Dependence of specific heat on electric field in $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ ferroelectric perovskites

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The electric field dependence of the specific heat of an anharmonic $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ ferroelectric crystal has been calculated in its paraelectric phase from Silverman-Joseph Hamiltonian augmented with fourth order phonon coordinates using double times Green’s functions. The electric field dependent soft mode contribution to the specific heat is described by appropriate Einstein terms. The variation of the specific heat with temperature and defect parameters has been discussed for different values of field strengths. The effect of defects on specific heat can be observed in the presence of anharmonicity. The specific heat decreases with increase in external field and increases with increase in temperature which is in agreement with the previous results. As the Curie temperature is approached, the Cochran soft mode is held to be responsible for the anomalous behaviour of specific heat.

Keywords: Anharmonicity, Curie temperature, Defects, Soft mode frequency, Specific heat, Ferroelectric perovskites

1 Introduction

It is well known that the temperature dependence of several properties of ferroelectrics results from the temperature dependence of the low lying transverse optic mode of vibration. In contrast to other systems, in ferroelectrics, the frequency corresponding to the transverse optic mode of the zero wave vector is imaginary (i$\omega_o$) in the harmonic approximation, showing that harmonic forces alone are not sufficient to stabilize the system. The stabilization of this mode can only be brought about by considering that anharmonic interactions which can stabilize the soft mode, is of the fourth order. One of the very interesting properties of these crystals is the electric field and defect dependence of the low frequency transverse optic mode (TO). Reviews of the phenomenon are available in the literature. The effect of the electric field on the Cochran modes in SrTiO$_3$ and KTaO$_3$ was studied by Steigmeir, showing an upward shift in the TO-mode frequency which reduces the TO-LA interactions. These studies show remarkable influence of electric field on 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. 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. The dependence of specific heat on temperature, defect and applied electric field is a reflection of soft mode frequency on these systems. 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 be zero and lattice displacements associated with this mode become unstable. Lawless has measured the anomalous specific heat of pure soft mode dielectrics experimentally at low temperatures. Baluni and Naithani have theoretically studied the electric field dependence of displacive ferroelectric crystals with impurities.

In this paper, an important ferroelectric material barium calcium titanate ($\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$) has been studied which is a solid of family composed of barium titanate ($\text{BaTiO}_3$) and calcium titanate ($\text{CaTiO}_3$) with its Curie temperature varying over wide range. When calcium atoms were introduced to ‘A’ site in perovskites 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. Among the perovskites mixed systems, $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ (BCT) is an interesting series because of its unique ferroelectric properties which are suitable for various potential
applications. It has been identified as a leading material for under cooled detector fabrication, photorefractive mirrors and as a gate insulator of oxide semiconductors FET in the thin film form\textsuperscript{18}. A current review on Ba\textsubscript{1-x}Ca\textsubscript{x}TiO\textsubscript{3} is available in the literature\textsuperscript{19,27,29}.

The aim of present work is to study the variations of the specific heat of polycrystalline mixture of Ba\textsubscript{1-x}Ca\textsubscript{x}TiO\textsubscript{3} in the presence of electric field in paraelectric phase, 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 is taken into account. Their effect on the anharmonic coupling coefficient in the Hamiltonian is neglected. The effect of electric field and impurities on soft mode frequency and hence, on specific heat is observed in the presence of anharmonicity. Only the contribution of soft mode towards specific heat is taken into account, in general, it is accepted that low temperature specific heat data estimated from the acoustic spectrum (e.g elastic constants) can be in error by as much as an order of magnitude. The effect of an external field on the specific heat of the polycrystalline mixture of Ba\textsubscript{1-x}Ca\textsubscript{x}TiO\textsubscript{3} in its paraelectric phase can be observed in the presence of anharmonicity\textsuperscript{20}. Around the Curie point temperature \(T_c\), the Cochrans soft mode is held responsible for anomalous behaviour of specific heat\textsuperscript{21}. The variation of specific heat with temperature, defect and electric field is discussed and results obtained are compared with the earlier experimental and theoretical results. A considerable review on specific heat of pure and mixed crystal is available in literature of many researchers\textsuperscript{15,16,21} and references therein.

2 Theory

2.1 Hamiltonian and Green’s function

The Hamiltonian which includes the anharmonicity up to the fourth order in the potential energy due to interaction of soft mode coordinates, resonant interaction and scattering terms are considered. The impurities introduced are characterized by the different value of mass as compared to the host atoms and the modified nearest neighbour harmonic force constants around their sites. Their influence on the anharmonic coupling coefficients in Hamiltonian is neglected. The modified transformed Hamiltonian\textsuperscript{12} of a mixed displacive ferroelectric in paraelectric phase which includes defects and electric field is used in the present study.

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

\[
G_o^o(\omega+i\varepsilon) = << A_o^o(t); A_o^o(t') >> (\omega+i\varepsilon) \quad \ldots(1)
\]

\[
G_o^o(\omega+i\varepsilon) = G'(\omega) + G''(\omega) \quad \ldots(2)
\]

Writing Eq. (1) in the Dyson’s equation form by solving Green’s function with the help of modified transformed Hamiltonian and by Fourier transforming, one obtains:

\[
G_o^o(\omega+i\varepsilon) = \omega_o^o/\pi[(\omega_o^o)^2-(\omega_o^o')^2(\omega)-i\Gamma_o^o(\omega)] \quad \ldots(3)
\]

where \((\omega_o^o')^2(\omega)\) is defect and field dependent soft mode frequency and can be written as:

\[
(\omega_o^o')^2(\omega) = -(\omega_o^o)^2 + 4\omega_o^o D(0,0) + \omega_o^o E^2(96g^2V-24gD') + 4 \omega_o^o g + \Delta_o^o(\Omega) \quad \ldots(4)
\]

where \(\Delta_o^o(\omega)\) and \(\Gamma_o^o(\omega)\) are shift and half width of the soft phonon mode with defects, anharmonicity and electric field, \(\omega_o^o\) is the soft mode frequency of pure harmonic crystal, \(D(0,0)\) is defect dependent term for \(k=0\) (wave vector) depending upon changes in the force constants; \(g\) is a term from transformation operator \([S \rightarrow -igEB_o^o]\); \(V\) and \(D'\) are electric moment terms. The real part of the pole of \(G_o^o(\omega+i\varepsilon)\) in Eq. (3) would give the temperature dependent soft mode frequency \(\Omega(T)\) of the Cochrans mode in the presence of electric field and defects as the self consistent solution of Eq. (4). as \([\Omega(T) \approx \omega_o^o(\omega)]: \)

\[
(\Omega)^2 = -(\omega_o^o)^2 + 4 \omega_o^o D(0,0) + 4 \omega_o^o Q' + \Delta_o^o(\Omega) \quad \ldots(5)
\]

where \(Q'\) can be expressed as:

\[
Q' = \sum_k \beta^i(k) \langle A_k^\lambda, A_k^\lambda \rangle = \sum_k \beta^i(k) \eta_k^\lambda. \quad \ldots(6)
\]

\(\Delta_o^o(\omega)\) is the shift in the presence of anharmonicity, defect and electric field contributing terms, respectively and can be written as:

\[
\Delta_o^o(\omega) = \Delta_1(\omega)+\Delta_2(\omega)+\Delta_3(\omega)+\ldots\ldots+\Delta_{10}(\omega) \quad \ldots(7)
\]
where $\Delta_s(s\omega) (i=1,2,3,\ldots,10)$ are the real parts of the Green’s function and the values of $\Delta_s, s(\omega)$ are given by:

$$\Delta_1(\omega) = |D(-k,0)|^2 2\Omega/(\omega^2-\Omega^2) \quad \ldots 7(a)$$

$$\Delta_2(\omega) = -|C(-k,0)|^2 2\Omega/(\omega^2-\Omega^2) \quad \ldots 7(b)$$

$$\Delta_3(\omega) = |D(-k,k)|^2 2\omega_{k1}\omega_{k2}/(\omega^2-\omega_{k1}\omega_{k2}) \quad \ldots 7(c)$$

$$\Delta_4(\omega) = |C(-k,k)|^2 2\omega_{k1}\omega_{k2}/(\omega^2-\omega_{k1}\omega_{k2}) \quad \ldots 7(d)$$

$$\Delta_5(\omega) = E^2[(4g^2a^2/(k^2) + 4a(k)^2)] 2\omega_{k1}\omega_{k2}/(\omega^2-\omega_{k1}\omega_{k2}) \quad \ldots 7(e)$$

$$\Delta_6(\omega) = |F(k)|^2 \delta'(\omega_{k1}'\omega_{k2}'\omega_{k3}'\omega_{k4}')/(\omega^2-\omega_{k1}'\omega_{k2}'\omega_{k3}'\omega_{k4}') \quad \ldots 7(f)$$

$$\Delta_7(\omega) = [\delta(k^2)\delta(\omega_{k1}'\omega_{k2}'\omega_{k3}'\omega_{k4}')] \times\Gamma(1+2\Omega/\omega_{k1}'\omega_{k2}'\omega_{k3}'\omega_{k4}') \quad \ldots 7(g)$$

$$\Delta_8(\omega) = E^2[16g^2 \sum_{k1,k2} \Omega(-k,k1,k2)^2 + 4g\sum_{k1,k2} \Omega(-k,k1,k2)^2] \delta'(\omega_{k1}'\omega_{k2}'\omega_{k3}'\omega_{k4}') \quad \ldots 7(h)$$

$$\Delta_9(\omega) = E^2[(4g^2\delta(\omega_{k1}'\omega_{k2}'\omega_{k3}'\omega_{k4}')/(\omega^2-\omega_{k1}'\omega_{k2}'\omega_{k3}'\omega_{k4}')) \quad \ldots 7(i)$$

$$\Delta_{10}(\omega) = \sum_{k1,k2} \Omega(-k,k1,k2)^2 \delta'(\omega_{k1}'\omega_{k2}'\omega_{k3}'\omega_{k4}') \quad \ldots 7(j)$$

In terms of Einstein function, the expression for the $C_v$ can be expressed as:

$$C_v = k_B \sum E(\omega) \quad \ldots 9$$

where $k_B$ is Boltzmann constant and $\omega$ is defined as

$$\omega = \hbar \Omega_{AED}/k_B T \quad \ldots 10$$

where $\Omega_{AED}$ is soft mode frequency of Ba$_{1-x}$Ca$_x$TiO$_3$ perovskites in the presence of anharmonicity, defect and electric field and $E(\omega)$ is the Einstein function given as:

$$E(\omega) = (\omega^2)^2 \exp(\omega/(\exp\omega - 1))^2 \quad \ldots 11$$

We get the specific heat at constant volume by substituting ($k=0$) for soft phonon mode and putting $E(\omega)$ from Eq. (10) in Eq. (8) as:

$$C_v = k_B \sum E(\omega) \quad \ldots 12$$

Putting $\omega$ from Eq. (9) in Eq. (11), we get:

$$C_v = k_B \hbar \Omega_{AED}/k_B T \quad \ldots 13$$

If the temperature is not so high the temperature and electric field dependence of the soft mode frequency in Eq. (4) can be expressed as:

$$\Omega_{AED} = \Omega_{AD} \quad \ldots 14$$

where $T' = T + \Delta T$ and $\Delta T = 1.9 \times 10^{-3}$ Volt/cm.

So for the variations of specific heat with temperature, defect and electric field, the dependence of soft mode frequency on temperature, defect and electric field will be considered.

2.3 Variation of soft mode frequency with electric field in Ba$_{1-x}$Ca$_x$TiO$_3$

The Curie temperatures ($T_c$) of Ba$_{1-x}$Ca$_x$TiO$_3$ for different values of $x = 0.0,0.05,0.10,0.15$ are taken from Ref. 28. Soft mode frequency ($\Omega$) for zero field case of Ba$_{1-x}$Ca$_x$TiO$_3$ for different values of $x = 0.0,0.05,0.10,0.15$ has been calculated. 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 changes according to the relation, $\Delta T = 1.9 \times 10^{-3}$, where $E$ is the electric field in V/m. With the help of Eq. (13)
taking electric field as a parameter, the soft mode frequency for different values of \(x=(0, 0.05, 0.10\) and 
\(0.15)\) is calculated. The variation of soft mode frequency (\(\Omega\)) versus electric field with temperature 
as a parameter for different values of \(x\) is shown in the 
Fig. 1(a-d). Soft mode frequency increases with 
increase in electric field which is in good agreement 
with previous results\(^{14,17,24,25}\).

2.4 Variation of specific heat at constant volume with electric 
field in \(Ba_{1-x}Ca_xTiO_3\) perovskites

Using Eq. (12), the specific heat at constant volume 
of \(Ba_{1-x}Ca_xTiO_3\) mixed crystal for different values of 
\(x=(0, 0.05, 0.10\) and \(0.15)\) at different values of 
electric field has been calculated. Fig. 2(a-d) shows 
the variation of specific heat at constant volume with 
temperature for different values of electric field taking 
different values of \(x=(0, 0.05, 0.10\) and \(0.15)\). Taking 
a particular temperature as a reference, it is observed 
that specific heat at constant volume (\(C_v\)) decreases 
with increase in electric field in all the cases.

3 Results and Discussion

The treatment adopted here shows the comparative 
variation of specific heat at constant volume of 
\(Ba_{1-x}Ca_xTiO_3\) for different values of temperature, 
impurities and electric field in the presence of 
anharmonicity. Green’s function and Dyson’s 
equations 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 \(Ba_{1-x}Ca_xTiO_3\) 
ferroelectric perovskites. In the present study, the 
Hamiltonian proposed by the Silverman and Joseph\(^{26}\) 
has been distinguished in terms of creation and 
anihilation operators. At microwave frequencies, the 
findings are in good agreement with previous 
experimental and theoretical results.

![Fig. 1 — Variation of soft mode frequency of \(Ba_{1-x}Ca_xTiO_3\) with electric field at different temperatures for different values of \(x\) (a) \(BaTiO_3\) (\(x=0\)), (b) \(Ba_{0.95}Ca_{0.05}TiO_3\) (\(x=0.05\)), (c) \(Ba_{0.90}Ca_{0.1}TiO_3\) (\(x=0.10\)) and (d) \(Ba_{0.85}Ca_{0.15}TiO_3\) (\(x=0.15\))](image-url)
It is clear from Eq. (12) that the electric field dependence of specific heat is the consequence of the field dependence of soft mode frequency. Also, it is evident from Eq. (4) that the square of soft mode frequency varies directly as the square of the applied electric field. So the soft mode frequency increases with the increase in electric field which is in confirmation with the experimental and theoretical results\textsuperscript{16,27}. Hence, one can observe that this frequency is stabilized in the presence of defect, electric field and anharmonicity. If all the above effects are neglected, this frequency is imaginary due to cancellation of competing forces.

From Eqs (4) and (12), it is clear that the presence of an electric field will increase the soft mode frequency and hence, will decrease the specific heat in confirmation with experimental results of Lawless\textsuperscript{14}, who explained the decrease in specific heat in KTaO$_3$ and SrTiO$_3$ with electric field at constant temperature. He has also described the field dependence of the soft mode frequency using Lyddance-Sachs-Teller-devonshire formalism\textsuperscript{28} while in this study dependence is described by making use of a Hamiltonian proposed by Silverman and Joseph\textsuperscript{26} and recent thermal Green’s function technique. Also soft mode contribution to the specific heat is described by appropriate Einstein’s terms.

It is clear from Fig. 1(a-d) that the soft mode frequency varies with varying concentrations. It is higher when Ca impurity is doped in pure BaTiO$_3$ crystal and decreases monotonically with decrease in the Ca impurity doped in the crystal. Taking any temperature as a reference, the soft mode frequency increases with increase in electric field. The results are in good agreement with previous results of other researchers.
The variations of specific heat at constant volume with temperature at different electric fields and defect concentrations are shown in Fig. 2(a-d). The specific heat increases with increase of temperature in all the cases (Fig. 2). It is also observed from Fig. 2 that taking any temperature as reference the specific heat decreases with increase in electric field in all the cases studied. The variations are in good agreement with previous studies\(^{14,16}\). Recently, the Greens function technique has been applied in studying various properties of Ba\(_{x}\)Sr\(_{1-x}\)TiO\(_3\) and Ba\(_{1-x}\)Ca\(_x\)TiO\(_3\) (Refs 23, 30).

References