Raman studies of antiferroelectric phase transition in lead ytterbium niobate based perovskite compound

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Abstract.

The change in inverse dielectric susceptibility ($\chi^{-1}$) associated with the phase transition is related to the hard-mode frequency shift ($\omega_0$) as \( \Delta(\chi^{-1}) = R \omega_0^2 \), where the proportionality constant R of the equation can be determined from the experimental data. This relation of \( \Delta(\chi^{-1}) = R \omega_0^2 \) between the changes in $\chi^{-1}$ and $\omega_0$ was verified for the antiferroelectric phase transition observed in 0.94PYN [Pb(Yb1/2Nb1/2)O3]-0.06PT[PtO3].

1. Introduction

When the phonon frequency changes in the phase transition are within 2% of their harmonic frequencies, perturbation theory can be applied to predict a coupling between an anomalous phonon of Einstein mode frequency $\omega_k$ and order parameter $Q$, leading to \( \Delta(\omega_k^2) = A Q^m + B Q^{2m} \) with $m=1$ or $2$ as determined from symmetry restrictions [1]. For optically active modes we have $A > B$ in most cases, when this Einstein mode is defined as the hard-mode.

Hard-mode spectroscopy [1] is applied to analyze the phase transition on the basis of phonon frequency shifts. It has been applied to phase transitions of Pb(Sc1/2Ta1/2)O3 [2], quartz [3], Pb(Zr0.52Ti0.48)O3 [4], (Sr0.70Ca0.30)TiO3 [5] and La1/3LiTiO3 [6]. Local bonds associated with the site symmetry change can be changed in bond length, bond angle, etc. in the phase transition, when the corresponding phonon modes will change in frequency and mode symmetry accordingly. Hard-mode spectroscopy makes use of this change represented by [1] $\Delta(\omega_k^2) \propto Q^2 \propto \Delta \chi^{-1}$.

In the present study of ours, an antiferroelectric system of 0.94PYN[Pb(Yb1/2Nb1/2)O3]-0.06PT[PtO3] is studied for the experimental verification of this hard-mode relation.
2. Nondegenerate hard-mode

Phase transition can be assumed to change the potential energy of the crystal in the form

\[ V(Q, q) = \frac{1}{2} \omega_0^2 q^2 + \frac{1}{2} Aq^2Q^2 \]

where \( \omega_0 \) is the phonon frequency in the Einstein solid approximation of Slater dynamics \[7\], \( Q \) the order parameter, and \( q \) the phonon coordinate. We can derive \[8\] a relation between the hard-mode frequency shift \( \omega_Q \) and the change in inverse dielectric susceptibility \( \Delta(1/\chi^{'}) \):

\[ \omega_Q^2 = \frac{N e^2}{m} \left( \frac{1}{\chi_T^s} - \frac{1}{\chi_E^s} \right) = A Q^2 \]  

(1)

where subscripts \( T \) and \( E \) represent phases of nonzero \( Q \)(below \( T_C \)) and \( Q = 0 \) (above \( T_C \)) respectively. This expectation will be examined in our antiferroelectric system of \( \text{Pb}(\text{Yb}_{1/2}\text{Nb}_{1/2})\text{O}_3\)-\( \text{PbTiO}_3 [\text{PYN-PT}] \).

3. Experimental results

Perovskite structures can be shown to include \( T_d(\text{Pb}), O_h(\text{Yb}, \text{Nb}, \text{and Ti}) \), and \( C_{4v}(\text{O}) \) sites in the paraelectric phase, but the antiparallel displacement of \( \text{Pb} \) ions changes the site group symmetries in the antiferroelectric phase. This antiferroelectric ordering reduces \( T_d \) symmetry, for example, to \( 3C_{2v} \) site symmetries. This symmetry change also brings about a change in vibrational modes, which can be analyzed by use of correlation methods. There are four Raman active modes \( (A_{1g} + E_g + 2F_{2g}) \) in the \( Fm\overline{3}m \) symmetry of PYN-PT system \[9, 10\]. With the change in site group symmetry, the correlation table of compatible symmetry transformations predicts splittings of degenerate vibrational modes. The nondegenerate \( A_{1g} \) mode in \( T_d \) site symmetry will be transformed to the \( A_g \) mode in \( C_{2v} \) site symmetry and three degenerate modes are expected to exhibit splittings. Doubly degenerate \( E_g \) mode may be separated into two \( A_g \) modes, and triply degenerate \( F_{2g} \) mode will be split into \( B_{1g} + B_{2g} + B_{3g} \) modes. Previous structural studies \[9-13\] and our Raman scattering spectra of PYN-PT at different temperatures confirm these symmetry changes of the antiferroelectric phase transition. The degenerate modes need a more complete analysis of polarization dependence using a single crystal sample, and the Raman spectroscopic changes of nondegenerate modes will be more preferable for our ceramic polycrystalline samples to be used in comparison with the dielectric measurements for analyzing the phase transition of our PYN-PT system.

The processing details for growing our polycrystalline PYN-PT samples and characterization of the structures have been reported elsewhere \[9-10\]. Raman spectra of our samples were obtained by a double-grating monochrometer (Jobin Yvon U-1000) and a water-cooled PM tube in the backscattering geometry. \( \text{Ar}^+ - \text{Kr}^+ \) mixed gas ion laser was used for excitation at output power of 200mW and wavelength of 488.0 nm. The sample was heated in a heating stage (Linkham) from 303K to 593K for measuring the temperature dependence of Raman spectra. The Peakfit software program (Jaden Scientific) was used for deconvolution of the Raman bands. In the best fit routine, peak wave number, full width at half maximum and peak intensity for all the component of Raman bands are taken as unconstrained variables, with each component band assumed as a symmetric Lorenzian contribution. The sample specimens were coated for electrodes by silver paste. Impedance/gain-phase analyser (Hewlett Packard 4194A) was employed for measuring dielectric constant at 100Hz as a function of temperature.

Figure 1 shows Raman spectra of the PYN-PT sample obtained in both paraelectric and antiferroelectric phases. There are two narrow and two broad Raman bands observed at 533K, when
PYN-PT has Fm$\overline{3}$m structure of paraelectric phase. The Raman band at around 800 cm$^{-1}$ is assigned to the $A_{1g}$ mode of the octahedral perovskite unit [12, 13]. The Raman band below 100 cm$^{-1}$ may be assigned to the $F_{2g}$ lattice mode, because heavy Pb atoms at the $F_{2g}$ symmetry site contribute to the mode displacement resulting in the low vibrational frequency due to large reduced mass [11-14]. A very broad Raman band at around 300 cm$^{-1}$ may be another $F_{2g}$ mode, because the band exhibits a three-component splitting below the antiferroelectric transition temperature.

Fig. 1. Raman spectrum of PYN-PT at 533K (paraelectric phase) and 303K (antiferroelectric phase). Laser fluorescence lines(x) are not completely filtered.

For a quantitative analysis on the hard-mode we choose a well defined $A_{1g}$ Raman band to measure the hard-mode shift. Although a $B_{1g}$ band near 200 cm$^{-1}$ also shows temperature dependence as large as the $A_{1g}$ Raman mode, it is not convenient to be applied for the nondegenerate hard-mode studies due to the correlation splitting effect from the $F_{2g}$ Raman mode. This mode can also have a nonlinear coupling with other phonons, because the phonons of this frequency range can be easily influenced by the symmetry breaking excitations of external vibrations. For that reason we leave the $B_{1g}$ band near 200 cm$^{-1}$ out of our present concern until a full solution derived relation is available for degenerate hard-modes.

Fig. 2. Temperature dependence of $\omega^2$ in PYN-PT for $A_{1g}$ Raman band across the antiferroelectric phase transition at $T_N$.

In the vibrations of the octahedral unit in the PYN-PT sample the $A_{1g}$ mode is involved directly with the bonds between the B site cation and the nearest neighbor oxygens. The ordering displacement of B site cations in the octahedra can thus be confirmed [12-15] by a quantitative analysis of the $A_{1g}$
Raman band. The square values of the band peak wave numbers are plotted as a function of temperature in Fig. 2. The frequency shift of this hard-mode is observed to increase discontinuously at 493K. This frequency shift of the $A_{1g}$ Raman band is related to the hard-mode frequency shift $\omega_h$. If the wave number of this Raman mode at $T>493K$ (paraelectric phase) is assigned to $\omega_e$ and to $\omega_r$ at $T\leq493K$ (antiferroelectric phase), the hard-mode frequency shift $\omega_h$, can be obtained as a function of temperature in the antiferroelectric phase.

![Graph showing inverse dielectric susceptibility in PYN-PT](image)

Fig. 3. Inverse dielectric susceptibility ($\chi^{-1}$) in PYN-PT as a function of temperature across the antiferroelectric transition at $T_N=493K$ (*), and temperature dependence of $\omega_h^2$ equivalent to $Q^2$ (°), where $Q$ represents the order parameter of the phase transition. Inset shows temperature dependence of the ratio $\Delta(\chi^{-1})/\omega_h^2$ across the antiferroelectric transition in PYN-PT.

Dielectric constant measured as a function of temperature at 100Hz is shown in Fig. 3. Since very low dispersion is expected in this low frequency region, this dielectric data can be taken as an asymptotic representation of static dielectric constant. Temperature dependence of inverse susceptibility presented in Fig. 3 confirms that our 0.94PYN-0.06PT system has the first order transition of antiferroelectric ordering. This result of ours, in agreement with the previous studies [9-15], implies that the original soft-mode theory for continuous phase transitions may not be applicable to this first order phase transition. However, the essentials of the soft-mode theory can be still borrowed in our hard-mode frequency shift dealing with the first order transition. To test the applicability of our remodelling to the first order transition, the order parameter in this phase transition may be defined from Fig. 3, where the temperature dependence of $\omega_h^2$, proportional to $Q^2$, is presented. The linear proportionality relation between $\Delta(\chi^{-1})$ and $Q^2$ can be seen from Fig. 3. To make it quantitative, we evaluate the proportionality constant from Eq. (1). Let $R$ denote the proportionality constant of the hard-mode relation Eq. (1), which can be rearranged to give

$$\frac{\Delta(\chi^{-1})}{\omega_h^2} = \frac{m}{Ne^2} = R \, .$$

(2)

This proportionality constant is presented in Fig. 3, where we can see a constant value of $R$ in the antiferroelectric phase ($T<493K$), compatible with the hard-mode frequency shift behavior. This constant value $R$ is evaluated to be $-1.6 \times 10^{-7} \text{cm}^2 \pm 1.6 \times 10^{-8} \text{cm}^2$, whereas in the region $T>493K$
this constant \( R \) can not be defined because the hard-mode frequency shift \( \omega_Q \) is so defined as to emerge with the phase transition order parameter. With our system exhibiting the first order phase transition, precursor domains may be formed in the vicinity of the transition point [14, 15]. The formation of heterogeneous domains invalidates the present hard-mode frequency shift model, where the dielectric anomaly of phase transition is assumed to be derived from a linear response of the uniform hard-mode shift. Except this narrow region of phase transition discontinuity our simple approach based on Slater dynamics can be verified to be working well as seen from Fig.3.

4. Discussions

Our work is concerned with a phase transition represented by a site symmetry breaking which effect vibrational structures, where the governing interactions can be approximated by an Einstein oscillator mode coupling with a local order parameter of the phase transition. The dielectric anomaly of phase transition is also assumed as governed by a linear response of the hard-mode shift. The proportionality constant can be seen to have a dimension as given from Eq. (2).

\[
R = \frac{\Delta(\chi^{-1})}{\omega^2} = \frac{m}{Ne^2} \sim \frac{[\text{kg}]}{[\text{C}^2/\text{m}^2]} = \frac{[\text{kg} \times \text{m}^2]}{[\text{C}^2/\text{m}]} \tag{3}
\]

The denominator \([\text{C}^2]/[\text{m}]\) has the dimension of electrostatic binding energy, whereas the numerator \([\text{kg} \times \text{m}^2]\) has the dimension of moment of inertia. From this dimensional relation, the proportionality constant \( R \) may be considered as a measure for the moment of inertia of dipoles induced by a small change of the binding energy due to the atomic rearrangements. This proportionality constant may be expected to increase with cooperative ordering of dipoles. That is, the proportionality constant will be a measure of ordering for dipoles.

It will be interesting to examine how the Slater dynamic parameters \((N, m, e)\) determining the proportionality constant \((R)\) should vary with the phase transition. Fig.3 suggests a close relation between the hard-mode shift \((\omega^2)\) and the dielectric constant anomaly \((\chi^{-1})\) of phase transition.

Previous studies could reveal the cationic ordering at B sites by studying the frequency change of the \(A_{1g}\) Raman mode [14, 15]. Temperature dependence of the hard-mode frequency shift \(\omega_Q\) is captured in Fig.3, where the frequency shift of the \(A_{1g}\) Raman mode was converted to the hard-mode frequency shift to be compared with the emerging order parameter of phase transition. We can thus support the view that the cationic ordering at B sites may be responsible for antiferroelectric ordering in PYN-PT.

Only oxygen ions are expected to make displacements in the \(A_{1g}\) mode if a perfect \(Fm\overline{3}m\) symmetry is maintained. However, with the cationic ordering displacements, B site cations can be also involved in the \(A_{1g}\) mode excitation so that the effective mass may be increased in the \(A_{1g}\) mode vibration with the antiferroelectric ordering, and the vibrational frequency of the \(A_{1g}\) mode is expected to decrease accordingly [14, 15]. The \(A_{1g}\) Raman mode can thus be a useful probe for the cationic ordering at B sites in the perovskites. Frequency of the \(A_{1g}\) mode is observed to decrease in the orthorhombic phase in comparison to that in the paraelectric cubic phase as depicted in Fig.2. This frequency shift to lower frequencies also implies the B-site cations may be displaced off the symmetry center in the orthorhombic phase. Dipole moments of PYN-PT are expected to be coupled with volume change and strain, so the antiferroelectric PYN may also become ferroelastic. For a more confirming picture of structural details
in PYN-PT such as antiparallel displacements of the off-center cations at B sites, high resolution structural studies are required in the vicinity of the phase transition.

5. Conclusion
The hard-mode shift representation of the site symmetry breaking local displacements is the underlying assumption of the present extension. A proportionality constant of the hard-mode relation can be interpreted in terms of a rotational mobility associated for ordering dipoles. Hard-mode studies of PYN-PT antiferroelectrics confirm the cationic ordering at B sites to play an important role in the antiferroelectric phase transition of perovskite systems. The B-site cationic ordering and thus polarization may be closely related to the relaxor–type (volume) strain response in PYN-PT system.

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