

CHAPTER 9

ELECTRICAL CONDUCTIVITY MEASUREMENTS

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9.1 Introduction

The electrical conductivity is an important elegant experimental tool to probe into the structural defects and internal purity of the crystalline solids. Unlike metals and semiconductors where the electron is the charge carrier, electronic conduction is not an usual phenomena in insulators because of the large energy gap. In insulators, the factors contributing to electrical conductivity are the crystal defects such as isolated anion or cation (Schottky defect), cation substitutional impurities, cationic interstitials (Frenkel defects), colour centres, etc. Most of the earlier investigations on alkali halides¹⁻⁵⁾, tin iodates⁶⁾, rare earth tungstates^{7,8)}, Schultenite⁹⁾ and on ilmenite¹⁰⁾ described the electrical conductivity in terms of electrons (or holes), polarons and impurities thereby the mechanism of ionic conductivity.

The measurements of ionic conductivity has been one of the classical methods for the determination of energies of defect creation

and migration in ionic solids. In solid caused of ionic structure, the conduction is mainly caused by the displacement of ions liberated due to thermal fluctuations. At low temperature, it is most weakly bound ions, particularly impurity, ions, that are free to drift. At high temperatures, some ions detach from the sites of crystal lattices. Conduction in dielectrics with an atomic or molecular lattice structure is only associated with impurities. At room temperature, the lattice is electrically neutral due to pairing of various defects. Also, some carriers are observed as trapped at defect sites, which accounts for the very low conductivity of ionic materials at room temperature. Supplying thermal energy to the sample serves to thermally generate, the charge carriers because of the breaking of the weaker bonds, thus enhancing electrical conduction. The investigation of electrical conductivity in association with thermal variation has been studied in this chapter to understand the mechanism of charge transport.

9.2 Experimental

The single crystals of RHT used in the present investigation, were grown by employing the gel technique, as described in Chapter 5. The orthorhombic disphenoidal crystals of the sizes $10 \times 4 \times 3 \text{ mm}^3$ were selected. To obtain pellet samples of RHT, the crystals grown in the laboratory were finely ground and the resulting powders were compressed into a die of diameter 1.0 cm and thickness 0.3 cm under a pressure of 1100 kg cm^{-2} using a hand operated hydraulic press. The average particle size for sample was $150 \mu\text{m}$.

The electrical conductivity measurements were carried out in the temperature range 300 to 470 K. The single crystal or the pellet, as the case may be, was mounted between the flat silver electrodes in an ordinary conductivity cell. The silver paste was applied on both the experimental surfaces for firm contact. It was then enclosed in a resistance heated furnace and the temperature of the sample was monitored using a platinum-rhodium thermocouple ($\pm 1^\circ\text{C}$). The temperature of the samples

increased by regulating the input power. The rate of heating could be maintained linear for a reasonably large range of temperatures. The resistance of the sample is measured by a EBM (India) Million Megohmmeter (Model No. EBM 115). The accuracy in the measurement of resistance in the range $10^6 \Omega$ to $10^{14} \Omega$ is 5 %. The readings of the megohmmeter were recorded when the values became steady. The measured values of resistance at different temperatures were converted into the electrical conductivity (σ) by knowing the area and thickness of the samples while the dimension of the crystals were measured with the help of a travelling microscope of least count 10^{-3} cm. Prior to the conductivity measurements, the samples were heated and cooled for two to three cycles to avoid moisture in the samples.

9.3 Results and Discussion

The dc conductivity, σ $\text{ohm}^{-1} \text{cm}^{-1}$ at different temperatures for pellet as well as for RHT single crystals samples are summarized in Table 9.1.

Table 9.1Values of Electrical Conductivities (σ) of RHTDifferent Samples

Temperature of the sample in K	Electrical conductivity (σ) of the samples in (ohm ⁻¹ cm ⁻¹)	
	Pellet x 10 ⁻¹³	Single crystal x 10 ⁻¹³
323	2.305	2.946
332	3.477	4.409
342	4.403	5.642
352	5.651	7.373
364	8.061	10.71
373	10.08	12.20
383	12.32	17.15
393	16.12	23.28
402	21.21	37.28
412	35.05	61.42
422	57.58	96.10
432	83.59	149.90
442	129.70	234.20
452	174.10	301.20

The variation of $\ln \sigma$ with the reciprocal of absolute temperature of the pellet and crystal samples are illustrated in Figure 9.1. It is clearly seen from the figure that the value of $\ln \sigma$ for crystal samples are always higher than for pellet samples for a given temperature over the temperature range investigated. This may be explained due to the fact that when the electric field is applied on the two opposite surfaces of the crystal the charge carriers move freely in the crystal and reach the other electrode, while in the case of polycrystalline pellet samples all charge carriers cannot reach the other electrode. Some will be trapped at the grain boundaries and give rise to interfacial polarization.

The variation in the electrical conductivity observed in Figure 9.1 yield different straight lines and it is in accordance with the relation :

$$\sigma = \sigma_0 e \mu \exp \left[\frac{-E_g}{kT} \right] \quad (9.1)$$

where σ_0 = is the number of charge per cm^3 ,

e is the electronic charge,
 μ is the mobility of charge carriers,
 E_g is the activation energy of the process,
 k is the Boltzman constant, and
 T is the temperature of the sample.

The linear variation of plots are broken at a temperature T , of nearly 393 K, thereby giving two straight lines with different slopes for both samples. The differential thermal analysis (Figure 8.5, Chapter 8) experiments failed to show any phase change of the crystal in the temperature range studied, and in particular, at critical temperature, T , so that the author believes that there exist two types of conduction in this material, one at low temperature and the other at high temperature, by the way of extrinsic and instrinsic conduction respectively.

The hydrogen atoms linked between $(Rb)^+$ and $(HCOOH)_2^-$ ions may also act as impurities. Thus the extrinsic conductivity is due to $(Rb)^+$ and $(HCOOH)_2^-$ ion vacancy impurities or both. The activation energy in the extrinsic range is therefore

a measure of energy required to move the permanent defects. In the intrinsic range, where the electrical conductivity is predominantly due to the movement of defects produced by thermal activation, it is associated with the pure crystal. As pycnometric density (2.263 gm cm^{-3}) and X-ray density do not differ in this crystal, there may be a small concentration of Frenkel defects in the stoichiometric crystal, which seem to be dominant in electrical conduction in the sample. The estimated values of activation energies for pellet and single crystals are given in Table 9.2. It is clearly seen from this table that the activation energies for crystals are higher than that of pellet samples.

9.4 Conclusions

1. The variation σ in dc conductivity of single crystal and pellet samples are studied in the temperature range between 300 to 470 K.
2. The electrical conductivity of the crystalline samples are larger than that

Table 9.2Activation energies of different samples of RHT

Particular of the sample	Activation energy in eV	
	Low temperature range	High temperature range
Pellet	0.652	0.162
Single crystal.	0.734	0.237

of pellet samples.

3. The electrical conductivity in the case of RHT crystals is intrinsic above 393 K and extrinsic below 393 K.
4. The extrinsic conductivity is dominated by $(\text{Rb})^+$ and $(\text{HCOOH})_2^-$ ion impurities while the intrinsic conductivity is due to Frenkel defects.
5. The activation energy for the electrical conduction process is estimated. The activation energy for crystals are higher than that of pellet samples.

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Captions of the figures

Figure 9.1 Variation of electrical conductivity
with temperature for single crystal
(●) and pellet (▲) samples
of RHT.

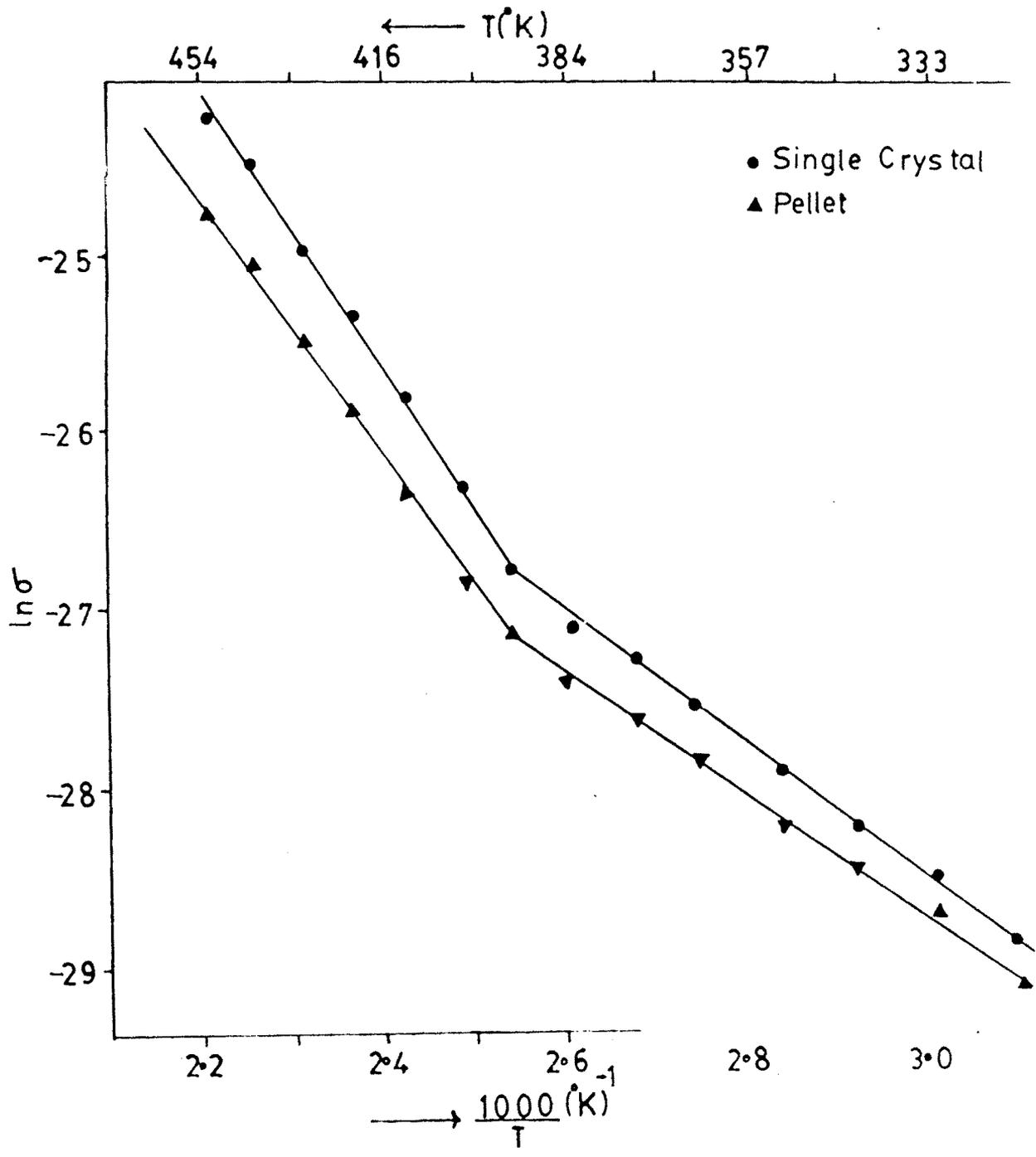


Fig. 9.1