Theoretical study of ABO₃ type perovskite with reference to KNbO₃

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Received 2 April 2004; revised 28 June 2005; accepted 4 July 2005

One-dimensional model study has been carried out for KNbO₃ system by the model Hamiltonian proposed by B D Silverman. Third and fourth order coupling constants, change in coupling constants by doping, spring constants, shift and width have been calculated and the variation of polarization mode frequency and polarization per unit electric field with temperature ($T$) has been obtained for KNbO₃ system. The values obtained are also compared with the values obtained by the Hamiltonian proposed by Pytte.

Keywords: Perovskite, Polarization, Shift and width, Spring constants

1 Introduction

The compounds KNbO₃ and NaNbO₃ possess room temperature structures and both are based upon the mineral perovskite. Above 435°C temperature KNbO₃ exhibits a simple cubic structure. On cooling, the perovskite cell undergoes a deformation to tetragonal symmetry. Further cooling below 225°C results in another phase transformation and the perovskite cell possess monoclinic symmetry.

From the structural point of view, in ABO₃ perovskites there are three main features to be recognized. Firstly, the corner linked “O” octahedra are usually, only distorted to a minor extent, so that to a first approximation, we can treat them as rigid units. Secondly, off-centering of B-cation inside the octahedron can occur, which is associated with the phenomenon of ferro or anti-ferroelectricity. The sense of the displacement in one-octahedron is that, one corner displacements of the B-cations give chain dipoles; two corner give sheet dipoles and three corner a single three-dimensional dipole. Thirdly, the octahedron may tilt in a variety of configurations and have a considerable effect on the lattice parameters. Structure with tilted octahedral shows abnormal elasticities, whether or not dipole moments are present, and also have larger mean linear expansions than structures in which the orientation of the octahedral is fixed by symmetry. The cubic-tetragonal ferroelectric structural transition of KNbO₃ was distributed to the condensation of a soft lattice vibrational mode in which rigid oxygen-octahedral vibrate against the potassium and niobium atoms. The rigidity of these octahedra was ascribed to the strength of the oxygen-oxygen bonds compared with those between potassium-oxygen and niobium-oxygen. In the lower temperature tetragonal-orthorhombic and orthorhombic-rhombohedral transitions the oxygen octahedral remains rigid, the directions of their displacements are along [001], [011] and [111] in the tetragonal, orthorhombic and rhombohedral phases, respectively. These lower temperature structural transitions can also be attributed to the condensation of soft lattice vibrational mode. The magnitudes and directions of atomic displacements account for the observed changes in spontaneous polarization of KNbO₃, when the effective atomic changes are estimated from infrared and dielectric data. With these displacements, Cochran’s soft mode theory of ferroelectricity yields good values for the Curie constants describing temperature dependence of the dielectric constants. The temperature and frequency dependence of width in sodium potassium niobate mixed system is described elsewhere.

2 Model Description

The niobium and oxygen ions are coupled chains in the [100], [010], and [001] directions of the unit cell. The oxygen ions are constrained to move only perpendicular to the unit cell. The niobium ions are allowed a displacement in an arbitrary direction however, the component of motion along one chain is
taken to be uncoupled from motions along the other chains. We can also say that shear forces are neglected. The potassium ions are assumed to be fixed in position. This model will allow the motion of the niobium and oxygen ions to be described by a superposition of the modes of a linear chain.

The energy of a chain is:

\[
H_0 = -\frac{1}{2} \sum_i \left( \frac{aP^0}{2e_0} \right) E \exp \left\{ \left( \frac{aP^0}{2e_0} \right) \right\} \sum_i (x_i - u_i),
\]

\[
= \frac{1}{2} \sum_i (\frac{aP^0}{2e_0}) \sum_i (x_i - u_i),
\]

\[
= \frac{1}{2} \left( \frac{aP^0}{2e_0} \right) \sum_i (x_i - u_i),
\]

where, \( x_i \) and \( u_i \) are the displacements from equilibrium of the oxygen and niobium ions, respectively; \( n \) is the number of electronic charges on each ion; \( m \) the mass of each ion; \( K \) the spring constant coupling for nearest neighbours, \( E \) the applied electric field and \( P^0 \) is the polarization.

The Hamiltonian is next written in terms of the complex normal co-ordinate \( q_k \) is given by:

\[
x_i = \left( \frac{1}{2Nm} \right)^{1/2} \sum_k (q_k^0 - q_k^0) \exp(ikX_i^0),
\]

\[
u_i = \left( \frac{1}{2Nm} \right)^{1/2} \sum_k (q_k^0 + q_k^0) \exp(ikU_i^0),
\]

where, \( X_i^0 \) and \( U_i^0 \) are the equilibrium positions of the oxygen and niobium ions, respectively.

Substituting Eq. (2) into Eq. (1), we obtain:

\[
H_0 = \frac{1}{2} \sum_k \left[ P_k^0 P_k^0 + (\omega_k^0)^2 q_k^0 q_k^0 \right]
\]

\[
+ \frac{1}{2} \sum_{k=0} \left[ P_k^0 P_k^0 + (\omega_k^0)^2 q_k^0 q_k^0 \right]
\]

\[
+ \frac{1}{2} \left[ (p_0^0)^2 + \omega_k^0 (q_0^0)^2 \right] - neE_i \left( \frac{2N}{M} \right)^{1/2} q_0^0,
\]

\[
\]

where, \( \omega_0 \) is the natural frequency of the optical mode \((k=0)\).

Applying local field term:

\[
E_i = \left( \frac{1}{b} \left[ E_i^2 + \frac{a}{2e_0} P \right] \right)^{1/2}
\]

And polarization term:

\[
P^2 = \left( \frac{ne}{8\pi^3} \right) \left( \frac{2N}{m} \right) q_0^0
\]

For soft mode frequency Eq. 5 takes form

\[
\omega_0^2 = \omega_0^2 - \frac{(ne)^2 a}{4e_0 md^3 b} \text{ or } \omega_0^2 = \omega_0^2 - V_0^2
\]

A transition to the ferroelectric state occurs when the polarization mode becomes unstable \((\omega_0^2 = 0)\). This is believed due to the cancellation of the short-range repulsive forces by the dipolar forces.

3 Imperfection Damping

Damping is due to the presence of imperfections in the lattice, e.g. impurities, dislocations, local strains etc. These imperfections will couple the polarization mode to other modes and provide a mechanism for the scattering of energy out of the driven mode.
Let us assume that a number of springs along a chain have modified spring constant \( K_1 \) due to the presence of interstitials or local strain. These modified springs are located randomly along a chain. The change in the Hamiltonian due to the presence of these springs is:

\[
H_{\text{imp}} = \frac{1}{2} K_1 \sum_{i=0}^{n} (x_i - u_{i+1})^2 + \frac{1}{2} K_1 \sum_{i=0}^{n} (x_i - u_{i-1})^2, \quad K_1 = K_t - K.
\]  

Considering the Hamiltonian proposed by Silverman, we have calculated the expressions for shift and width as follows:

\[
H = \frac{1}{2} \left( \sum_K p^2_k p^2_{-k} + \omega^2_k q^2_k q^2_{-k} \right) + \frac{1}{2} \left( \sum_{k=0}^{n} p^0_k p^0_{-k} + \omega^2_k q^0_k q^0_{-k} \right) + \frac{1}{2} \left( p^2_0 + \omega^2_0 q^2_0 + H_{\text{imp}} \right).
\]  

\[
H_{\text{imp}} = \left( \frac{K_1}{Nm} \right) \sum_K D(k) q^2_k q^2_{0}
\]

Solving the Hamiltonian by Green's function method we have:

\[
\omega^2_0 q_0 - \omega^2 q_0 + \frac{2K_1}{Nm} \sum D(k) q^2_k (t) \times \exp i(\omega^2_k - \omega^0_k) t = 0 \]  

\[
(\omega^2 - \omega^2_k) q^2_k (t) = -\frac{2K_1}{Nm} \sum D(k) q_0 \exp i\omega_0 t
\]

\[
q^2_k (t) = -\frac{2K_1}{Nm} \sum D(k) q_0 \exp i\omega_0 t \left( \frac{1}{(\omega^2 - \omega^2_k)} \right)
\]

Now putting value of \( q^2_k (t) \)

\[
(\omega^2 - \omega^2_k) q_0 (t) - \frac{2K_1}{Nm} \sum D(k) \left( \frac{1}{(\omega^2 - \omega^2_k)} \right) q_0 (t) = 0
\]

\[
\omega^2 = \omega^2_0 + \Delta(\omega) + i\Gamma(\omega)
\]

where,

\[
\Delta(\omega) \rightarrow \text{Shift and } \Gamma(\omega) \rightarrow \text{Width}
\]

\[
\Delta(\omega) = \left( \frac{2K_1}{Nm} \right)^2 \sum |D(k)|^2 R \left( \frac{1}{(\omega^2 - \omega^2_k)} \right).
\]

\[
\Gamma(\omega) = \left( \frac{2K_1}{Nm} \right)^2 \sum |D(k)|^2 \frac{\pi}{2\omega_k} [\delta(\omega - \omega^0_k) - \delta(\omega + \omega^0_k)].
\]

\[
\omega_0^2 = 5 \times 10^{25} / \text{Sec}^2 > \omega^2 \approx 5 \times 10^{22} / \text{sec}^2.
\]

The width (damping constant) \( \Gamma(\omega) \) can be evaluated by going to the limit of a chain of infinite length. The damping constant in the microwave frequency region is found to be:

\[
\Gamma(\omega) = \left( \frac{4K_1}{Nm} \right) \left( n/2N \right) \left( \frac{\omega}{(\omega^0)^3} \right),
\]

The loss tangent may be written as given by Silverman:

\[
\tan \delta = \frac{\Gamma}{\omega_t^2 - \omega^2}, \quad (\omega << \omega_T)
\]

Using Eqs. (13), (14) and (15), value of \( \Gamma, \Delta \) and change in spring constant \( (K^1) \) can be evaluated. These values are found

\[
\Gamma = 13.97 \times 10^{22} \text{ Hz},
\]

\[
\Delta = 6.48 \times 10^8 \text{ Hz},
\]

\[
K^1 = 1.2915 \times 10^{22} \text{ joule/m}^2, \text{ for KNbO}_3 \text{ system}
\]

Now considering Silverman expressions, we have calculated the frequency of the transverse polarization mode, soft mode frequency, fourth-order coupling constants and spring constant for KNbO3 in paraelectric phase.
Frequency of the transverse polarization mode is given by:

\[ \omega_i^2 = \frac{(ne)^2 ac}{4e_o md^2 b} (T - T_c) \]  \hspace{1cm} \text{... (17)}

Soft mode frequency is given by:

\[ \omega_0^{02} = \frac{(ne)^2 a}{4e_o md^2 b} \]  \hspace{1cm} \text{... (18)}

After putting values of \( a, e, c, d \) etc. from literature\(^8\), the value of frequencies comes out:

\[ \omega_i^2 = 6.63 \times 10^4 n(T - T_c)^{1/2} \text{Hz}, \omega_0^{02} = 1.9245 \times 10^{28} n^2 \text{ Hz.} \]  \hspace{1cm} \text{... (19)}

Variation of Polarization mode frequency \( (\omega_i^2) \) with temperature \( (T) \) have been evaluated and plotted in Fig. 1

4 Anharmonic Damping

We consider the damping due to third-order anharmonic interactions. Pauli\(^9\) calculated the effect of a third-order anharmonic interaction on damping of a linear chain of equal masses.

The third-order anharmonic energy of a chain is:

\[ H_{\text{anh}} = \frac{1}{4} \beta \sum_i [ (x_i - u_{i,1})^4 + (x_i - u_{i,1})^4 ] \]  \hspace{1cm} \text{... (20)}

where, \( \alpha \) is the third order coupling coefficient.

The equation of motion for polarization mode coordinate is:

\[ q_i^0 + (\omega_i^2 + i \Gamma) q_i^0 = (ne/b) E \exp(iot(2N/m))^{1/2}, \]  \hspace{1cm} \text{... (21)}

where,

\[ \Gamma = [64(2)^{1/2} \alpha^2 kT/m^3 (\omega_0^{05})^5 \omega] \]  \hspace{1cm} \text{... (22)}

Value of \( \alpha \) for KNbO\(_3\) comes out to:

\[ \alpha = 3.0414 \times 10^6 \text{ joule/m}^3. \]

The fourth-order anharmonic energy of a chain is:

\[ H_{\text{anh}} = \frac{1}{4} \beta \sum_i [ (x_i - u_{i,1})^4 + (x_i - u_{i,1})^4 + c.c. ] \]  \hspace{1cm} \text{... (24)}

where, \( \beta \) is fourth-order coupling constant.

Fourth-order coupling constant value for KNbO\(_3\) system comes out:

\[ \beta = \frac{m^2 c (\omega_0^{05})^4}{48K_\beta} = 2.624 \times 10^{-22} n^4 \text{ joule/m}^4 \]  \hspace{1cm} \text{... (25)}

Spring constant is found to be:

\[ K = \frac{(ne)^2 a}{16e_o d^2 b} = 2.18 \times 10^2 n^2 \text{ joule/m}^2 \]  \hspace{1cm} \text{... (26)}

Already we have calculated the change in spring constant, which is:

\[ K^1 = 1.2915 \times 10^2 \text{ joule/m}^2. \]
The number of electronic charges per ion is found to be \( n \approx 0.7 \) (approx.).

The line polarization of a chain is:

\[
P_s = \frac{\partial F}{\partial E_0} = \frac{2(e)^2 E_0 N}{m (\omega_0^2)} \cdot kT \cdot \frac{\beta E_0 N}{m (\omega_0^2)^2}
\]

which may be written as

\[
P_s = \frac{2(ne)^2 E_0 N}{m(4K/m)_{\text{eff}}} \cdot \frac{Ps}{E_0} = \frac{2(ne)^2 N}{m(4K/m)_{\text{eff}}}
\]

Using Eq. 28 variation of polarization per unit electric field \((Ps/E_0)\) with temperature \((T)\) has been shown in Fig. 2.

### 4 Results and Discussion

Using experimental results\(^{10}\) on dielectric constant and loss tangent for \(K_{1-x}Na_xNbO_3\)(Ref. 11), third and fourth-order coupling constants and anharmonic constants have been calculated. The values of coupling constants have been reported here. Temperature dependence of polarization mode frequency with temperature has been plotted in Fig. 1. The temperature dependence of polarization have been calculated and plotted in Fig. 2. Figures 1 and 2, show the anomalous behaviour at transition temperature, indicating the dominant role of soft mode in regards to phase transition. The values thus calculated as reference to one-dimensional model to \(KNbO_3\), are approximately justifying the values\(^{11}\) calculated with the help of Model Hamiltonian proposed by Pytte\(^{13}\).

### References