Ferroelectric two-level system and phase transition temperature monitoring of $\text{SrTiO}_3$
using dielectric resonance modes

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The ferroelectric phase transition temperature of a single crystal $\text{SrTiO}_3$ cylindrical puck inserted into a cylindrical copper cavity has been measured around 51 K using quasi $T_{E_{m,1,1}}$ and quasi $T_{M_{m,1,1}}$ electromagnetic modes. The observed results of such dielectric spectroscopy may be explained by implementing a quasi-harmonic approximation of phonons in the incipient ferroelectric crystal $\text{SrTiO}_3$ lattice. The resonant modes act as very sensitive probe by implementing measurements of Q-factor, transmission or frequency shift when cooling down to low temperatures around a few Kelvin. The resonator dielectric losses reveals different crystal unit structure states and ferroelectric phase transition in continuous cooling. The ferroelectric phase transition initiates a spontaneous polarization ($P_s$) forming a double-well potential in each crystal unit causing a two-level systems, which creates extra loss and changes the transmission characteristics and Q-factors of the modes. This process is able to describe resonator properties over a broad range of frequency. Landau’s theory of correlation length supports the reported observations as the implication of phonon wave vector $q_c = 0$ of central ion in crystal unit symmetry regarding soft-mode.

INTRODUCTION

As a microscopic view, crystal structure and collective dynamics of lattice (phonon vibration) have an important role on dielectric polarization and the possibility of ferroelectric (FE) phase transitions\cite{1,2}. In this work we have implemented the quasi $T_{E_{m,1,1}}$ (transverse electric) and quasi $T_{M_{m,1,1}}$ (transverse magnetic) modes of microwave dielectric resonator\cite{3,7} as a probing tool to monitor crystal asymmetry and such a FE phase transition with respect to temperature. Phonon quasi-harmonic approximation allows the analysis of crystal asymmetry and phase transitions as a simple perturbation theory. Any asymmetry in the crystal lattice changes the line width and on resonance transmission of the resonance modes, and hence forms a sensitive measurement while continuous cooling. We measured the phase transition temperature and structural asymmetry of a white opaque $\text{SrTiO}_3$ (STO) cylindrical crystal\cite{8} specimen using this process. The asymmetry in the crystal unit due to soft mode phonons, which create a dielectric anomaly in macroscopic state contributing to imaginary part of relative permittivity\cite{2,9}, and immediately changes the observable quantities like Q-factor, transmission or frequency shift with respect to temperature. Hence the excited dielectric resonance mode in the microwave regime acts as a frequency transducer of a conversion of the change of the lattice structure of the crystal into the most precise physical and measurable quantity which is frequency, thus works as a powerful sensitive tool for monitoring the nature of structural asymmetry of crystal unit and phase transitions\cite{10}.

$\text{SrTiO}_3$ crystallizes in a Perovskite structure of space group Pm3m with lattice constant 3.905 Å in cubic symmetry where the $\text{Ti}^{4+} - \text{O}^{2-}$ distance is 1.952 Å\cite{11,12}. Incipient FE states\cite{13} arises from paraelectric (PE) phase as a regular order-disorder or displacive structural phase transition of the crystal, and is defined as 1$^{\text{st}}$ order (first-order) or 2$^{\text{nd}}$ order (second-order) FE state according to the phase transition characteristics\cite{14}. The FE free energy equilibrium state’s qualitative agreement with dielectric polarization is explained by Landau’s theory\cite{15}. This phenomenological parameter\cite{15}, the dielectric polarization\cite{11}, reveals spontaneous polarization as an order-disorder parameter of double-well potential\cite{2,10} in the FE phase and shows rapid decrease of dielectric resonance mode’s Q-factor.

The crystal structure changes to lower symmetry in FE phase transitions, and the center-symmetric titanium ion in the octahedral structure of the crystal unit is substantially displacive instead of diffusive\cite{17,18}. The quasi $T_{E_{m,1,1}}$ modes and quasi $T_{M_{m,1,1}}$ modes are very sensitive to this FE phase transition produced spontaneous polarization due to soft mode produced displacement of center-symmetric ion of the crystal unit\cite{12}. This spontaneous polarization\cite{19} creates dielectric dipoles, and contributes to the net dielectric polarization of the crystal showing shift of frequency in the frequency-temperature characteristic curves. Characteristically the spontaneous polarization is a signature of FE phase, and cause of rapid decrease of Q-factor\cite{20}. Hence this incipient FE phase transition temperature can be monitored using
the WG modes as a phenomenon of the spontaneous polarization [14, 15].

Quasi-harmonic approximation of phonon [2, 21] is required to adapt the anharmonic states of FE asymmetry as a damped harmonic oscillation of the crystal lattice. Soft-mode [9, 15] and Hard-mode [16, 22] frequency shifts are described to explain the measurement of phase transition temperatures, and thoroughly monitored in terms of observable quantity Q-factor, transmission amplitude, and frequency shifts from the excited whispering gallery modes. Theoretical explanations support anharmonic approximation in FE phase showing its explicit temperature dependency. Experimental measurements are performed to validate the theoretical model with FE phase transition characteristics including two-level system of double-well potential in the lattice.

**SUPPORTING THEORY IN BRIEF**

**Spontaneous Polarization and Phase Transition Mechanisms with Temperature**

The phenomena of PE to FE phase transitions are explained on the basis of Gibbs free-energy state of the crystal lattice and the divergence of Landau correlation length with respect to temperature (T). In this way, the dielectric behaviour with respect to free-energy $\phi$ in the lattice [1, 23] can be justified qualitatively [14]. The expression of this free-energy in terms of phenomenological parameter (dielectric polarization) [2, 15] may be written in the form of Taylor expansion with crystal symmetry constants $\alpha_0, \alpha_{11}$ and $\alpha_{111}$ in absence of external electric field stress ($E=0$) as [2]:

$$
\phi = \phi_0 + \frac{\alpha_0 (T - T_0) P_x^2}{2} + \frac{\alpha_{11} P_x^4}{4} + \frac{\alpha_{111} P_x^6}{6}
$$

(1)

The free-energy term $\phi$ is the sum of PE phase free-energy $\phi_0$ and FE phase energy in terms of polarization ($P(T)$) arises from small displacement of central ion of the octahedral structure of the Perovskite crystal due to cooling. As an one dimensional model, only x-component of $P$ is considered in this simple equation. The term $\phi$ is independent of polarization sign. The characteristics of this free-energy is schematically shown in Fig. 1 in arbitrary unit with symmetry constants $\alpha_0 = 1$, $\alpha_{11} = -1$ and $\alpha_{111} = 1$ for simplicity. Landau theory describes that the correlation length characteristics with respect to phenomenological parameter $P(T) [2, 15, 24, 27]$ reveals equilibrium energy state $\frac{\partial^2 \phi}{\partial P_x^2} = 0$ at the ferroelectric phase transition temperature $T_c$ of the crystal [1, 2, 15, 24, 27]. Applying this equilibrium condition of FE free energy, the spontaneous polarization $P_s$ shows two minima at $P_x = \pm P_s$ and a single maximum at $P_x = 0$ in case of $T \leq T_0$ and $T = T_0$, respectively. On the other hand, only a single minimum appears when $T \geq T_0$ (Fig. 1).

There is a continuous phase transition (second-order) at $T = T_c$. At the lower temperature ($T < T_0$), $P_s$ has the temperature dependence (calculated from equation-1 neglecting the higher order terms than $P_x^4$) as:

$$
P_s = \pm \left( \frac{\alpha_{11} (T - T_0)}{\alpha_{111}} \right)^{\frac{1}{2}}
$$

(2)

A first-order phase transition could appear at $T \leq T_c$ with $\alpha_{11} < 0$ showing a discontinuity in the characteristic curve of some crystals, until the complete disappearance of FE phase with rising temperature higher than $T_c$. This temperature $T_c \geq T_0$ is known as 1st order phase transition temperature. In this case, the expansion of free energy must be taken to higher order terms than $P_x^4$ for calculations [16].

**Mechanisms of Phonon and core-shell model**

All the lattice vibrations can be classified as acoustic phonon or optical phonon. In the lattice, atoms of the crystal unit cell vibrate in phase in acoustic mode. In the case when the neighbouring atoms are out-of-phase from each other in vibration due to different mass, then the vibrations give rise to an oscillating dipole moment of the unit cells forming elementary polarity, may be at low temperatures [9]. This type of mode of vibration with out-of-phase in the crystal lattice can soften the atom of symmetry centre in crystal unit and displaces a little from its position in cooling initiating FE phase with soft mode. This dynamic distortion of soft mode [1, 2, 9, 24] producing a small displacement of ion (atom of symmetry centre) in each unit cell structure with respect to temperature can be described in terms of a complete set of normal-mode of vibration (phonon) [16]. This mechanism of ferro-electricity is also described as a core-shell interaction of the displaced ion [1, 26, 29]. The inter atomic
outer most electron shells and nuclei cores interactions produces a spontaneous polarization.

It is assumed that in the anharmonic interaction of asymmetry, the lattice vibrations are operated under phase modulation from one unit cell to next with a transverse optic phonon wave vector \( q_c = 0 \) as the characteristics of soft-mode\[9\]. Quantum mechanics of the oxygen ion polarizability in core-shell interactions may imply as responsible for FE phase transition\[30\]. This is possible by stabilizing the free \( O^{2-} \) ion by a homogeneously 2–charged sphere, known as the Watson model\[31\]. The octahedral structure \( TiO_6 \) of \( SrTiO_3 \) crystal is tightly held within eight Sr atoms occupying \( Ti^{4+} \) ion in the center, and nonlinear polarizability of \( O^{2-} \) happens along \( Ti - O - Ti \) chain at the temperature \( T < T_o \). The \( Ti^{4+} \) ion displacement produces FE two-level system (Fig.1) with two FE free energy minima at \( \pm P_s \) in the \( TiO_6 \) complex.

The core-shell interactions\[1, 29\] among individual ion \( Ti^{4+} \) and oxygen in the \( TiO_6 \) cluster with interacting coupling constant \( g_2 \) of attractive coulomb interactions and coupling constant \( g_4 \) (directly related to oxygen polarizability)\[29\] are considered for the free-energy of the system \( \Phi \) as a contribution of rigid ion potential \( V_o \), polarizability potential \( V_v \), and temperature dependent SPA (Self-consistent Phonon Approximation). Hence, the free energy adopts the form\[1, 2\] 

\[
\frac{\partial \Phi}{\partial \langle W_1 \rangle_T} = \langle W_1 \rangle_T \left[ g_2 + g_4 \langle W_1 \rangle_T^2 + 3g_4 \langle W_1^2 \rangle_T \right]
\]  

(3)

which is zero for polarization displacement \( \langle W_1 \rangle_T = 0 \) and indicates paraelectric phase; or, \( \langle W_1 \rangle_T = \pm \left[ -\frac{g_2}{g_4} - 3 \langle W_1^2 \rangle_T \right]^{1/2} = \pm \left[ 2 \left( \frac{\langle W_1^2 \rangle_T}{T_o} - \langle W_1^2 \rangle_T \right) \right]^{1/2} \) in ferroelectric phase. This is analogous to Landau’s theory\[1, 2, 15\].

Explicit temperature dependency of soft-mode

The energy associated with the lattice vibrations is usually expressed in terms of the Hamiltonian of phonon \( H_{ph} \). For a crystal containing \( Z \) atoms in each unit cell, the \( 3Z \) phonon branches are labelled by \( \nu \). To make the equation compact, the mode label \( (q, \nu) \) is denoted by wave vector \( q \) and \( (-q, \nu) \) is denoted by wave vector \( -q \). The amplitude of each phonon of wave vector \( q \) and \(-q \) is represented by the mass weighted normal-coordinate \( Q_q \) and \( Q_{-q} \) respectively in the lattice\[2\]. To give an effective Hamiltonian in the anharmonic interaction of crystal asymmetry, the anharmonic interaction term \( V_4 \) of \( 4^{th} \) order in normal-coordinate thermal average are considered in the form of the Hamiltonian as\[2, 32\]

\[
H_{ph} = \frac{1}{2} \sum_q \omega_q^2 Q_q Q_{-q} 
+ \frac{1}{4} \sum_q \sum_{q'} V_4(q, -q, q', -q') \langle Q_q Q_{-q} \rangle Q_{q'} Q_{-q'}
\]

(4)

Hence the Hamiltonian can be rearranged considering anharmonic interactions with a set of renormalized phonon frequencies \( \tilde{\omega}_q \) (quasi-harmonic approximation) as in the following\[2\]:

\[
H_{ph} = \frac{1}{2} \sum_q \left[ \omega_q^2 + \frac{k_B T}{2} \sum_{q'} \right] \tilde{\omega}_q^2 Q_q Q_{-q} 
= \frac{1}{2} \sum_q \tilde{\omega}_q^2 Q_q Q_{-q}
\]

(5)

Now, the renormalized frequencies have an explicit temperature dependence as directly extracted from equation-(5)

\[
\tilde{\omega}_q^2 = \omega_q^2 + \frac{k_B T}{2} \sum_{q'} V_4(q, -q, q', -q') / \tilde{\omega}_q^2
\]

(6)

This equation has a self-consistent set of solutions for the renormalized frequencies\[32\] and this quasiharmonic approximation application is also called pseudo-harmonic approximation\[21\].

According to the soft mode behaviour, the crystal has a small displaceable distortion corresponding to renormalized frequency that can be expressed in normal mode coordinates\[16\] and viewed as a small modification of its symmetry structure. Eventually, \( \tilde{\omega}_q^2 = 0 \) for a zero displaceable distortion at a certain temperature \( T_o \) known as the transition temperature. From equation-(6)

\[
T_o = -2\omega_q^2 \left[ k_B \sum_q V_4(q, -q, q', -q') / \tilde{\omega}_q^2 \right]
\]

(7)

and thus

\[
\tilde{\omega}_q^2 = \left[ k_B \sum_{q'} V_4(q, -q, q', -q') / \tilde{\omega}_q^2 \right] (T - T_o)
\]

(8)

As a consequence the renormalized phonon frequency \( \tilde{\omega}_q \) has an imaginary value at \( T < T_o \) temperature\[2\].

The dependence of lattice energy at low temperature \( T < T_o \) can be approximated from equation-(1) by double-well potential \( V(P) \) (Fig.1) as described earlier. Now, the coefficient \( \alpha_o(T - T_o) \) of equation-(1) is equivalent to the square of the imaginary harmonic frequency \( \tilde{\omega}_q^2 \) which is arisen from temperature dependent soft-mode\[2\].
MEASUREMENTS AND RESULTS

Dielectric measurements of SrTiO$_3$ (STO) crystal

A cylindrical STO crystal specimen of 3.27 mm diameter and 3.66 mm height was used as a dielectric resonator for this study. The dielectric resonance mode families, quasi-TE$_{m,1,1}$ and quasi-TM$_{m,1,1}$ microwave modes in the range of frequencies 1 GHz to 11 GHz were estimated with azimuthal variations $m = 1$ to 4 by using computer simulation software based on the method-of-lines (MoL) \[4, 33\]. These modes excited in the STO dielectric resonator are experimentally determined with a Vector Network Analyzer (VNA) for measurements of modes in transmission $S_{21}$. By matching measured and simulated mode frequencies, the relative permittivity of the crystal has been estimated as $316 \pm 0.2$ at room temperature 295 ± 1 K.

Python computer software was used to record the variation of resonance frequency of quasi TE$_{1,1,1}$, quasi TE$_{2,1,1}$ and quasi TM$_{2,1,1}$ modes under continuous cooling from 275 K down to liquid-helium temperature (5 K). This frequency-temperature characteristics from 275 K down to 25 K is shown in the figure 2, and also from 75 K down to liquid-helium temperature (5 K) is shown in the separate figure (Fig.3) for highlighting the curves including the trends of the curve to be flat after 5 K. The TE$_{1,1,1}$ mode and TE$_{2,1,1}$ mode resonance frequency 4.555 GHz and 6.696 GHz decreased down to 456 MHz and 678 MHz respectively. The TM$_{2,1,1}$ mode resonance frequency 6.539 GHz decreased down to about 626 MHz (Fig.2 and 3). Also, there is a little peak in each characteristic curve around 105 K (Fig.2), and may be implied to the transition of crystal unit from cubic to tetragonal structure. The decrease of dielectric resonance mode frequency in the observed frequency-temperature characteristic curves indicates an increase of relative permittivity of the crystal up to about $3 \times 10^4$.

The temperature-frequency characteristic curves of different mode families crosses each other due to different polarization of mode. Influence of crystal asymmetry is seen at temperatures likely lower than phase transition temperature. Rate of change of the decrease of frequency with respect to temperature becomes rapid around 75 K, and it indicates transition stage of crystal unit to lower symmetry as an effect of soft mode. Marked frequency shift $\Delta \omega'$ and $\Delta \omega''$ in the figure 2 is due to anomaly of relative permittivity likely created from soft-mode. These trends ended showing the curve to be flat at a temperature lower than 5 K due to dielectric saturation. Rowley et al. \[23\] explained this characteristics as quantum criticality (Fig.3). This frequency-temperature characteristics of TE$_{2,1,1}$ mode is given individually in the figure 4 with logarithmic scale of temperature.
Ferroelectric phase transitions of $SrTiO_3$ crystal

Generally, two-level system of Gibbs free energy minima at $\pm P_s$ is generated in the ferroelectric phase (Fig. 1), and $P_s$ may be switched as $+P_s$ and $-P_s$ with travelling microwave in the crystal lattice [23, 35]. If the microwave is not strong enough to switch $P_s$ then still WG modes are capable to indicate the FE phase transitions by responding to the damping oscillation and dielectric anomaly. At the ferroelectric phase at $T < T_c$, this non-zero polarization is usually formed in terms of softening of an optical mode to the Brillouin zone center, which produces dipole by the separation of positive and negative charge centers in the crystal unit. A large imaginary permittivity due to this dipole moment initiates below phase transition temperature, and minimum loss of energy of the operating quasi-TE$_m,1,1$ and quasi-TM$_m,1,1$ microwave modes are occurred at the phase transition temperature $T_c$. According to Ginzburg-Landau theory, $\partial \phi / \partial T = 0$ at the FE phase transition temperature as a phenomena of particle correlation length divergence to infinity [15, 27], and ensures minimum energy loss of quasi-TE$_m,1,1$ and quasi-TM$_m,1,1$ modes.

Rowley et al. [24] suggested that FE transition of $SrTiO_3$ is occurred at higher than 50 K and quantum criticality arises down to 3 K. The FE phase transition temperature is determined by our experiment as 51 K at the observed highest $Q$-factor of the modes TE$_{2,1,1}$, and TM$_{2,1,1}$ in the Q-factor characteristic curves with respect to temperature (Fig. 5). Also in terms of maximum transmission ($S_{21}$) of the characteristic curves as shown in the Fig. 5, the FE transition temperature is apparently around 51 K. This indication is not so clear due to the flat region around transition temperature as a consequence of lower rate of change of transmission intensity due to corner variation of rhombohedral crystal symmetry in the transition zone of tetragonal to rhombohedral symmetry. As an observation of other structural symmetry transition on the basis of this transition characteristics, the crystal unit structural transition temperature from cubic to tetragonal shape may be identified as about 105 K according to the observed noisy tilt of transmission ($S_{21}$) in the transmission characteristic curve (Fig. 6). Similarly a peak in the curve of frequency-temperature characteristics are observed at this temperature (Fig. 6). Plausibly, the noisy part of the curve close to the tilt is the effect of geometric frustration of the crystal unit at the beginning of cubic to tetragonal structural transition, where atoms tend to stick to non-trivial positions on a regular crystal lattice conflicting inter-atomic forces leading to different structures [36]. Hence, it reveals the change of local arrangement of the crystalline lattice. However the non-trivial influence of thermal diffuse scattering is inevitable, a detailed examination shows that transmission noise of TM$_{2,1,1}$ mode is at higher or different temperature than TE$_{2,1,1}$ mode (Fig. 6) revealing different response of lattice among the modes. The frequency shifts $\Delta \omega'$ and $\Delta \omega''$ in Fig. 2 is due to the square of the imaginary frequency $\tilde{\omega}_q^2$ (see equation (8)) as a consequence of anomaly of imaginary permittivity relating to the temperature dependent soft-mode [2]. In addition, as the coefficient $\alpha_s(T - T_s)$ of equation (1) is equivalent to $\tilde{\omega}_q^2$ (see equation (8)), the measure of frequency shift reveals the strength of $P_s$ and the depth of the double-well potential (see equation (2)).

The FE phase transition is also indicated showing the loop formed by the transmission characteristic curves of TE$_{2,1,1}$ mode under external DC electric field $5.5 \times 10^3 \ \text{Vm}^{-1}$ across the crystal along its axis and without this external field in cooling from room temperature down to 4 K (Fig. 7). The loop starts formation at a temperature $T \approx 51 \ K$, which is the FE phase transition temperature. Likely, the local influence of this external electric field at the Ti$^{3+}$ site is $E_z = 5.83 \times 10^{-3} \ \text{Vm}^{-1}$. Apparently the soft-mode produced spontaneous polar-
ization is being influenced by the external electric field, which is revealed by higher transmission intensity of the $TE_{2,1,1}$ mode in the region of soft-mode at the temperature zone $T \leq 51$ K in this incipient FE crystal. Such a spontaneous polarization forms a $P_s(T) - T$ loop assimilating to the displayed $S_{21} - T$ loop of the figure revealing spontaneous polarization difference $\Delta P_s(T)$ due to external electric field $E_x$. In fact the $P_s - T$ loop is not a hysteresis loop rather it is a loop revealing spontaneous polarization variation $\Delta P_s(T)$ due to external electric field at the temperature below FE phase transition temperature, and confirms the existence of soft-mode.

Microwave power dependency was apparently low as predicted for this incipient ferroelectric crystal. The influence of microwave power becomes significant at lower temperatures less than 10 K, where transmission disappeared after 8 K at lower microwave power (Fig. 6) whereas the transmission was observed until down to 4 K by applying comparatively higher microwave power (Fig. 7).

**CONCLUSION**

Application of quasi $TE_{m,1,1}$ and quasi $TM_{m,1,1}$ microwave modes provide a technique to measure the FE phase transition temperature and thus works as an effective tool to diagnose microscopic asymmetry of crystal lattice. This technique is generally very effective for measurement of weak ferroelectric phase transitions where the traditional measurement process applying external electric field is inefficient. The phase transition temperature was accurately observed with the soft-mode contributing to the frequency shift in the frequency-temperature characteristic curves (Fig. 2 and 3). Mani et al. claimed a similar fact as dynamical effect in a typical order-disorder mechanism in the transitional region of crystal symmetry[36][38].

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