CHAPTER - V

DIELECTRIC PERMITTIVITY

5.1 INTRODUCTION

The most common and significant non-linear property of ferroelectric materials is the dielectric constant or dielectric permittivity (ε). Since the permittivity (ε) expresses the behaviour of polarization, it is clearly close to the heart of ferroelectricity. The dielectric constant (ε) is defined as the ratio of the capacitance of a capacitor filled with the dielectric material to that of empty capacitor and hence a dimensionless parameter. It is a rarely constant, but changes with applied field, stress, temperature and other parameters. It is well known that the spontaneous polarization of the material decreases with temperature and finally reduces to zero at Curie temperature increasing dielectric constant to a peak value. Polar dielectric materials characteristically have much higher values of ε (in the range 100-10000) than non-polar dielectric materials (ε in the range 1-10). The most polar materials show a large increase in ε at a temperature in the region of a crystalline phase transition temperature. This anomaly of ε, of the ferroelectric material at the Curie-weiss temperature shows maximum value of ε and material goes from polar phase (ferroelectric state) to non-polar phase (paraelectric state). In the paraelectric phase ε obeys the expression,

$$\varepsilon = \frac{C}{T-T_0} \qquad \ldots\ldots 5.1$$

where C is Curie constant, T_o is Curie-Weiss temperature. Equation 5.1 is the electrical equivalent of the Curie-Weiss behaviour observed in ferromagnetic materials. Similarly, an important dielectric property of the polar materials, is a dissipation factor i.e. tan δ which is a mere ratio of imaginary part to real part of ϵ. Most polar dielectrics are very good insulators and hence have a low value of tan δ. Tan δ like ϵ, also shows anomalous behaviour at T_c.

The most detailed study of titania ceramics on high dielectric constant was carried out by Von-Hippel et al (1946). Smolenskii. (1950) reported peakvalue of ϵ of $SrTiO_3$ ceramic in the temperature range 20-30^{0}k. The dielectric constant of $PbTiO_3$ ceramic was measured as a function of temperature by Shirane et al (1951). The dielectric constant of lead-strontium titanate series in the temperature range from-150^{0}c to 300^{0}c was measured by Nomura et al(1955).Akao et al (1955) reported that the temperature dependence of the real part of ϵ of Rochelle salt for different values of the measuring frequency. Marutake (1956) computed high values of dielectric constant in $BaTiO_3$. Granicher's (1958) dielectric measurements on single crystals of $SrTiO_3$ revealed that the Curie-Weiss law is obeyed at 95^{0}k. Few investigators except Rupprecht et al (1961) and Diamond (1961) observed an explicit relationship between ϵ and external applied electric field. Theory of Rupprecht is valid for small fields only and that of Diamond's theory is applicable to polycrystalline materials which are more lossy. Schlosser et al (1961) investigated that the capacitance and dielectric loss of crystal

wafers depend up on their thickness. Dielectric constant measurements of ferroelectric $NaNO_2$ crystal were made by Shoichiro Nomura (1961). Stern and Lurio (1961) used the phenomenological theory of Devonshire (1945, 1954) in which they determined the change in dielectric constant with applied electric field. The effect of different factors on the dielectric constant of $SrTiO_3$ was studied by Hegenberth (1964) and Samara et al (1965). Measurements of the dependence of dielectric constant on grain size of $BaTiO_3$, as a function of temperature were described by Miller (1967) . The variation of the dielectric constant and loss tangent at 1MHz as a function of d.c. voltage in (Ba-Sr) TiO_3 and (Pb-Sr) TiO_3 system was determined by Griffiths (1970). Coufora et al (1972) were studied dielectric properties of $(Ba_{1-x}-Sr_x)$ TiO_3 single crystal. The dielectric behaviour of different particle size powders of barium titanate, potassium ferrocyanide trihydrate and ammonium sulphate was studied by Mansingh et al(1974). The dielectric properties of $(Sr_{1-x}-Pb_x)$ TiO_3 solid solution at low temperatures and high pressures were studied by Martin et al **(1976)**. The results of variation of overall dielectric constant of $BaTiO_3$ single crystal with applied a.c. electric field and crystal temperature were reported by Deshpande et al (1977). Optical and dielectric studies on $SrTiO_3$ & $KTaO_3$ were carried out by Fujii et al (1977). Glass et al (1978) studied the dielectric constant variation of calcium orthovanadate and observed peak value of dielectric constant at the Curie temperature. Ismailzade et al (1980) were investigated dielectric measurements of polycrystalline samples of the rare earth arsenates $RAsO_4$ (R=Pr,Nd,Eu,Gd,Tb,Dy,Er or Yb) at

1 KH_2 frequency. V.K.Yanovski (1980) was studied temperature dependence of ε of $KNbO_3$ crystal. Further, Ismailzade et al (1981) discovered new oxide ferroelectrics RVO_4 (R=Nd,Eu,Gd,Tb,Dy,Ho,Er,Yb,Lu and Sc) and from the variation of ε with temperature observed maximum value of ε at ferroelectric Curie temperatures of these materials. Several physical properties of lead titanate such as measurement of DTA curve, dielectric constant, Raman scattering and microscopic observations have been made by Takashige et al (1981). The dielectric constant ε_c of poled tetragonal $BaTiO_3$ was measured in frequency range 0.1 to 6 GH_2 by Clemens et al(1981). Mathur et al (1981) were reported dielectric constant of mixed crystals of TGS and TGFB. Yamashita et al (1982) were measured dielectric constant of ceramic $BaTiO_3$ under high d.c. biasing field of 5 to 20 KV/cm. R.Chaves et al (1982) were studied dielectric constant of $SbSe_xS_{1-x}I$ in weak fields at 1KHz. Dielectric and pyroelectric properties of sintered discs of $NaVO_3$ were reported by Khan et al (1983) and observed anomalies in dielectric constant around 375-390°c. They also showed that the anomalous property of dielectric constant is independent of the electrode material used and poling of the sample. The rate of surface layers in dielectric measurements in oxide perovskites such as $SrTiO_3$ and $BaTiO_3$ was discussed by Stumpe et al (1984). Molokhia et al (1984) were investigated the dielectric constant of $BaTiO_3$ doped with Yb_2O_3 at different concentrations at different temperatures. Similarly, Issa et al (1984) studied dielectric properties of $BaTiO_3$ doped with Gd_2O_3 having different concentrations. S.H.Chavan and P.G.Kulkarni (1985) studied dielectric and hysteresis properties of ferroelectric solid solutions of barium-strontium and

barium-calciun **titanate.** Jamadar et al (1986) investigated dielectric constants of lead-barium and lead-strontium titanate. Patil et al (1989) investigated dielectric properties of KVO$_3$, LiVO$_3$ and their solid solutions. Recently, Patil et al (1990) have studied dielectric properties of KVO$_3$ doped with Nd$_2$O$_3$ and Kashid et al (1990) also have studied temperature dependence of dielectric constant of KVO$_3$ and LiVO$_3$ doped with different concentrations of Gd$_2$O$_3$.

In this investigation, the temperature dependence of dielectric constant of KVO$_3$ doped with Er$_2$O$_3$ for various concentrations are studied.

5.2 EXPERIMENTAL

The dielectric permittivity (ϵ) of the ferroelectric material is generally measured by using method based on the principle of comparison of two capacities. The ratio $\dfrac{c_1}{c_2} = \epsilon$, is called dielectric constant, where c_1 is capacity of capacitor filled with the substance and c_2 is the capacity of the empty capacitor containing air. The LC resonant circuit is used for the determination of capacitance as shown in Fig. 5.1. The circuit consists of inductance L, C$_s$ the calibrated variable capacitor and C capacitor in which the specimen may be placed. The experimental arrangement used for the measurement of dielectric constant at various temperatures is shown in Fig. 5.2, which consists of an electrically heated furnace with a temperature controller arrangement and the digital capacitance bridge (LCR METER VLCR 7). The
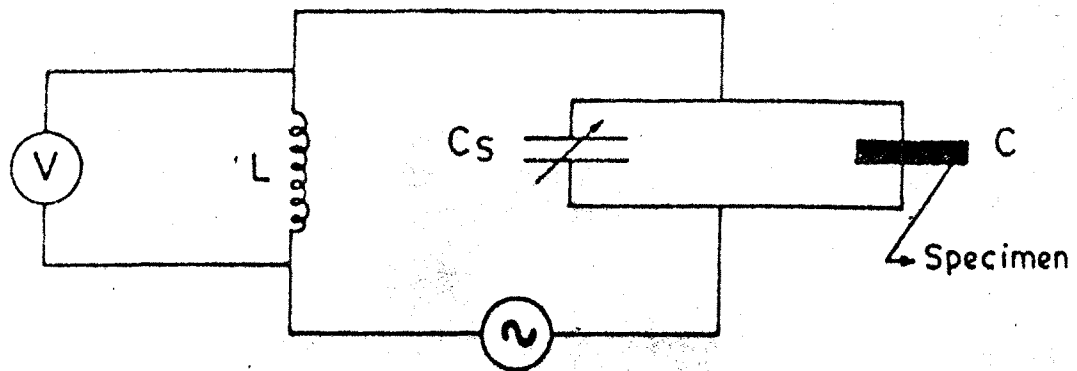
Fig. 5·1 — SCHEMATIC DIAGRAM OF APPARATUS FOR THE
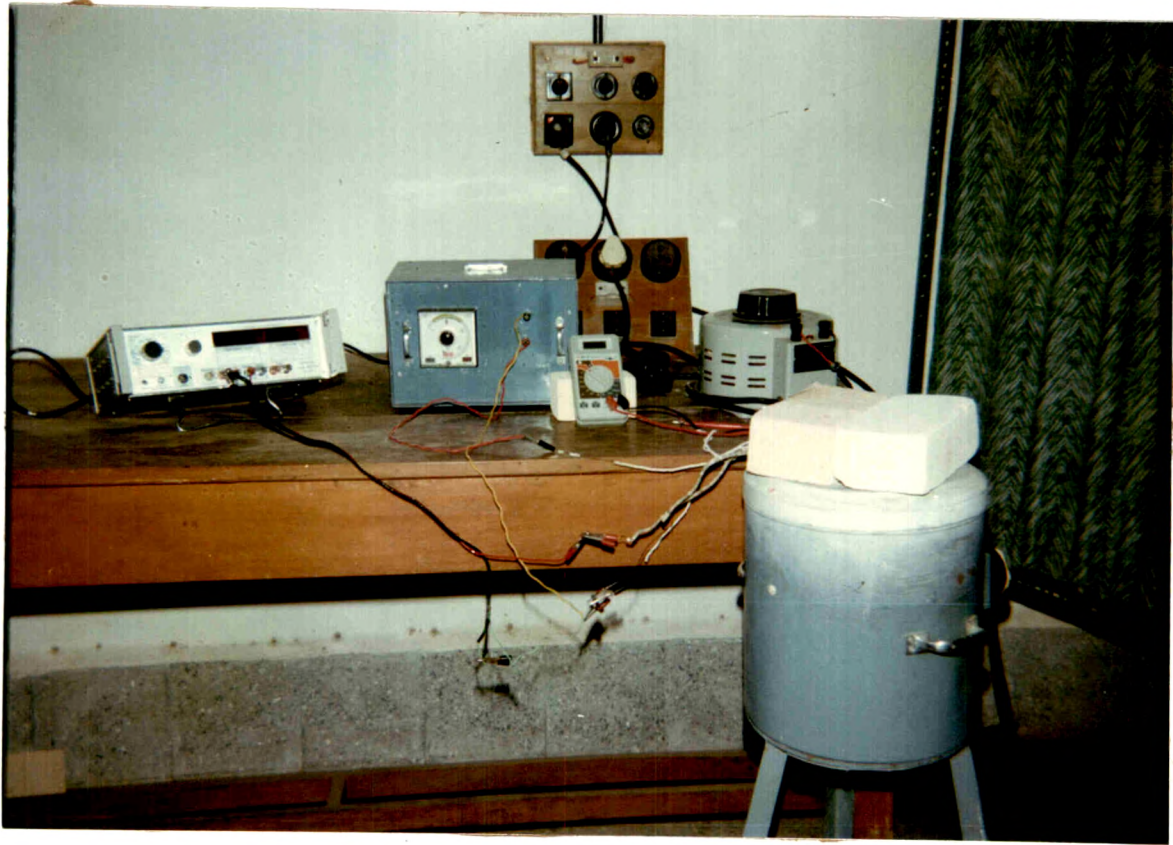MEASUREMENT OF DIELECTRIC CONSTANT.

Fig. 5.2 : Experimental set-up for measurement of dielectric permittivity.

pellets of the samples of undoped KVO_3 and doped KVO_3 with Er_2O_3, having thickness about 1 mm were sintered at 750^0c and then faces of pellets were coated with thin layer of silver paste to achieve good electrical contact with electrodes in a sample holder. From the capacitance measurement data and capacitance of air in the empty capacitor dielectric constants at different temperatures were calculated by using above mentioned method. The variation of dielectric constant with temperature of undoped and doped KVO_3 with different concentrations of Er_2O_3 (0.025 to 3 mol %) is shown in Fig. 5.3.

5.3 RESULTS AND DISCUSSION

Fig. 5.3 reveals us that the dielectric constant of undoped and doped KVO_3 with Er_2O_3 having different concentrations (0.025 mol % to 3 mol %) is temperature dependent. It is also seen that the maximum(peak) values of dielectric constant of different samples are observed at different temperatures indicating their Curie temperatures. The Curie temperatures of these samples are quite in good agreement with the Curie temperatures confirmed by dielectric hysteresis study as well as pyroelectric measurement technique. Fig. 5.3 shows the decrease in Curie temperature of KVO_3 as dopant (Er_2O_3) concentration in it increases. The peak values of ε , Curie temperature and density of the samples are summarized in Table 5.1.
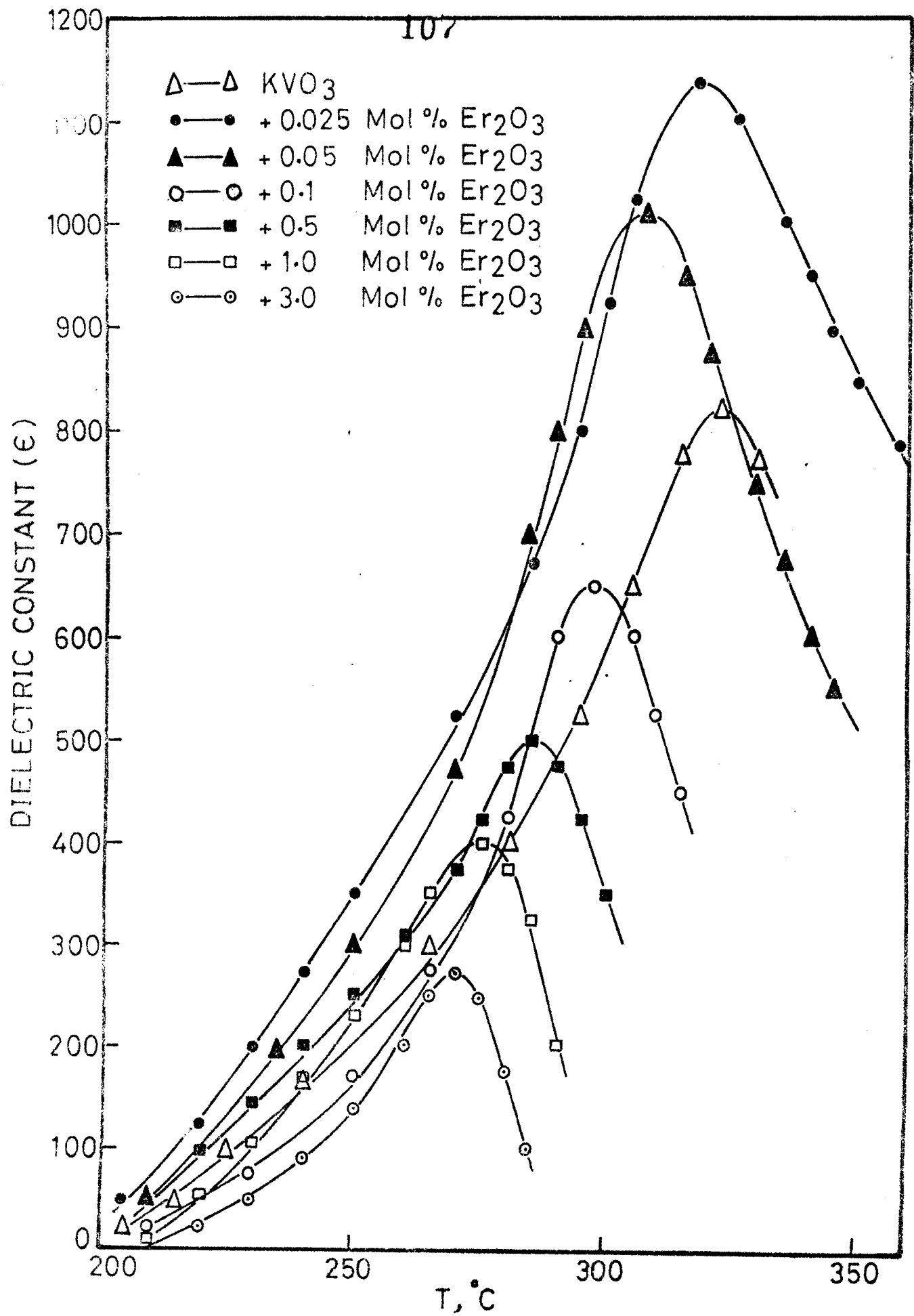
Fig.5.3 VARIATION OF DIELECTRIC CONSTANT WITH
TEMPERATURE FOR UNDOPED AND DOPED KVO₃ WITH
Er₂O₃.

TABLE 5.1

ϵ_{max} CURIE TEMPERATURE AND DENSITY OF SAMPLES

Er_2O_3 content Mol %	ϵ_{max}	Curie Temp. ^oC	Density gm/cc
0.000	820	322.5	2.50
0.025	1140	317.5	2.61
0.050	1010	307.5	2.58
0.100	650	297.5	2.51
0.500	500	285.0	2.47
1.000	400	275.5	2.43
3.000	275	260.0	2.40

Table 5.1 shows ϵ_{max} is higher for KVO_3 samples containing 0.025, 0.05 and 0.1 mol % Er_2O_3 and it is smaller for samples containing 0.5, 1 and 3 mol % Er_2O_3, as compared to ϵ_{max} for undoped KVO_3. The dielectric constant ϵ_{max} is highest for 0.025 mol %. Er_2O_3 in KVO_3 This table also indicates that ϵ_{max} is a function of density of the sample showing ϵ_{max} is higher for higher density of KVO_3 doped with 0.025 mol % Er_2O_3. This indicates that dielectric saturation state is observed for 0.025 mol % doping of Er_2O_3 in KVO_3. Fig 5.3 also shows broad peak nature for all the samples indicating diffuse phase transition at Curie temperature.

From the present investigation following conclusions could be drawn.

CONCLUSIONS

1. Dielectric constant varies with temperature for undoped and Er_2O_3 doped KVO_3 samples. i.e. it increases with temperature showing a peak value at the Curie point and decrreases with further rise in temperature, obeying the Curie-Weiss law.

2. Peak value of ε represents Curie temperature of that sample.

3. ε_{max} is different for different samples.

4. Curie temperatures of all the samples are matching with those confirmed by dielectric hysteresis and pyroelectric measurement experiments.

5. ε_{max} is maximum for the KVO_3 containing 0.025 mol % of Er_2O_3 indicating the dielectric saturation state of ferroelectric ceramic.

110

R E F E R E N C E S

Ahmed et al	(1982), Phys. Stat.Sol.(a) 69, 103.
Akao H. and Sasaki T.	(19555), J.Chem.Phys. 23, 2210.
Chavan S.H. and Kulkarni P.G	(1985), Ind. J.Phys. 60 A, 124-132.
Chave R. and Others	(1982), Phys. Stat. Sol.(a) 73, 367.
Clemens R.,Luther G and Muser H.E.	(1981),Phys.State. Sol. A-64, 637.
Coufora P.,Muser H.E. Novak J. and Janousek V.	(1972), Czech. J.Phys. B-22, 485.
Deshpande et al	(1977), Ind.J.Pure and Appl.Phys.15,477.
Diamond H.	(1961), J.Appl.Phys.32,909.
Fujii Y. and Sakudo T.	(1977), Bull. Acad.Sc.USSR.Phys. Ser.41,30.
Granicher H.	(1958), Archiv.Sci.(Geneva).11,28.
Glass A.M.;Abrahams S.C. and Ballman A.A.	(1978),Ferroelectrics. 17, 579.
Hegenberth E.	(1964), Phys. State.Sol. 6, 333.
Ismailzade I.H.,Ismilov R.M. and others	(1980), Ferroelectrics 23, 35.
Ismailzade I.H. and Others.	(1981), Ferroelectrics. 31, 45.
Issa M.AA. Molokhia N.M. and Nasser S.A.	(1984), J.Phys.D(4B). 17. 571.
Jamadar V.M., Patil T.A. and Chavan S.H.	(1986), Ind.J.Pure and Appl.Vol-24,561-5.
Kashid A.P.,Patil R.T. and Chavan S.H.	(1990), Ind.J.Pure and Appl.Phys.(Accepted)
Khan A.H., Ghare P.B. and Narayanan P.S.	(1983), Bull. Mat. Sci.(Ind).5, 133.
Mathur S.C.,A.K.Batra. and Singh H.	(1981), Ferro.Vol-39, 1197-1200.

Mansingh A and Bawa S.S.   (1974), Ind.J.Pure and Appl.Phys.12,483.

Martin G., Hegenberth E.   (1976), Sov.Phys. Solid State 18, 143.
and others.

Marutake M.I.   (1956), J.Phys. Soc. Japn. 11, 807.

Miller C.A.   (1967), Britt.J.Appl.Phys.18,1689.

Molokhia N.M.,Issa M.AA   (1984),J.Am.Cer.Soc.(USA).67,289.
and Others.

Nomura S. and Sawada S.   (1955), J.Phys.Soc.Jpn. 10, 108.

Patil T.A.; Jamadar V.M.   (1988), Ind. J.Phjys. 62a, 87-89.
and Chavan S.H.

Patil N.B.; Patil R.T.   (1990), Mat. Res. Bull (Commu.).
and Chavan S.H.

Rupprecht G. Bell R.O.   (1961), Phys. Rev. 123, 97.
and Silverman B.D.

Samara G.A. and Giardini A.A.(1965), Phys.Rev.140, A-954.

Schlosser H. and Drougard   (1961), J.Appl.Phys. 32, 1227.
M.E.

Shirane G. and Hoshino S.   (1951), J.Phys. Soc. Jpn. 6, 1227.

Shoichiro and Nomura   (1961), J.Phys. Soc. Jpn. Vol-16.

Smolenski G.A.   (1950),Zhur. Tech.Fiz-20, 137.

Stern E. and Lurio A.   (1961), Phys. Rev. 123, 117.

Sumpe R., Wagner D.   (1984), Ferroelectrics. 56, 149.
and Bauerle.

Takashige M. and Nakamurat.   (1981), Ferroelectrics. 37, 654.

Von-Hippel A. and others   (1946), Ind. and Eng.Chem.38,1097.

Yamashita K. and Others   (1982), Yogyo-Kyo Kaishi(Jpn).90,339.

Yanovskii V.K.   (1980), Sov. Phy.S.s.,22(7)..