

Raman study of phase transition in ferroelectric $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{TiO}_3$

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Abstract. Raman scattering investigation of phase transition in the ferroelectric $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{TiO}_3$ is reported. The results suggest onset of significant dynamic disorder at 105°C. This corroborates findings of recent structural study regarding large positional disorder associated with Ti and O1 atoms well below the tetragonal to cubic transition temperature ($\sim 150^\circ\text{C}$).

Keywords. Raman scattering; phase transition; ferroelectric.

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1. Introduction

The tetragonal (ferroelectric) to cubic (paraelectric) phase transition in BaTiO_3 (BT) is characterized by a sharp peak in dielectric permittivity around 130°C. Solid solutions like $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ ($x < 0.4$) on the other hand exhibit broadened transitions termed as diffuse phase transitions (DPT). DPT is not necessarily related to crystalline inhomogeneity but it is intrinsic in nature [1]. It is believed that phase changes are influenced by large polarization fluctuations in these systems [2]. It has been shown recently [3] that partial substitution of Ba by Ca results in broadening of the dielectric peak as well as shifting of the peak position to higher temperatures ($\sim 150^\circ\text{C}$). In this paper we report detailed Raman scattering investigations in $\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ single crystal having a nominal value of $x = 0.05$. Interestingly, the intensities of E and A_1 modes which are Raman active in the tetragonal phase, disappear around 105°C, well before the temperature at which the dielectric function peaks, namely 150°C. We discuss the implication of these observations in conjunction with the results reported using neutron scattering and electron paramagnetic resonance studies.

2. Experimental details

$\text{Ba}_{1-x}\text{Ca}_x\text{TiO}_3$ (BCT) crystals were grown at Crystal Growth Centre, Anna University by Remelka technique using KF as flux. A mixture containing 30% ($\text{BaCO}_3 + \text{CaCO}_3 + \text{TiO}_2$) and 70% KF was taken in Pt crucible and heated to 1200°C. After a certain

soaking time temperature was lowered to 850°C. At this temperature, the flux was decanted and the crystals were cooled to room temperature. The grown crystals were recovered using hot-distilled water. By performing the growth run with a slow cooling rate of 3°C/h, and a soaking period of 15 h, high quality crystals with enhanced size were obtained [4].

The BCT sample used in our experiment was a parallelepiped of $2 \times 5 \times 5 \text{ mm}^3$ with the smallest side parallel to c -axis. Neutron diffraction measurements indicate that Ca^{2+} occupies Ba^{2+} site [5, 6]. The crystal space group is $P4 \text{ mm}$ and room temperature lattice constants are $a = b = 3.982 \text{ \AA}$, $c = 4.025 \text{ \AA}$ [6]. For determining the concentration of Ca, a small crystallite belonging to this lot was subjected to composition analysis using optical emission spectroscopic technique [7] which yielded a value of $x \approx 0.05$. Raman spectra were excited using the 5145 Å line of Ar^+ laser in backscattering geometry. The scattered light was analyzed with a home-made double monochromator and detected using a cooled photomultiplier in the photon counting mode [8]. In the tetragonal ferroelectric phase, $A_1(\text{TO})$ and $E(\text{LO}, \text{TO})$ polar modes were picked up from the bc face by employing $a(cc)a$ and $a(cb)a$ scattering geometry respectively. The $A_1(\text{LO})$ mode was recorded from the ab face in the $c(aa)c$ scattering geometry. The soft mode in the tetragonal phase has $E(\text{TO})$ symmetry. For the sake of comparison limited measurements were also carried out on a BaTiO_3 (BT) crystal.

3. Result and analysis

Existence of an overdamped soft mode in BaTiO_3 is well documented in literature [9, 10]. The frequency and damping of the mode are obtained by fitting the Stokes side of Raman spectra to $I(\omega)\alpha(n(\omega) + 1)\text{Im}G(\omega)$, where $G(\omega) = [\omega_0^2 - \omega^2 + i\Gamma\omega]^{-1}$ is the

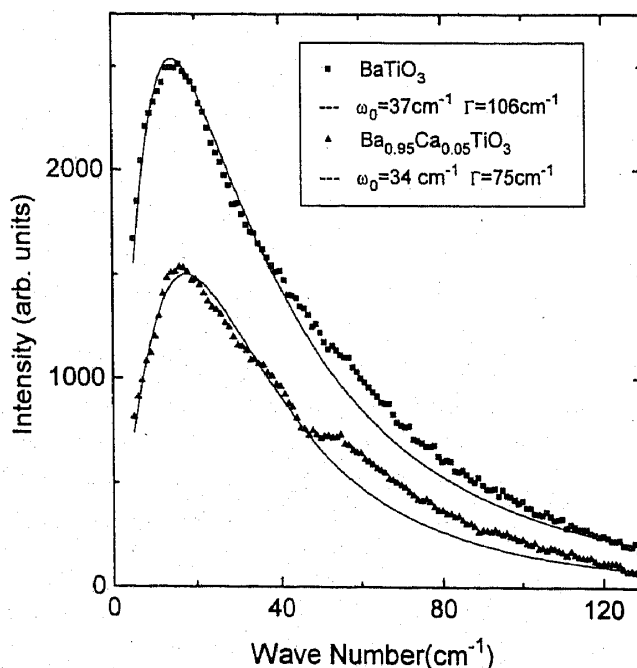


Figure 1. Raman line shapes of the $E(\text{TO})$ mode reduced by Bose population factor for BaTiO_3 and $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{TiO}_3$ in the tetragonal phase at 22°C.

response of a damped harmonic oscillator with frequency ω_0 and damping parameter Γ . Figure 1 shows the measured Raman line shapes of the soft mode, reduced by the Bose population factor for BT and BCT in the tetragonal (22°C) phase. The continuous line is a fit to the data. For BCT, the analysis yields $\omega_0 = 34 \text{ cm}^{-1}$ and $\Gamma = 75 \text{ cm}^{-1}$ at 22°C in the tetragonal phase. This may be compared with the corresponding values for BT; $\omega_0 = 37 \text{ cm}^{-1}$, $\Gamma = 106 \text{ cm}^{-1}$. In BCT we find additional intensity around 65 cm^{-1} , the origin of which is not clear.

To monitor the tetragonal (ferroelectric) to cubic (paraelectric) transition in BCT, intensity variation with temperature for the following modes was studied: (i) overdamped $E(\text{TO})$ mode, (ii) $A_1(\text{LO})$ mode at 720 cm^{-1} , and (iii) $A_1(\text{TO})$ mode which manifests as a dip at 180 cm^{-1} .

The results are presented in figures 2 and 3. It is seen that Raman intensity disappears between 100°C–105°C. Recent neutron diffraction study of structural phase transition in BCT [6] indicates presence of significant Ti disorder at 120°C. On the basis of structural data refinement, a displacement of 0.2 \AA is assigned to the Ti ion along the c -axis on either side of its mean position. Since $(c - a)$ which can be taken as a measure of the tetragonality of the unit cell is quite small ($= 0.025 \text{ \AA}$) in comparison, the local site symmetry of the TiO_6 octahedron can be regarded as pseudo-cubic. From symmetry arguments it then follows that the modes involving Ti and O atoms will be Raman inactive. It is interesting to note however that even though Raman scattered intensity from the normal modes disappear around 105°C, polarized quasi-elastic light scattering intensity is present in BCT above this temperature. The intensity profile $I_H(\omega)$ has been measured from 5 cm^{-1} to 100 cm^{-1} where it merges with the background level. The profile could be fitted to a function of the form $1/(1 + \omega^2\tau^2)$. τ can be regarded as a characteristic time scale for fluctuations in the system. τ varies from 10^{-12} s in the

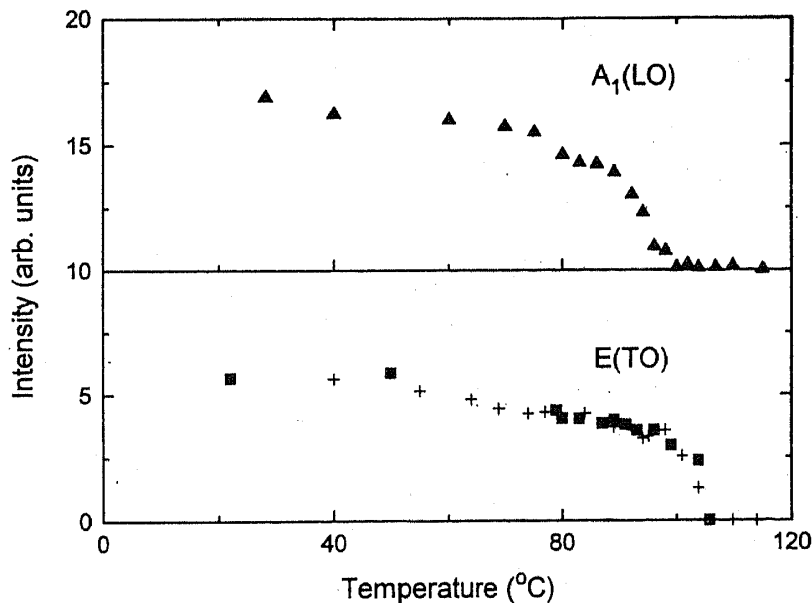


Figure 2. Integrated Raman intensity of $A_1(\text{LO})$ and $E(\text{TO})$ mode in the tetragonal phase of $Ba_{0.95}Ca_{0.05}TiO_3$. Crosses (+) and squares (■) belong to two different runs normalized at room temperature.

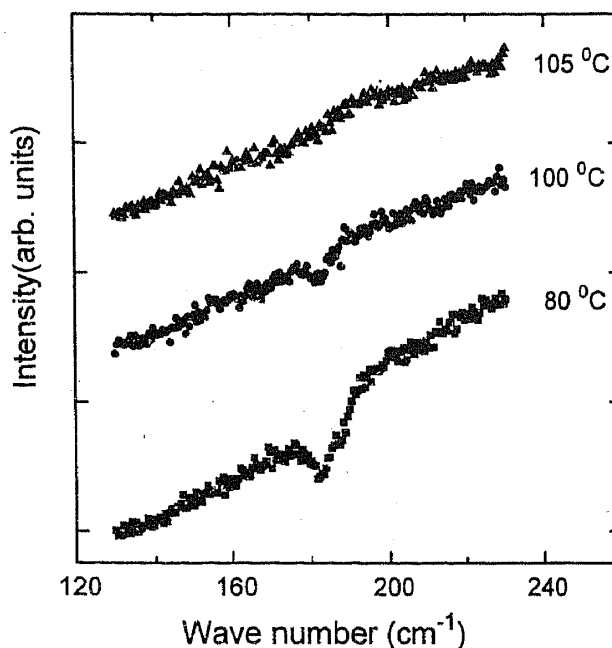


Figure 3. Raman line shape of the $A_1(TO)$ mode at 180 cm^{-1} in $\text{Ba}_{0.95}\text{Ca}_{0.05}\text{TiO}_3$ at three different temperatures.

pre-transition regime to 10^{-11} s in the post-transition regime (transition temperature $\sim 150^\circ\text{C}$). The integrated quasi-elastic intensity is plotted as a function of temperature in figure 4. This intensity which we attribute to disorder induced scattering is picked up *only* in the polarized scattering configuration. The above observation is consistent with a picture where dynamical disorder of Ti and O1 atoms is confined primarily along *c*-axis. Further, intensity drops considerably around 150°C . Structural investigations [6] also confirm that positional disorder of Ti and O1 atoms is very much reduced at this temperature as the crystal transforms from tetragonal to cubic phase.

It is of interest to make a comparison with BaTiO_3 . Raman measurements similar to BCT were carried out. There is evidence for onset of dynamical disorder as the transition temperature ($T_c \sim 130^\circ\text{C}$) is approached but *unlike* in BCT, fluctuations in BaTiO_3 do not lead to vanishing of Raman intensity below T_c .

The dielectric response (ϵ') of BCT can be understood on the basis of the results reported here. We note that the rising trend in ϵ' [3] commences at 100°C where dynamic disorder associated with Ti and O1 atoms also manifest in Raman spectra and ϵ' peaks around 150°C as the crystal transforms into the paraelectric phase.

The tetragonal \rightarrow cubic transition in BCT has also been investigated using EPR technique [11]. The EPR signal originates from Fe^{3+} ions residing at Ti sites. The authors find that the signal corresponding to the tetragonal phase disappears at 110°C but the cubic spectrum appears only above 160°C . The absence of any signal in the temperature range 110°C – 160°C is attributed to dynamic fluctuations in the system with a characteristic time scale of 6×10^{-11} sec. It is interesting to note that the temperature at which the EPR signal for the tetragonal phase disappears is not very different from the temperature at which Raman intensity also vanishes. This is not

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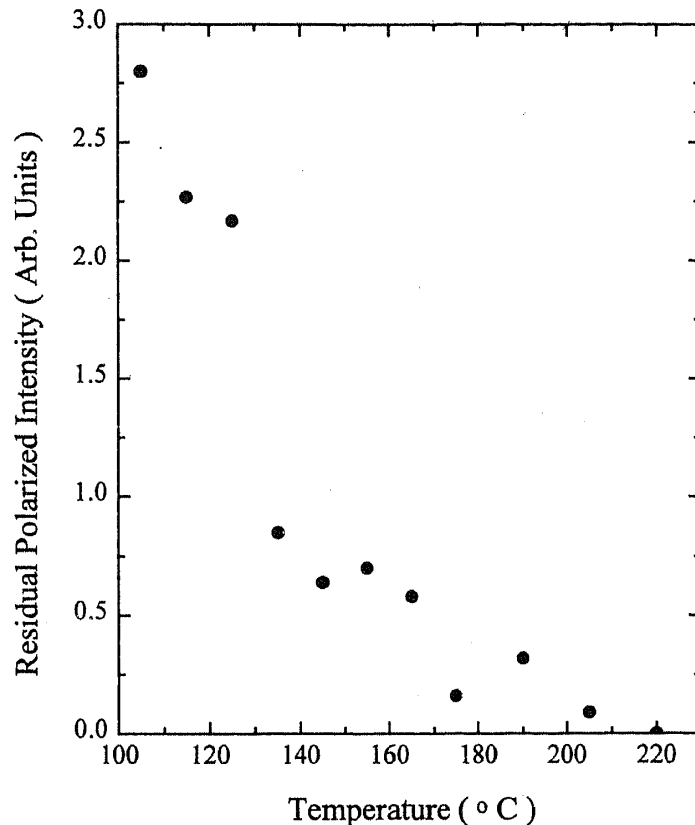


Figure 4. The integrated quasielastic polarized (I_H) intensity in the pre- and post-transition regimes for $Ba_{0.95}Ca_{0.05}TiO_3$ ($T_c \sim 150^\circ C$). Since I_H is practically temperature independent above $220^\circ C$, it has been subtracted out to obtain the contribution arising from dynamic disorder associated with phase change.

surprising since in both EPR and Raman scattering one is essentially probing local symmetry of the TiO_6 octahedron.

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