Field dependent dielectric behaviour of $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ ferroelectric perovskites

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The electric field dependence of complex dielectric constant of $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ ferroelectric crystal in paraelectric phase has been studied by using the method of double times thermal Green’s function and Kubo formalism. A general expression is derived from the Silverman-Joseph Hamiltonian by taking into account the change of mass as well as harmonic force constant between impurity atom and host lattice atoms with fourth order phonon coordinates. The frequency, temperature and electric field dependent dielectric constant of $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ crystal has been investigated. The dielectric constant increases with increase in temperature as well as with the applied electric field. The results are compared with the previous experimental and theoretical results.

Keywords: Dielectric constant, Ferroelectrics, Perovskites, Green’s function, Kubo formalism

1 Introduction

In the recent past, the dielectric, piezoelectric and optical properties of ferroelectric oxides have been studied, because of their applications in various electronic and optical devices. Ferroelectrics are the most typical non-linear dielectric materials. These crystals have the property to be polarized in the presence of external electric field. Polarization of these materials may be represented by small displacements of large number of charged particles of the matter. Domain structure studies have become one of the important properties in case of ferroelectric materials. From the domain structure, the direction of spontaneous polarization can be easily understood.

Several interesting temperature dependent properties of ferroelectrics result from the temperature dependence of low lying transverse optic (TO) mode of vibrations. A very interesting property is electric field dependence of low lying TO modes. The electric field dependent soft mode frequency in displacive ABO₃ type ferroelectrics has been investigated earlier by many researchers.

Due to large value of permittivity with suitable doping, these are used in capacitors with outstanding properties. These ferroelectrics have found applications in memory displays, optical communications, coherent optical processing, modulator beam reflectors and holographic storage media. The semiconducting ferroelectric 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 $\text{BaTiO}_3$, $\text{SrTiO}_3$, $\text{CaTiO}_3$ and $\text{KTaO}_3$. The studies of electric field dependent dielectric constant have been done by other researchers. The effect of electric field on the Cochran modes in the ABO₃ type perovskites was first studied by Steigmeir showing upward shift in transverse mode frequency which reduces transverse optic longitudinal acoustical (TO-LA) interactions. These crystals show diffused phase transition (DPT) of crystals and frequency dependence of the dielectric constant.

Barium calcium titanate ($\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$) is an ferroelectric material because of the significant variation in its physical and structural properties due to Ca substitution. A considerable review on dielectric properties of pure and mixed crystals is available in the literature. Deorani et al. have theoretically studied the temperature dependence of dielectric constant in $\text{BaTiO}_3$, $\text{SrTiO}_3$ and $\text{KTaO}_3$ crystals. The same properties for zero field case for $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ have been studied by Kumar et al. A current review on the $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ is available in the literature.

The field dependent dielectric properties in polycrystalline of $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ by forming the model Hamiltonian for the polycrystalline mixture of ferroelectric perovskites and then applying it to $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ have been studied theoretically in the present paper. Double times thermal Green’s function is used to obtain thermally averaged correlation...
functions and hence, the observable quantities with the help of the modified model Hamiltonian by taking into account the anharmonic effects up to fourth order with substitutional defects and electric moment terms. In this formulation, the real part of the dielectric constant $\varepsilon'$ will lead to an expression for the change in Curie temperature ($T_c$) by the presence of electric field. We have accounted the effect of defect concentration and electric field on the real part of the dielectric constant of a displacive ferroelectric material in paraelectric phase and results obtained are in good agreement with previous experimental results.

2 Theory

The Hamiltonian that is considered here includes the anharmonicity up to fourth order in the potential energy due to interaction of soft mode coordinates, resonant interactions and scattering terms. The Hamiltonian used here is the same as used in our previous paper. The notations used are the same and in the same sense as used in Ref. 23.

We introduce the Green’s function for studying the dielectric constant as:

$$G_0^0 (t-t') = << A_0^0 (t); A_0^0 (t') >> \ldots (1)$$

or

$$G_0^0 (\omega + i\varepsilon') = G' (\omega) - G'' (\omega) \ldots (2)$$

Solving the equation of the motion for the Green’s function Eq. (1) with the help of modified Silverman-Joseph Hamiltonian Eq. (2) of (Ref. 23), Fourier transforming and writing it in the form of Dyson’s equation one obtains,

$$G_0^0 (\omega + i\varepsilon') = \omega / \{ \Pi (\omega^2 - v_0^o)^2 (\omega) = -2 \omega \Gamma_0^o (\omega) \}, \ldots (3)$$

where $(v_0^o) (\omega)$ is stabilized soft mode frequency, $\Gamma_0^o (\omega)$ is the phonon half-width for the soft optic mode.

$$(v_0^o)^2 (\omega) = (v_0^o)^2 + 4(v_0^o)^2 \sum_{\lambda,k} B_{\lambda,k}^2 (k) < A_k^2 + A_k \lambda >$$

$$+ 96g^2 v_0^o \nu E^2 - 24g v_0^o \nu D_1 E^2 + \Delta_0^o (\omega) \ldots (4)$$

where $\Delta_0^o$ is the shift in the presence of anharmonicity, impurities and electric field as:

$$\Delta_0^o (\omega) = \Delta_{A}(\omega) + \Delta_{D}(\omega) + \Delta_{E}(\omega) \ldots (4a)$$

The real part of the dielectric constant is related to soft mode phonon Green’s function as:

$$\varepsilon' (\omega) - 1 = -8\pi^2 N\mu^2 G' (\omega) \ldots (5)$$

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

$$\varepsilon' (\omega) - 1 = -8\pi^2 N\mu^2 (\omega^2 - \Omega^2)^2 \varepsilon_i (\omega^2 - \Omega^2)$$

$$+ 4\omega^2 (\Omega^0)^2; v_0^o \Omega \ldots (6)$$

where $\varepsilon_i$ is the static dielectric constant of material, $\mu$ is the mole dipole moment per unit cell and N is the total number of unit cells in the specimen and other symbols are as usual.

The frequency dependent dielectric constant (in the range $\Delta \tau \leq 1$) may be calculated using the relation (which is similar to that of Deorani):

$$\varepsilon' = \varepsilon_i (\omega_0^2) (\omega_0^2 - \omega^2) / (\omega_0^2 - \omega^2)^2 + 4\omega^2 (\Omega^0)^2; \omega_0 \Omega \ldots (7)$$

where $\lambda = \varepsilon_i (\tau) \omega_0^2$ is constant at certain temperature.

The soft mode frequency is very large as compared to the microwave frequency ($\omega / \Omega = 10^{-3}$) and no relaxation effects are observed and half width $(\Gamma_0^o (\omega) / 2 \omega_0)$ is such that $\Gamma_0^o (\omega) \ll 2\omega_0$. Due to this appreciable difference between the microwave frequency and the normal frequency of oscillator the real part of the dielectric constant [Eq. (7)] can also be written as:

$$\varepsilon' = \lambda / \omega_0^2$$

or

$$\varepsilon' = \lambda / (\Omega_{ADE})^2; \omega_0 = \Omega_{ADE} \ldots (8)$$

where $\Omega_{ADE}$ is soft mode frequency depends upon anharmonicity, defect and electric field.

The soft mode frequency for the optic mode could be written as :

$$\Omega_{ADE} = -(\omega_0^o)^2 - 2 \omega_0^o V + Y_1 + Y_2 T + Y_3 T^2 \ldots (9)$$

where $Y_2, Y_3$ are temperature dependent coefficients of $T$ and $T^2$, respectively in the expression of the square of soft mode frequency.
From Eqs (6),(8) and (9), \( \nu_0 \) is same as \( \omega_0 \), we conclude that:

\[
\epsilon'(T) = \lambda JK (T - T_c') + \xi T^2
\]

…(10)

where \( K \) is temperature independent constant, \( T_c' = (a/\beta) \) is paraelectric field dependent phase transition temperature, \( \xi = (\gamma/\beta) \) is non linearity constant, which characterizes the deviation of the temperature dependence of dielectric constant from the Curie-Weiss behaviour and is related to the third and fourth order coupling coefficients.

\[
a = -(\omega_k)^2 - 2 \omega_k \nu V + Y_1
\]

…10(a)

\[
\beta = Y_2 \text{ and } \gamma = Y_3
\]

…10(b, c)

If \( \xi \) is very small and \( T \) is not very high (i.e. in paraelectric phase, but in the vicinity of Curie temperature), then one can neglect the terms \( \xi T^2 \) from the denominator of the Eq. (10) and one gets:

\[
\epsilon'(T) = \lambda JK (T - T_c') \simeq C/(T - T_c')
\]

…(11)

where \( C = \lambda JK \) is Curie constant.

In general, electric field dependence of dielectric constant can be written as [from Eq. (11)],

\[
\epsilon' (T) \simeq C/(T - T_c')
\]

…(12)

where \( T_c' = T_c + \Delta T_c \)

…(12a)

\( \Delta T_c \) is change in Curie temperature due to applied electric field.

\[
\Delta T_c = 1.9 \times 10^{-3} \times E
\]

…(12b)

where \( E \) is applied field in (V/cm).

The temperature dependence of soft mode frequency of ferroelectric crystal is given by:

\[
\Omega(T) = K(T - T_c')^{1/2}
\]

…(13)

Also electric field dependent soft mode frequency can be expressed as:

\[
\Omega(E) \approx K(T - T_c')^{1/2}
\]

…(14)

From Eqs (13) and (14):

\[
\Omega(E)/\Omega(T) = [K(T - T_c')^{1/2}]/[K(T - T_c')^{1/2}]
\]

\[
\Omega(E) = \Omega(T)^{1/2} K(T - T_c')^{1/2}/K(T - T_c')^{1/2}
\]

\[
\Omega_{ADE} = \Omega_{AD} K(T - T_c')^{1/2}/K(T - T_c')^{1/2}\{\Omega_{ADE} \sim \Omega_{E} \text{ and } \Omega_{AD} \sim \Omega_{T}\}
\]

…(15)

where \( \Omega_{ADE} \) is field and defect dependent soft mode frequency and \( \Omega_{AD} \) is defect dependent soft mode frequency.

As Curie temperature changed in the presence of electric field for these perovskites, according to the Eq. (12b). Using Eq. (15) we have calculated the soft mode frequency of \( \text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3 \) for different values of \( x (= 0.0, 0.05, 0.10, 0.15) \) in different electric field strengths. The value of \( \Omega_{AD} \) is obtained from different parameters as discussed in our previous studies.

Hence, we have studied the variations of soft mode for different electric fields from Fig. 1. The variations are in good agreement with previous experimental and theoretical results of others.

Using Eq. (12), the variations of dielectric constant in paraelectric phase have been studied and these variations with temperature are shown in Fig. 2 for different field strengths. Taking a particular temperature as a reference, it is observed that dielectric constant increases with rise in applied electric field in all the cases. At a single value of electric field, dielectric constant decreases with increase in temperature in all the cases studied.

By using Eq. (7), we have calculated the dielectric constant for \( \text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3 \) for different values of \( x (= 0.0, 0.05, 0.10, 0.15) \) and electric field strengths. The variations of the dielectric constant with frequency for different electric fields is shown in Fig. 3.

3 Discussion and Conclusions

The technique used here leads one to a comparative variations of dielectric constant with the variation of frequency and temperature of \( \text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3 \) with different values of \( x (= 0.0, 0.05, 0.10, 0.15) \) in the presence of electric field. From Eq. (6), it is obvious that the value of dielectric constant depends on electric field, is a consequence of dependence of soft mode frequency on electric field. The value of dielectric constant increases with the increase in applied electric field.

Figure 1 shows the variation of soft mode frequency with temperature for different electric fields of \( \text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3 \) for different values of \( x (= 0.0, 0.05, 0.10, 0.01) \). When temperature increases soft
mode frequency increases for all values of $x$ in $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$. Taking any temperature as the reference, soft mode frequency increases with increasing electric field which is in agreement with experimental results.

Figure 2 shows the temperature dependence of dielectric constant in different electric field strengths of $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$, for different values of $x$ ($= 0.0, 0.05, 0.10, 0.15$). According to our results, as temperature approaches Curie's temperature ($T \rightarrow T_c$), dielectric constant sharply increases as difference ($T-T_c$) increases a sudden decrease in dielectric constant is observed, which is in agreement with experimental and theoretical results observed by Rupprecht and Bell$^{30}$, Kumar et al.$^{27}$, Kukreti et al.$^2$ Zhang et al.$^{21}$ and Jona and Shirane$^{31}$. It is evident from Figs 1 and 2 that the electric field is noticeable at low temperature side and ceases along the higher temperature side. The effect due to higher order anharmonic effects dominates upon the field effects as we move far away from the Curie temperature.

Figure 3 shows the variation of dielectric constant with the soft mode frequency for $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ at different values of $x$ ($= 0.0, 0.05, 0.10, 0.15$). When soft mode frequency increases dielectric constant first decreases for different values of applied field and at higher temperature both become constant for different values of $x$ ($= 0.0, 0.05, 0.10, 0.15$). The trend is the same for different values of electric fields. Taking a particular soft mode frequency as a reference, dielectric constant decreases with decrease of electric field. These variations are in good agreement with our previous studies.$^{26}$

Figure 4 shows the variation of dielectric constant with frequency for different electric fields in $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ for different values of $x$ ($= 0.0, 0.05, 0.10, 0.15$). The dielectric constant for any of the crystal is constant for frequencies $10^7 - 10^{11}$ Hz and above this range it suddenly decreases. The same variations are obtained for different field strengths and also for all compositions. Also it is clear that taking any frequency as reference, dielectric constant
increases with increase of electric field strength in Ba$_{1-x}$Ca$_x$TiO$_3$ for different values of $x$ (= 0.0, 0.05, 0.10, 0.15). These variations are in good agreement with our previous studies and of other experimental and theoretical results. The Ca substitution increases the dielectric constant by a less order as compared to the variations occur due to substitution of Sr atoms replacing Ba atoms in the crystal BaTiO$_3$. Recently, we have studied some physical properties of Ba$_x$Sr$_{1-x}$TiO$_3$ ferroelectric perovskites.

References