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Dielectric Behaviour of $Ba_xSr_{1-x}TiO_3$ Perovskites

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Abstract

Using the method of double – time thermal Green's functions and Kubo formalism, a general expression is derived for the complex dielectric constant of $Ba_xSr_{1-x}TiO_3$ ferroelectric crystal in the paraelectric phase taking into account the change of mass as well as harmonic force constant between impurity atom and host lattice atoms. The results are used to obtain an expression for the frequency dependence of the dielectric constant of $Ba_xSr_{1-x}TiO_3$ due to impurity and anharmonic scattering. To a first order approximation of the defect parameters the Curie temperature shift is found to depend only on the harmonic force constant changes between the impurity and host lattice atoms, and is proportional to the concentration of defects. The dielectric constant of ceramic $SrTiO_3$ can be enhanced by the addition of cation impurities like lead, barium, zirconium etc.

I. INTRODUCTION

It is now well known[1] that the lattice defects in the ferroelectric materials greatly influence their static dielectric constant in paraelectric phase. The effect of defects can generally be expressed by a change only in the Curie temperature T_c, without essentially changing the character of temperature dependence of the dielectric constant, that is, the Curie – Weiss law remains valid with practically the same Curie constant. Various impurities change the Curie temperature of the same material in different ways. For example the Curie temperature of $SrTiO_3$ increases on the substitution of Ba ions. The Curie temperature of $BaTiO_3$ increases on the substitution of Pb ions for Ba, while the Curie temperature T_c decreases on substitution of Sr ions for Ba and the change in Tc is negligible on substitution of Ca ions for Ba.

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We have theoretically calculated dynamic properties of perovskite type crystals in near past e.g. dielectric, electrical and acoustical properties of Barium Titanate[2], dynamics of soft mode in ferroelectrics[3],microwave absorption, Curie temperature & ultrasonic attenuation in ferroelectric solids[4], effect of electric field on dielectric & acoustical properties of ferroelectric solids[5] and soft mode dynamics of perovskite type crystals[6].

Ferroelectrics have found extensive applications in optical communication, memory display, coherent optical processing, modulators, beam reflectors and holographic storage media. Besides these, ferroeletrics are broadly used in ceramic industries. Semiconducting ferroeletric ceramics, having positive temperature coefficient of resistivity (PTCR) are used in temperature control and many other devices. The most intensively studied and widely used PTCR materials are those based on Barium Titanate. Although a large number of papers on PTCR materials are published only few reports on the dielectric spectrum of Barium Strontium Titanate are available.

We derive a general expression for the complex dielectric constant $\in$ at frequency, ω of a ferroelectric crystal having cubic symmetry in paraelectric phase, involving anharmonicities up to fourth order with substitutional defects of low concentration distributed at random, by using the method of time dependent Green's functions[7]. A considerable review on dielectric properties of pure and mixed ferroelectric crystals is available in the literature[2, 8 – 20]. Deorani et. al.[21, 22] have theoretically studied the temperature and frequency dependence of dielectric constant using the method of double time Green's function in Barium Titatnate, Strontium Titanate and Potassium Titanate, anharmonic ferroelectric crystals, using Silverman – Joseph's modified Hamiltonian taking into account anharmonic effect up to fourth order. There has been considerable interest in the physical properties of mixed crystals as they find interesting applications and their study helps in understanding basic mechanism of mixed crystal formation. Dependence of a physical property of a mixed crystal varies from system to system. The property may change in linear or nonlinear manner. For example solid solution of $BaTiO_3$ with other ferroelectrics of same class and also with certain compounds, which are not themselves ferroeletric possess ferroelectric properties and the change in the composition of the solid solution make it possible to regulate the Curie point within a broad range of temperature.

The aim of the present paper is to study theoretically the dielectric property in polycrystalline mixture of $Ba_xSr_{1-x}TiO_3$ by forming a model Hamiltonian for the polycrystalline mixtures of ferroelectric perovskites and than applying it to $Ba_xSr_{1-x}TiO_3$. Double time Green's function[21] technique is used to obtain thermally averaged correlation functions and hence the observable quantities with the help of model Hamiltonian taking into account anharmonic effect upto fourth order with substitutional defect. For simplicity the ions are assumed nonpolarizable. Such a formulation is particularly interesting as the real part of dielectric constant, $\in'$ will lead to an expression for the change in the Curie temperature resulting from the presence of impurities. We have taken into account the contribution of the soft mode frequency towards dielectric constant. The effect of defect on the real part of dielectric constant of a displacive ferroelectric material in paraelectric phase is discussed and results obtained are in agreement with the previous experimental and theoretical results.

2. HAMILTONIAN AND GENERAL FORMULATION

The Hamiltonian which includes the anharmonicity upto fourth order in the potential energy due to interactions of the soft mode coordinates, resonant interaction and scattering terms is considered. The impurities have been introduced characterized by a different mass than the host atoms and with modified nearest – neighbour harmonic force constants around their sites. Their influence on the anharmonic coupling coefficients in the Hamiltonian is neglected. The modified Silverman Hamliltonian of displacive ferroelectrics in paraelectric phase for zero field case, which includes defects is used in the present study and is exactly similar to eqn.(2) of our previous study[23]. The notations are used are the same and in the same sense as used by Naithani and Semwal[23] (for zero field case).

For the study of dielectric constant, we introduce the Green's function for the soft optic mode as:

$$G^{0}_{0}(t - t') = \langle\langle A^{0}_{0}(t) ; A^{0}_{0}(t') \rangle\rangle_{\omega + i\epsilon}. \qquad (1)$$

$$G^{0}_{0}(\omega + i\epsilon) = G'(\omega) - G''(\omega) \qquad (2)$$

Solving the egn. of motion for the Green's function (eqn.1) with the help of Modified Silverman Hamiltonian, (eqn.2, ref. 23), Fourier transforming and writing it in the form of Dyson's equations, one obtained,

$$G^{0}_{0}(\omega + i\epsilon) = \omega^{0}_{0}/\pi \left[\omega^{2} - (\nu^{0}_{0})^{2}(\omega) - 2\, i\omega\, \Gamma^{0^\circ}(\omega)\right] \qquad (3)$$

where $\nu^{0\,2}_{0}(\omega)$ is the stabilized soft mode frequency and $\Gamma^{0}(\omega)$ is the phonon half width for the soft optic mode.

The real part of the dielectric constant is related to soft mode Green's functions as,

$$\epsilon'(\omega) - 1 = -\,8\,\pi^{2} N\mu^{2}(0)\, G'(\omega) \quad . \qquad (4)$$

The real part of the complex dielectric constant [with the help of eqn.(3)] is given by :

$$\epsilon' - 1 = \frac{-\,8\,\pi N\mu^{2}(\omega^{2} - \Omega^{2})^{2}\,\epsilon_{s}}{(\omega^{2} - \Omega^{2})^{2} + 4\omega^{2}\Gamma^{0\,2}} \qquad : \nu^{0}_{0} \approx \Omega$$

or

$$\epsilon' = \frac{8\,\pi N\mu^{2}(\omega^{2} - \Omega^{2})^{2}\,\epsilon_{s}}{(\Omega^{2} - \omega^{2})^{2} + 4\omega^{2}\Gamma^{0\,2}} \qquad : \epsilon' \gg 1. \qquad (5)$$

Here, $\in_S$ is the static dielectric constant of the material, μ the dipole moment per unit cells, N the total no of unit cells in the specimen and other symbols are as usual.

The frequency dependent dielectric constant (in the range $\omega_T \leq 1$) may be calculated using the relation [which is similar to that of Deorani et. al.[22]] :

$$\in' = \frac{\in_S \omega_0^2 (\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + 4\,\omega^2 \Gamma^{0\,2}} \quad : (\omega_0 \approx \Omega \approx \nu)$$

$$\text{or } \in' = \frac{\lambda\ (\omega_0^2 - \omega^2)}{(\omega_0^2 - \omega^2)^2 + 4\,\omega^2 \Gamma^{0\,2}} \qquad (6)$$

where $\lambda = \in_S (T)\, \omega_0^2$ is constant at certain temperature. The soft mode frequency is very large as compared to the microwave frequency (as $\omega/\Omega \approx 10^{-3}$) and no relaxation effects are observed and half width $[\Gamma^0 (\omega) / 2\, \omega_0]$ is such that $[\Gamma^0 (\omega) << 2\, \omega_0]$. Due to this appreciable difference between the microwave frequency and the normal frequency of oscillation, the real part of the dielectric constant [eqn. (6)] can also be written as :

$$\in' = \frac{\lambda}{\omega_0^2} \qquad (7)$$

The soft mode frequency for the optic mode could be written a

$$(\nu^0_0)^2 (\omega) = -\,\omega_0^2 + \gamma_1 T + \gamma_2 T^2 \qquad (8)$$

where symbols have usual meanings. From eqn. (6) and (8) (ν^0_0 is same as ω^0_0), we conclude that

$$\in'(T) = \frac{\lambda}{K\,(T + \xi\, T^2 - Tc)} = \frac{C}{T + \xi T^2 - Tc}\ . \qquad (9)$$

Here, K is a temperature independent constant, Tc paraelectric phase transition temperature and ξ nonlinearity constant which characterizes the deviation of the temperature dependence of the dielectric constant from the Curie-Weiss behaviour and is related to the third- and fourth- order coupling coefficients.

If the parameter ξ is very small and the temperature is not very high (i. e. though in paraelectric phase but in the vicinity of Curie temperature Tc), than one can be neglect the term ξT^2 from denominator of eqn.(9) and one gets,

$$\in'(T) = \frac{\lambda}{K\,(T - Tc)} = \frac{C}{T - Tc} \qquad (10)$$

where c = λ / k is the Curie constant and Tc is the Curie temperature.

The soft mode frequency of ferroelectric crystal is given by :

$$\Omega^2 \sim (T - Tc)$$

$$\Omega^2 \simeq K\,(T - Tc). \tag{11}$$

In general the temperature & defect dependent soft mode frequency $\nu^0_0\,(\omega)$ can be expressed as:

$$\Omega^2_{T,D} \;=\; \Omega^2_T + \Omega^2_D\;. \tag{12}$$

Here, Ω^2_T is the temperature dependence part of the square of soft mode frequency and is given by :

$$\Omega^2_T = -\omega^{0\,2}_{0} + 4\omega^0_0 \sum_{k,\lambda} \beta^\lambda(k)\, N^\lambda_k - 2\,\omega^0_0 \,\mathrm{Re} \sum_{k,\lambda} |\,F(k)\,|^2\, x\, [N^a_k - N^0_k]$$

$$\frac{\omega^a_k + \omega^0_k}{\Omega^2 - (\omega^a_k + \omega^0_k)^2} - (N^a_k - N^0_k)\, \frac{\omega^a_k - \omega^0_k}{\Omega^2 - (\omega^a_k - \omega^0_k)^2}$$

$$+\, 8\omega^0_0\, \mathrm{Re} \sum_{k,\lambda} |\,\beta^\lambda(k)\,|^2 \tag{13}$$

and Ω^2_D is the contribution of defect on the square of soft mode frequency and its value obtained by :

$$\begin{aligned}\Omega^2_D \;=\;& 4\omega^0_0\, D(0,0) + \frac{4}{\omega_o^2} \sum_{k,\lambda} \frac{1}{(\omega^2 - \omega_{\surd}^2)} \{(\omega^0_0)^2\, \omega^\lambda_k\, D^\lambda(k^\lambda, 0)\\ &+ \omega^2\, \omega^\lambda_k\, C^2(k^\lambda,0,) + \omega^2\, \omega^0_0\, [C(k^\lambda,0)\, D^*(k^\lambda, 0)\\ &+ C^*(k^\lambda, 0)\, D\,(k^\lambda, 0)]\}.\end{aligned} \tag{14}$$

2.1 Defect variated soft mode frequency :

Using relation (11), we have calculated the ratio Ω^2 and $(T\text{–}T_c)$ for pure Strontium Titanate crystal at 400° K and taking approximation that this ratio is also the same for mixed crystal of $Ba_xSr_{1-x}TiO_3$. The Curie temperature of $Ba_xSr_{1-x}TiO_3$ for different values of x = 0.0,0.2, 0.5, 0.7, 0.8 etc. have been taken by best fit of data from reference[24]. Using again relation (11) we have calculated the soft mode frequency of $Ba_xSr_{1-x}TiO_3$ for different values of x. The variation of soft mode frequency verses defect parameter x of $Ba_xSr_{1-x}TiO_3$ have been shown in Fig. 1 for different values of x (= 0.0, 0.2, 0.5, 0.7, 0.8 etc).

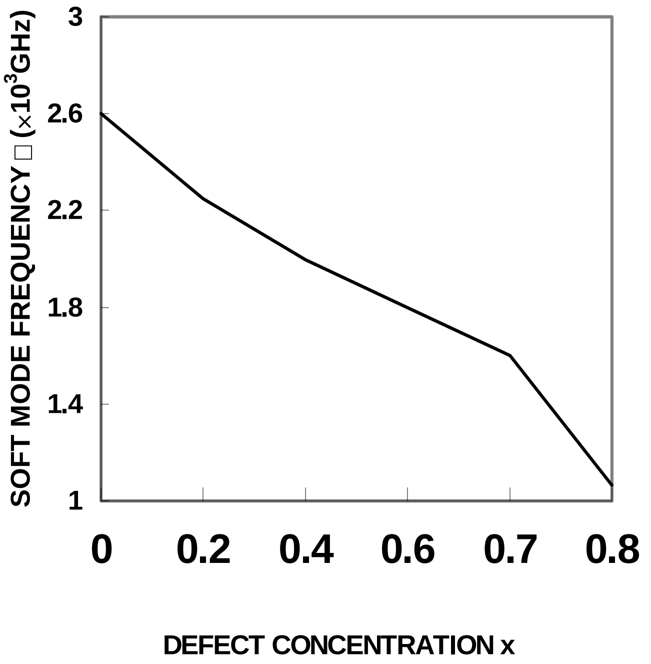

Fig 1-Variation of soft mode frequency with defect concentration (x) in baxsr1-xtio3 at 400k

2.2 Frequency variated dielectric constant :

Using the relation (7), we have calculated the dielectric constant at room temperature in the frequency range (10^7 – 10^{12} Hz) of $Ba_xSr_{1-x}TiO_3$ for the different values of x (= 0.0,0.2, 0.5, 0.7, 0.8 etc). Some calculated constants have been given in the Table 1 here. The Curie temperature of $Ba_xSr_{1-x}TiO_3$ for different values of x is obtained from Rupprecht and Bell[24] by best fit of data.

Table 1: Tc, Ω_o and λ for $Ba_xSr_{1-x}TiO_3$.

$Ba_x Sr_{1-x} TiO_3$	Tc	Ω_o	λ
$SrTiO_3$	37° K	2.6×10^{12} Hz	8.77×10^{28} Hz^2
$Ba_{0.2} Sr_{0.8} TiO_3$	105° K	2.34×10^{12} Hz	8.77×10^{28} Hz^2
$Ba_{0.5} Sr_{0.5} TiO_3$	218° K	1.84×10^{12} Hz	8.77×10^{28} Hz^2
$Ba_{0.7} Sr_{0.3} TiO_3$	280° K	1.495×10^{12} Hz	8.77×10^{28} Hz^2
$Ba_{0.8} Sr_{0.2} TiO_3$	324° K	1.068×10^{12} Hz	8.77×10^{28} Hz^2

We have shown the real part of the dielectric constant $\in'$ verses frequency in Fig. 2 in the paraelectric phase of $Ba_xSr_{1-x}TiO_3$ for different values of x (= 0.0,0.2, 0.5, 0.7, 0.8 etc). Solid curves are based upon our theoretical calculations while dotted are based upon experimental observations[25]. The variation of the dielectric constant $\in$ with frequency in the case of $SrTiO_3$ is in agreement with our theoretical[22] and experimental results[2] , while the results for $Ba_xSr_{1-x}TiO_3$ are similar to that obtained experimentally by the results of others workers [8,24,,26-28].

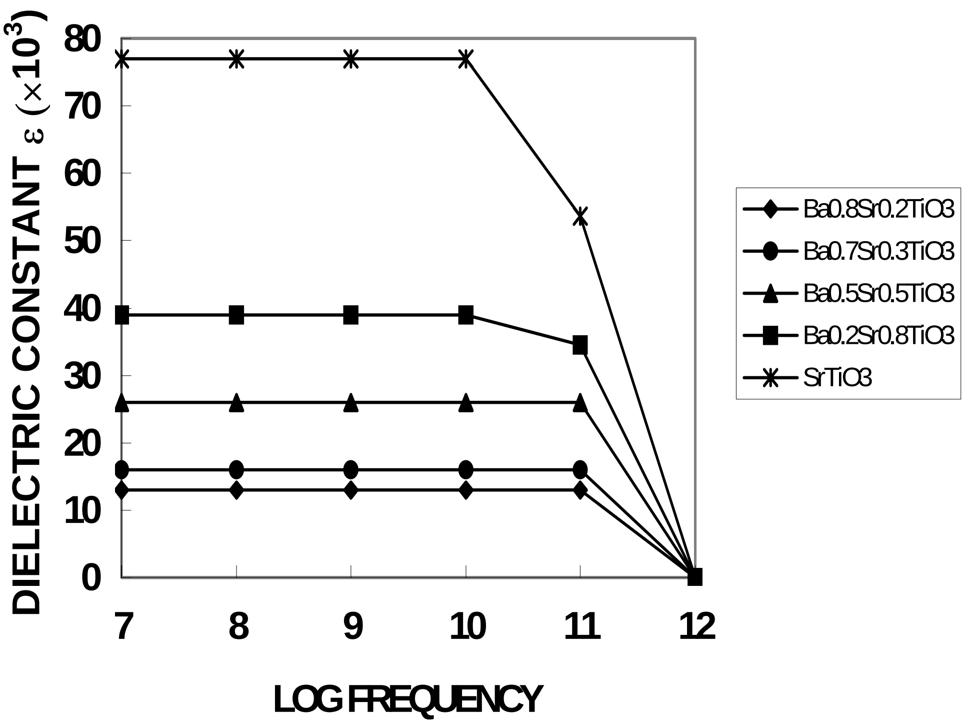

Fig.2 -Variation of dielectric constant with frequency at different soft mode frequency in baxsr1-xtio3

2.3 Temperature variated dielectric constant:

Using relation (10) we have calculated the dielectric constant in temperature range (50 - 700^0K) of $Ba_xSr_{1-x}TiO_3$ for different values of x (x=0.0,0.2,0.5,0.7,0.8). The value of Curie constant (C)is obtained from our previous study Deorani et.al.[22] . We have shown the variation of real part of dielectric constant with temperature in Fig.3 in paraelectric phase for $Ba_xSr_{1-x}TiO_3$ for different values of x and also the variation of reciprocal of dielectric constant with temperature in Fig.4 for same values of x.. The obtained linear variation of the reciprocal of the dielectric constant with temperature is in good agreement with the theoretical and experimental results of others[1,39].

3. DISCUSSIONN & CONCLUSIONS

The treatment adopted here leads one to see the comparative variation of dielectric constant with the variation of frequency and temperature of $Ba_xSr_{1-x}TiO_3$ with different values of x. In the present study the Hamiltonian proposed by Silverman[29] has been designed in terms of creation and annihilation operators. To evaluate the higher order correlation functions, the normalized Hamiltonian has been evaluated using the Green's function technique and Dyson's equation treatment.

The technique and approach used for obtaining the expression for dielectric constant in these perovskites is different from other workers. We have numerically estimated the dielectric constant of $Ba_xSr_{1-x}TiO_3$ and have shown the comparative variation of dielectric constant with frequency and temperature in these crystals. It is clear from eqn.(5) that the impurity dependence of dielectric constant is a clear consequence of defect dependence of soft mode frequency. So, in order to discuss the defect dependence of dielectric constant of displacive ferroelectrics, we first discuss the defect dependence of the soft mode frequency. It is clear from Fig.1 that the soft mode frequency varies with the variation of Barium concentration on the pure Strontium Titanate crystal. Fig.1 shows that the soft mode frequency has the highest value for a pure Strontium Titanate crystal and it continuously decreases when impurity of Barium increases. The soft mode frequency shows a sharp decrease at x=0.7, which is due to largest value of defect parameter α in above cases and has the lowest value for x=0.8 in the calculated ones.

It is evident from Fig.2 that an increase in frequency up to a certain range (10^7- 10^{11} Hz) does appreciable change in the dielectric constant of pure Strontium Titanate (i.e. when impurity is zero) but after this range (from 10^{11} -10^{12} Hz), the dielectric constant suddenly starts to decrease. The results are in good agreement with our previous theoretical[22] and experimental[2] results and also the results of other workers[8,324,26-28].

The variation is same for all values of x in $Ba_xSr_{1-x}TiO_3$. It is also evident from Fig.2 that when impurity concentration of Barium on pure Strontium Titanate crystal increases (i.e. value of x increase in $Ba_xSr_{1-x}TiO_3$), then the dielectric constant increases but the variation of dielectric constant with frequency is same for all the cases as in pure Strontium Titanate crystal case.

The dielectric constant of pure $SrTiO_3$ has the lowest value as compared to dielectric constant for mixed crystal. The increment in dielectric constant with the increment of the impurity concentration of Barium is due to the fact that soft mode frequency decreases with the increase of impurity of Ba on $SrTiO_3$. Fig.3 shows the variation of the dielectric constant with temperature of $Ba_xSr_{1-x}TiO_3$ for different defect concentration (i.e. different values of x) in paraelectric phase.

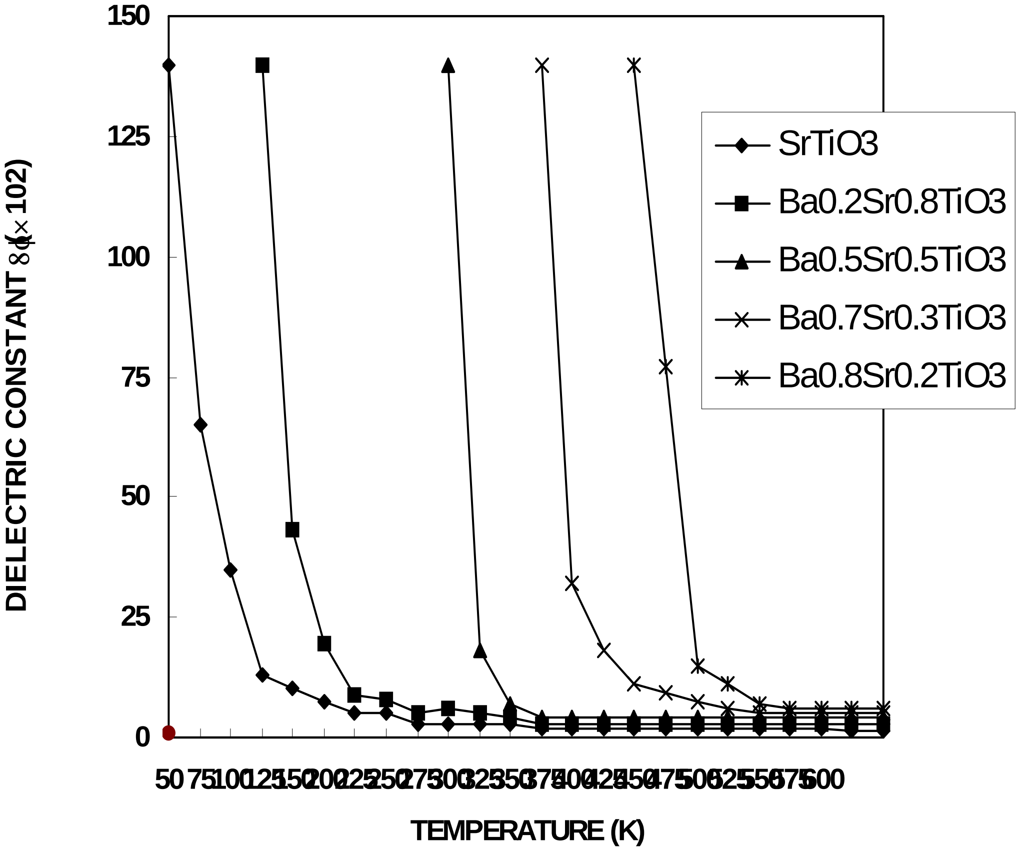

Fig.3-Varaiation of dielectric constant with temperature in baxsr1-xtio3 perovskites

It is evident from the figure that taking any temperature as a reference, the dielectric constant of pure $SrTiO_3$ Perovskite is the lowest as compared to the dielelctric constant for mixed crystal. It is also evident that in case of pure $SrTiO_3$ (i.e. x= 0 in $Ba_xSr_{1-x}TiO_3$), the dielectric constant increases sharply as $(T-T_c)$ decreases and has highest value as $T \rightarrow T_c$ and dielectric constant decreases as go away from Curie temperature and has small value at high temperature side. The trend is same in all the cases.

Fig. 4 shows the variation of the reciprocal of dielectric constant (1/ε) with temperature in $Ba_xSr_{1-x}TiO_3$ for different defect concentration (i.e. different values of x) in paraelectric phase. It is evident from the figure that taking any temperature as a reference, the reciprocal of the dielectric constant (1/ε) decreases with increase of the defect concentration (i.e.x) in $Ba_xSr_{1-x}TiO_3$ i.e. for pure $SrTiO_3$, the reciprocal of the dielectric constant has the highest value compared to the dielectric constant of mixed crystal.

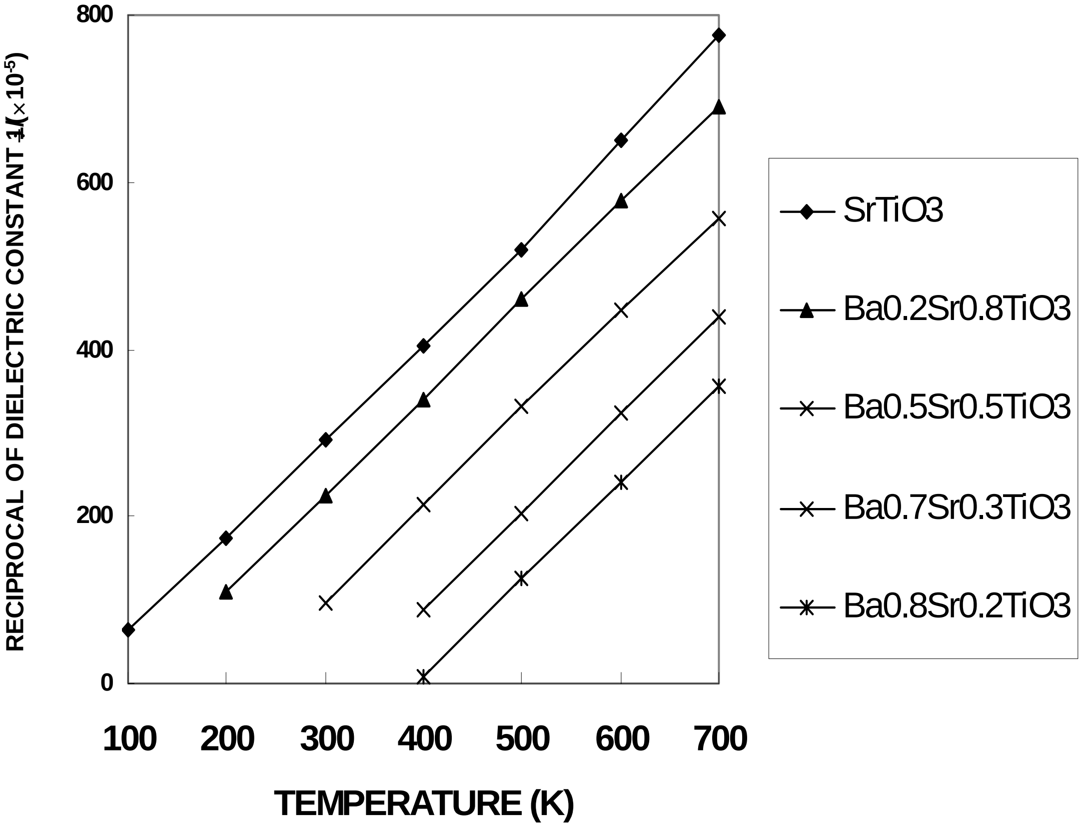

Fig.4-variation of reciprocal of dielectric constant with temperature in baxsr1-xtio3

It is also evident from Fig.4 that the reciprocal of the dielectric constant has a linear variation for pure $SrTiO_3$ and dielectric constant increases with the increase of temperature. The trend is same for all other concentrations also. This temperature dependence is due to the fact that the Curie temperature increases with the increase of the defect concentration. The results of the temperature dependence of the dielectric constant of $SrTiO_3$ are in close agreement with the results of the theoretical and experimental results of others[1,12-14,16] and also agree with Curie Weiss behaviour in the paraelectric phase if the temperature is not too high above T_c. Strong phonon phonon interaction due to vanishingly small frequency of the soft mode is held responsible for it. Our results for dielectric constant of pure and mixed crystal are also in close agreement with the results of others[1,12-14,16,31-33] . Anharmonicity is necessary in these crystals to observe these effects. In the vicinity of the Curie temperature, the soft mode frequency $[\Omega \propto (T-Tc)^{1/2}]$ becomes vanishingly small and hence, the dielectric constant decreases anomalously. Recently, we have applied the Green's function technique in observing the field dependent microwave loss[34] and attenuation constant[35] and KDP type ferroelectric36 also in displacive ferroelectics.

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