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Electrical conductivity in undoped and Mn^{2+}-doped $NaNO_2$ single crystals

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Abstract. Electrical conductivity studies in $NaNO_2$ single crystals with inherent impurities and also in crystals with added Mn^{2+} impurities have been reported. The heating conductivity runs of undoped and doped $NaNO_2$ crystals have been compared. The decrease in conductivity in cooling following a heating run has been attributed to the oxidation during heating leading to the bulk precipitation of impurities in the host. Above 170°C however the intrinsic defects are responsible for conduction. An anomaly is noticed in both the heating and cooling conductivity runs of the sample at about the Curie temperatures and has been found to show thermal hysteresis.

Keywords. Electrical conductivity; $NaNO_2$ single crystals; intrinsic defects; thermal hysteresis.

1. Introduction

Various physical properties of $NaNO_2$ have been extensively studied since its ferroelectricity was discovered by Sawada *et al* (1958). $NaNO_2$ undergoes a phase transition of first order from the ferroelectric to the sinusoidal anti-ferroelectric or incommensurate phase at 164°C (T_c: called the Curie temperature) followed by a second order phase transition to the paraelectric phase at $\sim$ 165°C (T_N: called the Néel temperature), the phase transitions being of an order-disorder type.

The electrical resistivity in pure sodium nitrite single crystals has been measured by Asao *et al* (1962) and Takagi and Gesi (1967). Their studies, however, did not throw any light on the nature of defects responsible for the observed conduction in this system. The electrical conductivity measurements in undoped and doped alkali halides and some low symmetry crystals (Barr and Lidiard 1970; Ramasastry and Murti 1968; Radhakrishna and Pande 1973) have nevertheless been proved to be fruitful in establishing the defect nature in corresponding crystal systems. To the best of our knowledge such measurements have not been reported in $NaNO_2$ crystals containing aliovalent impurities, though some EPR studies have been made in Mn^{2+}-doped $NaNO_2$ single crystals (Pandey and Upreti 1970 a, b; 1971). In this paper, we report the electrical conductivity measurements in undoped and Mn^{2+}-doped $NaNO_2$ single crystals.

2. Experimental

Single crystals of undoped $NaNO_2$ were grown from melt while those of Mn^{2+}-doped $NaNO_2$ by a solution method (Jain 1977) using GR grade (M/s Sarabhai M. Chemicals, India) sodium nitrite as the starting material. It was not possible to grow crystals of Mn^{2+}-doped $NaNO_2$ from melt as no stable dopant suitable for this purpose was available. The manganese concentration in our doped samples as determined by atomic absorption analysis was 140 ppm. The crystals were cut into platelets of approximate size $5 \times 5 \times 2$ mm. The smallest dimension of the platelet was along the crystal *b*-axis so that conductivity measurements could be made for current flow along this axis.

The DC conductivity was measured in the temperature range 85–253°C with an electrometer amplifier (ECIL EA 815). In order to get a good electrical contact, the opposite faces of the crystal specimen were coated with a thin layer of silver paint. A chromel/alumel thermocouple was kept just touching the crystal specimen to measure the temperature of the crystal for each observation. During observations, the heating/cooling rate was kept as small as half a degree per minute to allow the specimen to attain thermal equilibrium at any temperature. All the conductivity measurements were made in air and the maximum error in the measurement of temperature was $\pm 0{\cdot}5$°C. The polarization effects inherent in the DC conductivity measurements of ionic crystals were avoided by applying the electric field across the crystal only for a short duration of time (less than 20 sec) and noting the temporary pause of the meter needle.

3. Results

The results of the electrical conductivity measurements in single crystals of undoped and Mn^{2+}-doped $NaNO_2$ have been presented in figure 1 where the logarithm of conductivity σ is plotted as a function of reciprocal temperature in the temperature range 85–253°C. The graphs show conductivity results during heating and cooling runs for both types of crystals. The figure also shows the corresponding heating run plot obtained by using the data of Takagi and Gesi (1967) for their melt grown $NaNO_2$ single crystal. This plot is henceforth referred to as the "TG plot".

4. Discussion

The conduction process in sodium nitrite is evidently ionic (Zheludev 1971) and could thus occur either *via* vacancy jumps and/or through interstitial jumps of Na^+ ions. In the ferroelectric phase (below the Curie temperature) the conductivity values in the heating run of Mn^{2+}-doped $NaNO_2$ crystal are large as compared to those in the corresponding plot of undoped $NaNO_2$. This increase of conductivity shows that additional charge carriers participate towards conductivity in Mn^{2+}-doped $NaNO_2$. To derive such a conclusion by comparing the conductivity values in the heating run plots of undoped and doped crystals, grown by two different techniques (melt and solution) may normally appear ambiguous. The conductivity in a solution-grown crystal of an undoped material has been reported to be less than that of the corresponding melt-grown crystal (Ramasastry and Murti 1968; Mansingh and Smith 1971). But in the present case the situation is reversed because the solution grown Mn^{2+}-doped $NaNO_2$ crystal has a higher conductivity compared to the melt-grown crystal of undoped $NaNO_2$. Thus in our doped $NaNO_2$ crystals the role of Mn^{2+}

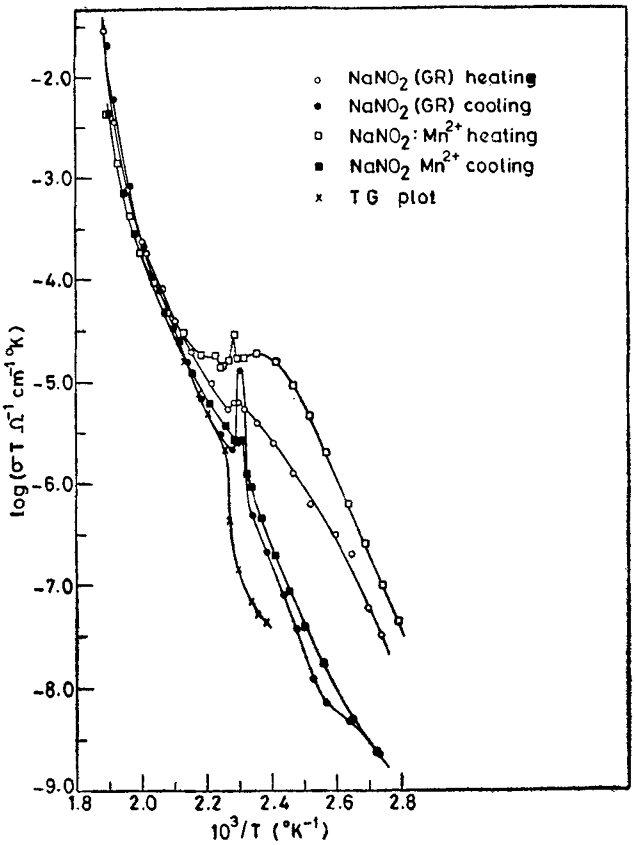

Figure 1. The temperature dependence of electrical conductivity σ for the undoped and Mn^{2+}-doped $NaNO_2$ single crystals in heating and cooling runs.

impurities towards increased electrical conduction is quite evident. Through EPR studies, it has been reported (Jain 1977) that when a divalent cation impurity (Mn^{2+}) is introduced in sodium nitrite, it replaces the sodium ion and a sodium ion vacancy is created to fulfil the charge neutrality requirement. Thus the additional charge carriers (extrinsic conduction) responsible for electrical conduction in Mn^{2+}-doped $NaNO_2$, are the sodium ion vacancies which move through the lattice with Na^+ ion jumps.

A comparison of the conductivity values in the heating run plot of undoped $NaNO_2$ with the TG plot, similarly shows that even in undoped $NaNO_2$ crystal there are appreciable number of charge carriers similar to those in Mn^{2+}-doped $NaNO_2$. This may be understood if it is considered that the starting host material has been reported to contain some aliovalent impurities: (Ca ~35 ppm), (Fe ~12 ppm), (Pb ~ 3 ppm) and (SO_4 ~ 36 ppm). Thus the undoped $NaNO_2$ crystal may consist of divalent and trivalent impurities.

The appreciably large values of conductivity in the heating runs below 170°C for both undoped and Mn^{2+}-doped $NaNO_2$, as compared to the corresponding cooling run values, may further be explained if it is presumed that divalent cation impurities imbedded in the crystal get oxidized and thus precipitated during the heating process (above 164°C). The oxygen for such an oxidation may probably be made available by nitrite ions with simultaneous creation of NO. In our studies the liberation of NO appeared quite imminent as the silver paint-crystal interface turned brown after each heating run. This liberation of NO also seems to establish that the precipitation of impurities in this system is irreversible. The crystal was also found turbid after measurements and it appears that this turbidity is due to microcracks created within the crystal as a consequence of escaping gas. These microcracks do not cause any detachment of electrodes because this would have resulted in decreased conductivity even in the intrinsic region contrary to our observations. The precipitation of impurity ions envisaged as above would cause the depletion of associated sodium ion vacancies from the crystal and thus result in a decrease in conductivity in cooling following heating. This phenomenon could also be explained on the basis of expulsion of impurities from the bulk of the crystal to its faces similar to what has been reported by Yacaman *et al* (1976) in alkali halide crystals doped with divalent impurities. The expelled metallic ions should get oxidized at the surface and one would thus observe blackening of Mn^{2+} -doped $NaNO_2$ crystal surface due to MnO formation. In the present case, however, the crystal did not appear blackened at the surface after heating. This accordingly shows that bulk precipitation mechanism dominates over that of expulsion. The depletion of charge carriers during heating can also explain the observed similarity in the cooling-run conductivity plots of undoped and Mn^{2+}-doped $NaNO_2$ crystals because a major portion of impurities in these crystals is made ineffective by bulk precipitation.

It is worthwhile to note that at temperatures above 170°C the conductivity plots in the heating and cooling runs match to a large extent for both undoped and Mn^{2+} -doped $NaNO_2$ crystals. These plots also match the " TG plot ". The matching for Mn^{2+} -doped crystal, however, starts at a somewhat higher temperature with the observation of an additional anomaly close to 177°C. The matching of all conductivity plots at temperatures exceeding 170°C indicates that the impurity ions are no longer responsible for conduction and that the conduction in this region may be due to the dominant intrinsic defects. The prominent intrinsic defects in this system are probably the interstitial sodium ions (Frenkel defects) because NO_2^- cannot be easily moved from their lattice sites due to their bigger size. The predominance of Frenkel defects over the Schottky defects in a similar system ($NaNO_3$) has been established by Murti (1967) through his theoretical investigation. The conduction in the paraelectric phase of $NaNO_2$ may thus be due to the motion of interstitial sodium ions and vacancies. The mobilities of these high temperature defects may not be equal and further vary differently with temperature explaining the high temperature curvature in the conductivity plots.

Finally, the cooling run plots of the two crystals do not exactly match the 'TG plot' indicating that some impurities with associated vacancies do remain in these crystals even after heating. The sharp fall in conductivity in the TG plot at low temperatures is further due to the fact that interstitials are eliminated at such temperatures leaving only a few impurity-generated vacancies.

In the cooling runs of both undoped and Mn^{2+}-doped $NaNO_2$ an anomalous peak in the conductivity plot is observed at 159·5°C. In the heating run of undoped $NaNO_2$, however, the anomaly is indicated at 162°C and for the sample with added Mn^{2+} impurities it is at 164°C. An anomaly is thus observed in the heating and cooling runs of both the samples at about the Curie temperature. The observed thermal hysteresis of 2·5°C in undoped $NaNO_2$ crystals and of 4·5°C in the corresponding doped crystal probably reflects the first order nature of the phase transition in $NaNO_2$ in concurrence with Sawada *et al* (1961), Hamano (1964) and Bohm and Hoffmann (1978).

A second anomaly has been observed at 177°C in Mn^{2+}-doped $NaNO_2$ crystal in its heating run. However, this has not been found in the undoped crystal with less impurities. It thus seems that the impurities have a role to make the anomalous behaviour detectable at 177°C. It would, however, be worthwhile to report that an anomaly at 178°C was for the first time reported by Hoshino and Shibuya (1961) and later by a number of other workers (Takagi and Gesi 1967; Sawada *et al* 1961).

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