Indian Journal of Pure & Applied Physics
Vol. 52, June 2014, pp. 391-394

Polarizability investigation by first order phase transition in the self-consistent phonon approximation for PSN system

Manish Uniyal* & S C Bhatt
Department of Physics, H N B Garhwal, University, Srinager Garhwal 246 174, Uttarakhand
*E-mail: mani_uniyal@hotmail.com

Received 1 September 2013; revised 23 December 2013; accepted 4 April 2014

Considering a quadratic Anharmonic model Hamiltonian and using double time temperature dependent Green's function method and Dyson's equation treatment, expression for polarizablity in the frequency response for mixed perovskite type ferroelectrics has been obtained. Using the experimentally observed temperature dependent dielectric constant, loss tangent, soft mode frequency and width for Na_{1-x} K_xNbO_3 (where $x = 0$, 0.4 and 0.5), the polarizablity has been calculated for these samples at 10 and 100 kHz.

Keywords: Phase transition, Model Hamiltonian, Ferroelectrics

1 Introduction

A model Hamiltonian has been proposed by Pytte[1] for understanding the structural phase transition in perovskite ferroelectrics, the phonon frequency, shift and width have not been explicitly calculated by them, because of early decoupling of correlation functions. The soft mode frequencies are determined for arbitrary temperature by calculating the equations of motion using the Model Hamiltonian and determining the required correlation functions by means of self-consistency conditions. The occurrence of ferroelectricity in perovskite type ceramics such as $Na_{1-x}K_xNbO_3$ has been established both theoretically and experimentally[2-5] with the existence of an optic mode of lattice vibration soft mode having wave number zero and a frequency, which is anomalously low and temperature dependent. Microscopic theories of displacive phase transitions have been based on a perturbation expansion of harmonic basis. Since the harmonic soft-mode frequencies are imaginary, the contribution of these modes in the anharmonic terms was neglected. A self-consistent model of the soft mode frequencies was first given by Boccara and Samara[6] by employing the renormalized phonon basis. Their formal treatment represented (the lowest order of) what is now called the self-consistent phonon approximation[7] (SPA). This approximation has been very successful in describing the anharmonic rare-gas solids, including the quantum crystals of solid helium.

Numerical calculations have shown that the SPA gives a first - order transition for a model ferroelectric containing only fourth order anharmonic interactions[8]. This result is surprising because the phenomenological Landau (Devonshire) theory predicts the transition to be second order, when only terms up to fourth order in the polarization are included[9-11]. Polarizability factor for $Na_{1-x}K_xTaO_3$ ceramics have already been study by the author[4]. Present result has been obtained by using our previous experimental results[12-14] with theoretically derived expression for polarizability

2 Theory

To illustrate the essential features of the SPA and to understand a first-order transition, it is instructive to consider a simple model Hamiltonian with a single degree of freedom:

$$H = 1/2\sum P^2(1) + {}^1\!/_2\,\Omega_0^2 \sum_a {}_1Q_1^2(1) - 1/2\sum{}_{11}$$
$$V(11')Q_1(1)Q_{1'}(1') + 1/2\Gamma_1 \sum Q_1^4(1) \qquad \ldots(1)$$

where $Q_{1,}$ is a localized normal mode coordinates describing the ion displacements in cell 1 and P(1) is the canonical conjugate momentum:

$$[Q_1, P_{1'}] = i\delta_{11} \qquad \ldots(2)$$

We set $Q_1 = Q_0 + U_1$, where the thermal average $Q_0 = Q_1 \langle Q_1 \rangle$ measures the distortion from the high temperature structure, while U_1 describes the average values. In SPA the free energy F = <H> - TS is obtained by using a harmonic trial density matrix[2]. The distortion Q_0 and the effective harmonic force constants are determined by minimizing the free energy. For the Hamiltonian given by Eq. (1) the extremum condition $\partial F/\partial Q^2 = 0$ takes the form:

$$Q_0[\Omega_0^2 - V(0) + \Gamma_1 Q_0^2 + 3\Gamma\Delta] = 0 \qquad \ldots(3)$$

where $V(0) = \Sigma_{II} V(II')$ and Δ is defined below. The effective force constants determine the self-consistent normal mode frequency. For this mode, it is given by:

$$\omega_q^2 = [\Omega^2 + v(0) - v(q) \sim \Omega^2 + a^2 q^2] \qquad \ldots(4)$$

where

$$\Omega^2 = [\Omega_0^2 - v(0) + 3r_1 Q_0^2 + 3r_1\Delta] \qquad \ldots(5)$$

Or in the distorted phase, using Eq. (3):

$$\Omega^2 = 2r_1 Q_0^2 ; \qquad \ldots(6)$$

The correlation function $\Delta = <U_i U_j>$ is determined with the help of the fluctuation dissipation theorem[6]:

$$\Delta = N^{-1}\Sigma_q 1/2\omega_q^{-1} \coth 1/2\beta\omega_q , \qquad \ldots(7)$$

for simplicity, we consider the limit $\omega_q / kT << 1$, Δ may be approximated by the Ornstein-Zemike form:

$$\Delta = kTN^{-1}\Sigma_q(\Omega^2 + a^2 q^2)^{-1} \qquad \ldots(8)$$

Evaluating the summation in the Debye-approximation, we obtain:

$$\Delta = \Delta_0 - \Delta_t \qquad \ldots(9)$$

where

$\Delta_0 = 3kT/\omega_d^2$ and $\Delta_T = \Delta_0(\Omega_d)\tan^{-1}(\omega_d/\Omega)$

On substituting in Eq. (9), we get:

$$\Delta = 3kT/\omega_d^2 - \Delta_0(\Omega/\omega_d)\tan^{-1}(\omega_d/\Omega)$$
$$= 3kT/\omega_d^2 - 3kT/\omega_d^2[\Omega/\omega_d^2(\Omega/\omega_d)\tan^{-1}(\omega_d/\Omega)]$$
$$3kT/\omega_d^2[1-(\Omega/\omega_d)\tan^{-1}(\omega_d/\Omega)] \qquad \ldots(10)$$

where $\omega_d = aq_D, q_D$ being the Debye wave vector. Δ_T denotes the contribution to Δ due to long wavelength fluctuation. For $Q_0 \neq 0$ Eq. (9) may be written as:

$$a(T - T_c) + r_1 Q_0^2 - 3r_1\Delta_T = 0 \qquad \ldots(11)$$

where

$$a = 9r_1 K_B / \omega_d^2 , \qquad \ldots(12)$$

$$T_c = a^{-1}[v(0) - \Omega_0^2]$$

and $v(0) = T_c a_{-}^{+}\Omega_0^2$ $\qquad \ldots(13)$

Because Δ_T is linear in Ω as $\Omega \to 0$, it follows from Eqs (6) and (11) that transition is first order. However, it is important that the linear term giving rise to the first order transition is entirely due to the long wavelength fluctuations.

On substituting Eqs (6,7,13) in Eq. (5), we get the expression as:

$$Q_0^2 = 9K_B/\omega_d^2[T_c - (1 - \Omega/\omega_d \tan^{-1}\omega_d/\Omega)T] \qquad \ldots(14)$$

On substituting the experimental results of soft frequency (Ω), natural frequency of the system (ω_d) for $\mathrm{Na_{1-x}K_xNbO_3}$(x=0,0.4 and 0.6)[2] we get the variation of Q_0^2 with temperature in Tables 1 and 2 and have been plotted in Figs 1 and 2, respectively.

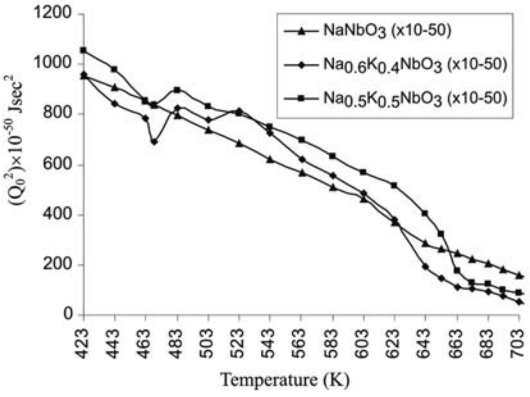

Fig. 1 — Variation of polorizability factor $(Q_0^2)\times10^{-50}$ with temperature for $\mathrm{Na_{1-x}K_xNbO_3}$ system at 10 kHz

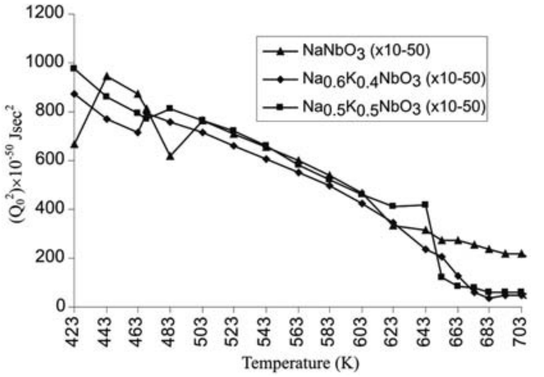

Fig. 2 — Variation of polorizability factor $(Q_0^2)\times10^{-50}$ with temperature for $Na_{1-x}K_xNbO_3$ system at 100 kHz

Table 1 — Variation of polarizability factor with temperature for $Na_{1-x}K_xNbO_3$ system at 10 kHz

Temp (K)	Q^2_0 (Eq.14)		
	$NaNbO_3$ ($\times10^{-50}$)	$Na_{0.6}K_{0.4}NbO_3$ ($\times10^{-50}$)	$Na_{0.5}K_{0.5}NbO_3$ ($\times10^{-50}$)
423	954.895	962.714	1056.414
443	904.904	844.019	976.681
463	852.924	783.587	852.924
468	835.296	688.712	838.053
483	795.972	823.544	897.129
503	738.568	776.852	829.465
523	682.972	815.001	802.164
543	622.856	723.200	750.817
563	565.904	617.903	695.447
583	510.850	555.869	634.879
603	463.300	483.549	570.107
623	370.992	381.849	515.551
643	284.823	196.032	405.398
653	263.154	145.408	324.038
663	243.402	113.768	177.184
673	223.966	106.400	126.017
683	203.671	096.366	124.345
693	182.924	073.992	101.700
703	160.912	054.014	090.128
713	137.814	031.730	077.608

Table 2 — Variation of polarizability factor with temperature for $Na_{1-x}K_xNbO_3$ system at 100 kHz

Temp (K)	Q^2_0 (Eq.14)		
	$NaNbO_3$ ($\times10^{-50}$)	$Na_{0.6}K_{0.4}NbO_3$ ($\times10^{-50}$)	$Na_{0.5}K_{0.5}NbO_3$ ($\times10^{-50}$)
423	668.997	873.761	977.585
443	943.662	769.213	863.139
463	873.264	713.708	792.220
468	810.662	791.180	768.264
483	620.877	755.427	811.023
503	763.925	712.427	765.688
523	710.318	660.914	719.177
543	652.552	608.618	662.722
563	599.171	553.835	584.074
583	541.224	493.945	523.370
603	465.379	423.840	460.859
623	330.773	342.661	409.512
643	313.281	236.576	417.828
653	272.239	204.288	121.636
663	274.047	126.288	086.964
673	255.696	059.664	076.659
683	237.390	037.154	063.008
693	220.847	047.595	061.110
703	220.847	047.595	061.110
713	183.783	005.966	038.420

3 Results and Discussion

Using our experimental[8] results for temperature and frequency dependence dielectric constant, tangent loss and width for $NaNbO_3$, $Na_{0.6}K_{0.4}NbO_3$ and $Na_{0.5}K_{0.5}NbO_3$, Polarizability factors obtained by first order phase transition in the self-consistent phonon approximation by using the formula obtained by Pytte[9], have been calculated for these mixed systems in continuation with our previous paper[7,8]. The polarizablity factor at 10 and 100 kHz frequency has been shown in Tables 1 and 2 and Figs 1 and 2, respectively. It is observed that polarizablity tends to decrease up to the first transition temperature (orthorhombic-tetragonal) thereafter, it increases and then tends to zero up to second transition temperature (tetragonal cubic). In the temperature range 465±20°C and 665±20°C anomalous behaviour has been observed due to phase transition. It can be understood that the polarization mode is temperature dependent.

Acknowledgement

The authors are thankful to Material Science Research Centre (MSRC), National Physical Laboratory (NPL), Delhi for laboratory facilities for preparation and characterization of the samples. Special thanks to Prof B S Semwal-Ex-Head and Prof R P Gairola, Head, Department of Physics, H N B Garhwal University, Srinagar Garhwal for valuable suggestion and encouragement.

References

1 Pytte E, *Phys Rev*, 5 (1972) 3758.
2 Uniyal M, Singh K, Bhatt S C, Ramchandra Rao M S, Pant R P, Suri D K & Semwal B S, *Indian J Pure & Appl Phys*, 41 (2003) 301.
3 Uniyal M & Bhatt S C, *Indian J Pure & Appl Phys*, 42 (2004) 341.
4 Uniyal M & Bhatt S C, *Indian J Pure & Appl Phys*, 50 (2012) 248.

5 Uniyal M & Bhatt S C, *Indian J Pure & Appl Phys*, 50 (2012) 915.

6 Boccara N & Sarma G, *Physics* (Long Is City, N Y) 1 (1965) 219.

7 Werthamer N B, *Phys Rev*, 1 (1970) 572.

8 Gillis N S & Koehler T R, *Phys Rev B*, 4 (1971) 3971.

9 Landau L D & Lifshitz E M, *Statistical Physics I,* Addison-Wesley, Reading Mass, (1958) Sect- 135.

10 A F Devonshire, *Advan Phys*, 3 (1954) 85.

11 Brout R, *Phase Transition* (Benjamin, New York, 1965).

12 Uniyal M, Bhatt S C, *Indian J Pure & Appl Phys*, 45 (2007) 609.

13 Uniyal M & Bhatt S C, *Inter J Materials & Chem*, 2 (2012) 47.

14 Uniyal M & Bhatt S C, *Proceedings of DAE-BRNS National Laser Symposium* (NLS-20) (2012) Jan 9-12.