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$T^{3/2}$ Contribution to the Specific Heat of $PbTiO_3$, $KNbO_3$ and $Ba_{1-x}Ca_xTiO_3$

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Abstract

A $T^{3/2}$ contribution to the low temperature specific heat of anharmonic ferroelectric crystal is calculated. This may be based on domain walls contribution because it is not present in paraelectric and antiferroelectric ferroelectrics. The variation of low temperature specific heat with temperature is discussed in $PbTiO_3$ and $KNbO_3$ and, the variation is discussed with defect concentration in case of $Ba_{1-x}Ca_xTiO_3$ ferroelectric perovskites for different values of 'x'.The effect of temperature and defect on low temperature specific heat can be observed in the presence of anharmonicity. Specific heat increases with increase in temperature in $PbTiO_3$ and $KNbO_3$ and, also with defect (for different concentration) in $Ba_{1-x}Ca_xTiO_3$ ferroelectric perovskites.

Keywords: Ferroelectric perovskites, Defects, Specific heat, Anharmonicity.

Introduction

A well known aspect of ferroelectric perovskites is that, a large number of their properties result from the temperature dependence of the low lying transverse optic mode of vibrations[1,2]. In ferroelectrics the frequency corresponding to the transverse optic mode of the zero wave vector is imaginary ($\iota\omega_o^0$) in the harmonic approximation as harmonic forces are not only sufficient to stabilize the system[3-8]. The dynamic properties of ferroelectrics will be affected[9-11] 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. Lawless[12-14] has measured the anomalous specific heat of pure soft mode dielectrics experimentally at low temperatures.

In our previous papers[15,16] we have discussed the variation of specific heat with temperature in and with temperature in $PbTiO_3$ and $KNbO_3$ and defect in $Ba_{1-x}Ca_xTiO_3$ ferroelectric perovskites in paraelectric phase by using modified Silverman-Joseph Hamiltonian for displacive ferroelectrics and the double time Green's function technique[2]. In the research papers[15,16] we have discussed the variation of specific heat in $PbTiO_3$, $KNbO_3$ and $Ba_{1-x}Ca_xTiO_3$ and such $T^{3/2}$ contribution to the low temperature specific heat was untouched.

The aim of the present work is to discuss the variation of low temperature specific heat with temperature is discussed in $PbTiO_3$ and $KNbO_3$ and, the variation is discussed with defect concentration in case of $Ba_{1-x}Ca_xTiO_3$ ferroelectric perovskites for different values of 'x'. The $T^{3/2}$ contribution to the low temperature specific heat is observed in $PbTiO_3$, $KNbO_3$ and $Ba_{1-x}Ca_xTiO_3$ ferroelectric perovskites. A considerable review on specific heat of pure and mixed crystal is available in literature of many researchers[14,17,18] and references therein.

Theory

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 modified transformed Hamiltonian[11] 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:

$$G_o^o(\omega+i\varepsilon) = \langle\langle A_o^o(t); A_o^o(t') \rangle\rangle (\omega+i\varepsilon) \tag{1}$$

$$G_o^o(\omega+i\varepsilon) = G'(\omega) + G''(\omega) \tag{2}$$

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:

$$G_o^o(\omega+i\varepsilon) = \omega_o^o/\pi[(\omega^2-(\upsilon_o^{o/})^2(\omega)-i\Gamma_o^{o\prime}(\omega)] \tag{3}$$

where $(\upsilon_o^{o\prime})^2(\omega)$ is defect and field dependent soft mode frequency and can be written as:

$$\begin{aligned}(\upsilon_o^{o\prime})^2(\omega) &= -(\omega_o^o)^2 + 4\omega_o^o D(0,0) + \\ &\omega_o^o E^2(96g^2V-24gD'_1)+4\,\omega_o^o g+\Delta_o^{o/}(\Omega)\end{aligned} \tag{4}$$

where $\Delta_o^{o\prime}(\omega)$ and $\Gamma_o^{o\prime}(\omega)$ are shift and half width of the soft phonon mode with defects, anharmonicity and electric field, ω_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 [$S = -igEB_o^o$]; V and D'_1 are electric moment terms. The defect dependent terms in the above equation will be zero while considering a pure crystal.

In our previous work[15,16]we have calculated the value of specific heat from the above mentioned technique as:

$$C_v = k_B\,(\hbar\Omega_{AED}/k_BT)^2\{\exp(\hbar\Omega_{AED}/k_BT)\}/[\exp(\hbar\Omega_{AED}/k_BT)-1]^2 \qquad (5)$$

Also in our previous work[19] for low temperatures the value of the specific heat for these crystals follow the relation

$$C = aT^3 + bT^{3/2}$$

or

$$CT^{-3/2} = aT^{3/2} + b \qquad (6)$$

where a and b are the constants. Since this is absent in the paraelectric and antiferroelectric phases and is independent of the presence of the defect concentration and also on the crystal whether it is displacive type or has H-bond, it suggests $T^{3/2}$ is due to domain walls.

Variation of specific heat at low temperatures

The value of constants ‘a’ and ‘b’ for $PbTiO_3$, $KNbO_3$ and $Ba_{1-x}Ca_xTiO_3$ are calculated from the best fit of data from our previous work[19,20]. The values of the Curie temperature for $PbTiO_3$, $KNbO_3$ and $Ba_{1-x}Ca_xTiO_3$ (for different values of ‘x’) are taken from the best fit of data from our previous work[21,22]. Specific heat at constant volume of the crystals taken under consideration has been calculated by using equation(6) at low temperatures. Variation of specific heat at low temperature has been given in the Fig.(1) for $PbTiO_3$ and $KNbO_3$(both pure crystals) and in Fig.(2) for $Ba_{1-x}Ca_xTiO_3$ (for x= 0.0, 0.05, 0.10 and 0.15).

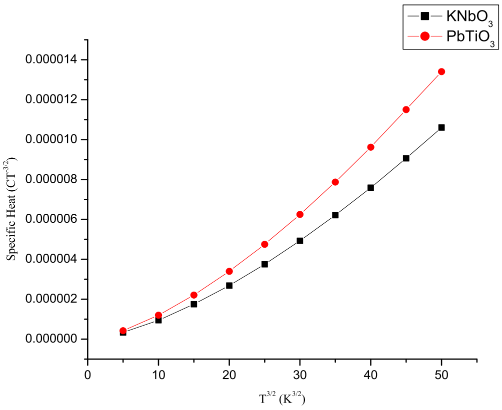

Figure 1: Variation of Specific Heat in $PbTiO_3$ and $KNbO_3$ferroelectric perovskites at low temperature with $T^{3/2}$.

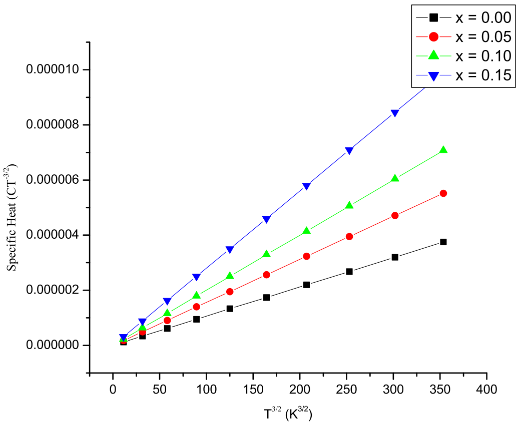

Figure 2: Variation of Specific Heat in $Ba_{1-x}Ca_xTiO_3$ (for x= 0.0, 0.05, 0.10 and 0.15) ferroelectric perovskites at low temperature with $T^{3/2}$.

Discussion and conclusions

Figs. (1) and (2) show the $T^{3/2}$ contribution to the specific heat at low temperatures for $PbTiO_3$, $KNbO_3$ and $Ba_{1-x}Ca_xTiO_3$ (for different values of 'x'). It is evident from the figure that specific heat at constant volume increases with increase in temperature at very low temperatures. It is also clear from the Fig.(2) that it also increases with increase in defect concentration in $Ba_{1-x}Ca_xTiO_3$ (for different values of 'x'). the trend is same for all the concentrations. Our results are in good agreement with the experimental[12-14,23, 24] and theoretical [19] results of the other researchers.

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