Electric field dependent sound velocity change in $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$
ferroelectric perovskites

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By using double time temperature dependent Green’s function technique, an expression for the sound velocity change in the mixed crystal perovskites ($\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$) has been obtained with the help of the modified Silverman-Joseph Hamiltonian. Third- and fourth-order anharmonic and electric moment terms in the modified Hamiltonian for $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ crystal perovskites have been considered. The effect of defect, electric field and anharmonic contributions on velocity change in $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ for paraelectric phase has been studied. The presence of higher order anharmonicity and electric moment terms decreases the sound velocity. In the vicinity of the phase transition, it decreases as the consequence of the soft mode. It also varies with electric field and defect concentration in $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$.

Keywords: Green’s function, Sound velocity, Ferroelectric perovskites

1 Introduction

In the recent past, due to excellent dielectric, piezoelectric and optical properties of ferroelectric oxides and its applications in various electronic and optical devices, studies on them have been undertaken. Barium titanate is one of the widely used ferroelectric materials in electronics industry, both in single crystal as well as in ceramic form. Because of its high permittivity with suitable doping, it is used in capacitors with outstanding properties. Also, it is possible to replace atoms of one kind in a pure crystal by atoms of another kind provided that the atoms are of similar size and valancy. This results in a crystal structure called a solid solution. When Ca atoms are doped to replace Ba atoms in the pure BaTiO$_3$ crystal substitutional solid solution $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ is formed. Solid solutions provide examples of point imperfections. The variations in the physical properties of the solid solution with composition can be easily established with the help of the single crystal of such materials. The interstitial atoms present at the interstitials of the solid solutions and the anion vacancies in omission solid solutions contribute to two types of imperfections usually involved to explain diffusion and electrolytic conductivity in the solids. In omission solution, the number of anion and cations is slightly less than required by the stoichiometry. The defect structure has been proposed to describe such crystal. The static and dynamic aspects of phase transition accompanying small displacements of atoms in perovskites can be investigated by using ultrasonic measurements in the vicinity of the phase transition. Low frequency acoustic velocities provide precise information about the equilibrium adiabatic properties of the system and the effects of the temperature and pressure can be readily studied.

Ultrasonic attenuation data provide information about dynamic behaviour and mechanism involved from the frequency and temperature dependence has been studied. In the structural phase, there exists anomalously large fluctuations which cause anomalous absorption of the sound waves as well as shift in the velocity due to coupling of elastic strains and the soft phonon modes. Theoretically, new ways of describing the critical phenomenon in terms of the fluctuation correlations have been of great importance. Emphasis on the dynamic aspects of the theory has increased which has naturally focused more attention on the ultrasonic work. The large variation in the velocity and the amplitude of the attenuation constant near the transition are usually referred to as anomalous. Such special variations are now described as critical. For single crystal, one must specify the values of the appropriate elastic stiffness constant $C_{ij}$. Due to piezoelectric electrostrictive effects, there is a strong coupling between the mechanical and the dielectric behaviour in all the ferroelectric materials. In the static limit, all the relationships between the anomalous dielectric and elastic properties can be predicted from
thermodynamics. The idea of coupling the acoustic and the polarization waves was treated from the phenomenological point with the damping of mixed polarization sound wave explicitly included. The velocity and the attenuation of the polarized sound wave near the Curie point are considered for a crystal of arbitrary symmetry. But detected expressions are developed for waves propagating along the crystallographic axes of the rhombic and the cubic ferroelectrics. As revealed experimentally as well theoretically, the soft or the ferroelectric mode plays an important role in displacive ferroelectrics. When the temperature approaches the paraelectric Curie-point $T_C$, the frequency of the soft mode becomes vanishingly small resulting in an increase of its amplitude. This anomalously large amplitude should influence the acoustic mode via phonon-phonon interactions and is expected to give rise to an anomalous behaviour of sound near $T_C$. The variation in physical properties of the solid solutions (Ba$_{1-x}$Ca$_x$TiO$_3$) with the composition can easily be established with the help of single crystals of such materials (BaTiO$_3$). Study on ultrasonic propagation in displacive ferroelectrics is available in the literature$^{8,10}$. The current review of barium calcium titanate (BCT) is given in the literature$^{2,11}$. The modified transformed Hamiltonian and the Green’s function technique and expression for the velocity change in displacive ferroelectric in paraelectric phase which includes defects and electric field, are used in the present study and is exactly similar as used in our previous studies$^{10,11}$ from the crystal model proposed by Silverman and Joseph by augmenting it with fourth order anharmonic interaction terms involving ferroelectric optic modes of lowest wave vector. It is assumed that the introduction of defects in the lattice causes changes in the harmonic force constants besides mass changes; their effect upon anharmonic coefficients is neglected. This is true for isovalent and non-polarizable defects because they cause change in the short range force only. For small concentration of defects the impurity-impurity interaction can be neglected. In the present problem, the change in transverse acoustic mode frequency of the wave can be written as:

$$\Delta \omega_k = \tilde{\omega}_k - \omega_k$$  \hspace{1cm} (1)

where the renormalized frequency $\Delta \omega_k = \tilde{\omega}_k - \omega_k$ is given by:

$$\tilde{\omega} = \omega_k + 2\beta^a(k) + \Delta_\omega(k)$$  \hspace{1cm} (2)

with

$$\omega_k = \tilde{\omega}_k = \omega_k^a + 2D(-k,k_i^a) + 2C(-k,k_i^a) + 8g^2E^2\beta^a(-k) + 4gE^2B^a(-k)$$  \hspace{1cm} (3)

and $\Delta_\omega(k)$ being the real part of the response function. Thus, using Eq. (1) one can obtain the expression of the sound velocity change$^5$. Taking the temperature variance of the soft mode frequency as $\Omega_\alpha(T-T_C)^{1/2}$ for small values of $k$ (in the limit $\omega \ll \Omega$), the temperature dependence of the sound velocity change can be expressed as$^{12}$:

$$\Delta c = -1/k[A_1 + A_2 E^2 + (A_3 + A_4 E^2) \frac{T}{(T-T_C)^{1/2}} + (A_5 + A_6 T + A_7 T^2) \frac{(T-T_C)^{1/2}}{T} + (A_9 + A_{10} E^2) T/(T-T_C) + A_{11} T^2/(T-T_C)^{1/2}]$$ \hspace{1cm} (4)

where $A_i$ ( $i = 1..11$) denote the temperature and electric field independent terms. $A_1$ is only defect-dependent, while the rest depends upon anharmonicity and electric moment terms. The expression given in Eq. (4) does not give the explicit temperature dependence of $\Delta c$ because of the renormalization effects. In the vicinity of the Curie temperature $T_C$ ($T \to T_C$), the ultrasonic velocity change decreases anomalously. The various temperature dependences of $\Delta c$ given in Eq. (4) are due to temperature variance of soft mode frequency $[\Omega_\alpha(T-T_C)^{1/2}]$ and higher order anharmonicities present in the crystal. $T$ and $T^2$ dependence of $\Delta c$ is due to third and fourth-order anharmonicities, respectively in the presence of
higher order electric moment terms. One can see from the Eqs (1-3) impurity affects change in velocity. The magnitude of the parameters $C$ (mass change) and $D$ (harmonic force constant changes) determines the magnitude of the defects to $\Delta c$. The electric field dependence of $\Delta c$ at a constant temperature (well above $T_c$) can be given as, $K_1+K_2 E^2$, where $K_1$ and $K_2$ are field independent coefficients. The relative magnitude and signs of the coupling coefficients determine the change in sound velocity due to an applied electric field. It is clear from Eq. (4) that in the vicinity of the Curie temperature $T_c$ ($T\rightarrow T_c$), the ultrasonic velocity change decreases anomalously reducing Eq. (4) for the low temperature limit, one obtains:

$$\Delta c = B_1+B_2 E^2 T^{-1/2} \left(T-T_c\right)^{1/2} \cdots (5)$$

where $B_1 = -A_1/k, B_2 = -A_2/k$ and $T'_c$ is the Curie temperature in the presence of electric field and defect, and is given as:

$$T'_c = T_c + \Delta T_c$$

with $\Delta T_c = 1.9 \times 10^{-3} \times E$

where $E$ is the electric field in V/cm.

Thus, in the low temperature range the law $(\Delta c = 1 / (T-T_c)^{1/2})$ can be valid to a good approximation to study these properties quantitatively.

3 Variation of Sound Velocity Change with Temperature at Different Electric Field Strengths

Impurity dependent Curie temperature $T_c$ in Ba$_{1-x}$Ca$_x$TiO$_3$ (BCT) for different values of defect concentrations ($x=0, 0.05, 01$ and $0.15$) have been taken from Ref. (13). We have calculated field and impurity dependent sound velocity change in Ba$_{1-x}$Ca$_x$TiO$_3$ ($x=0, 0.05, 01$ and $0.15$) at different temperatures, taking electric field as a parameter. The variation of the sound velocity change with temperature at different electric field for different values of $x$ ($x=0.0, 0.05, 0.10, 0.15$) is shown in Fig. 1 (a-d).

4 Discussion and Conclusions

In deriving the expression for the velocity change of sound, researchers have used different methods, approximations and symbols. We have used Green’s function technique and Dyson’s equation treatment in the presence of higher order anharmonic and resonant interaction. The Dyson’s equation treatment has been found convenient to derive shift and width of the frequency response function and hence, to describe the properties of mixed crystals.

The comparative variation of sound velocity change with temperature and impurity concentration in the presence of anharmonicity and electric field has been studied. In general, it is agreed that when the temperature $T$ approaches the paraelectric Curie temperature $T_c$, the frequency of soft mode decreases and sound modes couple strongly with the soft mode through the phonon-phonon interactions. These sound modes are longitudinal acoustic modes. In the case of the transverse acoustic modes, the interaction between the transverse acoustic mode and transverse soft mode is very small, so the expression for the sound velocity change of sound would not show any abrupt changes, as already reported experimentally by Barrett.$^{14}$ To evaluate the higher order correlation functions, the renormalized Hamiltonian has been used, using double time Green’s function technique and Dyson equation treatment. Both the mass change and force change constant changes due to doping, have been taken into account in the crystal Hamiltonian augmented with the higher order anharmonic terms.

Figure 1 (a-d) shows the variation of sound velocity change ($\Delta c$) with temperature in the presence of electric field in Ba$_{1-x}$Ca$_x$TiO$_3$ for different values of $x$ ($=0.0, 0.05, 01$ and $0.15$). These variations show that at a certain electric field, ultrasonic velocity decreases with increase in temperature.

The sound velocity decreases anomalously near the phase transition temperature for both the cases (Fig. 1). Taking any temperature as reference, sound velocity increases with the increase in electric field for both the solutions. The presence of higher order anharmonicity and electric moment terms decreases the sound velocity near the phase transition. In the vicinity of phase transition, the soft mode frequency which is imaginary in harmonic approximations becomes temperature dependent due to anharmonic terms. It becomes vanishingly small and these interactions cause an anomalous decrease in the ultrasonic sound velocity.

Our results are in good agreement with the theoretical results of Tani and Naoyuki.$^{15}$ and Nair and Nithani and Semwal.$^{5}$ However, Tani and Naoyuki.$^{15}$ using the correlation function of Mori.$^{16}$ have taken the anharmonicity up to third–order only in Silverman Joseph Hamiltonian for pure displacive ferroelectrics. We have taken the anharmonicity up to fourth-order in the presence of impurity and electric field. In
presence of defect and electric field, the combined effect is observed. In the absence of the electric field, the results agree with those of Kumar et al.\textsuperscript{17} Barrett\textsuperscript{14} has also shown the temperature dependence of ultrasonic velocity in KTiO$_3$ single crystal. Anharmonicity is necessary in these crystals to observe these effects. In the vicinity of the Curie temperature $T_c$, the soft mode frequency which is imaginary in harmonic approximations and becomes temperature dependent due to anharmonic terms, becomes vanishingly small and $N_0^o$ becomes anomalously large\textsuperscript{10}. Hence, these are interactions which cause an anomalous decrease in the ultrasonic sound velocity. Recently, we have applied the Green’s function technique in case of $(\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3)$ BCT ferroelectrics to study the field dependent dielectric constant\textsuperscript{18}, attenuation constant and specific heat\textsuperscript{19}.  

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\textbf{Fig. 1 — Variation of sound velocity change ($\mu$m/s) with temperature at different electric fields for (a) $x = 0.0$, (b) $x = 0.05$, (c) $x = 0.10$ and (d) $x = 0.15$}
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References


