Electric field dependence of specific heat in $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ ferroelectric perovskites

Ashish Kukreti, Ashok Kumar & U C Naithani
Department of physics, Garhwal University, Pauri Campus, Pauri(Garhwal), Uttarakhand 246 001

Received 6 May 2008; revised 1 September 2008; accepted 12 November 2008

The electric field dependence of the specific heat of an anharmonic $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ ferroelectric crystal has been calculated in its paraelectric phase from the Silverman-Joseph Hamiltonian augmented with fourth order phonon co-ordinates using double time Green’s functions. The electric field dependent soft mode contribution to the specific heat is described by appropriate Einstein terms. The variation of specific heat with temperature defect and electric field has been discussed. The specific heat decreases with increasing external electric field and increases with increasing temperature, in agreement with previous results. In the vicinity of Curie temperature, the Cochran soft mode is held responsible for the anomalous behaviour of specific heat.

Keywords: Barium strontium titanate, Defects, Soft mode frequency, Specific heat, Constant volume, Anharmonicity, Perovskites, Green’s function

1 Introduction

Barium strontium titanate ($\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$) is a solid solution family composed of barium titanate and strontium titanate with its Curie temperature covering a wide range. When strontium atoms were introduced to A site in perovskite barium titanate matrix to replace barium atoms, the phase transition temperature of paraelectric to ferroelectric decreases and the phase transition behaviour changes from sharp to diffuse.\(^1\) It is now well known that several interesting temperature dependent properties of ferroelectric results from the temperature dependence of the low-lying transverse optic (TO) mode of vibration. One of the very interesting property of these crystals is the electric field dependence of the low frequency TO modes\(^2\)\(^-\)\(^4\). The effect of electric field on the Cochran modes in $\text{SrTiO}_3$ and $\text{KTaO}_3$ was studied by Steigmeir\(^5\), showing an upward shift in the TO mode frequency which reduces the TO-LA interaction. All these studies reveal a remarkable influence of electric field on the ferroelectric soft mode frequency. So the dynamic properties of ferroelectrics will be affected in the presence of electric field because of the influence of the soft ferroelectric mode in the electric field.

In contrast to other systems, in ferroelectrics the frequency corresponding to the TO mode of the zero vector is imaginary in the harmonic approximation, showing that harmonic forces alone are not sufficient to stabilise the system. The stabilisation of this mode can only be brought about by considering that the anharmonic interaction that can stabilise the soft mode is of fourth order.

One of the most interesting property of these crystals is the defect dependence of the low lying frequency TO modes. The effects of the defects can generally be expressed by a change in Curie temperature $T_c$, without essentially changing the character of temperature dependence of the dielectric constant. In other words, the Curie-Weiss law remains valid with essentially the same Curie constant. Barium titanate is one of the most extensively studied perovskite ferroelectric materials. The solid solution of $\text{BaTiO}_3$ with other perovskite materials like $\text{SrTiO}_3$, $\text{CaTiO}_3$ and $\text{PbTiO}_3$ 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\(^6\). Among the perovskites mixed systems $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST) is an interesting series because of its unique ferroelectric properties which are suitable for various potential applications. BST has been identified as the leading material for under cooled detector fabrication, photorefractive mirrors and as a gate insulator of the oxide superconductors FET in the thin film form\(^7\). It is a complete solid solution and the amount of Sr causes a significant decrease of Curie temperature and changes in the dielectric properties. Different impurities can change the Curie temperature of the same material in different ways. For example on substitution of Pb ions...
for Ba ions in BaTiO$_3$ Curie temperature increases whilst it decreases on substitution of Sr ions for Ba ions, and change in $T_c$ is negligible on substitution of Ca ions for Ba.

Temperature and field dependence of the specific heat is a reflection of the temperature and field dependence of the soft mode frequency ($\Omega = (T - T_c)$). This effect is taken as direct evidence for the temperature dependence of polarization mode frequency. At transition temperature, the frequency of the soft mode tends to zero, and the lattice displacement associated with this mode becomes unstable. Lawless$^8$ has measured the anomalous specific heat of pure soft mode dielectrics experimentally at low temperatures. There is also much published work on the specific heat of pure and mixed ferroelectric crystals.$^9_{12}$

The aim of the present paper is to study variation in the specific heat of polycrystalline mixture of Ba$_x$Sr$_{1-x}$TiO$_3$ in the paraelectric phase, in presence of an external electric field, using Kubo formalism and Green’s function technique. The impurities introduced have a different mass from the host atoms and modified nearest neighbour harmonic force constant around their sites. The effect of differences between the mass and force constant of impurity and host lattice atoms resulting from the introduction of defects and electric field is taken into account. Their influence on the anharmonic coupling co-efficient in the Hamiltonian is neglected. The effect of electric field and impurities introduced are characterized by the nearest neighbour harmonic force constants around their sites. Their influence on the anharmonic coupling coefficients in the Hamiltonian is neglected. The modified transformed Hamiltonian of a mixed displacive ferroelectric in para-electric phase which includes defects and electric field is used in present study.$^6$

For the study of specific heat, Green’s function for soft optic mode is used as follows:

$$G_0^0(\omega + i\epsilon) = \langle\langle A_0^0(t); A_0^0(t')\rangle\rangle(\omega + i\epsilon) \quad ... (1)$$

$G_0^0(\omega + i\epsilon) = G'(\omega) - G''(\omega) \quad ... (2)$

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

$$G_0^0(\omega + i\epsilon) = \frac{\omega^0}{\pi[\omega^2 - (\nu^0_0)^2(\omega) - i\Gamma_0^0(\omega)\]]} \quad ... (3)$$

where $(\nu^0_0)^2(\omega)$ is defect and field dependent soft mode frequency and is given by

$$(\nu^0_0)^2(\omega) = -\omega^2_0 + 4\omega^2_0 D(0,0) + \omega^2_0 E^2(96g^2V - 24gD'_1) + 4\omega^2 g + \bar{\nu}^0(\Omega) \quad ... (4)$$

where $\bar{\nu}_0(\omega)$ and $\bar{\nu}_0^0(\omega)$ are the shift and half width of the soft phonon mode with defects, anharmonicity and electric field, $\omega^0_0$ is the soft mode frequency of pure harmonic crystal, $D(0,0)$ is the defect dependent term for $k=0$ wave vector depending upon changes in the force constants; $g$ comes in the transformation operator $[S = -ig E B^0_3]$; $V$ and $D'_1$ are electric moment terms.

The real part of the pole of $G^0_0(\omega + i\epsilon)$ in Eq. (3) would gives the temperature dependent frequency $\Omega(T)$ of the Cochran mode in presence of electric field and defect as the self-consistent solution of the Eq. (4).
as \((\Omega(T) = \Omega_0^g(\omega))\):

\[
\Omega^2 = - (\omega_0^g)^2 + 4\omega_0^gD(0,0) + 4\omega_0^g\overline{Q} + \Delta_0^g(\omega) \ldots (5)
\]

Here \(\overline{Q}\) is defined as

\[
\overline{Q} = \sum_i \beta^i(k) A_k^2 \Delta^i = \sum_i \beta^i(k) \eta_i^2 \ldots (6)
\]

and \(\Delta_0^g(\omega)\) is the shift in presence of anharmonicity, impurities and electric field as:

\[
\Delta_0^g(\omega) = \Delta_A^g(\omega) + \Delta_D^g(\omega) + \Delta_E^g(\omega) \ldots (7)
\]

where \(\Delta_A^g(\omega)\), \(\Delta_D^g(\omega)\) and \(\Delta_E^g(\omega)\) are the contribution in \(\Delta_0^g(\omega)\) due to anharmonic, defect and electric field parameters respectively.

Also in the high temperature range, and para-electric phase above the Curie temperature \(T_c\), the temperature dependence of square of soft mode frequency \([[(u_0^0)^2(\omega) = \Omega^2(\omega)]\] can be written as:

\[
\Omega^2(\omega) = - (\omega_0^g)^2 + \gamma_1T + \gamma_2T^2 \ldots (7a)
\]

where \(\gamma_1\) and \(\gamma_2\) are defect and temperature independent co-efficients which depend upon third and fourth order anharmonic terms.

2.2 General formulation

Specific heat at constant volume \(C_v\) for the crystal model considered here can be obtained as:

\[
C_v' = C_A + C_E + C_D
\]

or

\[
C_v' = C_A^{AE} + C_D
\]

where \(C_A\), \(C_E\) and \(C_D\) are the contribution due to anharmonicity, electric field and defect respectively.

In terms of the Einstein function \(^8,9\), the expression for \(C_v'\) can be written as:

\[
C_v' = k_B \sum_k E(Y_k') \ldots (9)
\]

Here \(k_B\) is Boltzmann constant and \(Y_k'\) is defined as

\[
Y' = Y_k' = h\Omega_{AED}/k_BT \ldots (10)
\]

where \(\Omega_{AED}\) is the soft mode frequency of Ba\(_x\)Sr\(_{1-x}\)TiO\(_3\) perovskites in presence of anharmoniciy, defect and electric field, and \(E(Y')\) is the Einstein function given by:

\[
E(Y') = Y'^2 \exp(Y'/\exp(Y' - 1)^2) \ldots (11)
\]

Substituting the value of the Einstein function \(E(Y')\) for soft phonon model \((k=0)\) in Eq.(9) the specific heat at constant volume is as follows:

\[
C_v' = k_B Y'^2 \exp(Y'/\exp(Y' - 1)^2) \ldots (12)
\]

Now substituting the value of \(Y'(Y_k'\) for \(k = 0\) from Eq. (10) into Eq. (12) gives

\[
c_v' = k_B (h\Omega_{AED}/k_BT^2 \exp(h\Omega_{AED}/k_BT)/(\exp(h\Omega_{AED}/k_BT) - 1)^2 \ldots (13)
\]

from which the soft mode frequency \(\Omega_{AED}\) of a ferroelectric crystal with impurities present can be calculated. If the temperature is not too high the temperature and electric field dependence of the soft mode frequency can be expressed as:

\[
\Omega_{AED} = (T - T_c^{*})^{1/2} = K(T - T_c^{*})^{1/2} \ldots (14)
\]

where \(K\) is a constant depends on temperature and electric field parameter and

\[
T_c^{*} = T_c + \Delta T_c
\]

with \(\Delta T_c = 1.9 \times 10^3 \times E\), where \(E\) is electric field measured in volt/cm\(^7\). Thus in order to study variation in specific heat with temperature and defect concentration in the presence of electric field, the dependence of soft mode frequency on temperature, defect and electric field will be considered.

2.2.1 Variation of soft mode frequency with electric field in Ba\(_x\)Sr\(_{1-x}\)TiO\(_3\) perovskites

The Curie temperature \((T_c)\) and soft mode frequency \((\Omega)\) for zero field of Ba\(_x\)Sr\(_{1-x}\)TiO\(_3\) for different values of \(x(0.0,0.1,0.2,0.5,0.7,0.8,1.0)\) have been taken from Kumar et al.,\(^{15}\) by best fit of data and are given in Table 1.

Now in order to consider the effect of an applied electric field on the soft mode frequency \((\Omega)\) and hence on the specific heat of a displacive ferroelectric crystal, it has been considered that the Curie–temperature changed with relation \(\Delta T_c = 1.9 \times 10^3 \times E\),
where \( E \) is electric field measured in V/cm. With the help of Eq. (14) taking electric field as parameter, the soft mode frequency for Ba\(_{x}\)Sr\(_{1-x}\)TiO\(_3\) for different values of \( x \) \((0.0, 0.1, 0.2, 0.5, 0.7, 1.0)\) is calculated. The variation of soft mode frequency(\( \Omega \)) versus electric field(\( E \)) with temperature as a parameter in SrTiO\(_3\), Ba\(_0.2\)Sr\(_0.8\)TiO\(_3\), Ba\(_0.5\)Sr\(_0.5\)TiO\(_3\), Ba\(_0.7\)Sr\(_0.3\)TiO\(_3\), Ba\(_0.8\)Sr\(_0.2\)TiO\(_3\), BaTiO\(_3\) respectively is shown in Figs 1(a)-(d). Soft mode frequency increases with increasing electric field and results are in good agreement with results of other workers\(^8,9,17,18\).

### 2.2.2 Variation of specific heat at constant volume (\( C'_V \)) with electric field (\( E \)) in Ba\(_{x}\)Sr\(_{1-x}\)TiO\(_3\) perovskites

Using Eq. (13), the specific heat at constant volume (\( C'_V \)) of Ba\(_{x}\)Sr\(_{1-x}\)TiO\(_3\) mixed crystal for different values of impurities concentrations \( x(0.0, 0.1, 0.2, 0.5, 0.7, 0.8, 1.0)\) at constant temperature has been calculated. Figs 2(a-d) show the variation of specific heat at constant volume (\( C'_V \)) with electric field taking temperature as a parameter in SrTiO\(_3\), Ba\(_0.2\)Sr\(_0.8\)TiO\(_3\), Ba\(_0.5\)Sr\(_0.5\)TiO\(_3\), Ba\(_0.7\)Sr\(_0.3\)TiO\(_3\), Ba\(_0.8\)Sr\(_0.2\)TiO\(_3\) and BaTiO\(_3\) respectively. Taking a particular temperature as a reference, it is observed that specific heat at constant volume (\( C'_V \)) decreases with increasing electric field in all the cases.

### 3 Results and Discussion

The treatment adopted here shows the comparative variation of specific heat at constant volume (\( C'_V \)) of Ba\(_{x}\)Sr\(_{1-x}\)TiO\(_3\) for different values of temperature, impurities and electric field in presence of anharmonicity. Green’s functions and Dyson’s equation are used in the presence of higher order anharmonic resonant interactions and scattering terms in the model Hamiltonian. The Dyson’s equation treatment has been found to be convenient for deriving the shift and width of the frequency response function. The treatment adopted makes it possible to see the relative variation in specific heat with temperature, defect and electric field in Ba\(_{x}\)Sr\(_{1-x}\)TiO\(_3\) ferroelectric perovskites. In the present study the Hamiltonian proposed by Silverman and Joseph\(^20\) has been designed in terms of creation and annihilation operators. At microwave frequencies the findings are in good agreement with previously published experimental and theoretical results.
It is evident from Eq. (13) that the field dependence of specific heat is a clear consequence of the field dependence of soft-mode frequency. It is clear from Eq. (4) that the square of the soft mode frequency varies directly as the square of the applied electric field strength. So the soft mode frequency increases with the increase in applied field in conformity with the experimental and theoretical results. Hence one can easily see that this frequency ($\Omega_{\text{AED}}$) is stabilized in the presence of defect, electric field and anharmonicities, if all the above effects are neglected this frequency ($\Omega_{\text{AED}}$) is imaginary due to cancellation of competing forces.

From Eqs (4) and (13), it is clear that the presence of an applied electric field will increase the soft mode frequency and hence will decrease the specific heat in confirming with the experimental results of Lawless, who has explained the measured decrease in the specific heat of KTaO$_3$ and SrTiO$_3$ with electric field at a constant temperature as a soft mode effect. He has described the field dependence of the soft mode using Lyddance-Sachs-Teller-Devonshire formalism, while in this study this field dependence is described by making use of a Hamiltonian proposed by Silverman and Joseph and the recent powerful thermal Green’s function technique.

Also the soft mode contribution to the specific heat is described by appropriate Einstein terms. Use of a unitary transformation renders the most significant first order dipole moment term to effect the specific heat via the applied electric field ($E$).

It is clear from Fig. 1(a) at temperature 400 K ($=T_c$ of BaTiO$_3$) that the soft mode frequency varies with varying concentration. It is higher with a pure strontium titanate crystal and decreases monotonically with increasing barium impurity concentration. Taking temperatures well above $T_c$ of BaTiO$_3$ ($\approx$ 400 K), the soft mode frequency decreases monotonically with increase of Ba impurity concentrations (upto the case of Ba$_{0.8}$Sr$_{0.2}$TiO$_3$). For pure BaTiO$_3$ the values are almost the same as of Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ and thus the both curves are overlapping, showing no remarkable difference. Also taking any temperature as a reference, the soft mode frequency increases with increase of electric field $E$, the variation is same for other temperatures. The results are in good agreement with the experimental and theoretical results of others.

The variations of specific heat at constant volume ($C'_v$) with electric field taking temperature as a parameter in SrTiO$_3$, Ba$_{0.2}$Sr$_{0.8}$TiO$_3$ Ba$_{0.5}$Sr$_{0.5}$TiO$_3$, Ba$_{0.7}$Sr$_{0.3}$TiO$_3$, Ba$_{0.8}$Sr$_{0.2}$TiO$_3$, BaTiO$_3$ respectively are shown in Figs 2 (a)-(d). It is clear from Fig. 2 (a) that taking any temperature as a reference, the specific heat at a constant volume ($C'_v$) decreases with increasing electric field. The trend is same for all other cases. These variations are in good agreement with experimental and theoretical results of previous studies.

It is obvious that the soft modes due to their large occupation number should cause an appreciable scattering of other modes. It is the temperature dependent soft mode and the process involving it, that give rise to effects peculiar to a ferroelectric material. The influence of electric field on this modes also affects the introduction of soft mode with other modes, thus giving electric field dependence of various dynamic properties. The soft mode contribution to these properties is particularly important in the vicinity of Curie temperature ($T_c$) and is expected to give an anomalous behaviour. The temperature, defects and field dependent soft mode frequency, and hence of specific heat at constant volume ($C'_v$) with applied field is noticeable in the vicinity of the Curie-temperature. In the high temperature region, the field effect ceases and the change in $C'_v$ arises mainly due to higher order anharmonic terms. Recently the Greens function technique is applied in observing the field dependent properties of BST ferroelectric pervoskites. A current review on BST is available in the literature.

References