

Sound attenuation in $Ba_{1-x}Ca_xTiO_3$ ferroelectric perovskites

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Theoretical expression of attenuation constant of anharmonic $Ba_{1-x}Ca_xTiO_3$ ferroelectric crystal in paraelectric phase using double times temperature dependent Green's function technique, is derived. The variation of attenuation constant with frequency and temperature has been studied by considering third- and fourth-order anharmonic interactions, taking electric field as an important parameter. The mass and force constant change due to the presence of impurity atoms in Silverman-Joseph Hamiltonian augmented with higher order anharmonic terms. The effect of electric field, defect and anharmonicity on stabilization of the soft mode frequency has also been studied. The attenuation constant increases with increasing temperature and frequency in the presence of an electric field. In the vicinity of the Curie temperature, attenuation constant increases anomalously.

Keywords: Attenuation constant, Anharmonicity, Defect, Ferroelectrics, Curie temperature

1 Introduction

The study of propagation behaviour of the ultrasonic waves near a phase transition, gives valuable information about the static aspects such as equilibrium adiabatic properties of the system and the effect of the temperature, pressure and external fields. The ultrasonic absorption data give information about the dynamic aspects. From the temperature, frequency and defect dependence, the mechanism involved can be understood. Ultrasonic measurements provide a sensitive tool to study the phase transition in solids¹. These studies have played an important role in characterizing the behaviour of a system near the cooperative phase transitions (Cooperating – ordering of the dipoles which give rise to the spontaneous polarization, is destroyed by the thermal agitation above the Curie temperature) and critical points. Theoretically, new ways of describing critical phenomenon in terms of fluctuation correlation have been of great importance. The large variations in the strength of attenuation near the transition are usually referred anomalous. Such special variations are referred to as critical. As revealed experimentally as well as theoretically¹⁻⁵, the soft or ferroelectric mode plays an important role in displacive ferroelectrics. As the temperature approaches the Curie temperature (T_c), the soft mode frequency becomes vanishingly small $\{\Omega^2 \approx (T-T_c)\}$ resulting in increase in its amplitude, which should influence the acoustic mode due to phonon-phonon interactions and is expected to give rise to an anomalous behaviour of sound near T_c .

Non-destructive ultrasonic techniques are used to study physical properties of the materials by measuring the ultrasonic velocities and attenuations. So, ultrasonic attenuation is very important physical quantity just like thermal conductivity, specific heat, elastic constants, etc⁶. A considerable review on pure and mixed ferroelectric crystals showing sound attenuation is available in the literature⁷⁻¹¹ and references therein.

The phenomenological theory of sound attenuation near transition point has been developed by Landu and Kalatnikov¹². The characteristic behaviour of the soft mode in displacive ferroelectrics like $BaTiO_3$, $SrTiO_3$, etc. can be discussed by the degeneracy of the soft mode with the longitudinal acoustic mode for large wave numbers. The idea of coupling of elastic strain and soft phonon mode was suggested by many researchers^{6,13-15}, where the coupling, which is quadratic in polarization and linear in strain, is described in terms of electro-strictive coupling. There is not any appreciable critical behaviour shown by the velocity of transverse wave. So the interaction of the soft mode phonon with each other and with acoustic phonons give the main contribution to the low frequency attenuation. Only interactions with the longitudinal sound remain in the vicinity of the Curie temperature when soft mode frequency tends to zero. $Ba_{1-x}Ca_xTiO_3$ (BCT) has wide range of applications and some more beneficial properties as compared to other ferroelectrics such as mechanical strength (towards heat and moisture), presence of ferroelectric

properties without broad range of temperature and is easy to manufacture.

Several researchers¹⁶⁻¹⁹ have derived expressions for attenuation constant in displacive ferroelectrics. Kumar *et al.*²⁰ have studied the attenuation constant in $Ba_xSr_{1-x}TiO_3$ perovskites for zero field case. Kukreti *et al.*²¹ have investigated the attenuation constant in $Ba_xSr_{1-x}TiO_3$ in case of different field strengths.

The attenuation constant in polycrystalline mixture of $Ba_{1-x}Ca_xTiO_3$ above the phase transition temperature with the variation of the frequency and temperature taking electric field as a parameter and to correlate the results with the results of other researchers have been studied theoretically in the present paper. Here the general expression of the sound attenuation has been obtained by augmenting the Silverman Hamiltonian with anharmonic terms up to third and fourth order. The effect of mass change and harmonic force constant changes between impurity and host lattice atoms in the presence of the electric field, through the consideration of defect. The defect, temperature, frequency and electric field dependence of the attenuation constant have been studied. In the vicinity of the Curie temperature (T_c), an anomalous behaviour of sound attenuation is predicted.

2 Theory

2.1 General formalism

The expression for the attenuation constant, as given by Tani and Tsuda⁸ can be written as:

$$\alpha = \Gamma_k(\omega)/c \quad \dots(1)$$

where c is sound velocity and Γ_k is the damping constant and is also defined as the width of the frequency response of acoustic phonon mode k .

2.2 Hamiltonian and Green's function

The Hamiltonian of the mixed ferroelectric crystal is similar to that used earlier in our previous study²¹ and the method used to construct the Hamiltonian is the same as used earlier^{15,22} from the crystal model proposed by Silverman and Joseph²³ by augmenting it with fourth order anharmonic interaction terms involving ferroelectric optic modes of lowest wave vector. It is considered that the introduction of the defect in the lattice causes changes in the harmonic force constants besides mass change and their influence upon anharmonic coefficient is neglected. This is true for isovalent and non-polarizable defects because they cause change in short range forces only.

The retarded double times thermal Green's function²⁴ for acoustical phonon can be written as:

$$G_{k,k'}^a(t-t') = \langle\langle A_k^a(t); A_{k'}^{a,\dagger}(t') \rangle\rangle = -i\theta(t-t')\langle A_k^a(t); A_{k'}^{a,\dagger}(t') \rangle \quad \dots(2)$$

Here $\theta(t)$ is Heaviside step function, $A_k^a(t)$ and $A_{k'}^{a,\dagger}(t')$ are the annihilation and creation operators of the acoustic phonon of the wave vector k while writing the equation of motion for the Green's function Eq. (2) with the help of the modified Hamiltonian²¹, Fourier transforming and writing it in the Dyson's equation form by using the methods used in our previous study²¹, one obtains:

$$G(\omega+i'\epsilon) = \delta_{k,k'}/2\pi [\omega - \omega_k^{a'} + i\Gamma_k(\omega)] \quad \dots(3)$$

where $\Gamma_k(\omega)$ is the damping constant and $\omega_k^{a'}$ is the field dependent stabilized acoustical frequency and is given as :

$$\omega_k^{a'} = \omega_k^a + 2\omega_k^a \Delta_k(\omega), \quad \dots(4)$$

$$\text{where } \omega_k^a = \omega_k^a + 8\omega_k^a gE^2 [2g\beta^a(k) - \beta^a(k)] \quad \dots(4a)$$

and

$$\Delta_k(\omega) = \Delta_k(\omega) + AE^2 \quad \dots(4b)$$

Here $\Delta_k(\omega)$ and $\Gamma_k(\omega)$ are expressions for the shift and width of acoustical phonon, respectively in the absence of the field. $\Delta_k(\omega)$ depends upon third and fourth order anharmonic coefficients in the presence of electric moment terms and the constant A depends upon third order anharmonic term only.

2.3 Temperature and field dependence of attenuation constant in $Ba_{1-x}Ca_xTiO_3$

The expression for the attenuation constant is given as according to the Eq. (21) in the literature²¹ as:

$$\alpha = \Gamma_k / c \quad \dots(5)$$

where the symbols have same significance and are used in same sense as used earlier.

Here the attenuation constant can be expressed as:

$$\alpha = \alpha_A(\omega) + \alpha_D(\omega) + \alpha_E(\omega) \quad \dots(6)$$

In the absence of applied electric field, $E = 0$

$$\alpha = \alpha_A(\omega) + \alpha_D(\omega) \quad \dots(6a)$$

The temperature, defect and field dependence of $\alpha(\omega)$ can be expressed as:

$$\alpha(\omega) = A_1 + (A_2 + A_3T + A_4E^2)T + (A_5 + A_6T + A_7E^2)[T / \times(T - T_c)^{1/2}] + A_8[T^2 / (T - T_c)^{1/2}] + A_9[T^2 / (T - T_c)] \quad \dots(7)$$

where A_i 's ($i = 1-9$) denotes the temperature and electric field independent term in $\Gamma_k(\omega)$. A_1 is only defect dependent while the rest depends upon impurity concentration, anharmonic force constants and electric moment terms. The expression given in Eq. (7) does not give the explicit temperature dependence of α because of renormalization effect. It is clear from the relation as T approaches T_c attenuation constant increases anomalously which is in agreement with the results of Tani⁸ and Pytte²⁵. In the presence of electric field at low temperature range for the reduced temperature, Eq. (7) becomes:

$$\alpha(\omega) = A_1 + A_4(T - T_c)^{3/2} + A_7E^2T / (T - T_c)^{1/2} \quad \dots(7a)$$

which is the same as obtained by Tani⁸. Here in the absence of electric field the attenuation constant can be written as:

$$\alpha(\omega) = \alpha_D(\omega) + \alpha_A(\omega) \quad \dots(8)$$

The symbols used in Eqs (7) and (8) are similar to be used earlier in previous studies²¹.

Comparing Eqs (7) and (8), we get:

$$\alpha_A(\omega) = A_4(\omega) / (T - T_c)^{3/2} \quad \dots(9)$$

$$\text{and } \alpha_D(\omega) = A_1 \quad \dots(9a)$$

$\alpha_A(\omega)$ for BaTiO_3 is obtained by the best fit of data from authors reported earlier¹⁹ and assumed that it remains unchanged by addition of impurity of Ca.

$$\text{and } A_1 = [D / T_c(\omega_0^0)]\alpha_0 \quad \dots(10)$$

where D is the defect parameter. α_0 for pure BaTiO_3 is equal¹⁹ to $0.4 \times 10^2 \text{ dBm}^{-1}$.

Also, the electric field dependent attenuation constant is given by:

$$\alpha_E(\omega) = [T / (T - T_c)^{1/2}]E^2A_7 \quad \dots(11)$$

where $T_c = T_c + \Delta T$, and $\Delta T = 1.9 \times 10^{-3} \times E$. E is the applied electric field and measured in V/cm.

The value of A_7 is calculated from the best fit of data from our previous study¹⁹ and is obtained as:

$$A_7 = 0.21 \times 10^4 \text{ S}^2\text{m}^{-1}\theta^{-1/2}$$

In the present study, only the net critical relaxation attenuation α_c above the phase transition temperature T_c in the presence of electric field, is concerned. The attenuation constant versus temperature for $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ with different values of defect concentrations (x) in the presence of electric field, for each value of x is plotted. This variation is linear which is in agreement with the authors previous studies^{19,20}. The attenuation constant increases with increase in impurity concentration and electric field.

2.4 Frequency dependence of attenuation constant in $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$

The frequency dependent attenuation constant can be represented as:

$$\alpha(\omega) = a_1 + a_2\omega^2 + a_3\omega + a_4\omega^4 \quad \dots(12)$$

where first three terms are due to anharmonic interactions and fourth term is due to defect contribution to the attenuation constant, respectively.

The frequency dependent attenuation constant can also be represented (Garland *et al.*²⁷) as:

$$\alpha(\omega) = \alpha_O + \alpha_D + \alpha_E \quad \dots(13)$$

Here α_O is the critical attenuation constant for pure crystal, α_D and α_E are electric field and defect dependent constants, respectively.

From Eqs [30 and 30(a)] of Ref.21, we get:

$$\alpha_D = a^4\omega^4 \text{ and } \alpha_E = a^2\omega^2 \quad \dots(14)$$

Eqs (12)-(14) show that defect dependence attenuation varies linearly with ω^4 .

$$a_4 = (D / T_c)^2 a_2 \text{ MHz}^{-4} \text{ s}^{-2} \text{ m}^{-1} \quad \dots(15)$$

where D is defect dependence parameter and T_c is Curie temperature, a_2 is calculated by the best fit of data¹⁹ and has value $a_2 = 4.1 \times 10^{-14} \text{ S}^2\text{m}^{-1}$ at temperature 398 K and frequency 10 MHz.

Using Eqs (13) and (14), we have calculated the attenuation constant for $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ mixed crystal with different values of x and plotted attenuation constant versus frequency curves for different values of x and different fields. Taking a particular field as a reference, it is observed that attenuation constant increases with increase in frequency in all the cases, which is in good agreement with previous results^{8,19-21}.

3 Results and Discussion

In the present work, an expression is derived for attenuation constant of sound and discussed its defect, frequency, temperature and electric field dependence in the $Ba_{1-x}Ca_xTiO_3$ ferroelectric perovskites, using double time thermal Green's function technique. Both the mass and force constant change due to doping, are taken into account, in the crystal Hamiltonian augmented with higher order anharmonic and higher order electric moment terms and give their contributions to various scattering processes. There are two scattering mechanisms present in the crystal: one is the various three- and four-phonon scattering amongst phonons due to higher order anharmonicity and the other is the electric field induced scattering due to electric moment terms in the presence of field. These two different scattering processes operate simultaneously having different values of the relaxation time for a particular acoustic phonon mode and the scattering rates are additive. It is shown that the acoustic width in the phonon frequencies is temperature dependent giving the temperature dependence of the attenuation constant. These temperature dependence is the direct consequences of the anharmonicity.

Figure 1 shows the variation of the attenuation constant with temperature at different electric fields for $Ba_{1-x}Ca_xTiO_3$ for $x = 0.05$. According to the present results, as temperature approaches towards the Curie temperature, attenuation constant increases. This variation is in good agreement with experimental results^{8,10} observed by Rupprecht and Bell²⁷ and our previous studies^{19,21}. The results are the same for all the values of x . Figure 2 shows the variation of attenuation constant with electric field, taking temperature as a parameter. It is clear from Figs (1 and 2) that attenuation constant increases with increase in electric field which is in agreement with previous results¹⁰. Figure 3 shows the variation of attenuation constant with frequency for different electric fields in case of $Ba_{1-x}Ca_xTiO_3$ for $x = 0.05$. It is evident from Figs (2 and 3) that attenuation constant increases with frequency and electric field which is in agreement with theoretical and experimental results of many researchers^{17,19,20}. Attenuation constant has less value in $BaTiO_3$ as compared to $SrTiO_3$.

Eq. (5) indicates that the dependence of the attenuation constant is a clear consequence of the field dependence of $\Gamma_E(\omega)$ [Eq. (15) of the Ref. (21)] and hence of $\Gamma_{E'}(\omega)$ [Eq. (12) of Ref. 21]. $\Gamma_E(\omega)$ varies

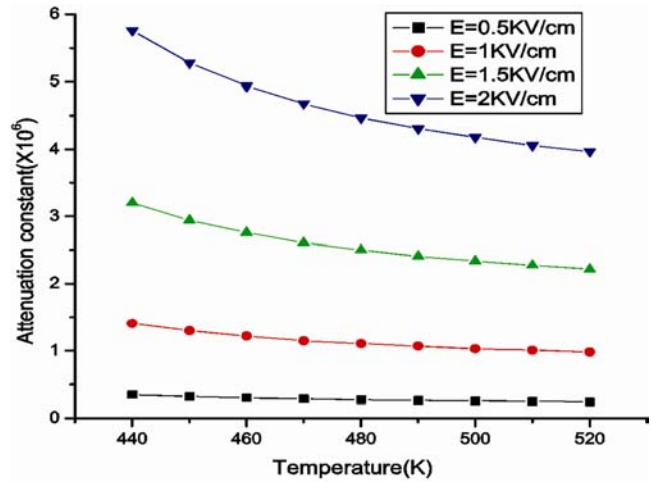


Fig. 1 — Variation of attenuation constant with temperature at different electric fields in $Ba_{1-x}Ca_xTiO_3$ ferroelectric perovskites for $x = 0.05$

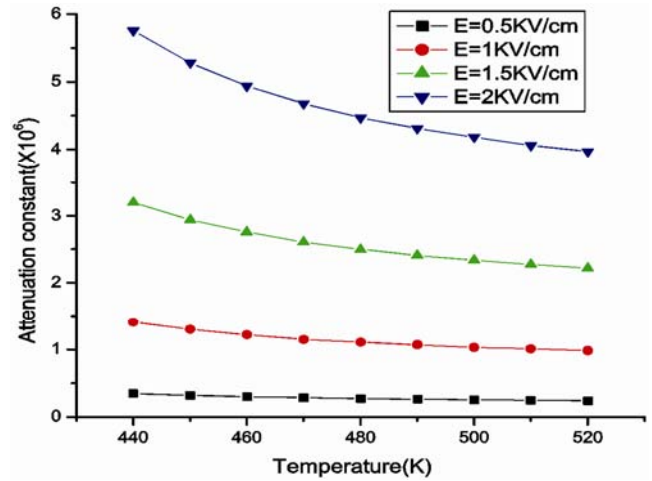


Fig. 2 — Variation of attenuation constant with electric field at different temperature in $Ba_{1-x}Ca_xTiO_3$ ferroelectric perovskites for $x = 0.05$

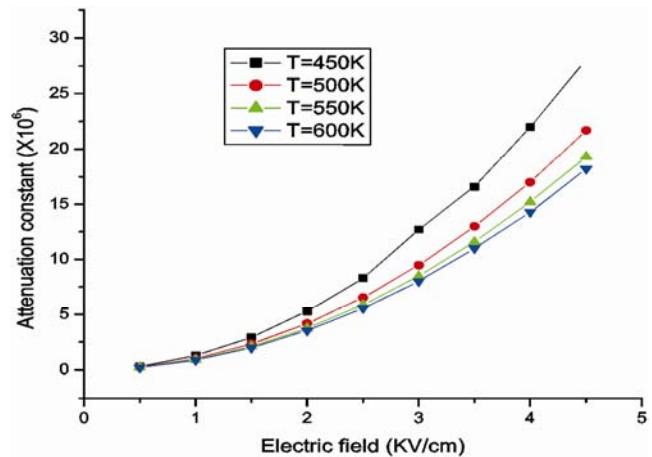


Fig. 3 — Variation of attenuation constant with frequency at different electric fields in $Ba_{1-x}Ca_xTiO_3$ ferroelectric perovskites for $x = 0.05$

directly as the square of the electric strength and thus, the attenuation constant increases with the increasing field. The results obtained are in good agreement with the results of Tani and Tsuda⁸ and Heuter and Neuhaus¹⁰. A considerable review on $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ is available in the literature²⁹.

4 Conclusions

In the present study, an expression is derived for the attenuation constant of sound and discussed its dependence on defect, electric field, temperature and frequency in a mixed anharmonic crystal ($\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$). The variations of mass and force constant due to doping are taken into account the third and fourth order anharmonicities and electric dipole terms. For the derivation of the expression of the attenuation constant, Green's function technique and Dyson's equation treatment have been used. The Dyson's equation treatment is very useful to derive shift and width of the frequency response function and is convenient to describe the properties of mixed crystals.

It is now clear that the attenuation constant increases as $T/(T-T_c)^{3/2}$. The attenuation constant in case of $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$, for all values of x increases with the increase in $T/(T-T_c)^{3/2}$. For phonons of small half width in harmonic approximation, the inverse relaxation time and hence, the attenuation constant is proportional to fourth power of phonon frequency, neglecting the changes in the force constants. But due to the modification of the changes in the force constants, this dependence changes from ω^4 to ω^2 . The experiments on the electric field dependent attenuation constant in mixed crystals in the vicinity of Curie temperature seem not to have been done except in BaTiO_3 mixed with lead (Pb) by Heuter and Neuhaus¹⁰ showing an increase in attenuation constant with the increasing electric field. Our results are in good agreement with those of Heuter and Neuhaus¹¹.

In the vicinity of Curie temperature, the soft mode frequency, which is imaginary in harmonic approximations and becomes temperature dependent due to anharmonic terms, becomes vanishingly small and N_0 [Eq. (19) of the Ref. 21] becomes anomalously large and hence, the attenuation constant increases anomalously. These results agree with the results of Tani and Tsuda⁸. The soft mode frequency is stabilized in the presence of defects, anharmonicity and electric field. The impurity, anharmonicity and electric field increase with the soft mode frequency. The treatment adopted here leads one to see the

comparative variations of the sound with the variations of the defect and electric field parameters. Attenuation constant has less value in ($\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$) as compared²¹ to ($\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$). Recently, dielectric constant²², microwave losses³⁰, specific heat³¹ and attenuation constant²¹ in case of $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$, has been studied.

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