CHAPTER V

D.C. ELECTRICAL CONDUCTIVITY

5.1 INTRODUCTION

The importance of an understanding of conductive processes cannot be overestimaed. Besides the obvious application to thermistors and barrier layer capacitors, the ability to control conductivity, and usually to keep it very low, is highly important to the piezoelectric uses of ceramics. Compositions which are too conductive are difficult to pole, tend to overheat in high power applications, and generally have undesirably high dielectric loss which limits efficiency.

Electrical conductivity is one of the essential charceristics of a substance and the elucidation of the conductivity is of primary importance. In particular, the electrical conductivity of ferroelectrics with simplest perovskite structure is not well understood. It is found that the point defects are responsible for many electrical properties of ABO_3 (A = Pb, Ba, Sr B = Ti) oxides belonging to perovskite family. The first step in the understanding of electrical transport in any solid is to know whether conductivity is ionic or electronic or mixed (partially ionic and electronic). There are several ways of determining the nature of conductivity. The simplest way is to measure d.c. conductivity as a function of time using electrodes which block ionic conduction. In the case of pure ionic conduction, d.c conductivity decreases with time and tends to become zero after sufficiently long time, whereas for a pure electronic conductor it is essentially independent of time. For mixed conduction it decreases with time but tends to stabilize at some finite constant value, which is the electronic contribution.

As far as ionic conductivity is concerned, interstetial conduction seems diffcult owing to vary compact structure of a peroveskite. Therefore creation of vacancies in the ceramic because of incomplete solid- state reaction or doping, appears the possible mode for ionic conduction. It has been observed that the perovskite structure tolerates substantial amount of vacancies, (79). Therefore, variation of conductivity with substitution is to be discussed in the light of possible mode of vacancy formation.

The seebeck co-efficient measurements on these systems indicate, whether the conduction is due to holes or electrons. A position vacancies in ABO₃ system attract electrons to complete the electronic shell of the surrounding oxygen, they act as an acceptor causing the

presence of holes in the lattice according to the relation.

$$v_A - v_A + 2h$$
(5.1)

Where V represents a vacancy. Similar effects are produced because of substitution also A positive ion replacing a higher valance cation acts as an accepter that is k^{1+} for Ba²⁺. In contrast a possitive ion replacing another of lower valancy acts as a donar e.g. sb⁵⁺ for Ti⁴⁺.

Resistivity of single crystal $BaTiO_3$ is very large, of the order of 10^{12} and shows a instrinsic conductivity both above and below the transition temperature. In case of ceramics the pores and imperfections create the donor and acceptor sites reducing the order of resistance.

As far as understanding the behaviour of compensated off valence substitution, the analysis could not vary straight forward. The sites where Ti^{4+} is replaced by Fe^{3+} or Cr^{3+} acceptor sites will be created, while the positions where Ti^{4+} replaced by b^{5+} donor siter will be created. The over-all conduction will then be the interbalances between these two types of conduction mechanisms.

In the present work, investigations are carried out on the variation of d.c. electrical conductivity with temperature in the solid solutions of $(BaFe_{x/2}Sb_{x/2})Ti_{(1-x)}O_3$ and $BaCr_{X/2}Sb_{X/2}Ti_{(1-X)}O_3$. These solid solutions being ferroelectric materials, possess large values of piezoelectric properties

near the transition temperature, and make them attractive in devices requiring piezoelectricity.

5.2Experimental

The experimental setup used for the study of d.c. conductivity of ferroelectric solid solutions of $(BaFe_{x/2}Sb_{x/2})Ti_{(1-x)}O_3$ and $BaCr_{x/2}Sb_{x/2}Ti_{(1-x)}O_3$ shown in fig. 5.1.

The experimental setup is discussed in sec. 2.6 The electrical conductivity is measured in the constant voltage mode, using a voltage sourse and a nano-ameter.

The pellets of above solid solutions were used in the form of dises (diameter lcm and thickness about 2mm). The pellet is placed in two copper strips for good electrical contact.

The d.c. conductivity investigation were based on the d.c. resistivity data obtained by two probe method. To ensure ohmic contact between pellet and electrode interface, the current through pellet was measured as a function d applied d.c. voltage at constant temperature and a linear region is selected to apply the constant voltage. We shall put a few observations regarding the conductivity behaviour.

1) The resistivites observed are very high and are of the order of 10^7 to $10^8 \ \Omega$ -m single crystal BaTiO₃ possesies the resistivities of 10^{11} to $10^{12} \ \Omega$ -m.

 The conductivity is measured in the linear region of I-V. characteristics.

3) Conductivity decreases with time indicationg the ionic conduction prevalent in these compositions.

4) No region of positive temperature co-efficient of the resisitivity is observed, as expected. The PTCR phenomenon is observed for donor doped $BaTiO_3$ ceramic specimens (79). This non-observance suggests that both the donor and acceptor contributions are prevalant to decide the conduction phenomenon for the FeSb as well as CrSb substitutions.

5) The conductivity appears to obey the conventional equation

$$6 = 6g exp - \frac{\Delta}{kT}$$

Where \bigwedge_{u} is the activation energy k is the Boltzman's constant. 6g basically determines available number of sites for conduction to take place.

(fig. 5.2-5.6 show variation of log 6 as a function of for $BaFe_{X/2}$ $Sb_{X/2}$ $Ti_{(1-X)}O_3$ with x = 0.025, 0.05, 0.1, 0.2and 0.4. Arrows in the graph indicate the Tc_2 and Tc_1 , as determined from the E vs T behaviour.

For the FeSb subititution the Tc_1 , recorded from the behaviour of dielectric constant is too low 100°c and conductivity was very low to be measured accurately. In the temperature range near Tc_2 300°c the current passing through the sample for 50-100v/cm electrical field across the sample in the range of few nano-amperes.

The $\triangle u$ for the temperture above To₂ $\triangle u_2$, more as compared to the one below Tc₂, $\triangle u_1$, and other ceramics e.g. (80) and is the consistent with measurements on single crystal BaTiO₃. Both u_2 and u_1 are observed to decrease with increasing level of FeSb substitution, table 5.1.

 Δu represents combined effect of creation of vacancies with increasing temperature as well as energy required to promote migration of ions in the vacncies available. Decreeasing Δu_1 and Δu_2 with concentration of FeSb is to be attributed to the Ba Fe x/2 Sb 4/2 Ti $_{1-x}$ O₃



^{Ti}0.975⁰3.

 $\langle i \rangle$









t:

TABLE 5.1

x	Δu above TC ₂	∆u below TC ₂
	Δu_2	Δu_1
0.25	0.8626	0.4767
0.05		0.3137
0.1	0.4831	0.3105
0.2	0.4436	0.2740
0.4	0.2090	0.1113

The Variation Of $extsf{Du}$ With Composition For FeSb

The Variation Of \triangle u With Composition For Composition CrSb

x	∆ u ₂	<u>∧</u> u ₁	∆ uø
	Δ u above TC ₂	Δ u above TC $_2$	Δ u below Tc ₁
0.025	0.3623	0.6161	Ø.1629
0.05	0.3078	0.2786	0.1752
0.1	0.4679	0.8626	
0.2	0.3220	0.6133	0.3044
0.4	0.3810	0.5176	0.0940

reduction in avaible vacancies as the substitution level is invresed.

Further the resistivity of the material at T=570 k TC_2 is observed to pass through a maximum for X = 0.025 fig 5.12 the present investigations show similar trend in the parameter 'c/a', sec 3.4 and dielectric constant sec 4.3 Further investigations of transport phenomenon are reequired to come to any concrete conclusion.

[fig 5.7 - 5.11 show variation of log 6 as a function of

to $10^{3/T}$ for BaCr_{x/2} Sb_{X/2} Ti_(1-X)⁰3

For CrSb system the overall behavior of conductivity obeys equ 5.1, but there different regions of activation energy are observed for temperatures

1) $T < TC_1 (\Delta u_0)$,

2) $Tc_1 < Tc_2$ (Δu_1) amd

3) $T > Tc_2 (\Delta u_1)$.

It has been observed table 5 that $\Delta u_1 > \Delta u_2$ as well as $\Delta u_1 > \Delta u_2$. The increase in Δu as T increases above $Tc_1, \Delta u_1 > \Delta u_3$,

could be attributed to reduction in amount of energy required for migration of the ions in the available vacancies and creation of additional vacancies both.







T



Fig. 5.9 : Plot of log 6 versus 1000/T for Ba Cr Sb .05

(8)





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Fig. 5.11 : Plot of log 6 versus 1000/T for Ba $Cr_{0.2}Sb_{0.2}Ti_{0.6}3$.

Though unusual but as the temperature is increased further $\triangle u$ again decreases $\triangle u_2 < \triangle u_1$ for T>Tc₂. This may indicate a structural charge occuring in the system. Within the new structure the available rate of charge of creation of vacancies may reduce or safurate and effective activation energy may reduce again. To confirm this logic, further investigations on these systems are must. The variation of crystal structure with temperature and the measurements of seebeck co-efficient are a few parameters of relavance in this case.

The resistivity at T = 588 k for this series also is observed to pass through a maximum for x = 0.1 fig 5.12 this observation is similar to the observations on FeSb system.

We wish to make a mention again of the fact that the investigations are too elementary to come to any definite conclusion about the effect of compensated off valency substitutions to modify the physical properties of perov skite systems in general.

· (1)



Fig. 5.12 : Variation of the resistivity with concentration for

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