CHAPTER-VII

SLMMARY AND CONCLUSIONS

Ferroelectrics, include the most significant polar materials both from a basic view point and from an applications view point. They possess some of the most interesting dielectric, pyroelectric, piezoelectric, thermal, optical and electrical properties. They have particularly high values of pyroelectric, piezoelectric and dielectric coefficients; because of the inherently high degree of internal ordering in them. As ferroelectrics possess fascinating and challenging properties they are used in varity of device applications such as memories, displays, printers, logic circuits, light modulators, deflectors, frequency changers detectors etc. In view of this, an attempt has been made in the present work, to prepare undoped and doped KVO_3 with Er_2O_3 by ceramic method study X-ray diffraction, E.P.R, dielectric hysteresis, and to pyroelectricity, dielectric constant and d.c. electrical conductivity. The results have been presented in the chapters II to VI of this dissertation.

The first chapter of this dissertation intended to provide the general introduction to the field of 'ferroelectrics.'It covers historical development, characteristic properties, classification of ferroelectrics and theoretical approach based on some ferroelectric materials. The second chapter gives procedure of the preparation of the samples, X-ray diffraction analysis and E.P.R. studies of different samples. Undoped and $\operatorname{Er}_2O_3(0.025$ to 3 mol%) doped KVO₄ were prepared

by ceramic method reported by Feigelson et al (1972) and Hawthorne and Calvo (1977). The lattice parameters of these samples were calculated from X-ray diffraction patterns by using least square method (Gauss, 1930). The pellets of these samples were prepared using a hydraulic press. These pellets were sintered at about 450°c for 3 hours and the two faces of the pellets were coated with thin layer of air drying silver paste. These pellets were used for the experimental investigations. In Chapter III, we have determined Curie temperatures of different samples and measured coercive field by using modified form of Sawyer and Tower circuit (1930). The pyroelectric behaviour of the samples was studied in chapter IV by using dynamic method devised by Chynoweth (1956) to measure pyroelectric parameters. Chapter V deals with dielectric constant measurement at 1 KHz frequency, by the method based on the principle of 'comparison of capacities.' In chapter VI, we have studied the d.c. conductivity of the samples in which, d.c. resistivity was measured two probe method in the temperature range covering their transition by temperatures. Also, the nature of conductivity (ionic, electronic or mixed) was determined by studying time dependence of the conductivity of the sample.

In this chapter, a brief account of the conclusions drawn in the present work is given;

The X-ray diffraction analysis showed that there is no change in the lattice parameters for undoped and Er_2O_3 (0.05 to 3 mol %) doped KVO₃. But it was observed that KVO₃ doped with 0.025 mol % Er_2O_3 shows

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appreciable change in lattice parameters. It shows appreciable decrease in volume of the unit cell. From this we can conclude that the added Er_2O_3 (0.025 mol %) in KVO₃ supports the substitution of Er^{3+} for K¹⁺ in the lattice of KVO₃.E.P.R.studies of undoped KVO₃ and 0.0225 mol % Er_2O_3 doped KVO₃ showed that Lande 'g' factor changes appreciably due to addition of Er_2O_3 in KVO₃ showing possibility of substitution of Er^{3+} for K¹⁺ in the lattice of KVO₃.

The dielectric hysteresis loop was observed for all the samples, indicating their ferroelectric behaviour. The shape of hysteresis loop (polarization versus electric field) is found to be temperature dependent. The half-width measurement of the hysteresis loop gives directly coercive field of the sample. It is confirmed that quite above the room temperature the hysteresis loop width decreases with increasing temperature and vanishes at the Curie temperature, indicating the temperature dependence of the coercive field (Fig. 3.10). It is found that Curie temperature and coercive field are strongly depending on Er₂O₂ content in KVO_3 . We further learned that as Er_2O_3 concentration increases, Curie temperature of KVO_3 decreases from $322.5^{\circ}c$ to $260^{\circ}c.It$ is similar with the results reported by Kuroda and Kubota (1980). The coercive field is maximum for KVO₃ doped with 0.025 mol % Er_2O_3 indicating substitution of K^{1+} by Er^{3+} . This result is also confirmed by increase of density of the same sample i.e. decrease of unit cell volume of KVO_3 doped with 0.025 mol % Er_2O_3 . For further increase of Er_2O_3 content in KVO_3 represents decrease in coercive field indicating defects created

in the ceramic due to substitution of Er^{3+} for K^{1+} .

The pyroelectric studies of the samples show that the pyroelectric current and pyroelectric coefficient are temperature dependent. These pyroelectric parameters show peak values for the samples indicating their Curie temperatures. The maximum peak values are observed for KVO_3 doped with 0.025 mol %, showing maximum change in spontaneous polarisation w.r.t. temperature at its Curie temperature. This result is directly related with the density of the samples and hence for KVO_3 doped with 0.025 mol % Er_2O_3 sample density is high indicating rather more solid state interaction that takes place in it. This also confirms that the solubility limit of Er_2O_3 in KVO_3 lattice is 0.025 mol %.

Undoped and $\mathrm{Er}_2\mathrm{O}_3$ (0.025 to 3 mol %) doped KVO₃ samples show anomalous dielectric behaviour at their Curie temperatures (Fig. 5.3); which is the peculiarity of the ferroelectric material. The peak value of dielectric permittivity (ϵ_{max}) strongly depends on $\mathrm{Er}_2\mathrm{O}_3$ content in KVO₃ as well as density of the sample. ϵ_{max} is higher for KVO₃ having 0.025 mol % $\mathrm{Er}_2\mathrm{O}_3$. This indicates that the dielectric saturation state is observed for 0.025 mol % $\mathrm{Er}_2\mathrm{O}_3$ doping in KVO₃. This high value of ϵ_{max} indicates good ferroelectric behaviour of the sample. Further increase of $\mathrm{Er}_2\mathrm{O}_3$ concentration shows decrease of ϵ_{max} representing inclination of ferroelectric material towards the non-ferroelectric behaviour.

The d.c. electrical conductivity studies of the samples showed a sharp change in the d.c. conductivity at the phase transition temperature of the sample (Fig. 6.4). It is confirmed that the d.c.

conductivity of the sample in ferroelectric state is smaller than that in the paraelectric state. The sample of KVO_3 containg 0.025 mol ${}^{0}_{0}$ Er $_{2}O_{3}$ shows high conductivity as compared to other samples. This also indicates that 0.025 mol $% \text{ Er}_2\text{O}_3$ content in KVO₃ may represent the solubility limit of $\operatorname{Er}_2 \operatorname{O}_3$ in KVO₃ lattice, producing more solid state reaction in the material. This might be due to decrease in grain size and hence due to increase in density of the sample. Similarly, due to doping of Er_2O_3 in KVO₃ there is possibility of substitution of K^{1+} by Er^{3+} producing vacancies in the lattice. Due to more mobile K^{1+} ions and their vacancies activation energy of the sample containing 0.025 mol % Er_2O_3 is very small; and hence the sample is more conductive The Table 6.1 shows activation energies for samples both in paraelectric and ferroelectric states indicating their large values in paraelectric state as compared to ferroelectric state. It is confirmed that for all the samples the conductivity is of mixed type (i.e. ionic + electronic) in ferroelectric state and it is of electronic type in paraelectric state (Fig. 6.3).

The summary and conclusions of the present work indicate that the ferroelectric properties of ceramic KVO_3 doped with 0.025 mol % Er_2O_3 are pronounced and would be useful for applications in future.