CHAPTER - IV

DIELECTRIC CONSTANT

C H A P T E R - I V

DIELECTRIC CONSTANT

4.1 Introduction :

Dielectric substances are those which do not have free electrons but their behavior in electric field is interesting. Under the influence of external electric field, the dielectrics get polarized. Dielectric constant which is often referred to as the dielectric permittivity is the ratio of the capacitance of a capacitor filled with a material to that of empty capacitor. In some ferroelectrics, the temperature dependence of dielectric constant above the transition temperature is expressed by equation 1.1, chapter -I. Polar dielectric materials characteristically have much high values of ε (in the range of 100-10,000) than the non-polar dielectric materials (ε in the range 1-10). In addition, most of the polar materials show a large increase in ε at a temperature in the region of phase transition temperature. In paraelectric phase i.e. above Curie temperature (T_c), the dielectric constant obeys the relation -

$$\varepsilon = \frac{C}{T-T_o} \qquad T > T_c \qquad \qquad \ldots (4.1)$$

Since equation 4.1 is the electric equivalent of the Curie-Weiss behavior observed in the ferroelectric materials, T_o in equation 4.1 is termed as the Curie-Weiss temperature

which does not coincide with the Curie point T_c and C is usually referred to as the Curie constant (Merz 1953, Drougard and Young 1954). At the Curie temperature (T_c), the large signal saturation polarization (spontaneous polarization) falls to zero. The dielectric constant in ferroelectric materials is rarely constant, but varies with applied field, temperature and other parameters. The nonlinearity of dielectric behavior is a significant characteristic of ferroelectrics.

An important small signal electric property of a polar dielectric material, especially from an application view point, is dissipation factor. This is usually measured in terms of $\tan\delta$ (a dimensionless quantity), where $\tan\delta$ is the ratio of the imaginary part to the real part of ϵ . Most of polar dielectrics are very good insulators and hence have a low value of $\tan\delta$ typically in the range 0.01-0.3. $\tan\delta$, like ϵ , also shows anomalous increase at T_c. In polar dielectrics ϵ and $\tan\delta$ remain fairly constant over a wide range of frequencies. In single crystal materials a decrease or relaxation exhibited by ϵ and $\tan\delta$ is only observed at frequencies as high as 10^8 to 10^{11} Hz. The relaxation frequencies vary significantly for different materials. Ceramics usually have a lower relaxation frequency than single crystal materials because of additional effects of the dispersion frequencies associated with multidomains.

Ismailzade et al (1981) discovered new oxide ferro-electrics RVO_4 (R=Nd, Eu, Gd, Tb, Dy, Pr, Er, Yb, Lu and Sc) and from the temperature dependence of dielectric constant maximum value of ϵ was observed at Curie temperature. Dielectric dispersion in $NaVO_3$-single crystal was reported by Matsuda (1974) in a frequency range between 100 Hz and 3 MHz and observed two remarkable dielectric dispersions along the C-axis. Bonsack (1971) has shown that addition of niobium of low concentrations (0.10 to 0.12 at.%) into $BaTiO_3$ increases the dielectric constant to 10^5 and tan δ to 0.1. Dielectric constant and loss tangent of $BaTiO_3$ doped with Yb_2O_3 were investigated at different temperatures, by Molokhia et al (1984). They have shown that both ϵ and tan δ continuously decrease with increasing dopant concentration due to the decrease in grain size. Factors affecting the permittivity of Gd-doped $BaTiO_3$ were studied by Issa et al (1984), showing the permittivity dependence on the type of solid solution formation and defective grain boundary layers. Effect of grain size on T_c and ϵ was studied by Martirena et al (1974) for ferroelectric ceramics.

In order to explore further the role of additives and impurities in giving rise to higher dielectric constants, we have studied the effect of Fe_2O_3-doping in $NaVO_3$, and the temperature dependence of dielectric constant, at a fixed 1 KHz frequency.
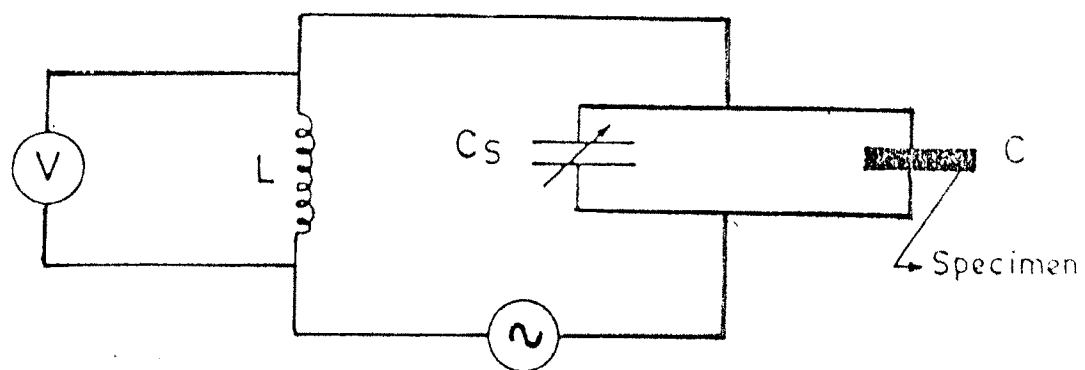
Fig.4·1– SCHEMATIC DIAGRAM OF APPARATUS FOR THE
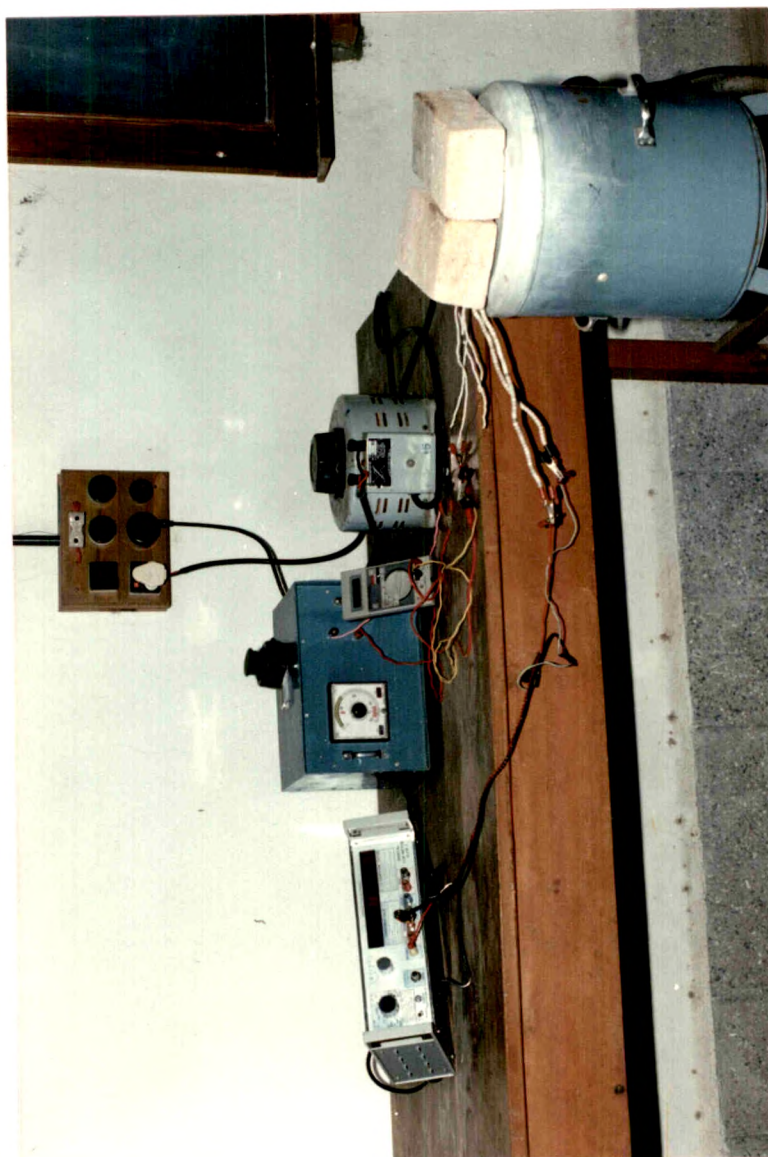MEASUREMENT OF DIELECTRIC CONSTANT

FIG. 4.2 : EXPERIMENTAL SET UP TO MEASURE THE DIELECTRIC CONSTANT

4.2 Experimental Details :

The dielectric constant measurements were carried out by the usual method based on a comparison of the capacity C" of a capacitor filled with the substance and the capacity C' of the empty capacitor. The dielectric constant is the ratio C"/C'. Determination of the value of the capacitance may in principle be accomplished by an LC resonant circuit as shown in Fig. 4.1 where C_s is the calibrated variable capacitor and C is the capacitor in which the specimen can be placed. The experimental set up used is shown in Fig. 4.2. It consists of a digital capacitance bridge (LCR meter VLCR-7), a globar furnace and a temperature controller. The samples, in the pellet form were heated in the globar furnace and capacities were measured at various temperatures and at a fixed 1 KHz frequency. The dielectric constants were calculated from capacitance measurement data.

4.3 Results and Discussion :

The dielectric constant (ε) as a function of temperature for $NaVO_3$ doped with Fe_2O_3 is shown in Fig.4.3. It shows that the dielectric constant of the samples strongly depends on the temperature and Fe_2O_3 content. The dielectric constant at the Curie peak for the samples containing 0.025 to 0.5 mol% of Fe_2O_3 was found to be increased with respect to that of undoped $NaVO_3$ ceramic. While the peak dielectric constant for the samples containing 1.0 to 5.0 mol % Fe_2O_3 was found to be decreased. Fig. 4.4 represents the variation
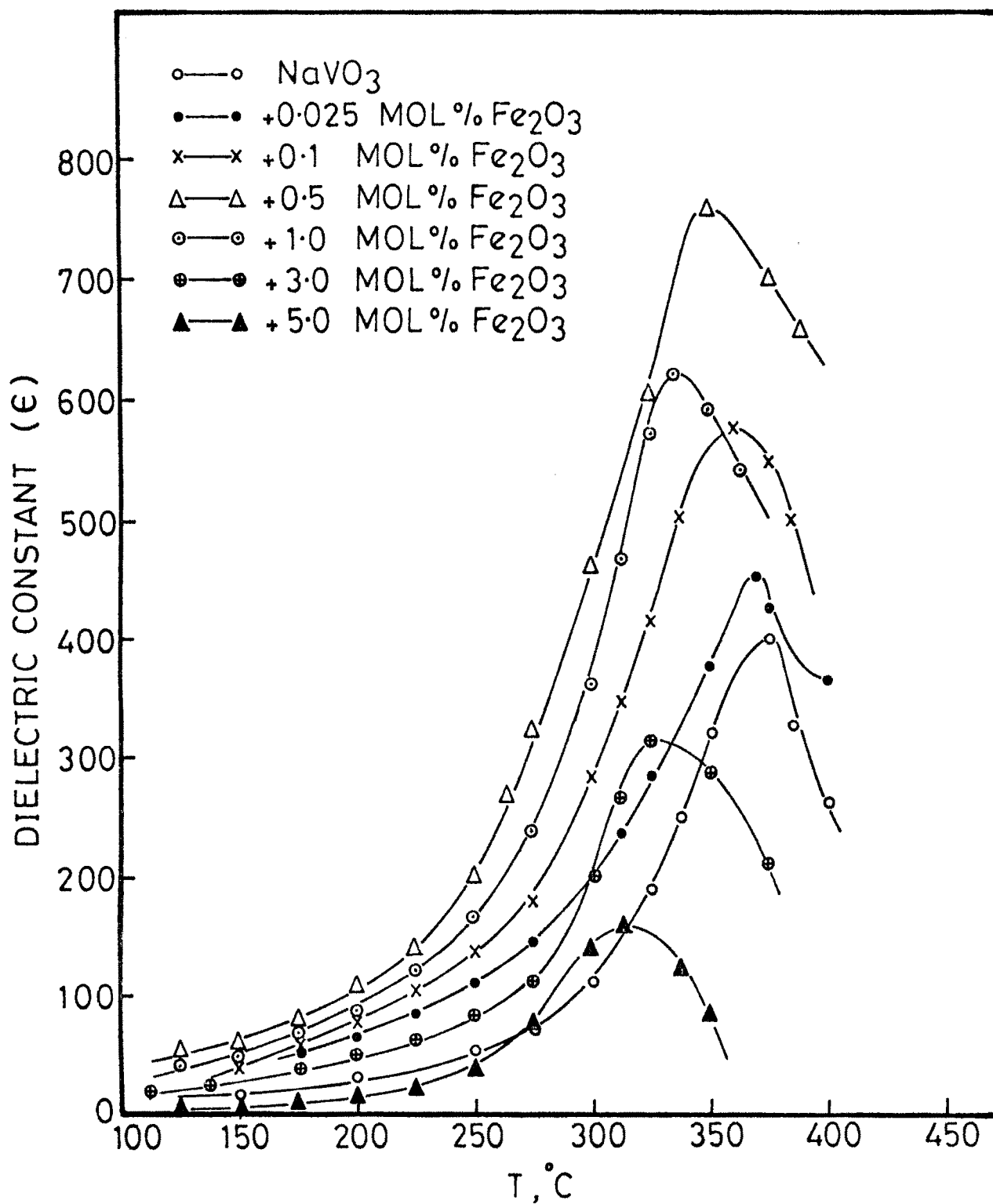
Fig. 4·3 – VARIATION OF DIELECTRIC CONSTANT WITH
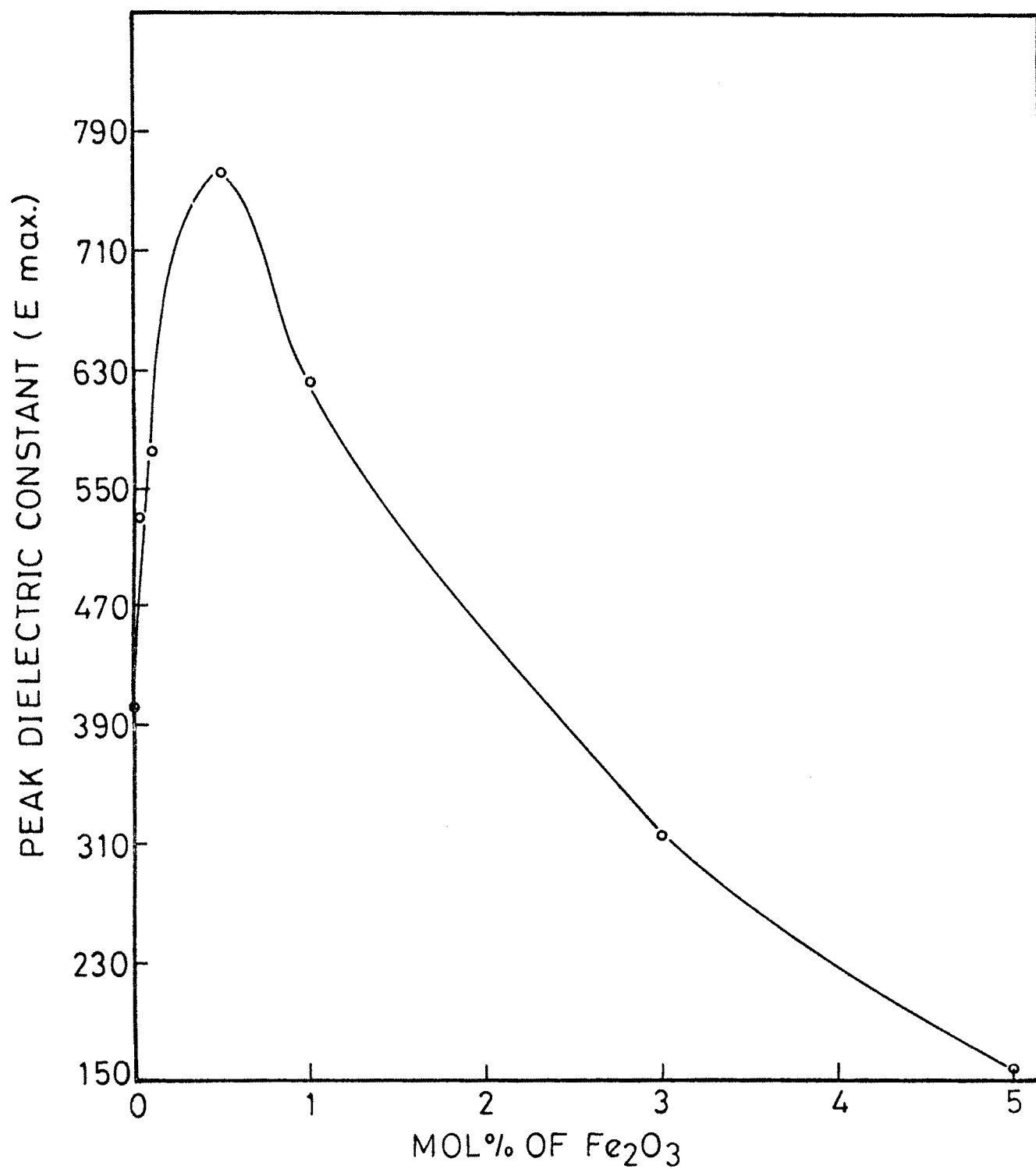TEMPERATURE FOR Fe_2O_3-DOPED $NaVO_3$

Fig.4·4 : PEAK DIELECTRIC CONSTANT OF $NaVO_3$ AS A FUNCTION OF MOL % Fe_2O_3 CONTENT

of peak dielectric constant as a function of Fe_2O_3 content. From this graph the samples can be divided into two groups. For the first group of samples (0.025 to 1.0 mol%) the variation with respect to solute concentration $_\lambda$of peak dielectric constant is larger than that for second group of samples (3.0 to 5.0 mol%).

The addition of Fe_2O_3 (from 0.025 to 5.0 mol%) to $NaVO_3$ shows lowering of Curie temperature. The dielectric constant rises sharply at the Curie point of each sample and above this temperature it decreases according to the Curie-Weiss law, which is the general feature of ferroelectrics.

The increase in the peak dielectric constant for the samples containing 0.025 to 0.5 mol%. Fe_2O_3 may be explained in the light of the type of solid solution formed between $NaVO_3$ and Fe_2O_3. A solid solution of the type

$$Na^+ \left[V^{5+}_{1-x} \ Fe^{3+}_x \ (vacV^{5+})_x \right] O_3$$
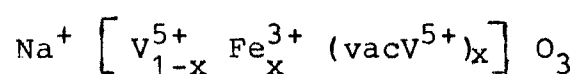
is assumed to be formed between Fe_2O_3 and $NaVO_3$, where vacV is a vacancy in the lattice. Creation of Na^+ vacancy and inclusion of Na^+ interstitial is more favoured as they sit in the interstices of chains of VO_2-O-VO_2-O-VO_2.... . These chains are more $_\lambda$less like large molecules. The similar type
of substitutions were reported by Issa et al (1984) and Bonsack (1971). We can say that the replacement of V-sites in $NaVO_3$ ceramics by Fe ion is most probable. Thus, as a result of formation of this solid solution, an increase in

the polarization should be expected. This increase in the polarization arises from those charge carriers which tend to become trapped and accumulate at lattice defects (V-vacancies). It will produce an apparent increase in the ε (space charge or interfacial polarization effect). Khan (1971) attributed the high permittivity of Nb-doped $BaTiO_3$ with concentrations of 0.19 to 0.93 at % of Nb, to the interfacial polarization effect. Also the space charge effects are probably responsible for the change in permittivity at low frequency. The increase in the polarization and hence ε , may also be explained by formation of the solid solution of the following type.

$$Na \left[V_{1-x}Fe_x \right] O_{3-x}$$

OR

$$\left[Na_{1-x}Fe_x \right] \left[V_{1-x}Fe_x \right] O_3$$
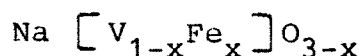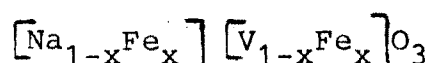
First case of solid solution formation indicates the deviation from oxygen stoichiometry giving rise to increase in the polarization due to entrapping of carriers at oxygen vacancies. The second type indicates formation of vacancies of Na and V in equal measure due to substitution by Fe.

The permittivity was found to depend upon the additives and increase in permittivity was attributed mainly to densification and grain size (Bonsack 1971). In the present situation, the densities of the samples increase with increase of Fe_2O_3 content from 0.025 to 0.5 mol% and decrease

for higher mol% (1.0 to 5.0 mol%) of Fe_2O_3 content (Table 4.1). This may be the reason for change in peak dielectric constant with respect to Fe_2O_3 content. The maximum value of peak dielectric constant for 0.5 mol% of Fe_2O_3 additive can be attributed to a rather greater solid state interaction that takes place in the material. It may represent

TABLE 4.1

Parameters describing Curie temperature, dielectric constant (ε_{max}) and density.

Fe_2O_3 content (mol%)	Curie temp. ($T^{o}C$)	ε_{max}	Density (gm cm^{-3})
0.0	375	400	2.66
0.025	370	450	2.74
0.1	360	575	2.79
0.5	350	760	2.85
1.0	335	620	2.77
3.0	325	315	2.71
5.0	315	160	2.68

the solubility limit of Fe_2O_3 in $NaVO_3$ lattice at which the dielectric saturation is attained. Similar results were obtained for Fe_2O_3 doped PZT (Weston et al 1969) and for Al-doped $BaTiO_3$ (Tawfik et al 1978).

According to the recent studies, the effect of domain wall motion and grain size is regarded as the important

factor contributing to the permittivity (Martiena and Burfoot 1974). The decrease of permittivity at the Curie peak for $NaVO_3$ doped with concentrations of Fe_2O_3 from 1.0-5.0 mol% is attributed to the inclusion formation of non-ferroelectric (Fe_2O_3) material on grain boundaries which hinder the domain wall motion. (Inclusions observed in microstructure studies) The peak values of dielectric constant, Curie temperature and the ceramic densities for doped and undoped $NaVO_3$ are summarised in Table 4.1.

For all samples the dielectric constant decreases with increasing temperature beyond the phase transition point i.e. in the paraelectric state. This is because in non-polar dielectrics, temperature has no impact on the polarization process. The electronic polarizability of a dielectric material is temperature dependent. However, as the dielectric expands under heat, the number of polarized molecules per unit volume decreases with increasing temperature. This shows that permittivity must also decrease with increasing temperature.

As has been noted earlier, in polar dielectrics dipoles are incapable of orientation within the low temperature region, since in this case the relaxation time τ is very high. But as temperature increases τ decreases and dipole polarization comes into play, which effects a substantial rise in permittivity. A further increase in tempe-

rature, however, adds to the random vibrational motion of molecules, which become progressively less susceptible to orientation. This process results in a typical 'dipole' maximum on the ε-T characteristic for each sample.

Conclusions:

1) Dielectric constant of each sample increases with temperature reaching a peak value at the Curie point and decreases with further rise in temperature, following the Curie-Weiss law.

2) Addition of Fe_2O_3 in $NaVO_3$ effectively modifies the dielectric properties of $NaVO_3$.

3) Peak dielectric constant increases with increasing Fe_2O_3 content from 0.025-0.5 mol% and it decreases with increasing Fe_2O_3 content from 1.0-5.0 mol %.

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