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Uniaxial mechanical stresses and their influence on the parameters of the ferroelectric phase transition in pressure-treated barium titanate

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ABSTRACT

The dependence of the $E(TO)$ line in Raman spectrum of a $BaTiO_3$ powder on applied uniaxial pressure up to 14 GPa are obtained and the values of residual mechanical stresses are evaluated. The second harmonic generation technique is used to obtain the width and temperature of the cubic-to-tetragonal phase transition in the powder treated by uniaxial pressures. The interrelations between the phase transition width, temperatures, and residual mechanical stresses are established. These interrelations differ from expectations based on known hydrostatic pressure-induced effects in $BaTiO_3$.

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$BaTiO_3$; second harmonic generation; residual mechanical stresses; ferroelectric phase transition

1. Introduction

Pressure and temperature treatments of ferroelectric powders are the basic procedures in the production of ferroelectric ceramics [1]. Nevertheless, physical processes accompanying pressure treatment and annealing have not been fully studied up to now. Recently, it has been shown [2, 3] that the temperature and width of the cubic-to-tetragonal phase transition (further – the “phase transition”) in the barium titanate ($BaTiO_3$) powder increase after treatment by uniaxial mechanical pressures. Moreover, the properties of this pressure-treated $BaTiO_3$ powder became similar to the properties of relaxor ferroelectrics [4]. It was demonstrated [2, 3] that the phase transition parameters changed due a random distribution of residual mechanical stresses inside the sample. These residual stresses can be partially erased by thermal annealing. Random mechanical stresses cause random electric fields, which are considered to be the reason for relaxor properties. It is believed that random electric fields also cause the relaxor behavior in ferroelectric crystals with compositional disorder [5–7].

A challenging question arises fore pressure-treated $BaTiO_3$ powder: what is the magnitude of residual stresses and how do they depend on the applied pressures? It is known that applied (or residual) pressures cause a shift of a narrow Raman $E(TO)$ line near 307 cm^{-1} [8]. The spectral position of this line can serve as a measure of mechanical stresses. For this

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purpose, an interrelation between the optical phonon frequency and the applied mechanical pressure should be established. To reproduce the way of ceramic sample production, the applied pressures should be uniaxial. This is important, because hydrostatic and non-hydrostatic stresses applied to ferroelectric crystals and ceramics lead to different effect for the phase transition [9–12].

The parameters of the ferroelectric phase transition can be determined by different experimental techniques (dielectric spectroscopy, differential scanning calorimetry, etc.). However, in the case of a broad ferroelectric transition, the results of different techniques can be significantly different. At the same time, it has been demonstrated [2, 3, 13, 14] that the second harmonic generation (SHG) technique is a powerful tool for investigation of the phase transitions from centrosymmetric (SHG is forbidden) to non-centrosymmetric (SHG is allowed) phases. According to Ref. [15], the SHG intensity $I_{2\omega}$ for a number of ferroelectrics is described by:

$$I_{2\omega} \propto \langle P_s^2 \rangle \quad (1)$$

where $\langle P_s \rangle$ is an averaged spontaneous polarization. Therefore, the temperature dependence of the SHG intensity reflects the polarization behavior (including the residual polarization in the paraelectric phase). It has been demonstrated [2, 3] that the temperature dependence of the derivative $d(\sqrt{I_{2\omega}(T)})/dT$ can characterize the temperature maximum (T_m) of the phase transition.

The goal of the present work is to find a relation between the position of the E(TO) Raman line and uniaxial mechanical stresses and to study effects of residual mechanical stresses of the pressure-treated barium titanate powder on the parameters of the ferroelectric phase transition.

2. Experiment

Barium titanate powder was manufactured by Aldrich. Pressure-treated samples in the form of pellets were prepared from the powder by uniaxial pressure from 1 to 4 GPa. Some samples were annealed by 900 °C. The particle size was about 2 μm or less.

In high-pressure Raman experiment, the BaTiO₃ powder was placed between the diamond anvil cell (DAC) in the EasyLab μScope DAC device (UK). The high-pressure experiments were performed at $T = 295$ K. A gasket made of stainless steel with an initial thickness of 0.25 mm was used. Holes approximately 150–200 μm in diameter were drilled in the gaskets pre-indented to a thickness of about 86 μm . The pressure applied to the powder was monitored by the shift of the $^5\text{D}_0 \rightarrow ^7\text{F}_0$ fluorescence band of the Sm²⁺ ion in a small SrB₄O₇:Sm²⁺ crystal placed in the vicinity of the sample. We did not use a liquid mixture, which was usually done to produce a hydrostatic pressure [8]. Back-scattering Raman spectra were recorded by using a triple-grating Horiba Jobin Yvon T64000 spectrometer equipped with DAC experiment. A 514 nm laser with a power of 5 mW was used as a Raman excitation source.

The Raman spectra of the pressure-treated and annealed samples were recorded in the backscattering geometry by a FTIR Raman Vertex 70 (Bruker) with a spectral resolution of 0.5 cm⁻¹. The excitation laser wavelength was 1064 nm.

SHG integral intensity from a Nd:YAG laser was measured in the backscattering geometry. A wavelength of this laser is 1064 nm, the pulse duration of 0.6 ns, repetition rate of

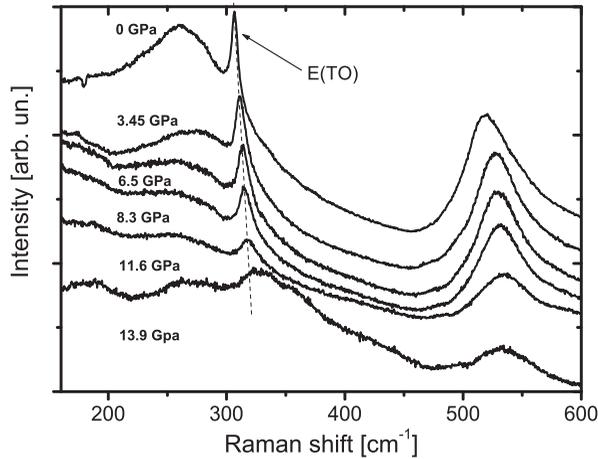


Figure 1. Room temperature Raman spectra in the BaTiO₃ powder at different applied pressures. These results were obtained on the «EasyLab μ ScopeDAC».

1 kHz and average power of 100 mW. Details of the SHG setup are presented in Refs. [13, 14].

3. Results and discussion

The experimental Raman spectra of the barium titanate powder under few representative pressures are shown in Fig. 1. It is seen that the $E(TO)$ line, which serves as an “indicator” of the tetragonal phase [16, 17], is found in all Raman spectra. According to theoretical and experimental data [18–22], only the cubic phase exists in BaTiO₃, if the external hydrostatic pressure is greater than 2 GPa. The inset in Fig. 2 shows that the luminescence line of of

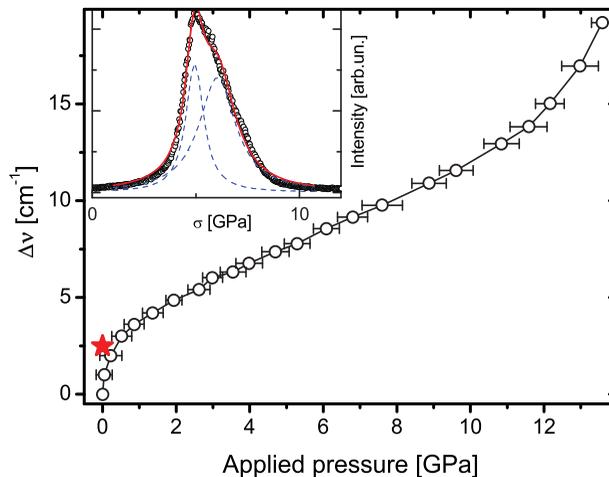


Figure 2. $E(TO)$ – phonon line spectral shift versus the applied pressure (circles). The star corresponds to the line position after pressure release. The inset shows the photoluminescence line of the SrB₄O₇:Sm²⁺ crystal under applied pressures of 5.5 GPa. The solid line is the cumulative fit of the experimental contour and the dashed lines are the Lorentzians.

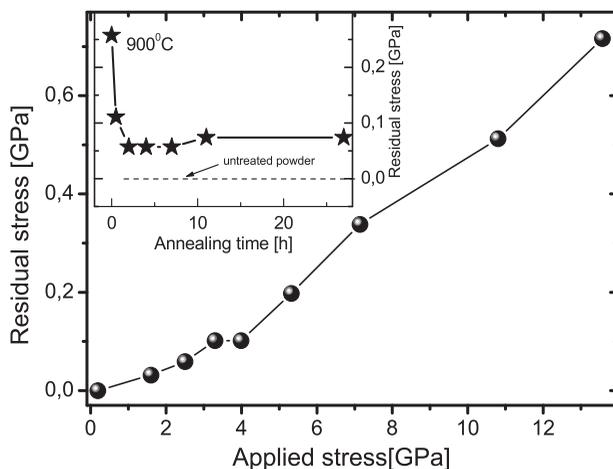


Figure 3. Residual mechanical stress versus the applied pressures. The inset shows the 900 °C annealing of residual stress in the BaTiO₃ powder pressed by 4 GPa.

SrB₄O₇:Sm²⁺ is described by a set (two or more) of Lorentzian contours. This means that the stress inside the powder is inhomogeneous as it would be expected in the case of non-hydrostatic pressure in a granular sample. This is in contrast with the case of hydrostatic pressures. We consider that the difference between the results of the present and previous [18–21] experiments is caused by non-hydrostaticity of the applied pressure.

The pressure-induced shift ($\Delta\nu$) of the $E(TO)$ line position versus the applied pressure is presented in Fig. 2. Details of $\Delta\nu$ evaluation from Raman spectra are described in Refs. [2, 3]. The value of $\Delta\nu$ after removal of the mechanical stress (13.6 GPa) is indicated by the star in Fig. 2. A non-zero value of $\Delta\nu$ for the pressure-treated powder means non-zero mechanical stresses inside the sample. The value of this stress can be estimated from Fig. 2. Similar experiments were carried out, wherein the applied pressure was varied from 0.04 to 13.6 GPa. As a result, the dependence of the residual mechanical stresses on the applied pressure was obtained (Fig. 3).

$E(TO)$ Raman line was studied in pressure-treated BaTiO₃ powders to estimate the residual mechanical stresses in these samples. The inset in Fig. 3 demonstrates that thermal annealing at 900 °C decreases the residual stress inside the sample, but not to zero. It seems that for complete erasure of the residual stress a higher annealing temperature should be used.

The temperature dependences of the SHG signal $I_{2\omega}(T)$ were measured in the samples with different residual stresses. The phase transition was characterized by the derivative $d(\sqrt{I_{2\omega}(T)})/dT$ found from the experimental data of $I_{2\omega}(T)$. The determination of the phase transition parameters from this derivative is discussed in details in Refs. [2, 3]. The found width of the phase transition (FWHM) and temperature of maximum T_m are shown in Fig. 4 versus the residual stresses. It is seen that T_m and FWHM increase, when non-hydrostatic pressure increases. This behavior is typical for the ferroelectric ceramics treated by uniaxial pressures [11–12], because non-hydrostatic pressure increases the stability of the tetragonal phase in BaTiO₃ [22]. The origin of nonlinear relation between FWHM and residual mechanical stresses seen in Fig. 4 is not clear and it is the subject of the further research.

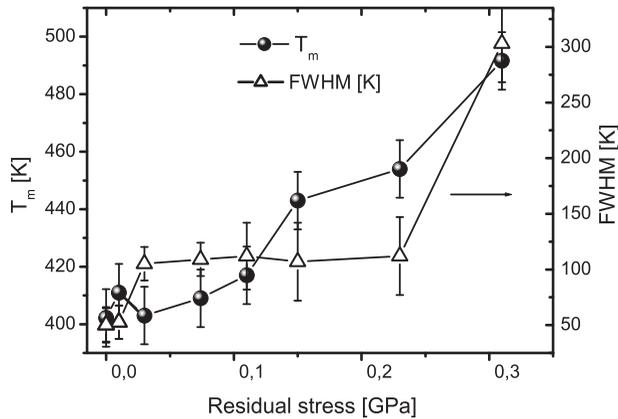


Figure 4. Phase transition temperature (circles, left axis) and FWHM of the phase transition (half width at a half maximum – triangles, right axis) in the pressure-treated BaTiO₃ powder versus the residual mechanical stress.

4. Conclusion

The dependence of the $E(TO)$ line position in a BaTiO₃ powder on the applied uniaxial stresses up to 14 GPa was obtained in Raman scattering. These data provide a calibration curve for the magnitude between the residual mechanical stresses and $E(TO)$ line position in pressure-treated samples. Obtained relation was used to study effects of the residual stresses in pressure treated BaTiO₃ powders on the phase transition. It was demonstrated that the residual stresses caused both broadening of the phase transition and increasing of the phase transition temperature.

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