Chapter X

IONIC THERMOCURRENT STUDIES OF DOUBLY DOPED NaNO₃ CRYSTALS

Abstract

Ionic thermocurrent technique has been used to study the relaxation of Ca²⁺ and Ba²⁺ impurity complexes in NaNO₃ crystals. The ITC spectrum of doubly doped NaNO₃ gives two well defined peaks (A and B) at temperatures 223 and 252K. The peaks A and B are identified as due to the reorientation of Ca²⁺-vacancy and Ba²⁺-vacancy dipoles. The analysis of the peaks yields activation energy values of 0.46 and 0.53 eV and values for pre-exponential factors as 5.46x10⁻⁹ and 3.79x10⁻⁹ sec respectively for dipoles formed by Ca²⁺ and Ba²⁺ with vacancies.
10.1 INTRODUCTION

As demonstrated in earlier chapters, ionic thermocurrent measurement is a powerful technique for studying point defects and their interactions in ionic crystals when these defects are created by the substitution of divalent impurities leading to the formation of composite structures such as the impurity vacancy (I-V) complexes [1,2]. Since these structures may have a dipole moment, it is possible to probe these defects with an electric field using techniques like dielectric loss and isothermal charging and discharging current measurements. A variety of defects in ionic crystals [3] have been investigated using ionic thermocurrent technique. It is also well known that many physical properties of ionic crystals are extremely sensitive to the presence of divalent cations [4]. The dispersion state of the dopant and the manner in which these cations are incorporated in the host lattice are dependent upon the thermal history of samples [5]. The impurity ions and vacancies can be presented as individual defects independent of one another or they may form aggregates into dimers, trimers or higher order complexes [6-8]. The first attempt to study the effect of double doping technique was reported by Morigaki et al. [9] in alkali halides containing divalent paramagnetic and diamagnetic ions [10]. This technique was used primarily to avoid magnetic exchange and dipole-dipole interactions. Later this technique
has been extended to study aggregation of kinetics in doped alkali halides. A major advantage of this technique is that it can also be used to remove the aggregation of impurities. The mechanism behind this technique is to dope the pure material with a divalent cationic and a monovalent anionic impurity simultaneously. The first experimental study of this kind was performed by Yokozava and Kazumata [11] in NaCl doped with Mn$^{2+}$ and F$^{-}$ impurities. It is believed that Mn$^{2+}$ vacancy complex is trapped and stabilised at F$^{-}$ impurity to form cation impurity-vacancy-anion impurity complexes [represented by (MV)$_{F^{-}}$]. Though the migration of (MV)$_{F^{-}}$ is not possible, only the rotation of MV dipole is possible. Thus the ITC study of such systems would ideally clarify the motion of bound vacancy in MV dipole associated with F$^{-}$ impurity. As a result it is possible to control the properties of dipole polarization of impurity vacancy complexes by this technique. In the present chapter a detailed study of the ITC measurements in crystals obtained by simultaneous doping by two different divalent cation impurities have been reported. Results are presented for NaN$\text{O}_3$ crystals doped simultaneously with Ca$^{2+}$ and Ba$^{2+}$. Such type of investigations have not been reported earlier in the literature for doubly doped non-cubic systems.
10.2 EXPERIMENTAL DETAILS

Single crystals of NaN\textsubscript{3} doped with various amounts of Ca(NO\textsubscript{3})\textsubscript{2} and Ba(NO\textsubscript{3})\textsubscript{2} (ranging from 0.02 to 0.1 mole %) were grown from melt using Bridgman technique. No precipitation of impurities were observed during the growth process. Samples with their broad faces parallel to the growth axis coated with aluminium electrodes using vacuum evaporation technique were used for the ITC studies. The ITC measurements were carried out in a metallic chamber described in chapter II using the usual procedure. The current measurements were made using an electrometer (Keithley, model 617) and a heating rate of 0.07K/sec was maintained throughout the entire temperature range of study (80 to 300K).

10.3 RESULTS OF ITC MEASUREMENTS

The ionic thermocurrent spectrum obtained for doubly doped specimens of NaN\textsubscript{3} containing 0.02 mole % Ca\textsuperscript{2+} and Ba\textsuperscript{2+} polarised at 300K with a fairly large field (3KV/cm) using a polarising time of 5 minutes is shown in figure 10.3a. The spectrum obtained shows two well defined current peaks (denoted as A and B in the increasing order of temperature) at temperatures 223 and 252K. It is observed that the magnitude of the current peak A is larger than that of the peak B. The current maxima for both these two peaks show linear relation with the
Figure 10.3a. ITC spectrum obtained for doubly doped (0.02 mole % Ca$^{2+}$ and Ba$^{2+}$) Na$_2$NO$_3$ crystal.
applied field as shown in figure 10.3b. The variation of the height of the current peak A and B as a function of poling temperature is shown in figure 10.3c. It shows a smooth decrease in the height of the current maxima with the rise in poling temperature. Figure 10.3d shows the ITC spectrum obtained for 0.02 mole % Ca\textsuperscript{2+} and 0.05 mole % Ba\textsuperscript{2+} doped NaNO\textsubscript{3} crystals. The ITC spectrum obtained by polarising the specimen at 300K for 5 minutes with a field of 3 KV/cm indicates that only the peak B is enhanced when compared with those in figure 10.3a. In this case also, the height of the current peaks show linear variation with increase in poling field and a decrease with increasing poling temperature. It is also observed that for higher Ba\textsuperscript{2+} concentration only the size of the peak B is found to increase, whereas the magnitude of the current peak A remains almost the same. Figure 10.3e shows the nature of the variation of the ITC peaks A and B for a doubly doped NaNO\textsubscript{3} (0.02 mole % Ca\textsuperscript{2+} and 0.05 mole % Ba\textsuperscript{2+}) crystal annealed at 400K for one hour. It is observed that both these peaks are found to be almost suppressed.

On the other hand the increase in doping concentration of Ca\textsuperscript{2+} in NaNO\textsubscript{3} for fixed doping concentration of Ba\textsuperscript{2+} impurity causes changes only for the peak A. It is found that, the size of the peak A increases in proportion to the concentration
Figure 10.3b. Variation of peak height with poling field for (1) peak A, (2) peak B.
Figure 10.3c. Variation of peak height with poling temperature for (1) peak A, (2) peak B, in a doubly doped NaNO₃ crystal.
Figure 10.3d. ITC spectrum obtained for doubly doped (0.02 mole % Ca$^{2+}$ and 0.05 mole % Ba$^{2+}$) NaNO$_3$ crystal.
Figure 10.3e. Variation of ITC peaks A and B for a doubly doped (0.02 mole % Ca\(^{2+}\) and 0.05 mole % Ba\(^{2+}\)) NaNO\(_3\) crystal annealed at 400K for one hour.
of Ca$^{2+}$ impurities added. The activation energy values evaluated from the peaks A and B in NaNO$_3$ doped with 0.02 mole % Ca$^{2+}$ and 0.05 mole % Ba$^{2+}$ by making use of the initial rise method [12] are found to be 0.46 and 0.53 eV respectively. It is also observed that no appreciable change occurs in the activation energy values for the range of doping concentrations used here.

10.4 DISCUSSION

Although it is clear that the ITC peaks A and B shown in figure 10.3a obtained for doubly doped NaNO$_3$ crystals give the characteristics of the impurities incorporated in the material, a tentative explanation regarding the origin of each of these peaks can only be arrived at by considering the effect of various experimental parameters on the nature of variation of ITC peaks. To identify the species responsible for the ITC peaks, let us consider the effect of substitution of the two different cationic impurities on the NaNO$_3$ lattice. It is well known that substitution of covalent impurities in a lattice create vacancies or interstitials depending on the nature of impurities substituted and hence they form impurity-vacancy (I-V) dipoles in the specimen. Supposing that simultaneous substitution of two different cationic impurities in the same lattice is made, they form two different types of dipoles provided that the dipole-dipole
interaction is absent (or small). Depending on the size of the added divalent cationic impurities dipoles are formed at nearest neighbour and/or next nearest neighbour positions. Experimental results obtained here clearly show that the current peaks obtained for the doubly doped specimens of NaNO₃ are due to the formation of cation impurity-vacancy dipoles formed by the substitution of Ca²⁺ and Ba²⁺ impurity ions in the lattice. The amplitudes of these peaks preserved by a linear relation (shown in figure 10.3b) with the polarising field, clearly indicate the independent nature expected for the non-interacting dipoles. These conclusions are further supported by the results obtained for annealed samples. The observed suppression of ITC peaks with thermal annealing at higher temperature clearly shows that this process prohibits the formation of aggregate viz., Ca²⁺ vacancy and Ba²⁺ vacancy dipoles.

In order to identify the species responsible for the peaks A and B, we have extended the ITC studies on doubly doped crystals of NaNO₃ by changing the concentration of one of the species, while keeping the concentration of the other species fixed. It is observed that for higher concentration of Ba²⁺ impurities only the size of the peak B changed, which in turn unambiguously shows that the peak B can be attributed
to the I-V dipoles formed by Ba$^{2+}$ ions in the NaNO$_3$ lattice. Hence one can indirectly confirm that the peak A should be due to the presence of Ca$^{2+}$ impurities. This has been further verified by incorporating greater amount of Ca$^{2+}$ impurities in the NaNO$_3$ lattice and in this case it is noted that only the peak A is found to be increased as expected. Thus it is clear that the two ITC peaks obtained for doubly doped NaNO$_3$ are associated with Ca$^{2+}$-vacancy and Ba$^{2+}$-vacancy re-orientation. The activation energy for reorientation of these dipoles can be evaluated from the analysis of the ITC curve by making use of the equation,

$$kT^2_m = bE \gamma_0 \exp\left(\frac{E}{kT_m}\right)$$

where $b$ is the heating rate, $\gamma_0$ is the reciprocal frequency factor [2].

The activation energy values obtained for the peaks at 223 and 252K are 0.46 and 0.53 eV with pre-exponential factors of $5.46 \times 10^{-9}$ and $3.79 \times 10^{-9}$ sec$^{-1}$ respectively. Thus in the present investigations simple and direct identification of the species responsible for the ITC peaks has become possible.
10.5 CONCLUSIONS

The ionic thermocurrent studies carried out in Ca$^{2+}$ and Ba$^{2+}$ doped sodium nitrate crystals in the temperature range 80-300K lead to the following conclusions.

1. The ITC studies carried out in doubly doped NaNO$_3$ crystal show two distinct current peaks, one at 223K and the other at 252K.

2. Both the peaks show linear dependence with the applied field.

3. The temperature corresponding to the current maximum for both the two peaks is found to be independent of poling field and poling temperature.

4. The current maximum of both the two peaks is found to be decreased with increase in poling temperature.

5. No ITC peaks are found in the annealed specimens of doubly doped NaNO$_3$ crystals.

6. The peak at 223K is attributed to the reorientation of Ca$^{2+}$ vacancy dipoles and the peak at 252K can hence be due to the Ba$^{2+}$ vacancy dipoles. This conclusion is further verified by concentration dependences of the peaks.
7. The activation energy values for $\text{Ca}^{2+}$ and $\text{Ba}^{2+}$ vacancy dipoles are found to be 0.46 and 0.53 eV and the values for pre-exponential factors are $5.46 \times 10^{-9}$ and $3.79 \times 10^{-9}$ sec.

8. Dipole-dipole interaction has no significant effect in this system.
10.6 REFERENCES


