International Journal of Pure and Applied Physics
ISSN 0973-1776 Volume 6, Number 2 (2010), pp. 135–142

http://www.ripublication.com/ijpap.htm

Field Dependent Sound Velocity Change in Ba_xsr_{1-X} TiO_3 Ferroelectric Perovskites

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Abstract

An expression for the sound velocity change in anharmonic $Ba_xSr_{1-x}TiO_3$ ferroelectric crystal is obtained in presence of an external electric field, by using double time temperature dependent Green's function technique. We have considered higher order anharmonic and electric moment terms in modified Silverman Hamiltonian for it. The field, defect and anharmonic contribution change in sound velocity are separately discussed. The sound velocity decreases anomaously in vicinity of the Curie temperature. The presence of higher order anharmonicity and electric moment decreases the sound velocity. It varies with temperature and sound velocity decreases with addition of defect in $Ba_xSr_{1-x}TiO_3$.

Keywords: Greens function, Anharmonicity, defect, Ultrasonic velocity.

Introduction

In the recent years, much attention has been paid to the dynamical aspects of phase transition accompanying small displacements of atoms in perovskites. Ultrasonic measurements in the vicinity of the phase transitions are one of the useful tools to investigate both the static and the dynamic aspects of phase transitions. 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 the dynamic behavior and from the frequency and temperature dependences, much can be learned about the mechanisms involved.

Theoretically new ways of describing the critical phenomena in terms of fluctuation correlations have been of great importance. Emphasis of the dynamic aspects of the theory has increased markedly and this has naturally focused more attention on the ultrasonic work[1]. The large variations in the velocity and the amplitude of the attenuation near the transition are usually referred to “anomalous”. Such special variations are now described as ‘critical’. For single crystals, one must specify the direction and the polarization of the sound wave or 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 behavior in all the ferroelectric materials. In the static limit, all the relationships between the anomalous dielectric and elastic properties[2] can be predicted from thermodynamics.

The idea of coupling the acoustic and the polarization waves was treated from the phenomenological point of 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[3-6], the soft or the ferroelectric mode plays essential role in displacive ferroelectrics. That is 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 behavior of sound near T_c.

It is possible to replace atoms of one kind in a crystal by atoms of another kind, provided that the atoms are of similar size and valencey. This results in a crystal structure called a solid solution or more specifically, a substitutional solid solution. The solid solution $Ba_xSr_{1-x}TiO_3$ and its end member $BaTiO_3$ both have perovskite structure. Barium titanate is one of the most extensively studied perovskite ferroelectric materials. the solid solution of $BaTiO_3$ with other perovskite materials like $SrTiO_3$, $CaTiO_3$, $PbTiO_3$, $BaZrO_3$ etc. are extremely interesting materials from the point of view of fundamental studies of the properties of ferroelectrics as well as for a variety of applications[7,8]. The variation in physical properties of the solid solutions with the composition can be easily established with the help of single crystals of such materials. In a previous paper[9,10] authors have obtained an expression for the sound attenuation constant in anharmonic $Ba_xSr_{1-x}TiO_3$ (BST) ferroelectric crystal using double-time temperature dependent Green’s function technique and a Hamiltonian proposed by Silverman and Joseph.

The aim of the present paper is to study theoretically the variation of the change in ultrasonic velocity in polycrystalline mixture of $Ba_xSr_{1-x}TiO_3$ with temperature, electric field and impurities by using a model Hamiltonian for the polycrystalline mixture of ferroelectric perovskites and then applying it to $Ba_xSr_{1-x}TiO_3$. The mass and force constant changes due to defect are taken into account in the Silverman Joseph Hamiltonian augmented with the higher order anharmonic and electric dipole moment terms. The expression obtained for the sound velocity change is then discussed with the variation of temperature, impurity and electric field.

Green’s function technique and the expression for the velocity change

The modified transformed Hamiltonian and the Green’s function of a mixed displacive ferroelectric in paraelectric phase which includes defects and electric field is used in 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 influence upon anharmonic coefficients is neglected. This is true for isovalent and nonpolarizable 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,

$$\Delta\omega_k = \tilde{\tilde{\omega}}_k^a - \omega_k^a \qquad (1)$$

where the renormalized frequency $\tilde{\tilde{\omega}}_k^a$ is given by

$$\tilde{\tilde{\omega}} = \tilde{\omega}_k^a + 2\beta^a(-k) < A_0^0 ; A_0^0 > + \Delta_k(\omega) \qquad (2)$$

with

$$\omega_k^a = \omega_k^a + 2D(-k, k_1^a) + 2C(-k, k_1^a) + 8g^2E^2\beta^a(-k) - 4gE^2B^a(-k) \qquad (3)$$

and $\Delta_k(\omega)$ being the real part of the response function [4]· Thus, using Eq. (1) one can obtain the expression of the sound velocity change[4]· Taking the temperature variance of the soft mode frequency as *Ω α (T- T_c)*$^{1/2}$ for small values of *k* (in the limit *ω* << *Ω*), the temperature dependence of the sound velocity change can be expressed as,

$$\Delta c = -\frac{1}{k}\Big[A_1 + A_2E^2 + (A_3 + A_4E^2)T + (A_5 + E^2A_6T + A_7T^2)\frac{1}{(T-T_c)^{1/2}}$$

$$+ (A_8 + A_9T + A_{10}E^2)\frac{T}{(T-T_c)} + A_{11}\frac{T^2}{(T-T_c)^{3/2}} \Big] \qquad (4)$$

where $A_i^{'s}$ (*i* = 1,.., 11) denote the temperature and electric field independent terms in $\Delta_k(\omega)$ (Eq. (1) for *ω* << *Ω*). A_1 is only defect-dependent, while the rest depend upon impurity concentration, anharmonic force constants and electric moment terms. The expression (4) does not give the explicit temperature dependence of Δc because of the renormalization effects. The renormalized frequencies of each phonon mode appearing in real and imaginary parts of polarization operator may produce some change in the temperature dependence. The various temperature dependences of

Δc 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. The T and T^2 dependences of Δc are due to third and fourth-order anharmonicities respectively in the presence of higher order electric moment terms. One can see from the Eqs. (1), (2) and (3) impurity influences change in velocity. The magnitude of the parameters C (mass change) and D (harmonic force constant changes) determines the magnitude of the defects to Δc. The electric field dependence of Δc 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 decrease anomalously reducing Eq. (4) for the low temperature limit, one can approximate as

$$\overline{\Delta} c \quad = \quad A_1 + A_3 \times E^2 \ / \ (T - T_c')^{1/2} \tag{5}$$

where T_c' is the Curie temperature in presence of defect anharmonicity and electric field with

$$T_c' = T_c + \Delta T_c \tag{5a}$$

and $\Delta T_c = 1.9 \times 10^{-3} \times E$ (5b)

where E is electric field measured in Volt/cm.

Thus in the low temperature range the law $\Delta c \propto 1/(T - T_c')^{1/2}$ can be valid to a good approximation to study these properties quantitatively.

Variation of sound velocity change (Δc) with temperature in $Ba_xSr_{1-x}TiO_3$ ferroelectric perovskites in presence of electric field

Using Eq. (5) we have calculated the sound velocity change for $Ba_xSr_{1-x}TiO_3$ mixed crystal for different values of x(=0.25, 0.30 & 0.35) in presence of electric field for different temperature. The coefficients A_1 and A_3 for $Ba_xSr_{1-x}TiO_3$ with corresponding values of x have been taken from Kumar *et al.*[7] by best fit of data. A summary of the calculated values of A_1, A_3 and T_c for electric field dependence of sound velocity change (Δc) with temperature in $Ba_xSr_{1-x}TiO_3$ ferroelectric perovskites with x = 0.25, 0.30 & 0.35 are given in Table 1 here.

Table 1: Coefficient A_1, A_3 and T_c for $Ba_xSr_{1-x}TiO_3$.

Crystal	A_1 (m/sec)	A_3 (mK/sec)	T_c
$Ba_{0.25}Sr_{0.75}TiO_3$	-13421.2	182527.5	122 K
$Ba_{0.30}Sr_{0.70}TiO_3$	-5874.5	71133.9	142 K
$Ba_{0.35}Sr_{0.65}TiO_3$	-2494.7	25919.2	160 K

The variation of sound velocity change (Δc) with temperature in presence of electric field for $Ba_{0.25}Sr_{0.75}TiO_3$, $Ba_{0.30}Sr_{0.70}TiO_3$ and $Ba_{0.35}Sr_{0.65}TiO_3$ are shown in Fig 1(a) to 1(c). In the presence of electric field the sound velocity decreases with increases of temperature in agreement with previous theoretical and experimental results [4,7,8,12].

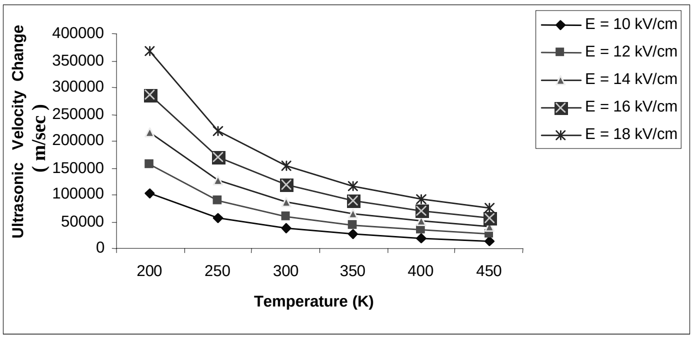

Figure 1(a) $Ba_{0.25}Sr_{0.75}TiO_3$.

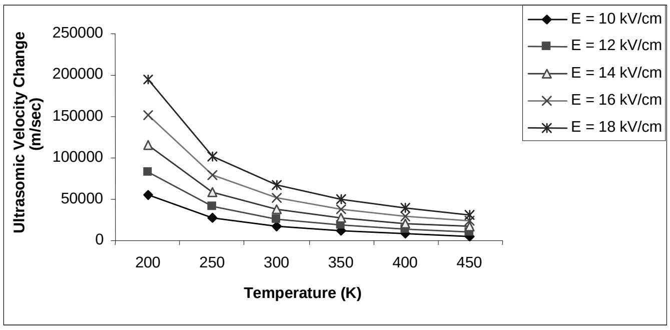

Figure 1(b) $Ba_{0.30}Sr_{0.70}TiO_3$.

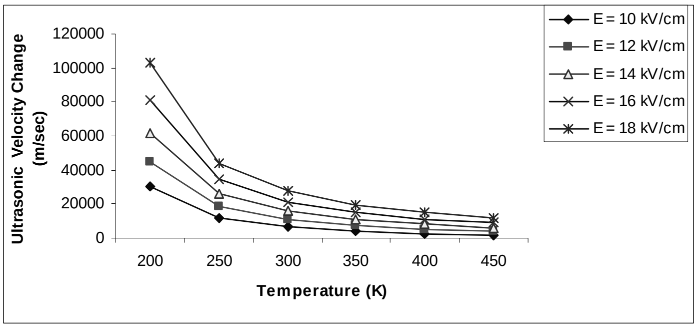

Figure 1(c) $Ba_{0.35}Sr_{0.65}TiO_3$.

Figure 1: Variation of sound velocity change(Δc) with temperature in $Ba_xSr_{1-x}TiO_3$ ferroelectric perovskites in presence of electric field.

Variation of sound velocity change (Δc) with defect in $Ba_xSr_{1-x}TiO_3$ ferroelectric perovskites in presence of electric field

Using Eq.(5) we have calculated the sound velocity change for $Ba_xSr_{1-x}TiO_3$ mixed crystal for different values of x(=0.25, 0.30 & 0.35) in the paraelectric phase (at temperature 300 K and 400 K). Ultrasonic velocity change (Δc) Vs electric field at different defect concentration are plotted in Fig. 2(a) to 2(b).

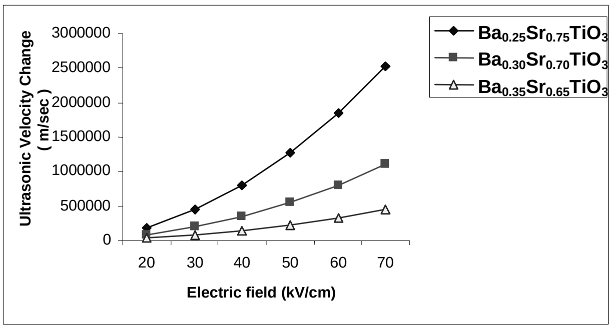

Figure 2(a) at T = 300 K.

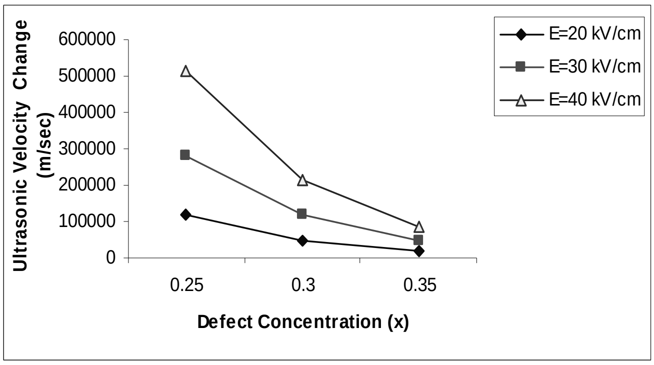

Figure 2(b) at T = 400 K.

Figure 2: Variation of sound velocity change (Δc) with defect in $Ba_xSr_{1-x}TiO_3$ ferroelectric perovskites in presence of electric field.

Discussion and conclusion

In deriving the expression for the velocity change of sound, different authors have used different methods, approximations and symbols. In the treatment adopted here we have used Green's function technique and Dyson's equation treatment in presence of higher order anharmonic, 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 treatment adopted here leads one to see the comparative variation of sound velocity change with temperature and impurity concentration in the presence of anharmonicity and electric field. 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 [13]. 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.

Figs. 1(a) to 1(c) shows the variation of sound velocity change (Δc) with temperature in presence of electric field in $Ba_xSr_{1-x}TiO_3$ for different values of x(=0.25, 0.30 and 0.35). These variations shows that at a certain electric field ultrasonic velocity decreases with increase of temperature.

Figs. 2(a) to 2(b) shows the variation of sound velocity change (Δc) with electric field and impurity concentration of Ba (i.e. x) in $Ba_xSr_{1-x}TiO_3$ crystal at certain temperature. These variations shows that at a certain temperature ultrasonic velocity decreases with increases of impurity concentration of Ba in $Ba_xSr_{1-x}TiO_3$ ferroelectric perovskites in the presence of electric field.

Our results are in good agreement with the theoretical results of Tani and Naoyuki [12] and Naithani and Semwal [4]. However, Tani and Naoyuki [12] using the correlation function of Mori [14] 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 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*[10]. Barrett[13] 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 $\tilde{N}_0^0$ becomes anomalously large[10] and hence these are interactions cause an anomalous decreases in the ultrasonic sound velocity. Recently we have applied the Green's function technique in case of ($Ba_xSr_{1-x}TiO_3$) BST ferroelectrics to study the field dependent dielectric constant[11], attenuation constant [9] and microwave loss[15].

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