Theoretical Investigation of Dielectric Properties of $KNbO_3$ Crystals

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ABSTRACT

Using experimental observed dielectric and loss behavior of potassium niobate crystals the temperature dependence of soft mode frequency, width, relaxation time, order parameter, fourth order coupling coefficients and anharmonic constants have been calculated. Anomaly has been observed in the behavior of soft mode frequency, width, relaxation time, and order parameter, near the transition temperatures in this compound.
Keywords *– Hamiltonian, perovskites, soft mode, relaxational behavior, transition temperature.*

1. INTRODUCTION

The perovskite type- ABO_3 crystals observe structural phase transition from the high temperature cubic phase to the low temperature tetragonal, rhombohedral (trigonal) or orthorhombic phase. The phase transition in perovskite crystals is, generally, assumed to be due to the instability of the temperature dependent low frequency optical phonon at transition temperature [1-3]. Depending on the relative magnitude of anharmonic interaction coefficients, different structural phases occur. By displacement of ions from special positions of the lattice of crystals having distorted perovskite structure several modes are involved in various transitions. Pytte [4] has proposed a model Hamiltonian to describe the ferroelectric transition in ABO_3 type compounds in terms of localized normal mode coordinates, elastic strains and large wavelength acoustic phonons. Expressions for free energy and normal mode frequencies have been obtained to describe the phase transition in these compounds, but the dielectric and other related properties could not be explained due to an early decoupling of various correlations in this study. Panwar and Semwal [5] modified the Pytte's Hamiltonian in terms of creation and annihilation operators. Using the systematic Green's function method and Dyson's equation the normal phonon frequencies, width and soft mode dynamics of perovskite type crystals were evaluated [5-8].

In the present study, temperature dependence of phonon frequency, width, order parameter, third and fourth order coupling coefficient and anharmonic constants of potassium niobate crystals have been calculated by correlating the theoretical expressions with the experimental results on dielectric measurements.

2. THEORY

Using the model Hamiltonian [5-8], double time thermal Green's function [9] method and Dyson's equation [10], renormalized soft phonon frequency and width have been calculated [5]. Using the Kubo formalism [11], the real part of the dielectric constant is given as:

$$K'(\omega) - 1 = -\frac{8\pi N \mu^2 \Omega_\lambda(q)\left\{\omega^2 - \hat{\Omega}_\lambda^2(q)\right\}}{\left[\left\{\omega^2 - \hat{\Omega}_\lambda^2(q)\right\}^2 + \Omega_\lambda^2(q)\Gamma_\lambda^2(q,\omega)\right]} \quad , \tag{1}$$

Where the symbols have their usual meanings [5-8], and tangent loss (tan δ), which is the ratio of imaginary and real part of dielectric constant is given by:

$$\tan\delta = -\frac{\Omega_\lambda(q)\,\Gamma_\lambda(q,\omega)}{\left\{\omega^2 - \hat{\Omega}_\lambda^2(q)\right\}} \quad , \tag{2}$$

In the presence of resonant interaction the relaxation time (τ) with the phonon width (Γ) is related as [12]

$$\tau_\lambda(q) = \Gamma_\lambda(q) \Big/ \hat{\Omega}_\lambda^2(q) \tag{3}$$

In the experimental range of frequencies $\omega << \hat{\Omega}_\lambda(q)$; for the temperature, at which $\Omega_\lambda(q)\tau_\lambda(q) << 1$, i.e., the systems for which no relaxation effect is observed;

and using relation (3) the Eq. (1) reduces to

$$K(\omega) = \frac{8\pi N \mu^2 \Omega_\lambda(q)}{\hat{\Omega}_\lambda^2(q)} \quad , \tag{4}$$

$$\text{or } K(\omega) \cong \text{Constant} \Big/ (T - T_c) \quad ;$$

This is Curie- Weiss law.

and, using relation (3), Eq. (2) reduces to

$$\tan\delta = \frac{\Omega_\lambda(q)\tau_\lambda(q)}{\left\{1 + \Omega_\lambda^2(q)\tau_\lambda^2(q)\right\}} \tag{5}$$

$$\cong \omega\left(\alpha + \beta T + \gamma T^2\right) \Big/ (T - T_C)$$

Where α is harmonic and defect contribution, β and γ are the contributions due to three- and four- phonon anharmonic interactions of the lattice, in the absence of anharmonicity they have zero value.

From Eq. (5), for small values of tan δ, one obtains

$$\tau_\lambda(q) = 1 \Big/ \{\Omega_\lambda(q)\tan\delta\} \tag{6}$$

In the first approximation the temperature dependence of phonon frequency ($\hat{\Omega}_{\lambda T}$) and width $\Gamma_{\lambda T}$ can be approximated to [7]

$$\hat{\Omega}_{\lambda T}^2 = \alpha + \beta T + \gamma T^2 \quad , \tag{7}$$

$$\Gamma_{\lambda T} = \alpha' + \beta' T + \gamma' T^2 \tag{8}$$

3. RESULTS AND DISCUSSION

Figures 1 (a) and (b) show the temperature dependence of soft mode frequency and width for $KNbO_3$, in orthorhombic and tetragonal phase, respectively. These values have been calculated from the dielectric measurement data of reference [13], using Eqs. (4) and (2). Similar results were obtained from our own dielectric measurements [14], which have been shown in Figs. 1 (c) and (d). The mode softening is visualized near the transition temperature. Using Eq. (6), calculated temperature variation of relaxation time for $KNbO_3$ has been given in Figs. 2 (a - d). It has been observed that the relaxation time for $KNbO_3$ decreases with increasing temperature, in the observed range.

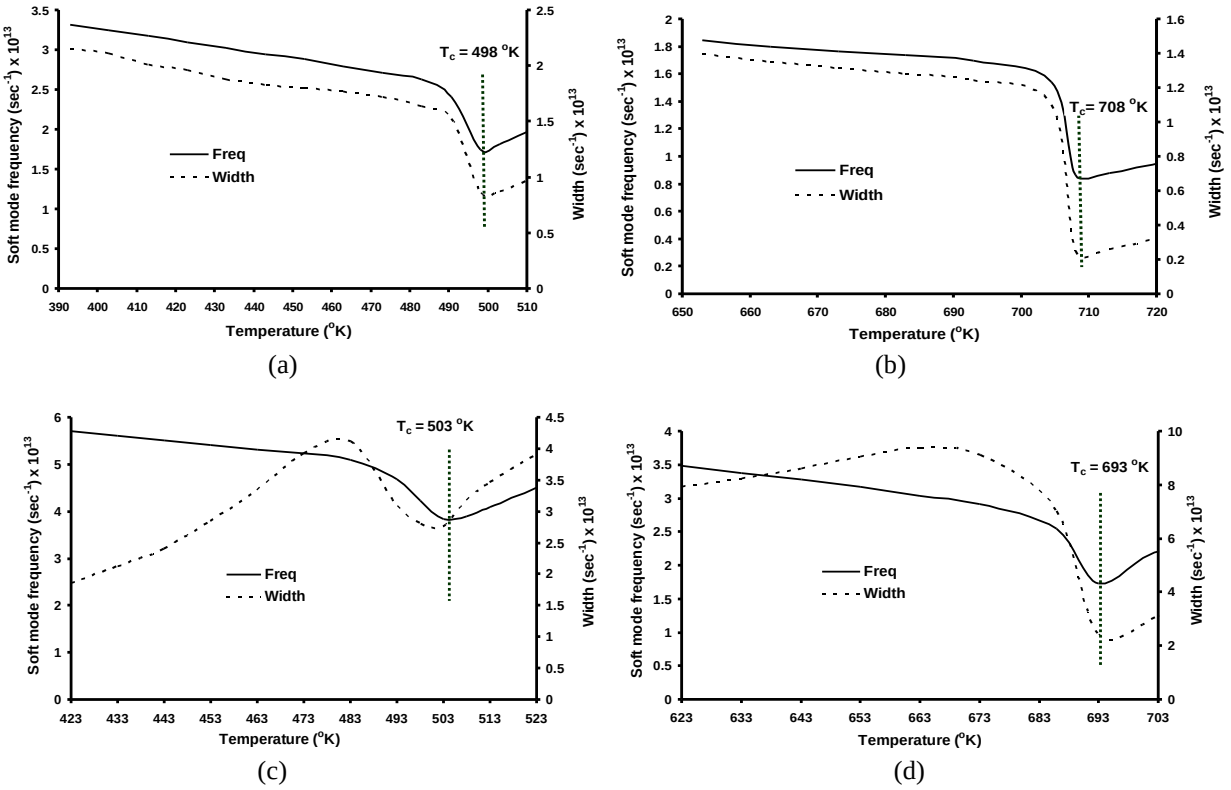
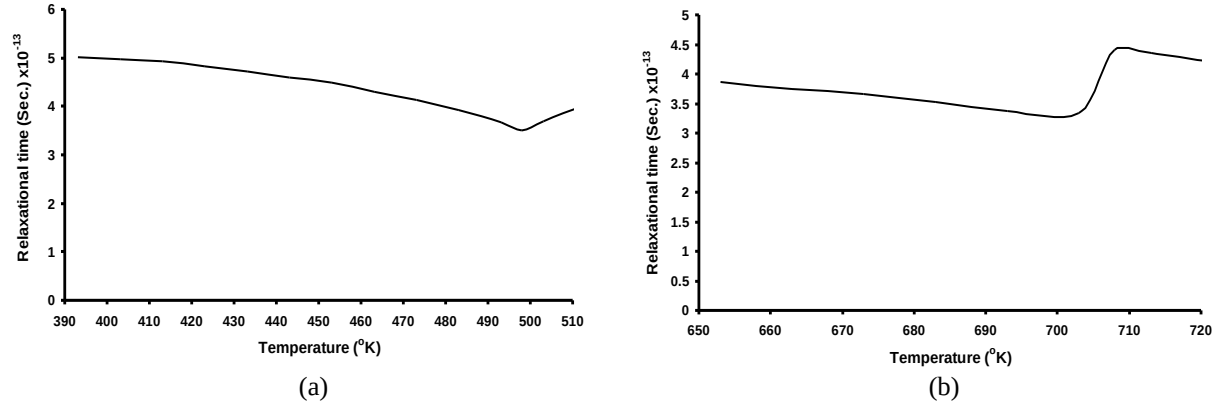
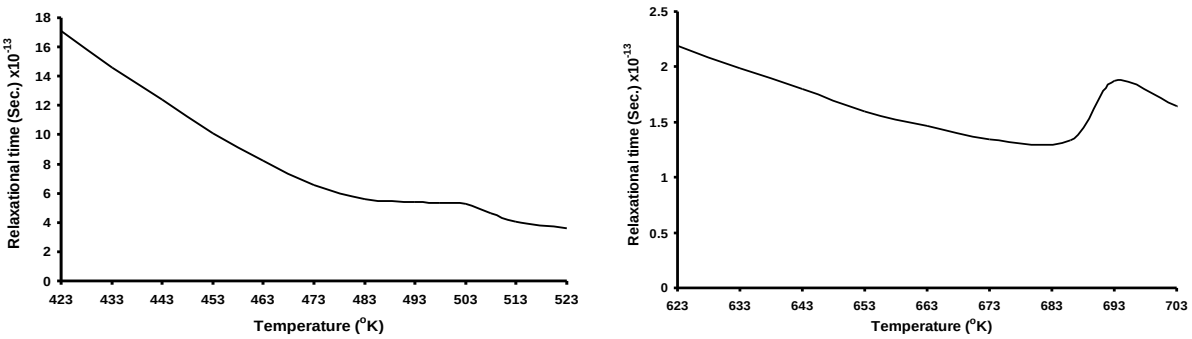


Fig. 1 Temperature dependence of soft mode frequency and width for $KNbO_3$ in (a) orthorhombic, (b) tetragonal phase (using data of reference [13], at 10 KHz) and (c) orthorhombic, (d) tetragonal phase (using our own data [14], at 10 KHz).





(c) (d)

Fig. 2 Temperature dependence of relaxation time for $KNbO_3$ in (a) orthorhombic, (b) tetragonal phase (using data of reference [13], at 10 KHz) and (c) orthorhombic, (d) tetragonal phase (using our own data [14], at 10 KHz).

Fitting Eqs. (7) and (8), with the reported [13] and our own results of dielectric measurements, calculated values of α, β, γ; α', β', and γ' for different phases of $KNbO_3$ have been given in Tables 1 and 2.

Table 1. Values of α, β, γ for different phases [*calculated from our own data (14)]

Parameter	**$KNbO_3$**			
	Orthorhombic		**Tetragonal**	
α (s^{-1})	-2.63×10^{28}	$*-1.59 \times 10^{28}$	-7.35×10^{27}	$*-4.60 \times 10^{27}$
β ($K^{-1}s^{-1}$)	1.26×10^{26}	$*.97 \times 10^{26}$	2.40×10^{25}	$*2.49 \times 10^{25}$
γ ($K^{-2}s^{-1}$)	-1.45×10^{23}	$*-1.22 \times 10^{23}$	-1.91×10^{22}	$*-2.50 \times 10^{22}$

Table 2. Values of α', β', γ' for different phases [*calculated from our own data (14)]

Parameter	**$KNbO_3$**			
	Orthorhombic		**Tetragonal**	
α' (s^{-1})	1.59×10^{14}	$*7.24 \times 10^{14}$	-2.59×10^{14}	$*-9.77 \times 10^{14}$
β' ($K^{-1}s^{-1}$)	-5.85×10^{11}	$*-3.51 \times 10^{12}$	8.57×10^{11}	$*3.02 \times 10^{12}$
γ' ($K^{-2}s^{-1}$)	6.03×10^{8}	$*4.37 \times 10^{9}$	-6.73×10^{8}	$*-2.12 \times 10^{9}$

The order parameter (A) is given by [15]

$$A^2 = \frac{9k_B}{m\omega_m^2}\left[T_c - \left\{1 - \frac{\hat{\Omega}}{\omega_m}\tan^{-1}\frac{\omega_m}{\hat{\Omega}}\right\}T\right], \quad (9)$$

where ω_m is the natural frequency of the system; and m is reduced mass of the system, given by

$$m = \frac{2m_o m_{Nb}}{m_o + m_{Nb}}; \quad \text{(for Nb-O system).}$$

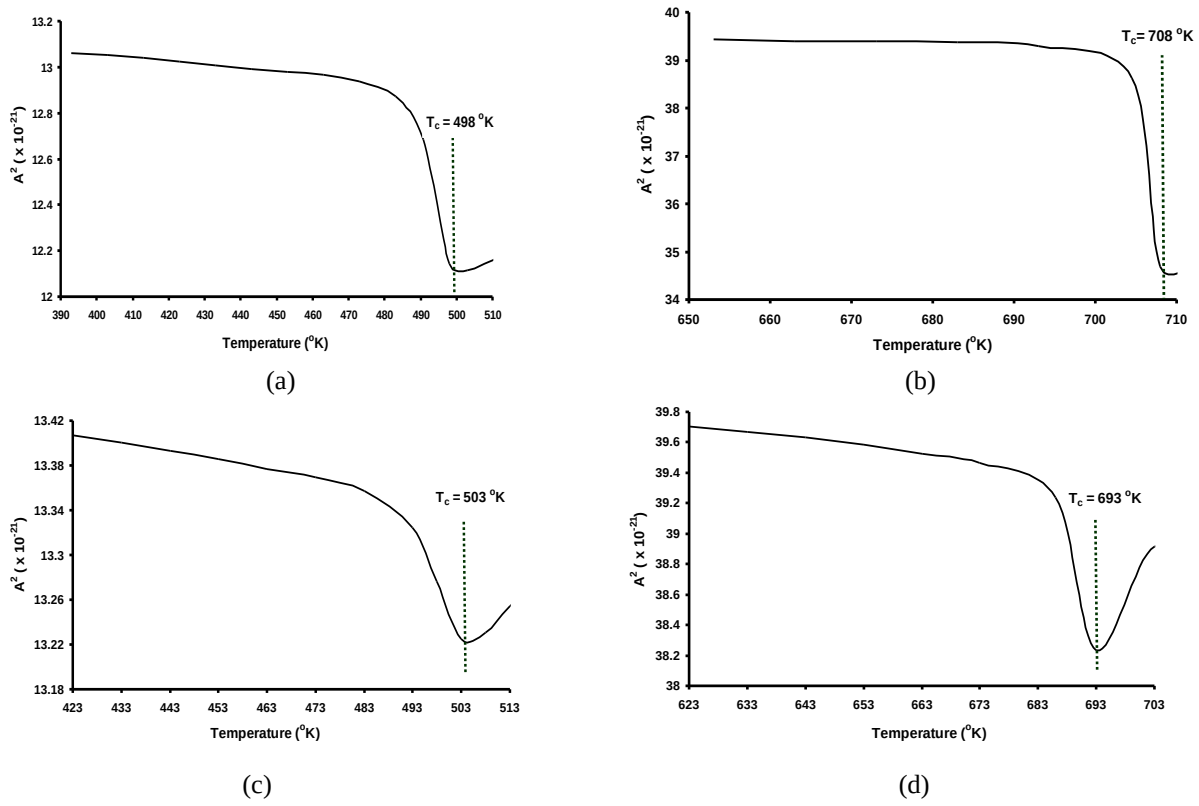


Fig. 3 Temperature dependence of A^2 for for $KNbO_3$ in (a) orthorhombic, (b) tetragonal phase (using data of reference [13], at 10 KHz) and (c) orthorhombic, (d) tetragonal phase (using our own data [14], at 10 KHz).

Table 3 Fourth order coupling coefficients for $KNbO_3$ (*calculated from our own data [14])

Parameter	$KNbO_3$	
$\Gamma_1 \times 10^{20}$ (J/m^4)	16.53	*54.92
$\Gamma_2 \times 10^{20}$ (J/m^4)	8.2	*27.46

Using the previously calculated values of $\hat{\Omega}$, A^2 has been calculated for $KNbO_3$, from Eq. (9), at different temperatures. The calculated temperature variation of order parameter (A^2) has been given in Figs. 3 (a – d). Fourth order coupling coefficients, Γ_1 and Γ_2, have been calculated for $KNbO_3$, and are given in Table 3. The fourth order coupling coefficient has been calculated, for $SrTiO_3$, by Silverman [16] with a different approach. Following Silverman [16], the fourth order coupling coefficient has been calculated for $KNbO_3$. Thus taking all the interactions into consideration, in the model Hamiltonian proposed by Pytte [4], and using Green's function method and Dyson's equation; expressions for phonon frequencies, widths and relaxation times, and hence for the dielectric constant and loss tangent have been obtained. The calculated expressions explain well the observed dielectric behavior of $KNbO_3$.

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