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Raman and AFM piezoresponse study of dense $BaTiO_3$ nanocrystalline ceramics

V. Buscaglia[a], M.T. Buscaglia[a], M. Viviani[a], T. Ostapchuk[b], I. Gregora[b], J. Petzelt[b], L. Mitoseriu[c,d,*], P. Nanni[c], A. Testino[c], R. Calderone[c], C. Harnagea[e], Z. Zhao[f], M. Nygren[f]

[a] *Institute for Energetics and Interphases – CNR, Via de Marini 6, Genoa I-16149, Italy*
[b] *Institute of Physics, Acad. of Sciences, Na Slovance 2, 18221 Praha 8, Czech Republic*
[c] *Department Chemical and Process Engineering, University of Genoa, P-le Kennedy, I-16129, Genoa, Italy*
[d] *Department of Electricity, Al. I. Cuza University, Bv. Carol 11, Iasi 700506, Romania*
[e] *INRS-EMT, University Québec, 1650 Lionel-Boulet, Varennes, QC, Canada J3X 1S2*
[f] *Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden*

Abstract

Dense nanocrystalline $BaTiO_3$ (BT) ceramics with grain sizes (GSs) below 100 nm obtained by spark plasma sintering (SPS), were investigated by micro-Raman spectroscopy in order to obtain information about the changes in the local order induced by size effects. The obtained spectra in the range 80–700 K showed the presence of all the crystalline phases of $BaTiO_3$, even in the finest structure (50 nm grain size ceramic), with particularities attributed to the high density of non-ferroelectric grain boundaries. The AFM piezoresponse study incontestably proved the ferroelectric switching at local scale in nanocrystalline $BaTiO_3$ ceramics at room temperature.

Keywords: Spark plasma sintering; Grain size; Ferroelectric properties; $BaTiO_3$

1. Introduction

The finite-size effects in ferroelectrics have attracted renewed interest in the frame of recent achievements of nanotechnology allowing to prepare ultrafine powders, ultrathin films and dense nanostructured ceramics and due to the developing of nanoscale investigation techniques.[1–5] The properties of fine ferroelectrics are different and often superior to those of conventional materials with coarse sizes. Therefore, the main limitation in microelectronics applications is related to the stability of the polar phase as well as the presence of a high density of interfaces with reduction of spatial dimensions.[1] The dielectric properties of $BaTiO_3$ (BT) ceramics as a function of grain size (GS) were extensively investigated and theoretically explained in terms of GS-dependence of the residual stresses, domain walls density, depolarising fields and surface/interface effects.[1,3,6,7] On the fundamental point of view, it is interesting to determine the smallest structure still exhibiting ferroelectric properties. Different values for such a critical size were reported for BT powders, films and ceramics, depending on the preparation techniques and on the mechanical and electrical boundary conditions.[1] Reliable data for the GS effects on the BT ceramics have been mostly reported for ceramics with GS above 0.5 μm; due to the difficulty of obtaining fully dense ceramics below this size, many of the GS effects previously reported in this range are strongly affected by porosity.[1] Dense BT ceramics with grains below 100 nm have been obtained only recently, using special densification methods.[3,8,9] The properties of nanocrystalline BT ceramics prepared by spark plasma sintering (SPS) technique were studied by XRD, calorimetric, and dielectric investigations.[8] A strong depression of the tetragonality down to $c/a = 1.003$

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[*] Corresponding author. Tel.: 40 32 144760; fax: 40 32 213330
E-mail address: lmtsr@uaic.ro (L. Mitoseriu).

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in comparison to 1.01 reported in BT ceramics with GS above 10 μm was found at room temperature together with a lowering of the Curie temperature with decreasing GS.[1] This strongly supports the existence of an important GS effect in addition to a "dilution" of ferroelectricity caused by the high density of non-ferroelectric grain boundaries.[3] The broadening of the anomaly of dielectric constant versus temperature and a small dispersion in the kHz range suggested possible GS-induced relaxor characteristics.[10] However, no high values of the dielectric constant as normally exhibited by the relaxors were found. In this study, information on the local polar character, phase transitions and switching properties of dense nanocrystalline ceramics, in addition to the overall macroscopic observations, were obtained by micro-Raman spectroscopy and by piezoresponse force microscopy. The results obtained for ceramics with mean grain size of around 50 nm are presented and discussed.

2. Sample preparation and experiment

Ultrafine high purity powders with narrow size distribution, prepared by precipitation from aqueous solution[11] were used for obtaining dense nanocrystalline ceramics with 97% relative density by SPS method (using Dr. Sinter 2050 – Sumimoto Coal Mining furnace).[12] The parameters of sintering and the microstructural characterisation of the SPS ceramics were described elsewhere.[8,9] The microstructure of the ceramic with 50 nm average grain size is presented in Fig. 1. The unpolarized Raman spectra of the ceramic samples were obtained using a micro-Raman spectrometer Renishaw in the temperature range of 80–800 K. The local polarization state was probed via converse piezoelectric effect using scanning force microscopy (Autoprobe CP Research, Thermomicroscopes; lock-in EG&G Instruments, 7260).[8] The mechanical oscillations were induced by ac voltage (0.4 V_{rms} at 16 kHz) to the tip (Micromash, CSC11B-series W_2C coated); the spring constant of the cantilever was 6 N/m and the free resonance frequency 150 kHz. A dc source (Keithley, model 2400) was connected in series with the tip for the hysteresis measurements.[13]

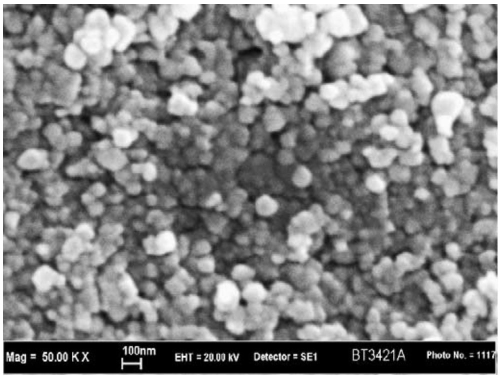

Fig. 1. Scanning electron image for nanocrystalline dense $BaTiO_3$ ceramic (chemical etching) with average grain size of 50 nm.

3. Results and discussion

The unpolarized Raman spectra of a 50 nm BT ceramic reduced by the Bose–Einstein temperature factor (Fig. 2) show all the main characteristics of the Raman activity in single-crystals and in coarse ceramics,[14–16] proving the existence of all the polar phases and the succession of transitions rhombohedral–orthorhombic–tetragonal–cubic (r–o–t–c) of BT, with some differences in the temperature range of stability of each phase. The main spectral features observed for 50 nm BT ceramics are: (a) two intense broad bands A1(TO1) at ∼265 cm^{-1} (which is a stiffened component of the soft mode phonon) and A1(TO4) at ∼513 cm^{-1}, (b) a sharp peak (silent) at ∼306 cm^{-1} (TO3-LO3) and the LO4 band at ∼717 cm^{-1}, both stable up to high temperatures in the c phase, (c) a small peak E(TO4) at ∼487 cm^{-1} present only in r and o phases, (d) E(TO1) and unresolved TO2-LO2 peaks at ∼166–186 cm^{-1} and some continuous scattering between the TO1 and TO2 modes even in the cubic phase, which was not observed in the coarse grained ceramics,[17] (e) a small broad mode ∼650 cm^{-1} not present in single crystal and coarse ceramics, but also found in polycrystalline films,[17] which was considered as being activated by a high degree of granularity in these systems.[18] A gradual softening of the main modes together with a broadening and decrease of the intensity with increasing temperature is observed. Unlike in single crystal and coarse ceramics,[14] few modes (TO3-LO3 and LO4) persist at temperatures few hundreds degrees above the t–c phase transition. This feature is not only due to second order Raman spectra at high temperatures, but mainly to the broken translation symmetry by the high density of grain

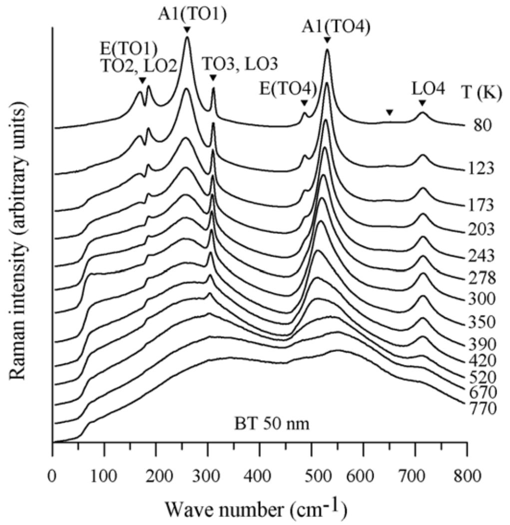

Fig. 2. Unpolarized reduced micro-Raman spectra of a BT ceramic sample with average grain size of 50 nm, at various temperatures.

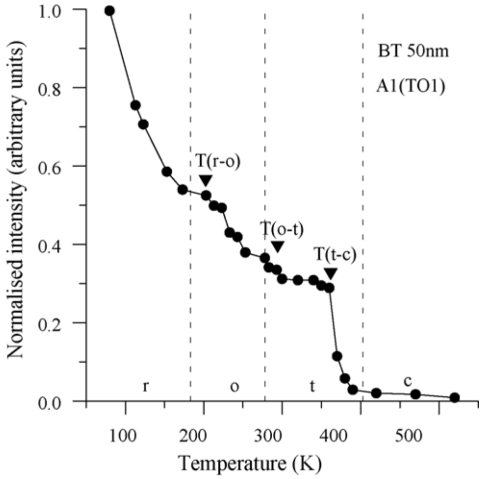

Fig. 3. Temperature dependence of the intensity of $A_1(TO_1)$ soft mode. The phase transitions in 50 nm BT are indicated with (▼). The temperature range of each structural phase in BT single-crystal (r, o, t, c) is shown with dotted lines.

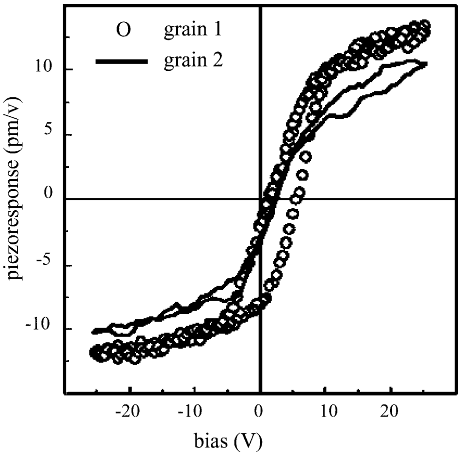

Fig. 4. Local piezoelectric hysteresis loops of the BT ceramic with grain size of 50 nm in regions of the sample marked as "grain 1" (○) and "grain 2" (—).

boundaries, defects or by possible short-range polar order regions existing in the cubic state, as commonly reported for relaxors.[10] It does not mean that diminishing GS at nanoscale level, a superparaelectric state is simply obtained in BT, but rather that a large number of regions with frozen polarization (ascribed probably to grain boundaries[19]) are present in the system. They could be non-switchable and not flipping between metastable states nor breathing and consequently not causing in this way a high dielectric response as in relaxors.

Some modes shows clear anomalies (frequency, intensity, damping) at the phase transitions, as for example the A1(TO1) soft mode (Fig. 3), allowing to determine the characteristic transition temperatures (apart o–t which is hardly detectable). The phase transitions take place with probable coexistence of mixed phases in a large range of temperatures.[17] A clear reduction of the t–c phase transition temperature from the value of micrometric ceramics (393 K)[1] to around 368 K in the 50 nm BT ceramic is indicated by the strong decrease of the A1(TO1) mode strength (Fig. 2), confirming the results of the dielectric data.[8]

The presence of the non-centrosymmetric phases below the Curie temperature shown by the Raman results is a necessary, but not sufficient condition for the existence of ferroelectricity. In order to probe the local ferroelectricity characteristics (i.e. the polarization switching), piezoresponse (PRS) force microscopy experiments were performed at room temperature. The observed PRS signal was much weaker that in the bulk BT[13] as a consequence of the reduced ferroelectric polarization related to the lower average tetragonality. Various regions were switched in both directions and a stable polarization was induced at the time scale of the experiment (8 h).[9] Changes of PRS up to a distance of about 500 nm from the poling area were observed in several experiments indicating some *trans*-granular dipole interaction. Typical hysteresis loops were locally recorded in some regions like grain "1" in Fig. 4, together with non-hysteretic behaviour found in other places (grain "2"). The non-hysteretic behaviour can be ascribed to the non-ferroelectric or "dead-layer" regions present in very small grains or at the border of grains. It resulted that 50 nm BT ceramics clearly preserves at local scale regions with ferroelectric behaviour that coexist with non-ferroelectric and with field-induced polarization regions. Macroscopically, the system shows in average a broad but well-defined ferro–para phase transition, as indicated by the spectroscopic and dielectric investigations.

4. Conclusions

Raman activity and the switching properties of dense $BaTiO_3$ ceramics with 50 nm average grain size obtained by SPS technique were investigated. All the symmetry phases present in single crystal and coarse BT ceramics were found, with particularities associated to the high density of grain boundaries. The phase transitions take place in a large range of temperatures in which the phases might coexist. The reduction of grain size causes a shift of the Curie temperature to 368 K, but 50 nm BT is macroscopically weakly tetragonal at 300 K. The system shows local switching with hysteretic character coexisting with non-hysteretic regions. The present results indicate that the critical GS for the ferroelectric behaviour in dense BT nanocrystalline ceramics is below 50 nm.

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