

## Soft-mode spectroscopy of BaTiO<sub>3</sub> thin films

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### Abstract

We present a detailed study of one highly ordered and two polycrystalline BaTiO<sub>3</sub> films of different thicknesses by far infrared and micro-Raman spectroscopy in the 10–550 K temperature range. The lowest-frequency phonon mode exhibits rather weak and smeared softening in comparison with its single crystal behaviour in all three films. A simultaneous presence of three soft-mode components, continuously changing with the temperature, is assigned to a gradual symmetry transformation within the film volumes. A modification of the soft-mode splitting in the highly ordered film can be explained by a constraint from the substrate. Polycrystalline films exhibit presence of polar modes in the Raman spectra up to 150 K above the single-crystal transition  $T_C$ .

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### 1. Introduction

In spite of the ceaseless debates on the central-mode type dispersion in BaTiO<sub>3</sub>,<sup>1–5</sup> the dominant role of the soft mode ( $F_{1u}(TO1)$  phonon) in its ferroelectric phase transitions remains incontestable. A strong dielectric dispersion descending down to  $\sim 1\text{--}5\text{ cm}^{-1}$  at the Curie point ( $\sim 410\text{ K}$ ) has been indicated by different experimental techniques<sup>3,6,7</sup> and assigned to the overdamped soft phonon mode. In the tetragonal phase this triply degenerate mode abruptly splits into two very distant components  $A_1(TO1)$  and  $E(TO1)$ .<sup>8</sup> The stiffened  $A_1$  component keeps its eigenfrequency around  $260\text{ cm}^{-1}$  without any drastic changes down to lowest temperatures. The overdamped  $E$  component at about  $40\text{ cm}^{-1}$  remains soft down to the tetragonal–orthorhombic phase transition, where it splits into the stiffened  $B_1$  and the soft  $B_2$  (at  $\sim 60\text{ cm}^{-1}$ ) components.<sup>8,9</sup> Finally, in the rhombohedral phase  $B_1$  and  $B_2$  are combined into one doubly degenerate  $E$  component, which is substantially stiffened in comparison with the tetragonal phase but still softer than the

$A_1$  component.<sup>9</sup> Such scenario of the soft-mode behaviour corresponds to the symmetry changes in BaTiO<sub>3</sub><sup>10</sup> and correlates with the temperature behaviour of the static permittivity.<sup>11</sup> The exact values of eigenfrequencies of  $B_1$  and  $E$  soft-mode components in the orthorhombic and rhombohedral phases have not been so far determined due to the absence of a single domain samples and ambiguous interpretation of the unpolarized spectra of multidomain samples.

In the present study we analyse the soft-mode dynamics of selected BaTiO<sub>3</sub> films in order to reveal possible deviations in their phase-transition sequences and dielectric responses from those of the single crystal. We discuss our findings in light of a number of possible causes, including effects of granularity and constraint imposed by the substrates.

### 2. Experimental

Table 1 presents a description of the three studied thin-film samples BTO1–3. Structure of the quasi-epitaxial BTO1 film was studied on a two-circle diffractometer (Huber) with the parallel beam optics,<sup>13</sup> while polycrystalline BTO2

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Table 1  
Structural characteristics of the studied BaTiO<sub>3</sub> films

Film	BTO1	BTO2	BTO3
Thickness (nm)	200	380	750
Substrate	(0001)-sapphire	(0001)-sapphire	(0001)-sapphire
Deposition method	MOCVD <sup>12</sup>	CSD <sup>14</sup>	CSD <sup>14</sup>
Layer growth	Quasi-epitaxial	Polycrystalline	Polycrystalline
Orientation	(1 1 1)	No texture	No texture
Stress-free lattice parameter (nm)	0.40083 ± 0.00018	0.40158 ± 0.00026	0.40158 ± 0.00028
Residual stress (MPa)	Compressive (80 ± 30)	Compressive (150 ± 80)	Compressive (140 ± 80)
Microstrain	(7.5 ± 1.5) × 10 <sup>-3</sup>	(4.4 ± 1.5) × 10 <sup>-3</sup>	(5.0 ± 0.7) × 10 <sup>-3</sup>
Microgeometry	Not found	Columns perpendicular to the substrate, ~100 nm in diameter	Columns perpendicular to the substrate, ~100 nm in diameter

and BTO3 were examined with the parallel beam optics attached to the Bragg–Brentano diffractometer (XRD 7 from Agfa/Seifert) at the constant angle of incidence 5°. As no line splitting was observed in either of the films, their structure was regarded as cubic for the calculation of parameters collected in Table 1. In-plane compressive strain was assigned to the difference in thermal expansion coefficient of BaTiO<sub>3</sub> and sapphire.<sup>13</sup> AFM indicated no clear granularity on the BTO1 surface, but well resolved grains on the BTO2 and BTO3 surfaces.

Far-infrared (FIR) transmittance measurements in the 20–300 cm<sup>-1</sup> frequency range (limited at high frequencies by the substrate transparency) and 10–520 K temperature interval, carried out using Bruker IFS 113v Fourier transform interferometer, were complemented by time-domain transmission terahertz spectroscopy (TDTTS) in the 8–50 cm<sup>-1</sup> range<sup>15</sup> at room temperature. Raman scattering spectra were obtained with Renishaw Raman microscope<sup>15</sup> in 80–550 K interval and reduced by the Bose–Einstein factor.

### 3. Results and discussion

Quasi-static permittivity, including the total phonon and electron contribution (Fig. 1), is evaluated from the fit to

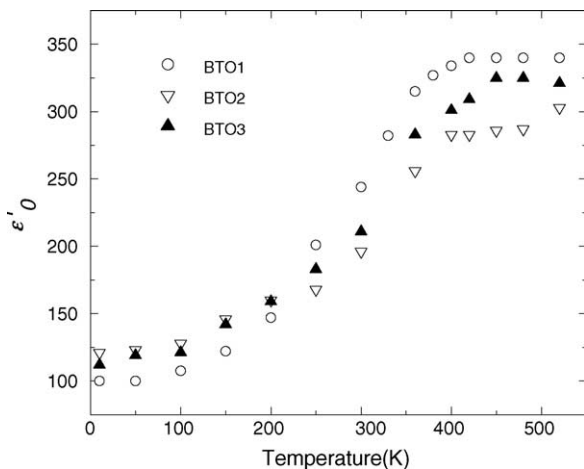


Fig. 1. Quasi-static permittivity evaluated from the fit of FIR spectra.

FIR transmittance spectra and TDTTS data with the classical damped oscillator model<sup>15</sup>. All three films exhibit similar results: above 500 K the permittivity almost attains the single-crystal values from IR reflectivity measurements<sup>8</sup>, but it does not show any anomaly on approaching 400 K. The loss spectra (Fig. 2) show a strong absorption peak below 50 cm<sup>-1</sup>, corresponding to the overdamped F<sub>1u</sub>E/B<sub>2</sub>(TO<sub>1</sub>) soft mode. It gradually weakens on cooling but does not vanish completely even at the lowest temperature, indicating that neither of the films undergoes a complete phase transformation into the lowest rhombohedral phase. The A<sub>1</sub>(TO<sub>1</sub>) peak at ~270 cm<sup>-1</sup>, on the contrary, weakens on heating, but due to the growing substrate absorbance we cannot conclude whether it vanishes above 400 K or not. For the same reason, the TO<sub>3</sub> mode at ~310 cm<sup>-1</sup> is revealed only at low temperatures in two thicker films. The spectral feature at ~180 cm<sup>-1</sup>, corresponding to unresolved E and A<sub>1</sub> components of the TO<sub>2</sub> mode, indicates an antiresonance in the case of BTO2 and BTO3 films. To improve the fit, we assumed it to couple with a broad absorption maximum at about 180 cm<sup>-1</sup> in BTO2 and 3 and at about 150 cm<sup>-1</sup> in BTO1. This absorption substantially strengthens below 300 K and its half-width is comparable with the half-width of the soft-mode components. Therefore we assigned it to the orthorhombic B<sub>1</sub> and rhombohedral E component of TO<sub>1</sub>. Its frequency in BTO1 is substantially lower than in BTO2 and in BTO3, that may indicate a larger A<sub>1</sub>–E rhombohedral and A<sub>1</sub>–B<sub>1</sub> orthorhombic splitting in BTO1 and consequently its higher anisotropy. Most probably, it is connected with the strong influence of the substrate on the (1 1 1)-ordered structure of the BTO1 film.<sup>13</sup>

It is important to underline that the obtained spectra of dielectric function are effective and together with intrinsic properties they may include geometric factors specific for a composite system built-up of variously oriented anisotropic particles. We have not introduced any geometrical parameter describing these effects into our model to escape possible ambiguities with non-regularity and grain-anisotropy of the thin-film structure. Hence, we can discuss only effective mode characteristics. In Fig. 3 we plotted effective mode eigenfrequencies obtained from our fit. To achieve a better agreement with experimental results we introduced additional oscillators at ~200 and ~110 cm<sup>-1</sup>, which do not correspond to

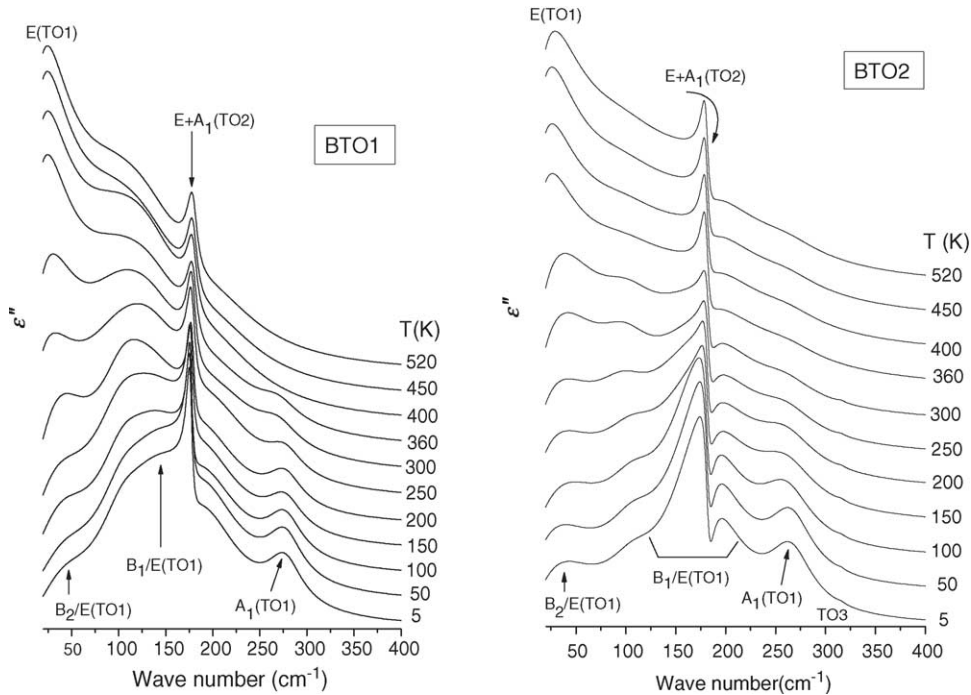


Fig. 2. Dielectric loss spectra of the BTO1 and BTO3 films, obtained from the fit of FIR transmittance. BTO2 spectra are qualitatively similar to those of BTO3 but with less pronounced phonon peaks.

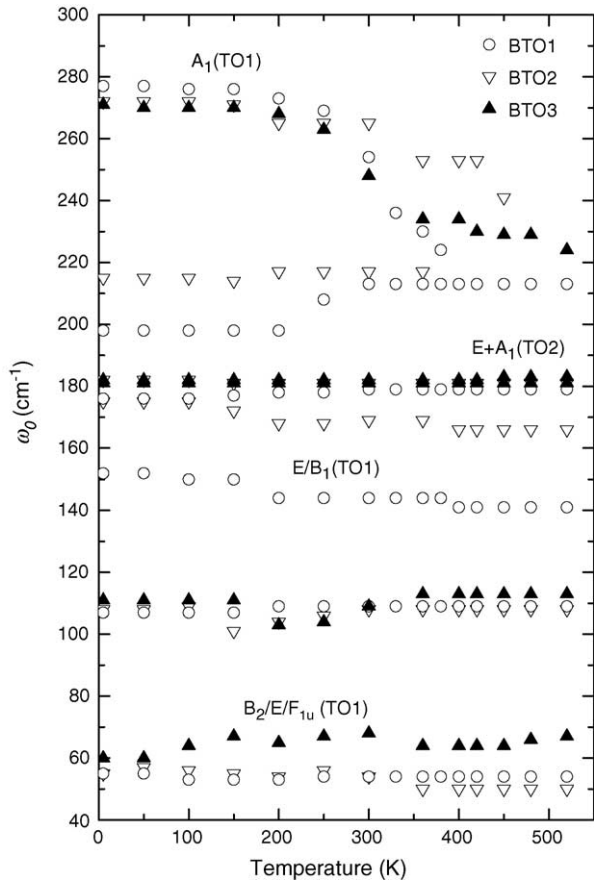


Fig. 3. Oscillator frequencies used to fit the FIR transmittance of the BTO1–3 films with the classical damped oscillator model.

any modes in single crystal.  $\omega_0$  of  $F_{1u}/E/B_2(TO1)$  appears almost temperature independent, but its loss maximum, more accurate characteristic of the soft-mode dynamics,<sup>3,6,7</sup> shows a small softening on heating up to 400 K with a subsequent saturation (Fig. 4) in BTO1 and 2. In BTO3 it displays a weak smeared minimum at 400–500 K, which is still less pronounced than in crystal. It speaks in favour of the incomplete transformation into the cubic phase.

Micro-Raman spectra are shown in Fig. 5 together with the room-temperature spectrum of the bare sapphire substrate. All spectra show interference features near TO2

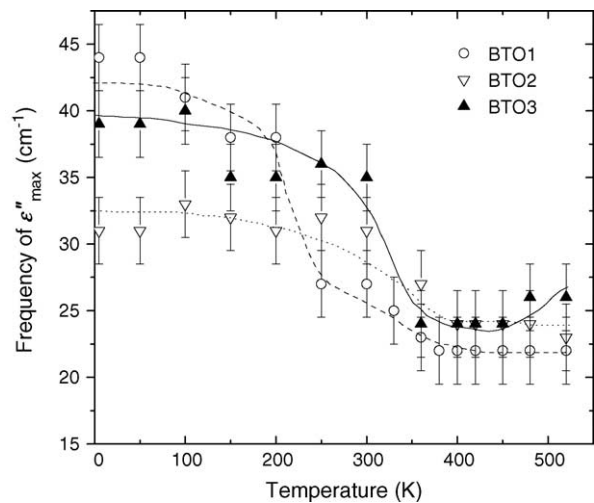


Fig. 4. Frequencies of the loss maxima indicating the overdamped soft-mode behaviour.

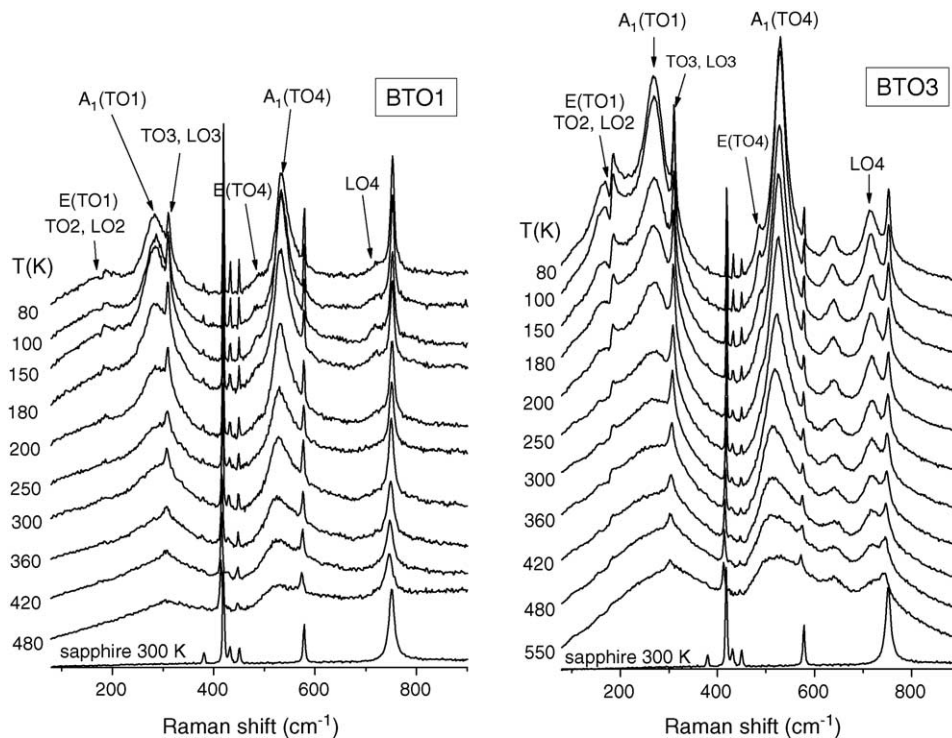


Fig. 5. Unpolarized micro-Raman spectra of the BTO1 and 3 films. BTO2 spectra are qualitatively similar to those of BTO3 with a slightly smaller intensity.

at  $\sim 180\text{ cm}^{-1}$ , strong and broad bands of  $A_1(\text{TO1})$  at  $\sim 270\text{ cm}^{-1}$  and  $A_1(\text{TO4})$  at  $\sim 530\text{ cm}^{-1}$ , sharp peak at  $\sim 310\text{ cm}^{-1}$  assigned to the silent TO3 mode and a well resolved maximum of LO4 mode at  $\sim 720\text{ cm}^{-1}$ . The spectral features are better resolved in the thicker BTO2 and 3 films, where we on heating observed a gradual softening of the  $A_1(\text{TO1})$  mode from 270 to  $240\text{ cm}^{-1}$ , of TO3 mode from 312 to  $306\text{ cm}^{-1}$ ,  $A_1(\text{TO4})$  mode from 530 to  $510\text{ cm}^{-1}$ . At higher temperatures, the last mode merges with E(TO4), lying at  $\sim 490\text{ cm}^{-1}$  at 80 K. Below 200 K all three films reveal an overlapping and/or interference between sharp TO2 mode and a broad maximum centred at about  $180\text{ cm}^{-1}$ , which we assign to the rhombohedral E(TO1) component of the soft mode. The extra mode at  $\sim 640\text{ cm}^{-1}$  observed in BTO2 and BTO3 may be connected with the granularity of the polycrystalline films as it has been suggested for bulk ceramics by Naik et al.<sup>16</sup> The other Raman peaks in our films correspond to those observed in single crystals,<sup>17</sup> but TO2 ( $\sim 180\text{ cm}^{-1}$ ) and TO3 ( $\sim 310\text{ cm}^{-1}$ ) modes in the BTO2 and BTO3 films do not vanish completely above the bulk Curie point up to the highest studied temperature (550 K), indicating some acentricity in the structure, at least local.

Identification of the tetragonal–orthorhombic phase transition from the spectra is the most delicate procedure. Even in single crystals the difference between these two phases is not pronounced in unpolarized Raman spectra. The lack of single crystal data in the orthorhombic phase makes this task impossible from our FIR data. However, we suggest a coexistence of the tetragonal and orthorhombic phases in a wide temperature range. A weakening of the E(TO1) and

strengthening of the  $B_1/E(\text{TO1})$  soft-mode component suggests that the tetragonal–orthorhombic transformation inside our films gradually occurs in the 250–400 K temperature range, but no definite conclusions can be drawn unless FIR measurements on  $\text{BaTiO}_3$  single crystal in the orthorhombic phase are performed. On the other hand, the coexistence of all three soft-mode components does not exclude a possible presence of a local monoclinic symmetry in our films.<sup>18</sup>

#### 4. Conclusions

Lowest phonon mode exhibits a very weak and smeared softening around 400 K in all three films. A simultaneous presence of three soft-mode components, exhibiting a continuous change of their parameters with temperature, indicates a gradual occurrence of all expected phase transitions within the volumes of all three films despite the fact that only cubic phase has been recognised by XRD at room temperature. We suggest a modification of the soft-mode splitting in the highly ordered film due to the constraint from the substrate. Polycrystalline films exhibit a presence of polar modes in Raman spectra up to 150 K above the single-crystal  $T_C$ .

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## References

1. Maglione, M., Bohmer, R., Loidl, A. and Hochli, U. T., Polar relaxation mode in pure and iron-doped barium titanate. *Phys. Rev. B*, 1989, **40**, 11441–11444.
2. Laabidi, K., Fontana, M. D., Maglione, M., Jannot, B. and Muller, K. A., Indication of two separate relaxators in the subphonon region of tetragonal BaTiO<sub>3</sub>. *Europhys. Lett.*, 1994, **26**, 309–314.
3. Petzelt, J., Kozlov, G. V. and Volkov, A. A., Dielectric spectroscopy of paraelectric soft modes. *Ferroelectrics*, 1987, **73**, 101–123.
4. Turik, A. V. and Shevchenko, N. B., Dielectric spectrum of BaTiO<sub>3</sub> single crystals. *Phys. Status Solidi (b)*, 1979, **95**, 585–592.
5. Clemens, R., Luther, G. and Muser, H. E., Dielectric behaviour of ferroelectric barium titanate in the microwave region. *Phys. Status Solidi (a)*, 1981, **64**, 637–645.
6. Vogt, H., Sanjurjo, J. A. and Rossbroich, G., Soft-mode spectroscopy in cubic BaTiO<sub>3</sub> by hyper-Raman scattering. *Phys. Rev. B*, 1982, **26**, 5904.
7. Ballantyne, J. M., Frequency and temperature response of the polarization of barium titanate. *Phys. Rev.*, 1964, **136**, A429–A436.
8. Luspín, Y., Servoin, J. L. and Gervais, F., Soft mode spectroscopy in barium titanate. *J. Phys. C: Solid State Phys.*, 1980, **13**, 3761–3773.
9. Laabidi, K., Fontana, M. D. and Jannot, B., Underdamped phonon in orthorhombic BaTiO<sub>3</sub>. *Solid State Commun.*, 1990, **76**, 765–768.
10. Last, J. T., Infrared-absorption studies on barium titanate and related materials. *Phys. Rev.*, 1957, **105**, 1740–1750.
11. Merz, W. J., The electric and optical behaviour of BaTiO<sub>3</sub> single-domain crystals. *Phys. Rev.*, 1949, **76**, 1221–1225.
12. Weiss, F., Lindner, J., Senateur, J. P., Dubourdieu, C., Galindo, V., Audier, M. *et al.*, Injection MOCVD: ferroelectric thin films and functional oxide superlattices. *Surf. Coat. Technol.*, 2000, **133**, 191–197.
13. Rafaja, D., Kub, J., Simek, D., Lindner, J. and Petzelt, J., Microstructure of Ba<sub>x</sub>Sr<sub>1-x</sub>TiO<sub>3</sub> thin films grown on sapphire substrates. *Thin Solid Films*, 2002, **422**, 8–13.
14. Jia, C. L., Urban, K., Hoffmann, S. and Waser, R., Microstructure of columnar-grained SrTiO<sub>3</sub> and BaTiO<sub>3</sub> thin films prepared by chemical solution deposition. *J. Mater. Res.*, 1998, **13**, 2206–2217.
15. Ostapchuk, T., Petzelt, J., Železný, V., Pashkin, A., Pokorný, J., Drbohlav, I. *et al.*, Dielectric response and soft-mode dynamics in SrTiO<sub>3</sub> thin films. *Phys. Rev. B*, 2002, **66**, 235406.
16. Naik, R., Nazarko, J. J., Flattery, C. S., Venkateswaran, U. D., Naik, V. M., Mohammed, M. S. *et al.*, Temperature dependence of the Raman spectra of polycrystalline Ba<sub>1-x</sub>Sr<sub>x</sub>TiO<sub>3</sub>. *Phys. Rev. B*, 2000, **61**, 11367–11372.
17. Perry, C. H. and Hall, D. B., Temperature dependence of the Raman spectrum of BaTiO<sub>3</sub>. *Phys. Rev. Lett.*, 1965, **15**, 700–702.
18. Pertsev, N. A., Zembilgotov, A. G. and Tagantsev, A. K., Effect of mechanical boundary conditions on phase diagrams of epitaxial ferroelectric thin films. *Phys. Rev. Lett.*, 1998, **80**, 1988–1991.