
CHAPTER - VI

SUMMARY AND CONCLUSIONS

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Ferroelectrics, having recently become increasingly important as materials of electronic devices, memories, displays, printers, logic circuits, light modulators and deflectors, are further studied in view of their versatility in the design of devices. PTC devices have also come up as detectors. Again the sensitive dependence of ferroelectric properties and electrical conduction on isovalent and offvalent impurities content holds promise of tailor-making of materials useful in device application. In view of this, an attempt has been made in the present investigation, to prepare NaVO_3 doped with Fe_2O_3 by ceramic method and studies were carried out on X-ray diffraction, microstructure, dielectric hysteresis, dielectric constant and d.c. electrical conductivity. The results have been presented in the chapters II to V of this dissertation.

The first chapter contains general introduction to the field of 'Ferroelectrics'. It covers historical background, classification and identification of ferroelectrics and sufficient theoretical background based on existing literature. Chapter II gives outlines of the preparation of the samples, X-ray diffraction analysis and micro-

structure studies. NaVO_3 doped with 0.025 to 5.0 mol % Fe_2O_3 was prepared by ceramic method reported by Sawada and Nomura (1950) and the lattice parameters of these samples were calculated from X-ray diffraction patterns. The pellets of these samples were prepared using a hydraulic press. These pellets were sintered at 500°C for four hours and the two faces of the pellets were coated with thin layer of silver paste and then used for the experimental purposes. Optical microscopy was carried out in our laboratory for the microstructure studies.

Chapter III deals with determination of Curie temperatures and coercive field measurements by using modified form of Sawyer and Tower circuit (1930). Dielectric constant investigations are reported in Chapter IV, by the method based on the principle of 'Comparison of capacities' at 1 K Hz frequency. The dielectric constants were measured at various temperatures of the sample. In Chapter V, we have presented the results obtained from the d.c. conductivity measurements. The d.c. resistivity measurements were carried out by two probe method covering the transition points. Also, the time dependence of the conductivity was studied to determine the nature of conductivity i.e. ionic, electronic or mixed.

In the following a brief account of the conclusions drawn in the present work is given.

The X-ray diffraction analysis showed that there is no appreciable change in the lattice parameters with increasing addition of Fe_2O_3 in NaVO_3 . From the optical microscopy we conclude that the added Fe_2O_3 from 0.025 to 0.5 mol % goes into the structure of NaVO_3 while at higher mol % of Fe_2O_3 inclusions form which were identified as reddish spots under the optical microscope.

Dielectric hysteresis studies of the samples confirmed their ferroelectric nature. The shape of polarisation versus electric field strength is square like for each of the samples and it was found to be temperature dependent. The hysteresis loop width decreases with increasing temperature and vanishes at the Curie temperature, indicating the temperature dependence of the coercive field (Fig.3.6). Curie temperature and coercive field are strongly depending on Fe_2O_3 content. As Fe_2O_3 content increases, Curie temperature of NaVO_3 continuously decreases. The decrease in Curie temperature is attributed to a greater degree of covalent bonding between Fe and O than that formed between V and O, the iron being substitutional or interstitial. The other possible effect in decreasing the T_c is that the carrier electrons would increase the stiffness of lattice and hence anharmonicity making the lattice more resistant to ordering. Coercive field of the sample increases with increasing Fe_2O_3 upto 0.5 mol % and decreases for higher concentrations of Fe_2O_3 . The increase in E_c with Fe_2O_3

content is due to increase in the structural rigidity caused by possible substitution of V by Fe. The decrease in E_c for higher contents of Fe_2O_3 is attributed to the defects created near the domain walls due to the formation of inclusions.

Sodium vanadate and its Fe_2O_3 -doped samples exhibit a strong anomaly of their electric permittivity at the transition point. This is a characteristic feature of a ferroelectric material. Dielectric constant of $NaVO_3$ was greatly influenced by Fe_2O_3 doping. The maximal permittivity value ϵ_{max} increases with Fe_2O_3 concentration from 0.025 to 0.5 mol % in $NaVO_3$, while the addition of Fe_2O_3 from 1.0 to 5.0 mol % causes a lowering of the maximal permittivity ϵ_{max} and a downward shift in temperature of maximum (Fig.4.3). This shift has been found to depend exponentially on the Fe_2O_3 content, hence it can serve as another parameter for doping effect measurements. The increased maximal permittivity with Fe_2O_3 content (0.025 to 0.5 mol %) may be ^{due} to the increase in polarization produced by trapped charge carriers at lattice defects or vanadium vacancies created by probable substitution of it by Fe ion. The increased maximal permittivity may also be attributed to the trapped carriers at vacancies created by sodium and vanadium with their equal substitution by Fe or at oxygen vacancies in two alternative models of solid solution formation. The maximum value of peak dielectric constant (Fig.

4.4), for 0.5 mol % of Fe_2O_3 content, can be attributed to a rather greater solid state interaction that takes place in the material. It may represent the solubility limit of Fe_2O_3 in NaVO_3 lattice at which the dielectric saturation is attained. The decrease in permittivity at the Curie peak for NaVO_3 doped with Fe_2O_3 from 1.0 to 5.0 mol % is attributed to the non-ferroelectric inclusions formed on the grain boundaries which hinder the domain wall motion.

Our results from the d.c. electrical conductivity measurements showed a sharp change in the conductivity at the phase transition point of the sample. The variation of conductivity of NaVO_3 with Fe_2O_3 content indicates a maximum conductivity for 0.5 mol % Fe_2O_3 content. The conductivity was explained on the basis of electron hopping mechanism $\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+}$ via changing valence of vanadium. The enhancement in the conductivity with Fe_2O_3 content presumes increase in charge carriers, while the decreased conductivity for higher Fe_2O_3 concentrations is attributed to scattering phenomenon, due to the formation of inclusions. As it is natural, the activation energy was found to be least for NaVO_3 doped with 0.5 mol % Fe_2O_3 . This may be due to the characteristic value of ΔE (0.3 eV) for $\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+}$ exchange mechanism in the limiting circumstances. The inclusions formed with higher Fe_2O_3 concentrations may cause for Fe^{3+} or Fe^{2+} to prefer the surface sites of

inclusions and hence may produce deficiency of these ions in the solid solution. This would make it difficult for electrons hopping via the said sequence and hence require higher activation energy for conduction. Our samples showed mixed ionic-electronic conductivity in the ferroelectric region and electronic nature in paraelectric region. The time dependence of conductivity in the ferroelectric region was attributed to the rotation of dipoles and domain wall motion. The transient that appears in the conductivity in paraelectric state may be due to the redistribution and readjustment of surface charges.

The aforesaid summary and conclusions of the present work indicate that the physical properties of ceramic sodium vanadate are greatly influenced by the introduction of ferric oxide as impurity which needs to be taken into consideration to use it for applications in future.

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