca²⁺ doped (250 ppm) specimens, while figure 9.3l shows variation of the current maxima for the peak A in Sr²⁺ doped specimens for a fixed field of 2KV/cm and poling temperature 300K. It can be noted that the current maxima decrease slowly with increase in poling time. It is also observed that, the effect of poling time is more pronounced in samples with high impurity concentration and for higher poling temperature.
Figure 9.3k. Variation of the current maxima as a function of poling time for the peak A in Ca$^{2+}$ doped (250 ppm) NaNO$_3$ crystal.
Figure 9.3. Variation of the current maxima as a function of poling time for peak A in $\text{Sr}^{2+}$ doped (250 ppm) $\text{NaNO}_3$ crystal.
9.3.7 Effect of heating rate

For studying the effect of heating rate, we have carried out the TSPC and TSDC measurements in samples with fixed values for impurity concentration, poling temperature, poling field/biasing field and poling time. In this case the height of the current maxima is found to be increased with increase in heating rate without affecting the total integrated charges for each peak.

9.3.8 Results obtained from DSC studies

The differential scanning calorimetric studies carried out in powdered NaNO₃ in the temperature range 110K to 300K with a heating rate of 10°C/m is shown in figure 9.3m. A sharp peak with a maximum at 265K has been observed in the case of pure sodium nitrate crystal.

9.4 DISCUSSION

It is obvious from the TSPC and TSDC, the current peaks (B) observed in both pure and doped NaNO₃ crystals that this material undergoes a phase transition at 263K. As already mentioned NaNO₃ undergoes an anomalous change in its electrical properties as revealed in \( \varepsilon \) vs T curve and in the monotonous change in resistivity at -30°C. It
Figure 9.3m. DSC spectrum of pure NaNO₃ material.
is suggested that the pronounced increase in the value of a.c. conductivity reflects a co-operative change in the polarizability of the structural units in the unit cell [19]. Therefore it is advisable to look for common reason which might be related to the characters of the nitrate group that leads to some kind of modification of the crystal field as long as neither the basic crystal structure nor the valency of the positive ions can be the effective factor. A change in the torsional rigidity or clamping of the permanent dipoles associated with the nitrate group may apparently be excluded since it would be likely to affect also the value of the lattice parameter. Therefore it is highly probable that the freezing of the reorientational motion of the NO$_3^-$ group about its threefold axis is responsible for the occurrence of this low temperature phase transition. Such successive blocking of the reorientational motion of the NO$_3^-$ ions taking place while cooling the crystal might lead to the splitting of the vibrational bands and a considerable contraction of the line. Such splitting in the internal and external modes of vibrations was observed experimentally in IR and Raman spectroscopy for the nitrate crystals, specifically for CsNO$_3$ and RbNO$_3$ [20-23]. Thus the change in the character of the vibrational mobility of the nitrate group should thus result in occurrence of phase transition in this method.
Therefore, the results obtained here from TSPC and TSDC along with the results obtained from the DSC studies clearly establish that pure NaNO₃ undergoes a phase transition at 263K. Also, the impervious nature of peak A at 263K in TSDC and TSPC to various experimental conditions strongly support the above conclusions.

The origin of the lower temperature peaks observed below 263K in both Ca²⁺ and Sr²⁺ doped NaNO₃ crystals in the TSPC and TSDC measurements can be explained by considering the role of the substituted divalent impurity ions in the NaNO₃ lattice. It is well known that electrical conduction in ionic crystals like NaNO₃ is a defect controlled property and this defect concentration increases exponentially with rise in temperature. In the case of NaNO₃ crystal the well confirmed experimental result [17] is that the electrical conductivity is considerably lowered by the addition of Ba²⁺ to the lattice (Contrary results have been observed for SO₄²⁻ and Sr²⁺ doped NaNO₃ in which, it is found that conductivity increases with the substitution of these ions). To compensate the excess charge of the added divalent positive ion impurity (Z²⁺), positive ion vacancies (V⁺) or negative ion interstitials (X⁻) may be created. If the mechanism of electrical conduction in this crystal is by the migration of either of these defects, the conductivity
must be enhanced. To account for the observed decrease in conductivity we should consider the effect of the above increase in number of negative carriers on the concentration of other defects such as negative ion vacancies \( (\text{V}_n^-) \) and positive ion interstitials \( (\text{X}^+) \). The concentration of positive ion vacancy \( [\text{V}_p^-] \), exists in equilibrium with the concentration of negative ion vacancy \( [\text{V}_n^+] \), and also with the concentration of positive ion interstitials \( [\text{X}^+] \). Similarly, the concentration of negative ion interstitials \( [\text{X}^-] \) exists in equilibrium with that of negative ion vacancy \( [\text{V}_n^+] \). These may be expressed by the following equations [24].

\[
[\text{V}_p^-][\text{V}_n^+] = \exp\left(-\frac{g_S}{kT}\right) = x_S^2 \quad (9.1)
\]

\[
[\text{V}_p^-][\text{X}^+] = \exp\left(-\frac{g_F}{kT}\right) = x_F^2 \quad (9.2)
\]

\[
[\text{X}^-][\text{V}_n^+] = \exp\left(-\frac{g_{AF}}{kT}\right) = x_{AF}^2 \quad (9.3)
\]

where \( S, F \) and \( AF \) stand for Schottky, Frenkel and Antifrenkel defects respectively, \( g \) for the free energy of formation of defects, and \( x \) for the concentration of either defects in pure crystal. It is understood from the expressions (9.1) to (9.3) that increase in \( [\text{V}_p^-] \) or \( [\text{X}^-] \) results in the decrease of \( [\text{V}_n^+] \) and/or \( [\text{X}^+] \). That is, the addition of divalent positive ion impurities into the lattice has the
The effect of decreasing the negative ion vacancies and/or positive ion interstitials. The conductivity will decrease if the process is mainly contributed by either anion vacancies or cation interstitials. Considerations based on both size and polarizability lead to the conclusion that nitrate ion should be less mobile. The nitrogen-oxygen bond is 1.2 Å with the oxygen having an ionic radius of 1.4 Å, whereas the ionic radius of Na⁺ is 0.95 Å. Likewise, the polarizability of the nitrate ion is 3.4 to 4.0×10⁻²⁴ cm³ while that of the sodium ion is 0.41×10⁻²⁴ cm³ [25]. Hence on account of the larger size of the nitrate ion, interstitial anions are less likely to occur and positive ion vacancies may be assumed to produce charge compensation. Thus it is highly probable that the substitution of divalent cationic impurities viz., Ca²⁺ and Sr²⁺ in a NaNO₃ lattice produce positive ion vacancies. These positive ion vacancies along with the divalent cationic impurities produce impurity-vacancy (I-V) complexes and their reorientations give rise to current peaks in TSPC and TSDC measurements. Thus the origin of the current peaks observed in doped NaNO₃ crystals can only be due to the formation of I-V complexes in this material by the substitution of divalent cationic impurities. Again, the effect of various experimental parameters on the variation of TSPC and TSDC current peaks (A) fully establishes that the origin
of the current peaks (A) are due to the I-V complexes. The activation energy values and pre-exponential factors evaluated from both TSPC and TSDC are found to be approximately the same. From this it is clear that, the results obtained for both pure and doped specimens of NaNO₃ are not the artifact of the technique used but is due to the innate properties of these materials.

The observed difference in size of the current peak in TSDC method compared to that in the TSPC can be explained as follows. During the TSDC process the dc electric field not only polarizes the sample but also causes partial dissociation and hence it build up an ionic space charge in the materials (As noted in section 9.3.5 this effect is much more at higher poling temperatures). Thus the effective number of I-V complexes which reorient on heating process is now reduced and this gives a smaller magnitude for TSDC peak (A). A reduction of the internal field due to space charge effect can also contribute to this phenomenon [26,27].

9.5 CONCLUSIONS

The results obtained for pure and doped NaNO₃ single crystals from TSPC and TSDC measurements lead to the following conclusions:
1. Both TSPC and TSDC measurements show a single current peak (A) in pure crystals and two peaks (A and B) in doped specimens of NaNO₃.

2. The temperature corresponding to the current maximum for peaks (A) in both pure and doped specimens is found to be 263K, whereas the temperature corresponding to the current maximum for peaks (B) in doped specimens is found to be dependent on the nature of impurity added.

3. The current peak (A) observed in both pure and doped NaNO₃ crystals at 263K can be assigned as due to the occurrence of a phase transition in this material at this temperature, apparently due to reorientation of NO₃ ion in the crystal lattice.

4. The current peaks (B) observed in doped specimens of NaNO₃ are due to the reorientation of I−V dipoles formed by the substitution of divalent cationic impurities in the pure NaNO₃ crystals.

5. The observed decrease in size of the TSDC peaks compared to that in the TSPC peak may be due to the formation of space charges in the TSDC process.
6. The activation energy values and pre-exponential factors evaluated for peaks (A) are found to be same in both TSPC and TSDC measurements.

7. The DSC studies also support fully well the results obtained for NaNO$_3$ from TSPC and TSDC measurements.
9.6 REFERENCES


