International Journal of Pure and Applied Physics
ISSN 0973-1776 Volume 6, Number 2 (2010), pp. 171–176

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

Electric Field Dependence of Soft Mode Frequency in $Ba_{1-X}ca_xtio_3$ Ferroelectric Perovskites

***Dushyant Pradeep, U.C. Naithani and Ashok Kumar**

Department of Physics, H.N.B. Garhwal Central University,
Campus Pauri (Garhwal), Uttarakhand, 246001, India
**E-mail: dushyant_pradeep@yahoo.co.in*

Abstract

An expression has been obtained for the soft mode frequency in $Ba_{1-x}Ca_xTiO_3$ ferroelectric perovskites in the presence of external electric field by using double time temperature dependent Green's function technique. The mass and force constants change due to the impurity atoms which are taken into account in the presence of higher order anharmonic and electric moment terms in the Silverman Joseph Hamiltonian. The soft mode frequency is obtained in the presence of both the electric field and defect concentrations of Ca in pure $BaTiO_3$. The soft mode frequency increases with increase in electric field and defect concentration.

Keywords: Soft mode frequency, Ferroelectric perovskites, Green's function, Anharmonicity.

Introduction

Now a day's ferroelectrics have become an important field of study due to their different physical, electrical and thermal properties. It is now well known that several interesting properties of ferroelectric perovskites depends upon temperature due to temperature dependence of low lying transverse optic mode of vibration[1].

Fatuzzo[2] has shown that the low frequency resonance in the far infrared can be shifted by electric field frequency in the microwave region. This shift was found large when the temperature of ferroelectric substance is slightly above the Curie temperature and the electric field dependence of the optic mode frequency arises from the anharmonic terms. The Raman scattering and frequency and the frequency shift of the soft mode in $SrTiO_3$, enhanced by thje electric field has been reported by Schaufele et.al.[3]. Warlock and Fleury[4] have also reported an electric field dependence of some soft optical phonon frequencies of $SrTiO_3$ in electric field

induced Raman scattering experiment. Warlock and Fleury[4] qualitatively interpreted their observations on the basis of the combination of the simple thermodynamic theory and slightly generalized L S T relations. A review of the work is available in the literature[5,6]. All these studies reveal a remarkable influence of the electric field on the ferroelectric soft mode frequency. The effect of impurity on soft mode frequency has been discussed by many researchers[7-9].

In the present paper an expression for the soft mode frequency in polycrystalline mixture of $Ba_{1-x}Ca_xTiO_3$ has been derived by forming a model Hamiltonian for polycrystalline mixture and then applying it to $Ba_{1-x}Ca_xTiO_3$ferroelectric perovskites. The mass and force constant changes are taken into account in the Silverman Joseph Hamiltonian[10] augmented with the higher order anharmonic and electric dipole moment terms. The variation of soft mode frequency with increasing electric field and with varying defect concentrations of Ca in pure $BaTiO_3$ has been studied.

Theory

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[11] of a mixed displacive ferroelectric in paraelectric phase which includes defects and electric field is used in the present study.

Green's function for soft optic mode is used as follows:

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

$$G_o^o(\omega+i\varepsilon) = G'(\omega) + G''(\omega) \quad (2)$$

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:

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

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

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

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 real pat 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 Cochran mode in the presence of electric field and defects as the self consistent solution of Eq. (4). as [$\Omega(T) \approx \upsilon_o^{o/}(\omega)$]:

$$(\Omega')^2 = -(\omega_o^o)^2 + 4\,\omega_o^o D(0,0) + 4\,\omega_o^o Q' + \Delta_o^{o\prime}(\Omega) \tag{5}$$

where Q' can be expressed as:

$$Q' = \sum_{\lambda,k} \beta^{\lambda}(k) \langle A_k^{\lambda}, A_k^{\lambda} \rangle = \sum_{\lambda,k} \beta^{\lambda}(k)\, \eta_k^{\lambda}. \tag{6}$$

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

$$\Delta_o^{o\prime}(\omega) = [\Delta_1(\omega) + \Delta_2(\omega) + \Delta_3(\omega) + \ldots\ldots\ldots + \Delta_{10}(\omega)] \tag{7}$$

where $\Delta_i,s(\omega)$ (i= 1,2,3,……,10) are the real parts of the Green's function and the values of Δ_i, $s(\omega)$ are given by:

$$\Delta_1(\omega) = |D(-k_a,0)|^2\, 2\Omega/(\omega^2-\Omega^2) \tag{7(a)}$$

$$\Delta_2(\omega) = -|C(-k_a,0)|^2\, 2\Omega/(\omega^2-\Omega^2) \tag{7(b)}$$

$$\Delta_3(\omega) = |D(-k,k_1^o)|^2\, 2\omega_{k1}^o/(\omega^2-\omega_{k1}^{o2}) \tag{7(c)}$$

$$\Delta_4(\omega) = |C(-k,k_1^o)|^2\, 2\omega_{k1}^o/(\omega^2-\omega_{k1}^{o2}) \tag{7(d)}$$

$$\Delta_5(\omega) = E^2[4g^2|F(k)|^2 + |A(k)|^2]\, 2\omega_k^o/(\omega^2-\omega_k^{o2}) \tag{7(e)}$$

$$\Delta_6(\omega) = |F(k)|^2\, \delta'(\omega_k^o/\omega_k^{o\prime}) \sum_{\pm} (N_0^o \pm N_k^{o\prime})(\Omega \pm \omega_k^{o/}) / \{\omega^2-(\Omega\pm\omega_k^{o/})^2\} \tag{7(f)}$$

$$\Delta_7(\omega) = |\beta a(k)|^2\, \delta(\omega_k^a/\omega_k^{a\prime})[(1+N_0^{o2}+2N_0^o N_k^{a\prime}) \times(2\Omega+\omega_k^{a\prime})/\{\omega^2-(2\Omega+\omega_k^{a\prime})^2\}(1-N_0^{o2})\,\omega_k^{a\prime}/\{\omega^2-(\omega_k^{a\prime})^2\}] \tag{7(g)}$$

$$\Delta_8(\omega) = E^2[16g^2 \sum_{k1k2} |\Phi(-k,k1,k2)|^2 + 4\sum_{k1k2} | \times C'(-k,k1,k2)|^2] \delta'(\omega_{k1}^o\omega_{k2}^a / \omega_{k1}^{o\prime}\omega_{k2}^{a\prime}) \times\sum_{\pm}(N_{k1}^{o\prime}\pm N_{k2}^{o\prime})(\omega_{k1}^{o\prime}\pm\omega_{k2}^{a\prime})/\{\omega^2-(\omega_{k1}^{o\prime}\pm\omega_{k2}^{a\prime})^2 \tag{7(h)}$$

$$\Delta_9(\omega) = E^2[64g^2|\beta a(k)|^2 + 4|\beta a(k)|^2]\delta'(\omega_k^a/\omega_k^{a\prime}) \times\sum_{\pm}(N_0^o\pm N_k^{a\prime})(\Omega\pm\omega_k^{a\prime})/\{\omega^2-(\Omega\pm\omega_k^{a\prime})^2 \tag{7(i)}$$

and

$$\Delta_{10}(\omega) = \sum_{k1k2}|\Phi(-k,k1,k2)|^2(2\delta)(\omega_{k1}^o\omega_{k2}^a/\omega_{k1}^{o\prime}\omega_{k2}^{a\prime}) \times[(1+N_0^oN_{k1}^{o\prime}+N_0^oN_{k2}^o+N_{k1}^{o\prime}N_{k2}^{o\prime}) \times(\Omega+\omega_{k1}^{a\prime}+\omega_{k2}^{a\prime})/\{\omega^2-(\Omega+\omega_{k1}^{a\prime}+\omega_{k2}^{a\prime})^2\} +(1-N_0^oN_{k1}^{o\prime}+N_0^oN_{k2}^o-N_{k1}^{o\prime}N_{k2}^{o\prime})$$

$$\times(\Omega-\omega_{k1}{}^{a'}-\omega_{k2}{}^{a'})/\{\omega^2-(\Omega-\omega_{k1}{}^{a'}-\omega_{k2}{}^{a'})^2\} \quad 7(j)$$

The notations used in the Eq.(7) are exactly similar and in the same sense as used in our previous calculations[12].

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:

$$\Omega_{AED} = \Omega_{AD}\,(E^2+1)^{1/2}\,(T-T_c')^{1/2}/(T-T_c)^{1/2} \quad (8)$$

where Ω_{AED} is electric and defect dependent soft mode frequency, Ω_{AD} is defect dependent soft mode frequency, both the quantities are taken in the presence of anharmonicity,

$$T_c' = T_c + \Delta T_c$$

and $\Delta T_c = 1.9\times10^{-3}$ Volt/cm.

So for the variation the dependence of soft mode frequency on temperature, defect and electric field will be considered.

Variation of soft mode frequency with electric field in $Ba_{1-x}Ca_xTiO_3$

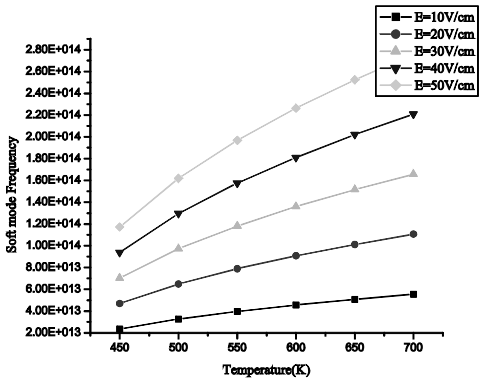
The Curie temperatures (T_c) of $Ba_{1-x}Ca_xTiO_3$ for different values of x(=0,0.05,0.10,0.15) are taken from the work of researchers[13]. Soft mode frequency (Ω) for zero field case of $Ba_{1-x}Ca_xTiO_3$ for different values of x(=0,0.05,0.10,0.15) has been calculated. In order to consider the effect of an applied electric field on the soft mode frequency (Ω) and hence, on the specific heat of a displacive ferroelectric crystal, it has been considered that the Curie temperature changes according to the relation, $\Delta T_c = 1.9\times10^{-3}\times E$, where E is the electric field in V/m. With the help of Eq. (8) 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 (Ω) 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].

Results and Discussion

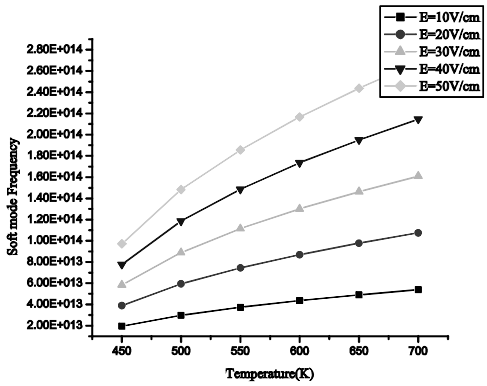
From Eqs (4) and (8), it is clear that the presence of an electric field will increase the soft mode in confirmation with experimental results of Lawless[14]. He has also described the field dependence of the soft mode frequency using Lyddance-Sachs-Teller-Devonshire formalism[20] while in this study dependence is described by making use of a Hamiltonian proposed by Silverman and Joseph[10] and recent thermal Green's function technique.

The treatment adopted here shows the dependence of soft mode of $Ba_{1-x}Ca_xTiO_3$ for different values of temperature, impurities and electric field in the presence of anharmonicity. In the present study, the Hamiltonian proposed by the Silverman and

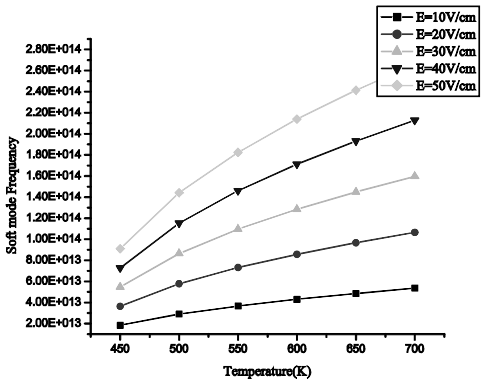
Joseph[26] has been distinguished in terms of creation and annihilation operators. At microwave frequencies, the findings are in good agreement with previous experimental and theoretical results. It is evident from Eq. (4) that the square of soft mode frequency varies directly as the square of the applied electric field. The variation of dependence of soft mode of $Ba_{1-x}Ca_xTiO_3$ for different values of temperature, impurities (for all x=0,0.05,0.10,0.15) and electric field is shown in the Figs.(1). So the soft mode frequency increases with the increase in electric field. The above results have also been compared with the experimental variations[4] shown in the Fig.(2). Thus our results are in good agreement with the experimental[4] (Fig.(2)) and theoretical results[18,19,21].



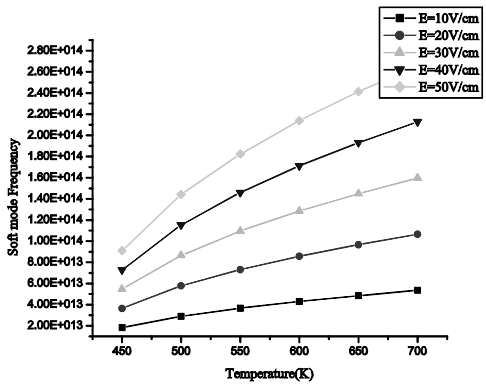
(a) $BaTiO_3$ (x=0)



(b) $Ba_{0.95}Ca_{0.05}TiO_3$ (x=0.05)



(c) $Ba_{0.90}Ca_{0.1}TiO_3$ (x=0.10)



(d) $Ba_{0.85}Ca_{0.15}TiO_3$ (x=0.15)

Figure 1(a) to 1(d): Variation of soft mode frequency of $Ba_{1-x}Ca_xTiO_3$ with temperature at different electric field strengths for different values of x.

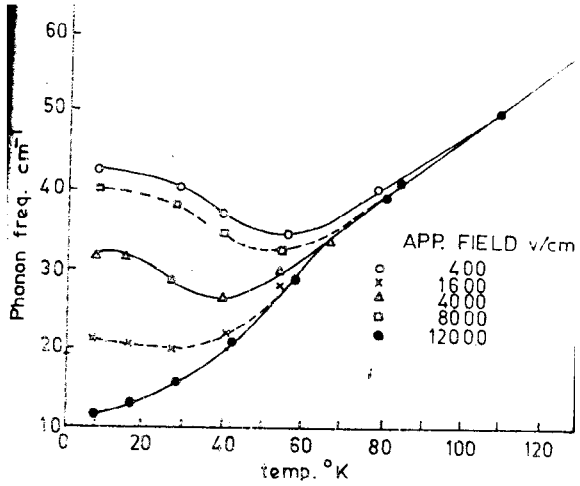


Figure 2: Experimental graph by Worlock and Fleury [4] showing the variation of soft mode frequency with temperature at different electric field strengths for different values of x.

Reference

[1] W Cochran, *Advance physics* 9,387,(1960).
[2] E Fatuzzo, *Proc Phys Soc London*, (GB) , 84, 709, (1964).
[3] R F Schaufele, W J Weber and B D Silverman, *Physical Letters* 25A, 47, (1967).
[4] J M Worlock and P A Flury, *Phys Rev Lett*, 19, 1176, (1967).
[5] R P Gairola and B S Semwal, *Journal Phys. Soc. Japan* 42, 975, (1977).
[6] A J H Mante, *Physica*, 52, 577, (1971).
[7] B D Silverman, *Phys. Rev*. 125, 1921, (1960).
[8] G Ruprecht, R C Bell and B D Silverman, *Phys. Rev*. 123, 97,(1961).
[9] Rita Bahadur and P K Sharma, *Phys. Rev*. B12, 448,(1975).
[10] B D Silverman and R I Joseph, *Phys. Rev*. 129, 2062, (1963).
[11] U.C. Naithani and B.S. Semwal, *Pramana* 11, 423, (1978).
[12] U.C. Naithani and B.S. Semwal, *Pramana* 14, 149, (1980); 15, 371, (1980); 14, 19 (1980) 19.
[13] Weiwei Zhang, Zhigang Shen & Zhigangfeng Shen; *J Mat Sci*,41, 5743, (2006).
[14] W N Lawless, *Phys Rev B*, 16, 433,(1977); 18 ,2394,(1978).
[15] Wei Xiaoyong and Yao Xi, *Mater Sci Engg B*, 99, 74, (2003).
[16] W J Merz, *Phys Rev*, 91, 513, (1953).
[17] W Kanzig and N Maikoff, *Helv Phys Acta*, 24, 343, (1951).
[18] G.N. Baluni and U.C. Naithani, *Indian J Pure & Appl Phys* 24, 440,(1986).
[19] Cheng Xiarong and Shen mingrong, *Solid State Commun*, 141, 587, (2007).
[20] R H Lyddance, R G Sachs and F Teller, *Phys Rev*, 59, 673, (1941).
[21] Ashok Kumar, Ashish kukreti and U C Naithani, 47, 300, (2009).