

Electric Field Dependent Specific Heat of SrTiO₃, BaTiO₃ and KTaO₃ Ferroelectric Perovskites

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Abstract: The field dependent specific heat of anharmonic ABO₃ type displacive ferroelectrics (SrTiO₃, BaTiO₃ & KTaO₃) is studied using double time Green's function technique along with Silverman-Joseph modified Hamiltonian which includes anharmonicity up to the fourth order due to the interaction of the soft mode. The soft mode contributions to specific heat are described by appropriate Einstein terms. The variation of specific heat with temperature and electric field is discussed. The specific heat in all three crystals increases non-linearly with temperature. The specific heat decreases with increase in external electric field. The effect of electric field on specific heat is more prominent in low temperature sides in all three crystals. The effect of temperature reduces in low field region and the change in specific heat arises mainly due to higher order anharmonic terms. The results are in agreement with previous experimental and theoretical results.

Keywords: anharmonicity, Cochran mode, Green's function, soft mode, Specific heat.

I. Introduction

Ferroelectricity is one of the most fascinating properties of dielectric solids. Ferroelectrics are the crystals that show spontaneous polarization which is reversible by stress or electric field. This phase transition is exhibited within the limited temperature range, called the Curie temperature T_c and is associated with a change in crystal structures and the anomalous behavior of some physical properties. All these materials are piezoelectric and have high electromechanical coupling coefficients. The ferroelectric materials have been grouped together because they have some common characteristics. There are more than a thousand ferroelectric compounds. The most commonly studied are the perovskites and the alkali dihydrogen phosphates. The perovskites have ABO₃ type structure, where A is a first, second, fourth or even fifth group ion of appropriate valency and B is a transitional metal ion such as Ti, Nb, Ta, Zr etc. For example NaTaO₃, KNbO₃, BaTiO₃, PbTiO₃, SrTiO₃, BiFeO₃ and KTaO₃ etc. are all ferroelectric perovskites.

Ferroelectrics have become a subject of considerable interest in the past few years, because of their wide potential applications in different fields. Their properties reveal many interesting applications in the ceramic industry, optoelectric devices for use in optical communication, memory display, coherent optical processing, modulators, beam reflectors, light valves and holographic storage media etc. As compared with similar magnetic devices, ferroelectric memory devices are very small in size and mass, consume less power and are not sensitive to external magnetic fields. Memory devices are constructed from ferroelectrics distinguished by a rectangular cycle of electric hysteresis, a short time needed for switching over (i.e. the time for changing the direction of spontaneous polarization).

It is now well known that several interesting temperature dependent properties of ferroelectric result from the temperature dependence of the low lying transverse optic mode of vibration [1]. One of the very interesting properties of these crystals is the electric field and temperature dependences of the low frequency transverse optic (TO) mode. The effect of electric field on the Cochran modes in SrTiO₃ and KTaO₃ was studied by Steigmeir [2], showing an upward shift in the TO-mode frequency which reduces the TO-LA interaction. All these studies reveal a remarkable effect of electric field on ferroelectric soft mode frequency. So the dynamic properties of ferroelectrics will be affected in the presence of electric field [3, 4] because of the effect of electric field on soft ferroelectric mode.

Low temperature specific heat of ferroelectric, superconducting and amorphous materials has been studied by several researchers [5,6]. These studies show that ferroelectric materials with field dependent low-lying modes will have associated field dependent specific heats at low temperatures [7]. The specific heat of all the three crystals (SrTiO₃, BaTiO₃ and KTaO₃) decreases with increase in applied electric field and this decrease is due to the hardening and splitting of the soft TO-mode frequency. There is also some published work on the specific heat of pure and mixed ferroelectric crystals [8-13]. A current review for perovskites type ferroelectric crystals is available in the literature [14-17].

The aim of the present work is to study theoretically the variation of specific heat with temperature and electric field both qualitatively and quantitatively using the method of double time temperature dependent Green's function in anharmonic ferroelectric crystals such as SrTiO₃, BaTiO₃ and KTaO₃ using a model Hamiltonian for ferroelectric crystal, augmented with anharmonicity up to fourth order. The expression for the specific heats of displacive type ferroelectric materials such as SrTiO₃, BaTiO₃ and KTaO₃ in paraelectric phase in presence of external electric field is obtained. We used double time Green's function technique to obtain thermally averaged correlation function and hence, the observable quantities with the help of Silverman-Joseph modified Hamiltonian which includes anharmonicity up to fourth order. The contribution of soft modes towards specific

heat has been taken into account. As in general, it is agreed that low temperature specific heat data can reveal the position(s) of low-lying vibrational levels in soft mode dielectric materials. The contributions from these levels are so large that specific heat data estimated from the acoustic spectrum (e.g. elastic constants) can be in error by as much as in order of magnitude. Also the soft mode contribution to the specific heat is described by appropriate Einstein terms. We make use of a unitary transformation which renders the most significant first order dipole-moment term to affect the specific heat via the applied electric field. The effect of an external electric field on the specific heat and soft mode frequency has been discussed in paraelectric phase for SrTiO₃, BaTiO₃ and KTaO₃ crystals. The properties of ferroelectric crystals are investigated both theoretically and experimentally by many workers. Calculated results have been compared with the results of other workers.

II. Theory

2.1 Green's function and the soft mode frequency

For the study of specific heat, we have used Silverman-Joseph modified Hamiltonian which includes anharmonicity up to fourth order in the potential energy similar to our previous study for zero defect case [4]. The interaction of the soft mode coordinates, resonant interactions, scattering and electric dipole moment terms are considered in the Hamiltonian.

To evaluate the expressions for various dynamic properties in presence of the electric field, we introduce the retarded double-time thermal Green's function for the optical phonon as:

$$G_0^0(t-t') = \ll A_0^0(t); A_0^0(t') \gg = -i\theta(t-t') \langle A_0^0(t); A_0^0(t') \rangle \quad \dots (1)$$

Where $\theta(t-t')$ is the usual Heaviside step function and the symbol $\langle \rangle$ denotes the statistical average. $A_0^0(t)$ and $A_0^0(t')$ 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. (1) with the help of the modified Hamiltonian, Fourier transforming and writing it in the Dyson's equation form, one obtains:

$$G_0^0(\omega + i\epsilon, E) = \frac{\omega_0^0}{\pi} [\omega^2 - \tilde{\nu}_0^0(\omega) - 2\omega_0^0 i \Gamma^0(\omega, E)] \quad \dots (2)$$

Where $\tilde{\nu}_0^{02} = \omega_0^{02} + 2\omega_0^0 \Delta^0(\omega, E)$... (3)

Here $\omega_0^{02} = \tilde{\omega}_0^{02} + \langle [F(t); A_0^0(t')] \rangle$... (4)

And $\tilde{\omega}_0^{02} = \omega_0^0 [\omega_0^0 + 2V + 12\Gamma'_1 gE + 24\Gamma'_2 g^2 E^2]$... (5)

Where the notations used are exactly similar and in the same sense as used in our previous calculations [12].

In Eqs (3) and (4), $\Delta^0(\omega, E)$ and $\Gamma^0(\omega, E)$ are the field dependent shift and width for the soft mode respectively, and are given by:

$$\begin{aligned} \Delta^0(\omega, E) = & 18\Gamma_1^2 N \left[\frac{2\Omega}{\{\omega^2 - (2\Omega)^2\}} \right] + 4\Gamma_2^2 (1 + N^2) \left[(1 + N^2) \frac{3\Omega}{\{\omega^2 - (3\Omega)^2\}} - (1 - N^2) \frac{\Omega}{\omega^2 - \Omega^2} \right] + \\ & 16 \sum |H|^2 \cdot \left[\frac{(N_k^a \pm N_k^0)(\Omega_k^a \pm \Omega_k^0)}{\omega^2 - (\Omega_k^a \pm \Omega_k^0)^2} \right] + \left[288\Gamma'_2 g^2 E^2 + 8NE^2 \times \sum |B^\lambda(k)|^2 \cdot \frac{2\Omega}{\{\omega^2 - (2\Omega)^2\}} \right] + \\ & \left[(-4|A|^2 \sum |F|^2 + 64g^2 E^2 \sum |H|^2) \frac{N\omega}{\omega^2 - \Omega^2} \right] \quad \dots (6) \end{aligned}$$

And $\Delta^0(T, E) = AT + BT^2 + CTE^2$... (7)

$$\begin{aligned} \Gamma^0(\omega, E) = & 9\pi\Gamma_1^2 N \{ \delta(\omega - 2\Omega) - \delta(\omega + 2\Omega) \} + 2\pi\Gamma_2^2 \{ (1 + 3N^2) \{ \delta(\omega - 3\Omega) + \delta(\omega + 3\Omega) \} - (1 - N^2) \{ \delta(\omega - \Omega) - \\ & \delta(\omega + \Omega) + 8\pi |H|^2 \times (Nk^a \pm Nk^0) \delta\omega - \Omega k^a - \Omega k^0 + \delta\omega + \Omega k^a + \Omega k^0 + \pi 144\Gamma'_2 g^2 E^2 + 4E^2 \times B\lambda k 2N \cdot \delta\omega - 2\Omega - \delta\omega + 2\Omega + \pi \{ [-2A2 \\ & |F|^2 + 64g^2 E^2 |H|^2] N \cdot \delta\omega - \Omega - \delta\omega + \Omega \} \} \quad \dots (8) \end{aligned}$$

And $\Gamma^0(T, E) = AT + BT^2 + CTE^2$... (9)

Where the notations used are exactly similar and in the same sense as used in our previous calculations [12].

Eqs. (7) and (9) show the temperature and field dependence of shift and width, respectively of optic phonons in frequency response.

The soft mode frequency for optic mode [Eqs (3-5)] may be written as:

$$\begin{aligned} \check{\omega}_0^{02} = & \omega_0^0 [\omega_0^0 + 2V + 12\Gamma_1' gE + 24\Gamma_2' g^2 E^2] + \langle [F(t); A_0^0(t')] \rangle > \\ & + \omega_0^0 [36\Gamma_1'^2 N \left[\frac{2\Omega}{\{\omega^2 - (2\Omega)^2\}} \right] + 8\Gamma_2'^2 \left[(1 + N^2) \frac{3\Omega}{\{\omega^2 - (3\Omega)^2\}} - (1 - N^2) \frac{\Omega}{\omega^2 - \Omega^2} \right] + 32 \sum |H|^2 \cdot \left[\frac{(N_k^0 \pm N_k^0)(\Omega_k^0 \pm \Omega_k^0)}{\omega^2 - (\Omega_k^0 \pm \Omega_k^0)^2} \right] + [576\Gamma_2' g^2 E^2 + \\ & 16NE^2 \times B\lambda k 2.2\Omega\omega^2 - 2\Omega^2 + (-8A2 |F|/2 + 128g^2 E^2 |H|/2) N\omega\omega^2 - \Omega^2 \end{aligned}$$

$$\text{Or } \check{\omega}_0^{02} = \omega_0^{02} + 2\omega_0^0 V + \gamma_1 + \gamma_2 T + \gamma_3 T^2 + \gamma_4 E + \gamma_5 E^2 \quad \dots (10)$$

Where γ_2 and γ_3 are the coefficients of T and T^2 , respectively and γ_4 and γ_5 are the coefficients of E and E^2 respectively. The square of the soft mode frequency varies as the square of the applied electric field which is in agreement with the experimental result [18]. The effect of the electric field on this mode also affects the interaction of soft mode with other modes, thus giving rise to electric field dependence of various dynamical properties.

2.2 General formulation for specific heat at constant volume (C_V)

The specific heat at constant volume (C_V) for the model of the pure crystals considered here can be obtained as follows:

$$C_V = K_B \sum_k E(Y_k) \quad \dots (11)$$

Here K_B is a Boltzmann constant and Y_k is defined as

$$Y_k = \hbar \Omega_k / (K_B T) \quad \dots (12)$$

Where Ω is the field dependent soft mode frequency of ferroelectric perovskites and $E(Y)$ is the Einstein function given by:

$$E(Y) = Y^2 \exp Y / (\exp Y - 1)^2 \quad \dots (13)$$

Substituting the value of the Einstein function $E(Y)$ for soft phonon mode ($k=0$) in Eq. (1) gives the specific heat at constant volume as

$$C_V = K_B Y^2 \exp Y / (\exp Y - 1)^2 \quad \dots (14)$$

Now substituting the value of Y (Y_k for $k=0$) from Eq. (2) into Eq. (4) it gives

$$C_V = K_B (\hbar \Omega / K_B T)^2 \exp(\hbar \Omega / K_B T) / [\exp(\hbar \Omega / K_B T) - 1]^2 \quad \dots (15)$$

For quantitative purposes, the authors consider that the Curie temperature changes with the electric field as suggested by Walter J. Merz [19], which is given by:

$$T'_c = T_c + \Delta T \text{ with } \Delta T = 1.9 \times 10^{-3} \times E$$

Where E is applied electric field in V/cm.

If the temperature is not too high, the temperature dependence of the soft mode frequency is given by:

$$\Omega_{k,T} \approx \{k(T - T_c)\}^{1/2} \quad \dots (16)$$

$$\Omega \approx \Omega_{k,E,T} \approx \Omega_{k,T} (E^2 + 1)^{1/2} (T - T'_c)^{1/2} / (T - T_c)^{1/2} \quad \dots (17)$$

Where T'_c is the changed Curie temperature in presence of electric field.

Thus the study of variation of soft mode frequency with temperature and applied electric field is necessary to study the variation of specific heat with temperature and applied electric field.

III. Results

Using Eqs (16) and (17), the soft mode frequency for all three crystals has been calculated for different temperatures in presence of external electric field. The variation of soft mode frequency with electric field at different temperatures for SrTiO₃, BaTiO₃, and KTaO₃ crystals is shown in Figs (1, 2 and 3) respectively. Soft mode frequency increases with increasing electric field and temperature. These results are in good agreement with the results of other researchers [8, 19, 20].

Specific heat at constant volume C_V of SrTiO₃, BaTiO₃ and KTaO₃ pure crystals has been calculated using Eq. (15) for different values of temperatures in presence of different electric fields. Curves of C_V against electric field for SrTiO₃, BaTiO₃ and KTaO₃ crystals at different temperatures are plotted in Figs (4, 5 and 6) respectively. It is observed from Figs (4, 5 and 6) that the specific heat increases with increase in temperature for all three crystals and for a constant temperature, the specific heat decreases with the increase in applied electric field for all three crystals.

IV. Discussion & Conclusions

Green's function technique and Dyson's equation treatment have been used to obtain an expression for the specific heat of SrTiO₃, BaTiO₃ and KTaO₃ perovskites in presence of an external electric field by using a model Hamiltonian in presence of higher order anharmonic and electric moment terms. The anharmonic coefficients and higher order electric moment terms give their contribution to various scattering processes.

It is observed from Eq (10) that the field dependence of specific heat is a clear consequence of the field dependence of the soft mode frequency. So in order to discuss the field dependence of specific heat of ferroelectric perovskite crystals, we shall first discuss the electric field dependence of the soft mode frequency. 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 mode also affects the interaction

of soft modes with other modes, thus giving electric field dependence of various dynamic properties. The soft modes contribution to these properties is particularly important in the vicinity of T_C and is expected to give an anomalous behaviour. From eq. (10) it is clear that the soft mode frequency increases with the increase in applied electric field in conformity with the experimental results [18, 21]. Hence, this frequency is stabilized in the presence of electric field and anharmonicities. It is clear from Eqs (10), (11) and (12) that the presence of an applied electric field will increase the soft mode frequency and hence, will decrease the specific heat in conformity with the experimental results of Lawless [8]. Lawless [8] has described the field dependence of the soft mode using Lyddane-Sachs-Teller-Devonshire formalism [21], while we have described this electric field dependence by making use of a Hamiltonian proposed by Silverman and Joseph [22] and powerful thermal Green's function technique [12]. Also, the soft mode contribution to the specific heat is described by appropriate Einstein terms.

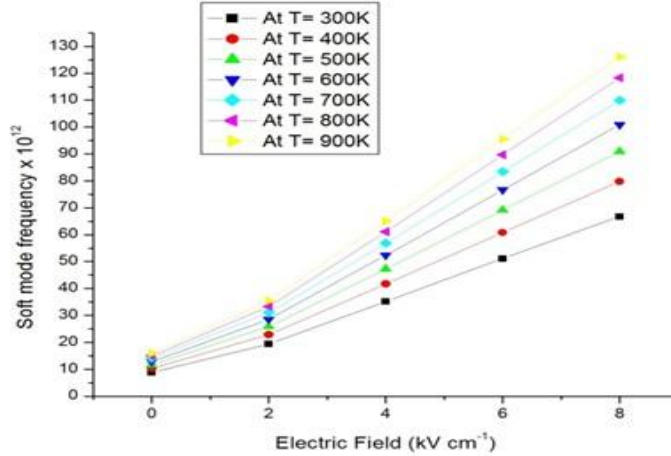


Fig. 1- Variation of soft mode frequency with electric field at different temperatures for SrTiO₃ crystal

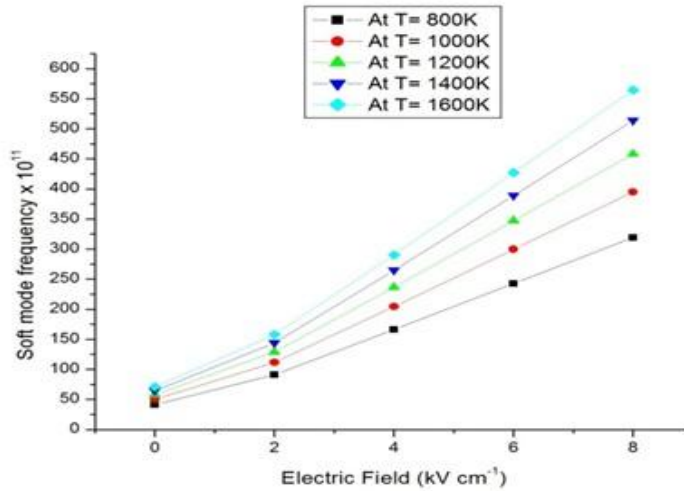


Fig. 2- Variation of soft mode frequency with electric field at different temperatures for BaTiO₃ crystal

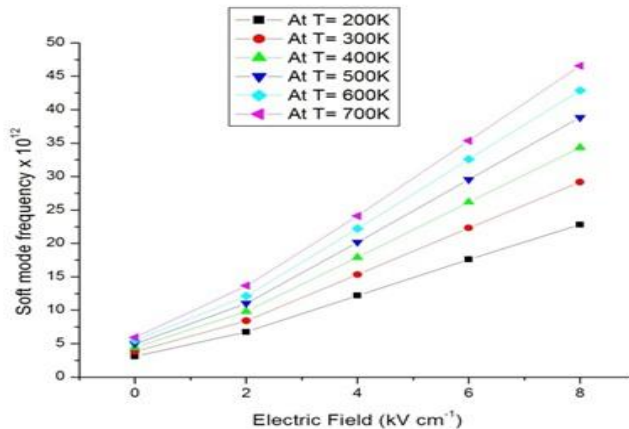


Fig. 3- Variation of soft mode frequency with electric field at different temperatures for KTaO₃ crystal

Figures (1, 2 and 3) show the variation of soft mode frequency with electric field at different temperatures for SrTiO₃, BaTiO₃ and KTaO₃ crystals respectively. The soft mode frequency increases with an increase in electric field. Taking any electric field as reference, the soft mode frequency increases with an increase in temperature. At low field's region, the temperature's effect is negligible for all the three crystals Fig. (1, 2 and 3).

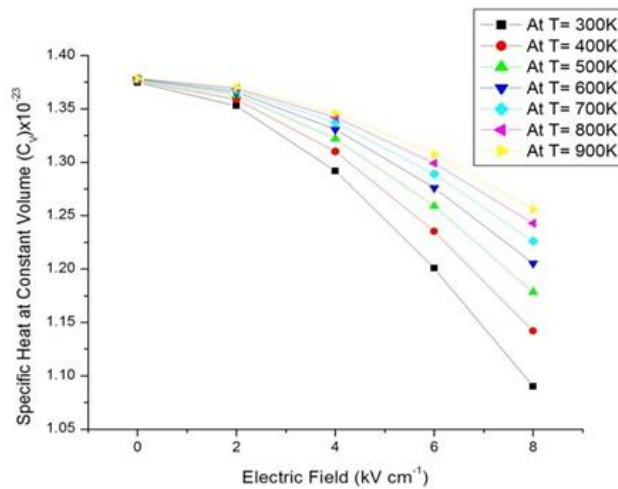


Fig. 4 – Specific heat at constant volume C_V versus electric field (in kV/cm) for SrTiO₃ at different temperatures

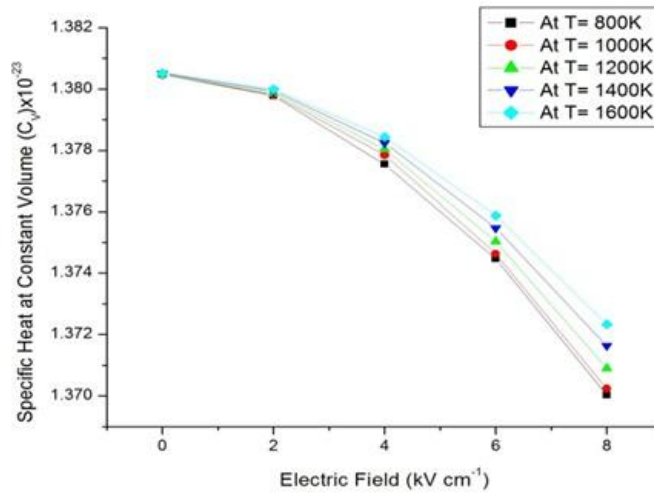


Fig. 5 – Specific heat at constant volume C_V versus electric field (in kV/cm) for BaTiO₃ at different temperatures

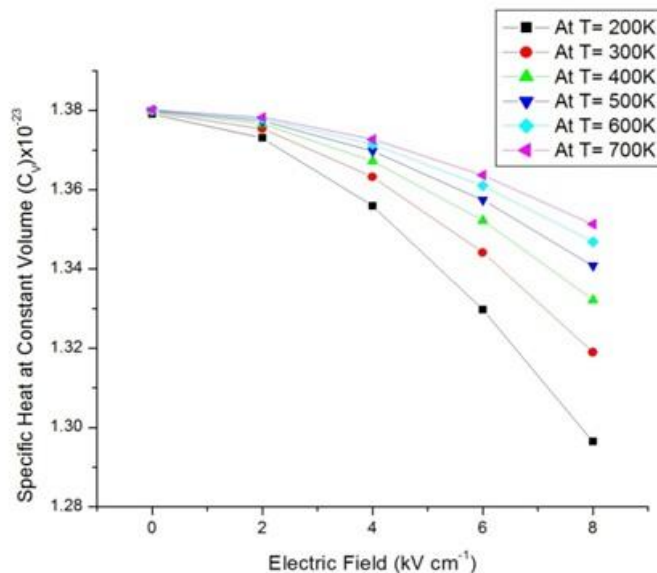


Fig. 6 - Specific heat at constant volume C_V versus electric field (in kV/cm) for KTaO₃ at different temperatures

Figures (4, 5 and 6) show the variation of specific heat with electric field at different temperatures for SrTiO₃, BaTiO₃ and KTaO₃ respectively. The specific heat at constant volume decreases with an increase in electric field. In low field region, the temperature's effect is negligible for all three crystals and the change in specific heat arises mainly due to higher anharmonic terms. Thus, our results are in good agreement with the experimental results obtained by Lawless [8] for ABO₃ type SrTiO₃ and KTaO₃ perovskites.

Strong phonon- phonon interactions due to vanishingly small frequency of the soft mode are held responsible for it. Anharmonicity is necessary in these crystals to observe these effects. Recently we have applied double time thermal Green's function technique in obtaining expression for electric field dependent inelastic scattering cross section of neutrons in BaTiO₃, SrTiO₃ and KTaO₃ displacive ferroelectric perovskites.[23]

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