Field dependent dielectric behaviour of \( \text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3 \) perovskites

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Using the method of double time thermal Green’s functions and Kubo formalism, a general expression has been derived for the electric field dependence of the complex dielectric constant of \( \text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3 \) ferroelectric crystal in the paraelectric phase from the Silverman–Joseph Hamiltonian augmented with fourth order phonon co-ordinates. The change of mass as well as harmonic force constant between impurity atom and host lattice atoms are taken into account. The frequency, temperature and electric field dependent dielectric constant of \( \text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3 \) crystal has been discussed. Dielectric constant increases with increase of applied field. The results are compared with previous experimental and theoretical results.

Keywords: Dielectrics, \( \text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3 \) perovskites, Green’s functions.

1 Introduction

Ferroelectrics are the most typical non-linear dielectrics. Due to their specific features they are broadly employed in many devices and have found a wide range of practical applications. It is now well known that several interesting temperature dependent properties of ferroelectrics result from the temperature dependence of the low lying transverse optic mode of vibration. One of the very interesting property of these crystals is the electric field dependence of the low frequency transverse optic mode.

Ferroelectrics have found applications in memory display, optical communication, coherent optical processing, modulator beam reflectors and holographic storage media. Besides these ferroelectrics are broadly used in ceramic industry. Semi conducting 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 barium titanate, strontium titanate and potassium tantalate. Studies on field dependent dielectric constant of ABO\(_3\) type perovskites are available in literature.\(^1\)-\(^4\) The effect of electric field on the Cochern modes in ABO\(_3\) type perovskites was first studied by Steigmeir\(^5\) showing upward shift in the transverse mode frequency which reduces the TO-LA interaction.

The aim of the present paper is to study theoretically the field dependent dielectric property in polycrystalline mixture of \( \text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3 \) by forming a model Hamiltonian for the polycrystalline mixture of ferroelectric perovskites and then applying it to \( \text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3 \). Double time thermal Greens function technique is used to obtain thermally averaged correlation function and hence the observable quantities with the help of a modified model Hamiltonian taking into account anharmonic effect up to fourth order with substitutional defect and electric moment terms. For simplicity the ions are assumed non polarizable. Such a formulation is particularly interesting as the real part of dielectric constant (\( \varepsilon' \)) will lead to an expression for the change in the Curie temperature resulting from the presence of electric field. The contribution of soft mode frequency towards dielectric constant has been taken into account. The effect of defect and electric field 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 Dielectric Constant

The electric field dependence of the complex dielectric constant in anharmonic ferroelectric crystals are calculated in its paraelectric phase from the Silverman–Joseph Hamiltonian augmented with fourth order phonon co-ordinates using double time Green’s function technique\(^6\).

For the study of dielectric constant, following Green’s function is used:
\[ G_0(t-t') = \ii \partial_x(t); A_0(t') \gg \omega + \ii \epsilon \]  
\( \text{or} \)
\[ G_0(\omega + i\epsilon) = G'(\omega) - G''(\omega) \]  

Solving the equation of motion for the Green’s function [Eq. (1)] with the help of modified Silverman-Joseph Hamiltonian [Eq. (2) of Ref. 6], Fourier transforming and writing it in the form of Dyson’s equation gives:

\[ G_0(\omega + i\epsilon) = \frac{\omega}{\pi} \left[ (\omega^2 - (v_0^2)^2) - 2i\omega\Gamma(\omega) \right] \]  

where \( \Gamma(\omega) \) is the phonon half width for the soft optic mode; \( (v_0^2)^2(\omega) \) is the square of stabilized soft mode frequency; and

\[ (v_0^2)^2(\omega) = (\omega_0^2)^2 + 4(\omega_0^2)\sum_{k,k'} B_k B_{k'} < A_{k+k'}^4, A_{k-k'}^4 > + 96g^2 \omega_0^2 V^2 - 24g^2 \omega_0^2 D^2 E^2 + \Delta_0^2(\omega) \]  

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

\[ \epsilon'(\omega) = -8\pi N\mu^2 G'(\omega) \]  

The real part of complex dielectric constant by using Eq. (3) is given as:

\[ \epsilon' - 1 = -\frac{8\pi N\mu^2 (\omega^2 - \Omega^2)^2}{(\omega^2 - \Omega^2)^2 + 4\omega^2 \Gamma^2}; \quad v_0^2 = \Omega \]

or

\[ \epsilon' = \frac{8\pi N\mu^2 (\omega^2 - \Omega^2) \epsilon_s}{[(\omega^2 - \Omega^2)^2 + 4\omega^2 \Gamma^2]^2}; \quad \epsilon' \gg 1 \]  

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

The frequency dependent dielectric constant [in the range \( \omega \tau \leq 1 \)] may be calculated using the relation14:

\[ \epsilon' = \frac{\epsilon_s \omega^2 (\omega^2 - \Omega^2)}{(\omega_0^2 - \Omega^2)^2 + 4\omega^2 \Gamma^2}; \quad (\omega_0 \approx \Omega \approx v_0) \]

or

\[ \epsilon' = \frac{\lambda (\omega^2 - \Omega^2)}{(\omega_0^2 - \Omega^2)^2 + 4\omega^2 \Gamma^2}; \]  

where \( \lambda = \epsilon_s (T)\omega_0^2 \) is constant at certain temperature.

The soft mode frequency is very large as compared to the micro wave 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 micro wave frequency and the normal frequency of oscillator the real part of the dielectric constant [Eq. (8)] can also be written as:

\[ \epsilon' = \frac{\lambda}{\omega_0^2} \quad \text{or} \quad \epsilon' = \frac{\lambda}{\Omega^2}\omega_0 = \Omega_{ADE} \]  

where \( \Omega_{ADE} \) is soft mode frequency which depend upon anharmonicity, defect and electric field.

The soft mode frequency for the optic mode could be written as7:

\[ \Omega_{ADE} = -(\omega_0^2)^2 - 2\omega_0^2 V + Y_1 + Y_2 T + Y_3 T^2 \]

where the symbols \( Y_1, Y_2 \) and \( Y_3 \) are the temperature independent, coefficients of \( T \) and \( T^2 \) respectively in the expression of square of soft mode frequency.

From Eqs (7), (9) and 10 \( (v_0^2) \) is same as \( \omega_0 \) we conclude that

\[ \epsilon'(T) = \frac{\lambda}{K(T + \xi T^2 - T')} \]  

where \( K \) is temperature independent constant, \( T' \) (\( = \alpha / \beta \)) is paraelectric field dependent phase transition temperature, \( \xi \) (\( = \gamma / \beta \)) is non-linearity 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.

\[ \alpha = -(\omega_0^2)^2 - 2\omega_0^2 V + Y_1, \quad \beta = Y_2, \quad \gamma = Y_3 \]

If \( \xi \) is very small and \( T \) is not very high (i.e., though in paraelectric phase but in the vicinity of Curie temperature \( T_c \) then the term \( \xi T^2 \) can be neglected from the denominator of Eq. (11) and

\[ \epsilon'(T) = \frac{\lambda}{K(T - T')} \approx \frac{C}{(T - T')} \]  

where \( C = \frac{\lambda}{K} \) is the Curie constant and \( T_c \) is the Curie temperature.
In general electric field dependence of dielectric constant from Eq. (12) can be written as:

$$\varepsilon' = \frac{c}{(T - T'c)} \quad \ldots \quad (13)$$

where

$$T'c = Tc + \Delta T \quad \ldots \quad (13a)$$

with

$$\Delta T = 1.9 \times 10^{-3} \times E \quad \ldots \quad (13b)$$

where $E$ is applied electric field in volt/cm².

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

$$\Omega(T) = K(T - Tc)^{1/2} \quad \ldots \quad (14)$$

Also the electric field dependant soft mode frequency can be expressed as

$$\Omega_{(E)} = K(T - T'c)^{1/2} \quad \ldots \quad (15)$$

where $T'c = Tc + \Delta T$ with $\Delta T = 1.9 \times 10^{-3} \times E$.

From Eqs (14) and (15)

$$\frac{\Omega_{(E)}}{\Omega_{(T)}} = \frac{(T - T'c)^{1/2}}{(T - Tc)^{1/2}} \quad \text{or}$$

$$\Omega_{(E)} = \Omega_{(T)} \left(\frac{T - T'c}{T - Tc}\right)^{1/2} \quad \text{or}$$

Fig. 1—Soft mode frequency verses temperature plot for different electric field: (a) SrTiO₃; (b) Ba₂Sr₂TiO₆; (c) Ba₅Sr₃TiO₁₃; (d) Ba₅Sr₂TiO₇; (e) Ba₈Sr₅TiO₁₃; (f) BaTiO₃
KUKRETI et al.: DIELECTRIC BEHAVIOUR OF Ba$_x$Sr$_{1-x}$TiO$_3$ PEROVSKITES

\[ \frac{\omega_{ADE}}{\omega_{AD}} \approx \left( \frac{T - T^*}{T - T_c} \right)^{1/2} \] … (16)

where $\omega_{ADE}$ is field and defect dependent soft mode frequency; $\omega_{AD}$ is defect dependent soft mode frequency.

2.1 Temperature variated soft mode frequency

It has been considered that the Curie-temperature changed in the presence of electric field for these perovskites with relation

$\Delta T = 1.9 \times 10^{-3} \times E$.

where $E$ is applied electric field in volt/cm.

Using Eq. (16), the soft mode frequency of Ba$_x$Sr$_{1-x}$TiO$_3$ is calculated for different values of $x$ (i.e. $x = 0.0, 0.2, 0.5, 0.7, 0.8$ and $1.0$) in different electric field strengths. The values of $\omega_{AD}$ (defect dependent soft mode frequency) are obtained.

The variation of soft mode frequency with temperature for different electric fields is shown in Fig. 1(a - f). The variations are in good agreement with previous experimental and theoretical results.

2.2 Temperature variated dielectric constant

Using Eq. (13), the values of temperature dependent dielectric constant in para electric phase are calculated. The variation of dielectric constant with temperature is shown in Figs 2(a-f) for different electric fields. Taking a particular temperature as a reference, it is observed that dielectric constant increases with increase of electric field in all the cases. It is also observed that taking electric field as a
parameter, dielectric constant decreases with increase of temperature in all the cases.

2.3 Soft mode frequency variated dielectric constant:

Using the Eq. (9), the dielectric constant of \( \text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3 \) is calculated for different values of \( x (x=0.0, 0.2, 0.5, 0.7, 0.8 \text{ and } 1.0) \) for the different corresponding values of soft mode frequency in the presence of different electric fields. The variations are shown in Figs 3(a-f).

2.4 Frequency variated dielectric constant:

By using Eq. (8) the dielectric constant of \( \text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3 \) is calculated for different values of \( x (x=0.0, 0.2, 0.5, 0.7, 0.8 \text{ and } 1.0) \) in the frequency range \( 10^7 - 10^{12} \) Hz for different field strengths. The variation of dielectric constant with frequency for different electric fields is shown in Figs 4(a-f).

3 Results and Discussion

The treatment adopted here shows the comparative variation of dielectric constant with the variation of frequency and temperature of \( \text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3 \) with different values of \( x (x=0.0, 0.2, 0.5, 0.7, 0.8 \text{ and } 1.0) \) in the presence of electric field. It is evident from Eq. (7) that the field dependence of dielectric constant is clear consequence of the field dependence of soft mode frequency. It is clear from Eq. (4) that soft mode frequency varies directly as the square of electric field strength.

Fig. 1(a-f) shows the variation of soft mode frequency with temperature for different electric field strengths of \( \text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3 \) for different values of \( x (x=0.0, 0.2, 0.5, 0.7, 0.8 \text{ and } 1.0) \). When temperature increases soft mode frequency first increases for all values of \( x \) and at higher temperature soft mode frequency decreases with increase of temperature for all the cases.
frequency becomes constant for all values of $x$ in $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (Fig. 1).

The soft mode frequency increases with increase of applied electric field and is in good agreement with the earlier experimental results\textsuperscript{10-13}. In the absence of the electric field the results are in good agreement with the results of Kumar \textit{et al.}\textsuperscript{9}, and in the absence of defect in pure crystals the results are in good agreement with the results of Lingwal \textit{et al.}\textsuperscript{7}.

Fig. 2(a-f) show the variation of dielectric constant with temperature in different electric field strengths of $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ for different values of $x$ ($x=0.0$, 0.2, 0.5, 0.7, 0.8 and 1.0). According to our results as temperature approaches towards Curie temperature (i.e. $T\rightarrow T_c$) dielectric constant sharply increases but as difference ($T-T_c$) increases a sudden fall of dielectric constant is observed. This variation is in good agreement with the experimental results of Rupprecht and Bell\textsuperscript{15}, Kumar \textit{et al.}\textsuperscript{9} and Jona and Shirane\textsuperscript{16}.

It is also evident from Fig. 1(a-f) and 2(a-f) that the field effect 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 effect as we move far away from the Curie temperature.

Figs. 3(a-f) shows the variation of dielectric constant with soft mode frequency for $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ at different values of $x$ ($x=0.0$, 0.2, 0.5, 0.7, 0.8 and 1.0). It is evident from the figures that when soft mode frequency increases dielectric constant first decreases for different values of electric field and at higher value of soft mode frequency dielectric constant becomes constant for all values of $x$. Trend is same for different values of electric field. Taking a particular soft mode frequency as a reference dielectric constant decreases with the decrease of electric field. These variations are in good agreement with previous study\textsuperscript{9}.
constant respectively. The variation of $\varepsilon''$ with frequency is shown by using the relation $\varepsilon''/\varepsilon' = \tan \delta$, where $\tan \delta$ is field, temperature and frequency dependent microwave loss in case of Ba$_{x}$Sr$_{1-x}$TiO$_3$ (Fig. 5). For simplicity this is shown at $E = 100$KV/cm in case of Ba$_{0.5}$Sr$_{0.5}$TiO$_3$. The trend will be the same for rest cases at different field strengths. It is seen that in the lower frequency region, the imaginary part $\varepsilon''$ increases with increasing frequency and shows a maxima at about $10^{11}$ Hz, while the real part $\varepsilon'$ does not change remarkably at lower frequencies. This dielectric response can be approximately described by the Debye type relaxation equations.

References