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# Features of Raman spectra in barium titanate pressed powder

I V Zaytseva<sup>1</sup>, A M Pugachev<sup>1</sup>, N V Surovtsev<sup>1</sup> and A S Krylov<sup>2</sup>

<sup>1</sup>Institute of Automation and Electrometry SB RAS, 630090 Novosibirsk, Russia

<sup>2</sup>Kirensky Institute of Physics Federal Research Centre KSC SB RAS, 660036 Krasnoyarsk, Russia

ZaytsevaIV@iae.sbras.ru

**Abstract.** Raman spectra in barium titanate powder under non-hydrostatic pressures are presented. The relationship between the pressure (up to 11 GPa) and the shift and the width of E(TO)-phonon line has been established. It has been found that under the action of uniaxial pressure a new Raman peak arises in the vicinity of 100 cm<sup>-1</sup>. It is shown that the Raman shift and width of both peaks increase depending on the applied pressure. These Raman lines broadening may be associated with an increase of the concentration of defect states in the volume of the sample.

## 1. Introduction

The primary method used in the manufacture of piezoelectric ceramics is a non-hydrostatic pressure treatment of the ferroelectric powders [1]. Studies of pressure treatment of ferroelectric powders are usually devoted to a case of hydrostatic pressures [2,3]. However, one can note that the effect of the non-hydrostatic pressure treatment may differ significantly from hydrostatic one. The phase transition temperature in BaTiO<sub>3</sub> powders is known to be decreased under the hydrostatic pressure [4] in contrast to the non-hydrostatic one. It was shown that residual mechanical stresses inside the pressure treated samples (mechanical stresses after removal of external non-hydrostatic ones) led to increase in the temperature and width of the ferroelectric phase transition from cubic to tetragonal phase. These pressures, caused by the formation of defects in the crystal cell, were studied in detail in Refs. [5-8]. The behaviour of the phase transition temperature (from tetragonal to cubic phase) in BaTiO<sub>3</sub> powders on the non-hydrostatic pressure is similar to analogous one in strained BaTiO<sub>3</sub> films grown on different substrates due to the existence of enormous strains [9-11].

It is known that Raman spectroscopy allows measuring the mechanical stress. In the case of barium titanate (BaTiO<sub>3</sub>), mechanical stresses can be determined by the shift of E(TO)-phonon line (near 307 cm<sup>-1</sup>) in Raman spectra [6,12]. However, a detailed study of the Raman spectra when non-hydrostatic pressures are applied directly to the powder was not carried out up to now.

The barium titanate crystal at room temperature passes into a cubic phase under applied hydrostatic pressure above 2 GPa. Therefore, it is important to investigate the position and width of E(TO) line in order to determine the phase of barium titanate at high non-hydrostatic mechanical stresses. In the present paper, we investigate the effect of heterogeneity or anharmonism, which should be reflected on the dependence of the E(TO) peak width under the mechanical pressure.

It was demonstrated that a new Raman line appeared under high pressure. In the present paper, this line is investigated in detail.



## 2. Experimental

High-pressure experiments were carried out in nominally pure BaTiO<sub>3</sub> powder (Aldrich) with a grain size less than 2 μm. Raman spectra of BaTiO<sub>3</sub> powder under high pressure were recorded at room temperature (296 K) in the EasyLab μScope DAC-HT(G) (UK). In the present experiments, the non-hydrostatic pressing was realised, due to the fact that no liquid pressure transmittance media was used. The value of mechanical stresses was measured by the shift of the Raman line in a diamond anvil near the surface of the sample. Details of this technique are described in Ref. [6].

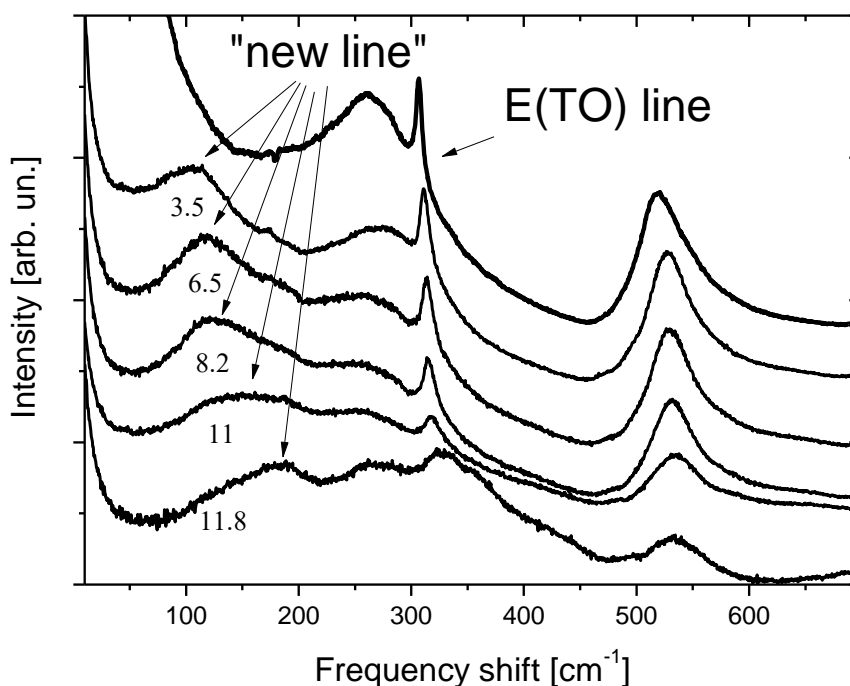
Raman spectra were measured in backscattering geometry. The laser beam was focused on the sample, and scattered light was collected by with a 50× Olympus LMPlanFl objective lens with N.A.=0.35. Raman spectra were excited by the Ar<sup>+</sup> ion laser Spectra-Physics Stabilite 2017 with λ=514.5 nm and power of 5 mW. Spectra of scattered light were recorded by the triple T64000 Horiba Jobin Yvon spectrometer.

## 3. Results and discussion

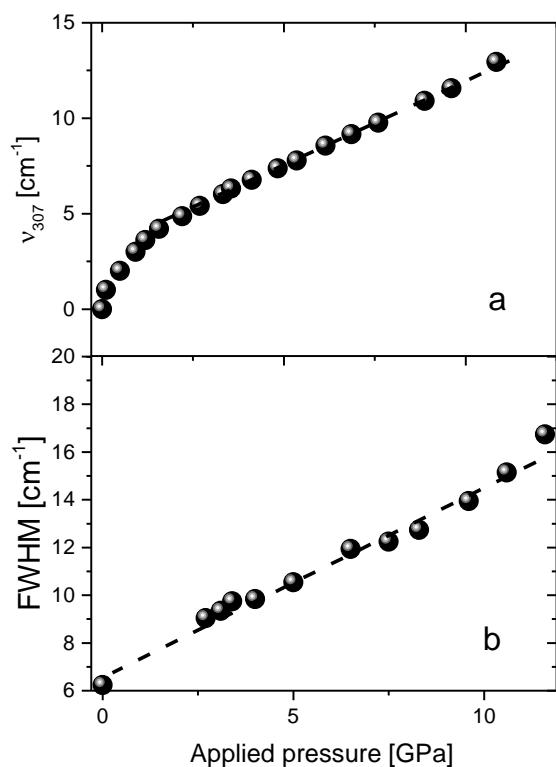
Typical Raman spectra under different non-hydrostatic pressures are demonstrated in Figure 1. It is clearly seen that:

1. E(TO) line is present at all applied mechanical stresses.
2. At non-hydrostatic pressures above 2 GPa a new line in the vicinity of 100 cm<sup>-1</sup> appears in the spectra.
3. When mechanical stresses are applied, the position of mentioned above lines shifts toward the higher frequencies, and the width increases. The dependences of the position and width of lines under study are shown in Figures 2 and 3.

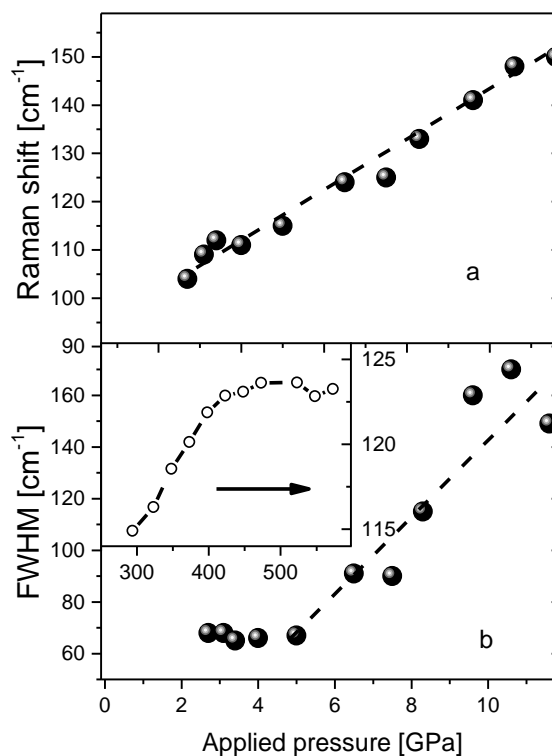
It is known that the line near 307 cm<sup>-1</sup> is a characteristic feature of the tetragonal (ferroelectric) phase in barium titanate [13]. The experimental fact that this line is manifested for the whole pressure range points out that the BaTiO<sub>3</sub> powder does not undergo the ferroelectric phase transition from tetragonal phase to cubic one under non-hydrostatic pressures up to 11 GPa. On the contrary, the



**Figure 1.** Typical Raman spectra under different non-hydrostatic pressures. The numbers indicate the values of non-hydrostatic pressures in GPa. Upper curve is a Raman spectrum at zero pressure.



**Figure 2.** Dependence of the (a) position and (b) FWHM of E(TO) line on the applied non-hydrostatic pressure.



**Figure 3.** Dependence of the (a) shift and (b) FWHM of the "new peak" on the applied non-hydrostatic pressure. The temperature dependence of the Raman shift of this peak at 5 GPa is shown in the inset.

hydrostatic pressure above 2 GPa applied to BaTiO<sub>3</sub> powder leads to the transition into the cubic phase [3]. We can propose that uniaxial mechanical stress causes a reorientation of domains by the ferroelastic effect. In this way, non-hydrostatic mechanical stress increases the density of domain (and dipole momentum, respectively) in a certain direction in originally unpolarized ceramics, which leads to the "conservation" of the ferroelectric phase.

Increasing the frequency of the E(TO) line shift presented in Figure 2a has been discussed earlier [12]. It is shown that the dependence of the line shift on the applied pressure can serve as an effective tool for determining mechanical stresses in ceramics obtained by pressing of barium titanate powder.

The full width of high maximum (FWHM) of the E(TO) Raman line is presented in Figure 2b. For this purpose, this line was fitted by the Voigt contour (the procedure of this fitting was described in Ref. [6] in detail). The Raman line width (Lorentz part of the contour) increases with increasing the pressure.

For a uniformly broadened line, one would expect a decrease in its width. Therefore, it should be noted that inhomogeneous broadening is observed in this experiment. The inhomogeneous broadening of this Raman line may be associated with a shortening of the corresponding lifetimes of vibration states. On the other hand, it could be caused by the appearance of the defect in the sample. Such inhomogeneous broadening can occur on much smaller scale, down to atomic one [14].

An increase of the non-hydrostatic pressure leads to the appearance of a new peak in the Raman spectra. It was first discovered in Ref. [15]. The dependence of the position of this peak on non-hydrostatic stresses is demonstrated in Figure 3a. In turn, the increase of FWHM of this line upon the pressure increase indicates an inhomogeneous broadening due to the anharmonicity of oscillations

(Fig. 3b). The temperature dependence of the Raman shift of this peak is presented in the inset in Figure 3b.

It is known that without the application of mechanical stresses, the soft mode in barium titanate is overdamped [16]. The question of whether a new peak is a manifestation of a soft mode can be answered by the temperature dependence of this peak. The temperature dependence of this line under the non-hydrostatic pressure of 5 GPa excludes its behaviour, which could be interpreted as a soft mode.

#### 4. Conclusion

The dependence of the Raman shift and width of E(TO) Raman line ( $307\text{ cm}^{-1}$ ) on applied non-hydrostatic pressures up to 11 GPa in the BaTiO<sub>3</sub> powder has been established. It is found that under the action of uniaxial pressure, a new peak appears in the vicinity of  $100\text{ cm}^{-1}$ . Its position, width, and temperature dependence, are measured. It is shown that the positions and widths of both peaks mentioned above increase depending on the applied non-hydrostatic pressure. These Raman lines' broadening may be associated with an increase of the concentration of defect states in the volume of the sample. The temperature dependence of this line under the non-hydrostatic pressure of 5 GPa excludes its soft mode behaviour.

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