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Plastic Deformation of BaTiO₃ Ceramics by High-pressure Torsion and Changes in Phase Transformations, Optical and Dielectric Properties

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Ceramics are generally brittle at ambient condition and they can hardly be deformed plastically. In this study, severe plastic deformation was successfully imposed on barium titanate ceramic powders by high-pressure torsion. A tetragonal-to-cubic phase transformation occurred, and the fraction and stability of the cubic phase increased by straining because of the formation of nanograins. BaTiO₃ exhibited photoluminescence and the yellow intensity increased after straining because of the formation of large fraction of grain boundaries. The dielectric constant of BaTiO₃ was unusually increased by nanograin formation while the Curie temperature remained constant.

Keywords: Severe Plastic Deformation (SPD), Ultrafine-Grained (UFG) Materials, Perovskite Oxides, Relative Permittivity, Capacitance

Barium titanate, BaTiO₃ (BTO), which belongs to the group of perovskite oxides with the general ABO₃ formula, has received much attention because of its dielectric,[1–5] piezoelectric [1,5,6] and ferroelectric [7,8] properties, as well as its mechanical and chemical stability.[9] Moreover, BTO has been widely investigated for its optical properties,[10] photoluminescence (PL),[11,12] photocatalysis,[13] proton conductivity [14] and phase transformations.[15–24] BTO transforms from a rhombohedral structure to an orthorhombic phase at –90°C, to a ferroelectric tetragonal phase at 5°C, and to a paraelectric cubic phase at 120°C under ambient pressure.[15–18] At ambient temperature, it exhibits a tetragonal-to-cubic phase transformation at 2 GPa [15–18] and it disorders at 5 GPa.[22] It was reported that the cubic phase can be stable or that several phases can coexist at ambient conditions due to the nanosize effect: 3 nm for nanowires,[19] 30–50 nm for nanograins,[23,24] and 5–26 nm for nanoparticles.[20,21]

Despite these results, there have been few reports on the effect of plastic strain on BTO phase transformations and subsequent changes in the physical properties. The main drawback is the technical difficulty of imposing plastic strain in hard and brittle ceramics with strong covalent or ionic bondings. However, some researchers reported that the high-pressure torsion (HPT) method, which is mainly used for metal processing,[25–28] is an effective technique for introducing plastic strain in ceramics.[29–33] In this work, intense plastic strain is imposed on BTO ceramic powders using the HPT method and the evolution of microstructure, phase transformations, PL and dielectric properties are investigated.

The material used in this study was commercial BTO powder with a purity level of > 96% and ~1 µm particle size. Almost 1 g of the powders was placed between two Bridgman anvils [34] under a pressure of 6 GPa and shear strain γ ($\gamma = 2\pi rN/h$; r : distance from disc center, N : number of turns, h : thickness of disc [26])

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was introduced by rotating the two anvils with respect to each other for either $N = 0$ (mere compression), 1/8, 1/4, 1/2, 1, 2, 5 turns at room temperature. The material had a disc shape with 10 mm diameter and 0.8 mm thickness after HPT processing.

After processing by HPT, X-ray diffraction (XRD) analysis was performed using Cu $K\alpha$ radiation. Raman spectroscopy and PL measurements were performed using a micro-Raman system with a 488 nm argon ion laser at 3.5 mm from the disc center. Cross section of sample was examined using scanning electron microscopy (SEM). For transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM), thin foils were prepared from material located at 4 mm away from the disc center using either the focused-ion-beam system or crushing. For dielectric measurements, the samples were sintered at 1,200°C for 2 h with a heating rate of 2°C/min. Two Au electrodes were attached to both sides of discs and the dielectric constant (permittivity of sample to permittivity of vacuum, 8.854×10^{-12} F/m) and the dielectric loss (dissipation of electromagnetic energy) were measured using an impedance analyzer at 1 Vrms and 1–2,000 kHz.

XRD analysis, as shown in Figure 1(a), confirms the presence of a tetragonal phase in the as-received powders as well as in the samples after only compression. The tetragonal peaks are not distinguishable after HPT processing either because of XRD peak broadening and/or phase transformation to a cubic phase. The peak broadening is visible more clearly in Figure 1(b), where the full-width-at-half-maximum (FWHM) is plotted against the imposed shear strain. The FWHM increases slightly with compression, but the increase is more significant after HPT straining, proving the occurrence of plastic deformation. It should be noted that the occurrence of steady states at large strains, as in Figure 1(b), has been reported in many other materials.[35–37]

The BTO microstructure at the steady state after HPT processing is shown in Figure 2. Nanograins form after processing, in agreement with earlier studies of grain refinement by severe straining.[25–28] While some grains have low misorientation angles as in Figure 2(a) (diffracted beams from the two grains exhibit a small angle in the selected-area electron diffraction (SAED) pattern), others have high misorientation angles as in Figure 2(b) (two grains A and B rotated by 40° with respect to each other). Note that the dark-field image in (a) was taken with the diffracted beams indicated by the arrow in the SAED pattern. Detailed microstructural examination confirms that the average grain sizes at the steady state are well into the nanometer regime (smaller than 100 nm and mainly in the range of 10–20 nm).

SEM micrographs of BTO samples after HPT processing for (a) $N = 0$ and (b) $N = 5$ and subsequent

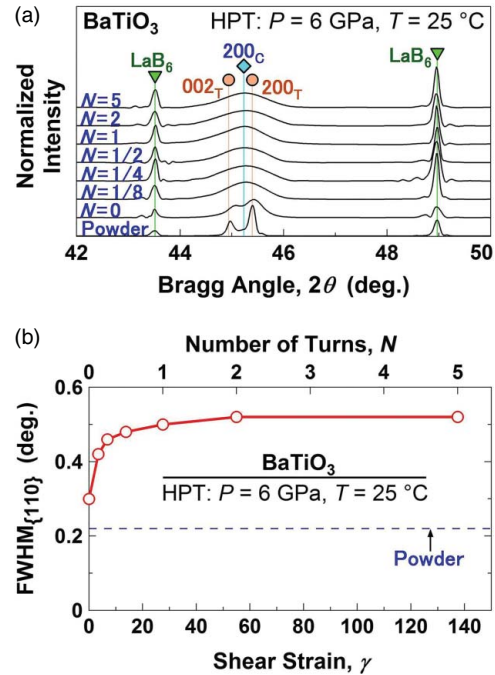


Figure 1. (a) XRD profiles for {200} peaks of samples processed for $N = 0$ –5 turns, including as-received powders (T and C indicate tetragonal and cubic phases, respectively); (b) variation of FWHM for {110} peaks of tetragonal and cubic phases plotted against shear strain and number of turns. LaB_6 powders were used to correct offset of the XRD detector.

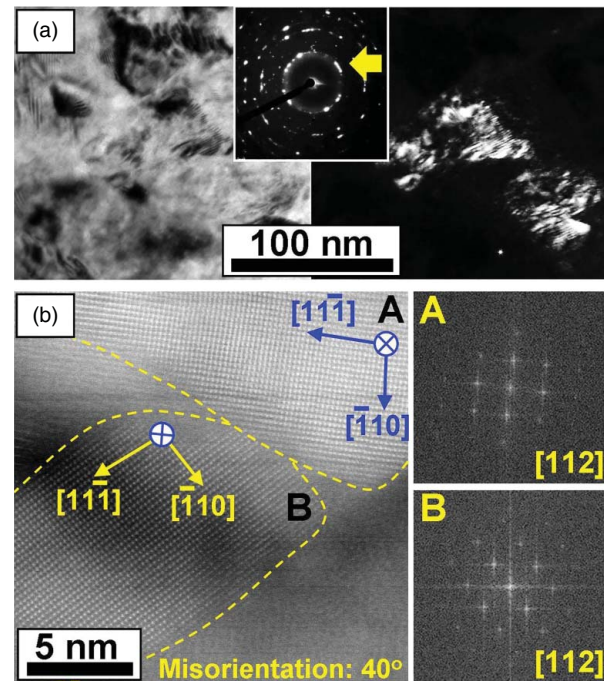


Figure 2. (a) TEM bright-field image (left), corresponding SAED pattern (center) and dark-field image (right), and (b) STEM lattice image (left) and diffractograms corresponding to grains A and B (right) for sample processed by HPT to steady state.

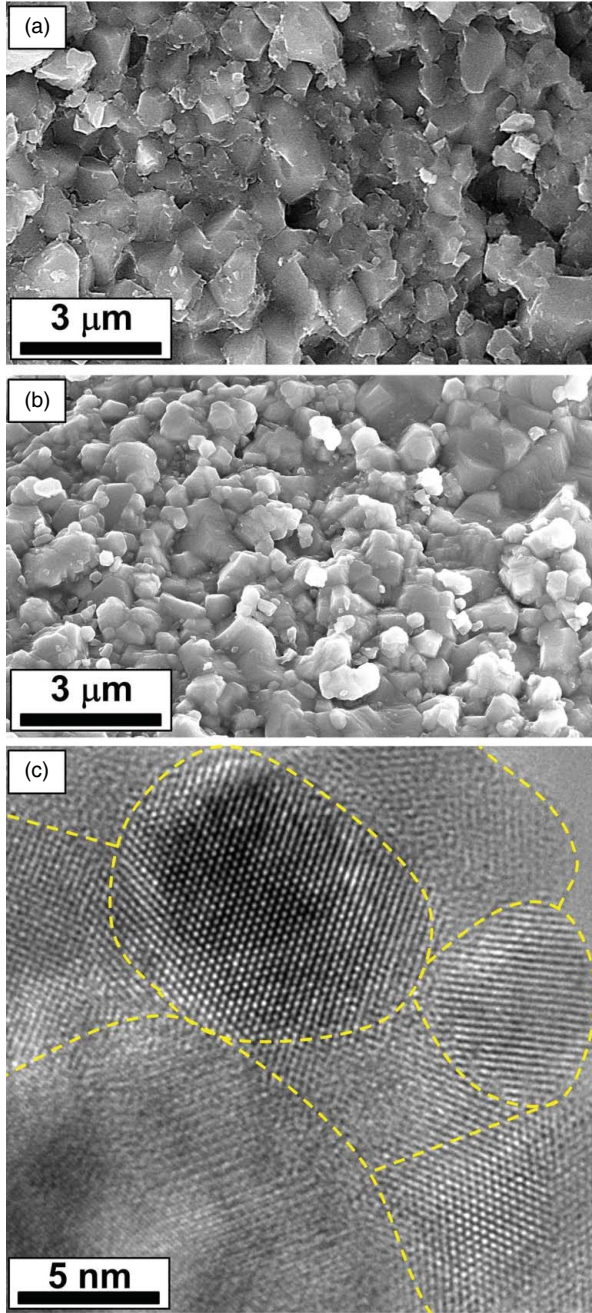


Figure 3. SEM micrographs for samples processed by HPT for (a) $N = 0$ and (b) $N = 5$ turns and subsequently sintered at $1,200^{\circ}\text{C}$. (c) TEM lattice image for sample processed for $N = 5$ turns and subsequently sintered at $1,200^{\circ}\text{C}$.

aging at $1,200^{\circ}\text{C}$ are shown in Figure 3. These micrographs suggest that the average grain sizes measured for 90–150 grains (regions separated by some boundaries in SEM micrographs) is $\sim 830\text{ nm}$ for $N = 0$ and $\sim 470\text{ nm}$ for $N = 5$. Although the average grain size measured for $N = 0$ is reasonably consistent with the initial particle size of the powders ($\sim 1\text{ }\mu\text{m}$), examinations using TEM clearly show that many nanograins

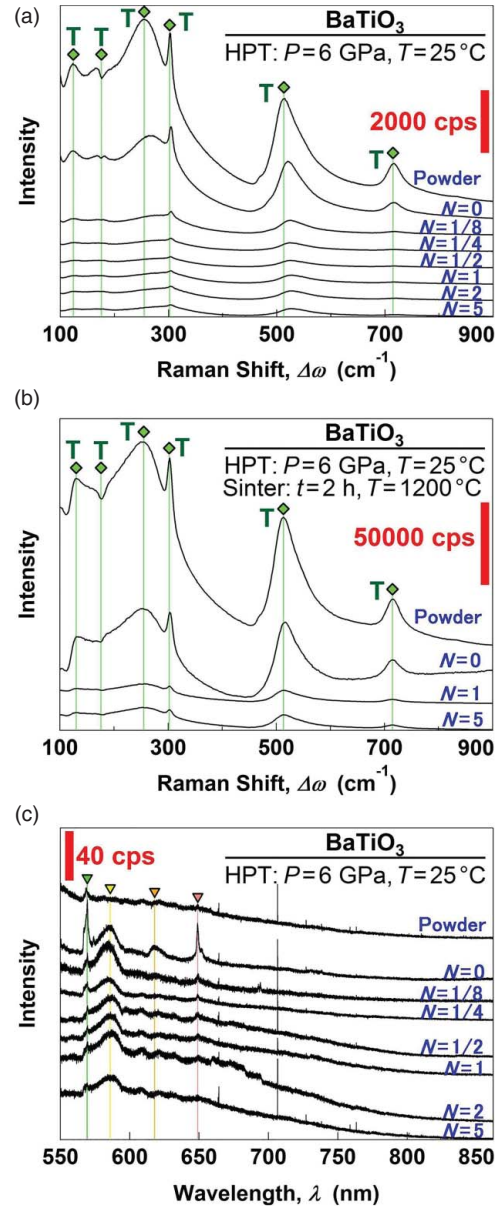


Figure 4. Raman spectra for (a) samples processed for $N = 0$ –5 turns and (b) samples processed for $N = 0$, 1 and 5 and subsequently sintered at $1,200^{\circ}\text{C}$, including as-received powders (T indicates tetragonal phase); and (c) PL spectra for samples processed for $N = 0$ –5 turns, including as-received powders. Note that different machines were used to acquire Raman spectra in (a) and (b).

(mainly in the range of 10–20 nm) are retained even after sintering the sample at $1,200^{\circ}\text{C}$, as visible in Figure 3(c).

Raman spectra in Figure 4(a) show that the peaks corresponding to the tetragonal phase become less visible after mere compression under 6 GPa. The intensity of tetragonal peaks decreases significantly after HPT processing at large strains ($N = 1$ –5 or $\gamma = 27$ –137), indicating that a decrease in tetragonality and a transition to the cubic phase could have occurred, consistent with the BTO phase diagram.[16–18] Details concerning

the BTO Raman spectra were reported elsewhere.[21–24] These results clearly show that, although substantial pressure is required to trigger the cubic-phase formation, the phase transition is facilitated with straining. This finding is consistent with earlier reports concerning the effect of strain on phase transitions in Ti,[38–40] Zr,[41] ZrO₂ [30] and some other metallic alloys.[42–44] The cubic phase present after HPT processing remains partially stable even after pressure release because of the formation of nanograins.[19–24] Figure 4(b) shows Raman spectra for the samples processed for $N = 0$, 1 and 5 and subsequently sintered at 1,200°C for 2 h. Figure 4(b) suggests that the crystal structure of BTO samples is mainly composed of tetragonal phase after sintering at 1,200°C.

The PL spectra in Figure 4(c) show that four peaks, corresponding to green, yellow, orange and red appear at 570, 590, 620 and 650 nm, respectively, after compression. Following HPT processing, the yellow intensity increases and the green, orange and red intensities decrease. These emissions are not due to direct transition of electrons between BTO valence and conduction bands, but they are instead attributed to the formation of lattice defects such as oxygen vacancies, excess oxygen and grain boundaries.[11,12] It was shown earlier that yellow intensity can increase as grain size decreases to the nanometer level,[11] which is consistent with the current results.

The BTO dielectric constant is plotted against (a) frequency and (b) temperature in Figure 5. The dielectric constant increases with the application of HPT, whereas the Curie temperature remains constant. The increase in dielectric constant appears to be more significant for larger numbers of turns, such as $N = 5$ or $\gamma = 137$. As shown in Figure 5(a), the samples processed for $N = 1$ and 5 exhibit better consolidation (relative density: 97%) than the sample processed for $N = 0$ (relative density: 93%). These results are consistent with the earlier reports on the improvement of consolidation of ceramics by HPT processing.[32,33] Figure 5(c) shows that the sintered samples exhibit similar dielectric loss, especially at temperatures in the range of 70–140°C. Therefore, the increase in dielectric constant is not due to the effect of dielectric loss. The dielectric constant of 5,000–14,000 after $N = 5$ is higher than values reported in the literatures,[1–5] suggesting that the current material should be promising for high-capacitance capacitors and for electronic devices that need efficient mechanical-electric energy conversion, provided that the material can be produced with a reasonable cost.

The increase in the BTO dielectric constant caused by HPT processing should be mainly due to the effect of grain size,[2–4] and partly due to good consolidation.[32,33] Earlier papers reported that the optimum grain size to achieve high dielectric constants

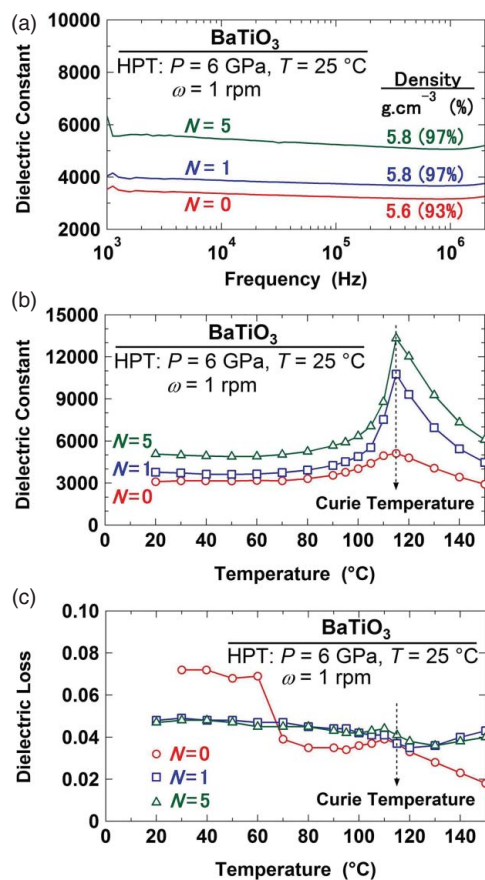


Figure 5. (a) Variation of dielectric constant against frequency at room temperature including density and relative density of the sintered sample, and variation of (b) dielectric constant and (c) dielectric loss against temperature at 1 MHz, for samples processed for $N = 0$, 1 and 5 turns, and subsequently sintered at 1,200°C for 2 h.

was in the range of 700–1,300 nm.[2,3,5] However, this present work suggests that the optimum grain size can shift even to the nanometer level after severe straining. The increase in the dielectric constant by nanograin formation through HPT processing is consistent with the theoretical models based on elastic field energy and domain wall energy.[2] These models suggest that the width of domains should decrease proportional to the square root of the grain size.[2] The reduction of optimum grain size is a challenging task for the development of high-capacitance multilayered ceramic capacitors.[3]

In summary, when severe plastic strain is introduced into BTO powders at room temperature, nanograins are formed and a tetragonal-to-cubic phase transformation occurs. The formation of cubic phase and its stability is facilitated by straining. The HPT-processed BTO exhibits PL and enhanced dielectric properties.

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