

Chapter - VII

SUMMARY
AND CONCLUSIONS

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The pure potassium niobate belongs to perovskite family of ferroelectrics, and is similar to Barium titanate. It is a typical ferroelectric which exhibits almost all the characteristic properties of ferroelectricity. Potassium niobates doped with various elements on the other hand are a new type of ferroelectrics. Also from a chemical and mechanical properties view point, these new system of doped semiconducting ferroelectric ceramics are found to be very stable. As regards their practical applicability, it may be noted that they exhibit ferroelectric property near and above room temperatures, and have significant electric conductivity and thermoelectric power characteristics, and hence are most promisingly the versatile materials.

The following explicit five studies, have been carried out on KNbO_3 and $\text{K}(\text{Ni}_x \text{Fe}_y \text{Nb}_z)\text{O}_3$ and are suggestive of significant characteristics of the materials developed by us.

I. a) The study of sample preparation of $\text{K}(\text{Ni}_x \text{Fe}_y \text{Nb}_z)\text{O}_3$ where $x=y=0, 0.02, 0.05, 0.10$ and 0.15 by ceramic method, so as to obtain low porosity ceramics.

b) X-ray diffraction and lattice parameters determination

for the ferroelectric phase of the ceramic at room temperatures.

- II. Experimental investigation of dielectric hysteresis loops, coercive fields and Curie temperatures of the samples.
- III. Measurement of dielectric constant at different temperatures.
- IV. D.C. conductivity measurement at different temperatures.
- V. Measurement of thermoelectric power at different temperatures.

Chapter I gives an historical account of development of ferroelectrics and a review of the thermodynamical theory. A short account of classification, characteristic and dielectric properties are also presented. Applications usually made are given at the end of this chapter.

Chapter II gives the method of preparation of ferroelectric material and details of pellet formation. X-ray diffraction studies have been carried out to confirm the formation of ferroelectric sample, and the characterisation of crystal structure. The lattice parameters are found to be consistent with those reported by Wood (1) and Shirane (2) et al. The lattice parameters are found to exist minimum for potassium niobate and increase with the impurities up to $x = y = 0.05$, then are found to decrease with further increase of impurity content.

In chapter III, the data on dielectric hystereses of ferroelectric samples have been reported. A modified form of Sawyer and Tower (3) circuit was used to determine the dielectric hysteresis loop and coercive field of potassium niobate and the said system. The hystereses loops observed for potassium niobate and the system at various temperatures are shown in Fig. 3.2 to 3.6. It was observed that the shape of hysteresis loop is temperature dependent. The hysteresis loop vanishes at curie temperature. The coercive field at various temperature was measured with the study of shape and half width of hysteresis loop. The coercive field increases with the increases in the impurity concentrations, while the curie temperatures lowered on addition of impurity concentrations.

In chapter IV studies on dielectric constant have been reported. The dielectric constant was determined at various temperatures for the potassium niobate and the system, from capacity measurement data, and is shown in Fig. 4.2 to 4.6. It is seen from these that the dielectric constant varies with temperature and shows the peak value at curie temperatures. These results are consistent with those reported by Shirane (2) et al, and Younskii (4). The dielectric constant increases with the impurities concentration.

In chapter V the data on d.c. electrical conductivity of potassium niobate and the system of ferroelectrics has been reported. The d.c. electrical conductivity was measured by two

probe method, in the temperature range covering their transition points, as shown in Fig. 5.3 to 5.7. The sharp changes observed at the phase transition temperature, is indicative of curie temperature of respective samples. The nature of electrical conductivity of all the samples reflects the ionic state of the materials. The activation energies were calculated both for the ferroelectric and the paraelectric studies. It was observed that the activation energy depends on impurities concentration. The activation energy in paraelectric state is more than that in the ferroelectric state. This is in accordance with Handerck (5) et al observations.

In chapter VI the data on thermoelectric power of potassium niobate and the system of ferroelectrics samples is shown in Fig. 6.2 to 6.6. For potassium niobate the seebeck coefficient is negative, indicating that majority carriers are electrons i.e. the material is an n-type semiconductor, which is quite consistent with the report of Srivastava et al (6). With the addition of impurities the transition temperature is found to decrease. Above transition temperature the sample exhibits a p-type of semiconductivity. Peaks of α -values are observed during both the n-type conduction and p-type conduction. As the impurities concentration increases the value of the peak temperature is found to decrease.

Taking into consideration all the experimental results of our studies of the potassium niobate and the system, the following can be said about the nature of transition in the ferroelectrics. The variation of coercive field with temperature, near the two transition temperatures for the KNbO_3 and Ni and Fe impurities system, leads to very interesting and physically significant aspects of the nature of order of transitions involved. In pure system, both Curie temperatures are of first-order transition type and they have been remarkably well reproduced in our results. With $x=y=0.02$ impurity substitution content the ferroelectrics system showed the orthorhombic \rightarrow tetragonal phase transition as a first-order type, while the tetragonal \rightarrow cubic phase transition is best probably a second-order type. Further the $x=y=0.05$ impurity substitution content showed a similar nature of the both transition temperatures, though the coercive field magnitude and transition temperatures differ considerably from those that of $x=y=0.02$ impurity substitution content system. Thirdly, with $x=y=0.10$, and 0.15 impurity substitution content the above said system exhibited minimum of the coercive field near the transition temperatures (598°K , 548°K). The nature of this variation, shows that both phase transition temperature, namely orthorhombic \rightarrow tetragonal and tetragonal \rightarrow cubic are seen to be of the second-order type. The

tetragonal \rightarrow cubic phase transition temperature strongly lowered so as to fall within the region of orthorhombic \rightarrow tetragonal transition temperature. From this last observation we may remark that tetragonal phase exists as an intermediate ferroelectric phase over a very limited range of temperature.

From the d.c. electrical conductivity of the system, it is observed that electrical conductivity not only depends on temperature but also on the impurities concentration. The electrical conductivity of the system decreases with time and tends to become zero after sufficiently long time. From this we can say that the electrical conductivity of the system is ionic nature in the ferroelectric phase as well in the paraelectric phase. But the activation energy of the system is higher in the paraelectric state.

Thermoelectric power shows a minimum at 498°k . Below this, the coefficient increases rapidly and above this temperature, thermoelectric power increases with the temperature and reaches a maximum value at 573°k . Thermoelectric power shows a second minimum at 685°k . Below this temperature α increases rapidly and above this temperature thermoelectric power increases with the temperature. These increases of the thermoelectric power is an interesting feature of the ceramic semiconducting samples studied in this work.

The system with impurity content $x=y=0.02$ clearly demonstrated a sudden change in the conductivity property at 460°k from n-type to p-type. This transition temperature from the conductivity change is lower than the temperature 498°k in the pure KNbO_3 sample, at the expected first-order phase transition of the ferroelectricity. A second-order transition temperature at which p-type to n-type conductivity is observed at 598°k , seems to be considerably lower than the temperature 685°k , that corresponding to KNbO_3 phase transition namely tetragonal \rightarrow cubic phase. The $x=y=0.05$, 0.010 and 0.15 impurity content system $\text{K}(\text{Ni}_x \text{Fe}_y \text{Nb}_z)\text{O}_3$ show a similar behaviour of thermoelectric power variation as a function of temperature as shown in Fig. 6.3 to 6.6. However, it may be noted that the change in the respective transition temperatures, first n-type to p-type and second p-type to n-type.

In general, it is seen from the figure the thermoelectric power α -depends mainly on temperature. It is clear that pure KNbO_3 is n-type with the number of free electrons n is by no means a constant. The dopant system $\text{K}(\text{Ni}_x \text{Fe}_y \text{Nb}_z)\text{O}_3$ on the other hand, clearly exhibits variation of thermoelectric power with charge concentration.

Further, the data plotted in the Fig. 6.3 to 6.6 indicates not only variation in charge carrier concentration but also type of charge carrier, which play an important role in the conductivity characteristics.

The system with the impurity content positively established the existence of an intermediate phase which is of p-type conductivity.

The change of the sign of seebeck coefficient with the temperature is indication of level of excitation between the two types of the states. The intermediate phase is obviously dominated by those states of oxygen defects which play an important role. The pure KNbO_3 has intermediate phase of conductivity which is only of n-type. Thus the pure KNbO_3 and the system $\text{K}(\text{Ni}_x \text{Fe}_y \text{Nb}_2)\text{O}_3$ differ markedly in the mechanism responsible for their electrical conductivity character. We may draw conclusion that the tetragonal phase of the ferroelectric conductivity behaviour seems to be not appreciably same as the intermediate phase electrical conductivity of the doped samples. The explanation lies mainly in the occurrence and nature of oxygen defects. The nuclear resonance data given in Chapter II supports this finding in the sense that the polarised state is not entirely ionic but is characterized by stronger interactions. This aspect becomes a subject matter of our further research. As

stated in Chapter II we emphasize that strong interactions between crystallites of the doped samples and their characteristic boundaries make these *new* ceramics as really the *novel* ceramics. The nature of crystallites and boundaries interactions differ since Ni and Fe dopants give rise to new intermediate phase existence, in these ceramics. Further consistent with the nuclear resonance data we observe covalency effects superimposed over the ionic oxygen defect behaviour of these ferroelectrics.

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