

# Macroscopic ferroelectricity and piezoelectricity in nanostructured BiScO<sub>3</sub>–PbTiO<sub>3</sub> ceramics

M. Alguero,<sup>1,a)</sup> H. Amorín,<sup>1</sup> T. Hungría,<sup>2</sup> J. Galy,<sup>2</sup> and A. Castro<sup>1</sup>

<sup>1</sup>Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, 28049 Madrid, Spain

<sup>2</sup>Centre d'Elaboration de Matériaux et d'Etudes Structurales (CEMES), CNRS, 29 rue Jeanne Marvig, BP 94347, 31055 Toulouse, France

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We have studied the macroscopic electrical properties of highly dense, nanostructured ceramics of BiScO<sub>3</sub>–PbTiO<sub>3</sub> with high Curie temperature and piezoelectric activity. Materials were processed by spark plasma sintering of nanocrystalline powder obtained by mechanosynthesis. Results indicate that the nanostructured material still presents the ferroelectric transition above 700 K. Ferroelectric switching is unambiguously demonstrated. Furthermore, ceramic disks were poled and their radial piezoelectric resonance was excited, which has not been achieved in nanostructured BaTiO<sub>3</sub> ceramics. © 2009 American Institute of Physics. [DOI: 10.1063/1.3056660]

The study of ferroelectric nanostructures is a highly topical research area.<sup>1</sup> Good examples are nanostructured polycrystals, which are necessary for the down scaling of ceramic technologies in microelectronics.<sup>2</sup> Ferroelectric polycrystalline films are also used in piezoelectric microelectromechanical systems,<sup>3</sup> and they are good candidates for implementing piezoelectric sensing and actuation in nanoelectromechanical devices.<sup>4</sup>

The feasibility of these ferroelectric ceramic based, miniaturized technologies depends on the scaling of the macroscopic functional properties with size. The existence of a fundamental size limit below which ferroelectricity vanishes is expected.<sup>5</sup> There are now solid evidences that ferroelectricity persists in nanoscale films,<sup>6</sup> wires,<sup>7</sup> and particles.<sup>8</sup> However, this does not guarantee the functionality of the ferroelectric ceramic nanostructured elements that depends on how macroscopic properties such as polarization switching and retain, linear polarizability, and piezoelectricity scale with the decrease in grain size. Reports on these effects on functional properties are scarce and mainly focused on tetragonal perovskite BaTiO<sub>3</sub>.<sup>9–11</sup> In these studies, a high permittivity of  $\approx 1600$  was reported for a material with a grain size of 30 nm.<sup>10</sup> However, only incipient,<sup>9</sup> or no<sup>10,11</sup> macroscopic ferroelectric switching was found, in spite of the nanostructured BaTiO<sub>3</sub> being in the ferroelectric state down to a size of 20 nm.<sup>11</sup>

Functional properties have not been reported for nanostructured morphotropic phase boundary (MPB) materials, which are used in most piezoelectric applications.<sup>12</sup> These are perovskite solid solutions with high electromechanical responses, resulting from a mechanism of polarization rotation between ferroelectric polymorphs.<sup>13</sup> The highest piezoelectric coefficients have been reported for single crystals of relaxor-ferroelectric solid solutions with MPB, such as Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>–PbTiO<sub>3</sub> and Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>–PbTiO<sub>3</sub>.<sup>14</sup> We recently succeeded in processing 0.92Pb(Zn<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>–0.08PbTiO<sub>3</sub> nanostructured ceramics with grain sizes of 15–20 nm by spark plasma sintering (SPS) of nanocrystalline powder obtained by mechanosynthesis.<sup>15</sup> However, the electrical properties indi-

cated that long range ferroelectric order does not develop at the nanoscale, but that instead the high temperature relaxor state is stabilized as a size effect.<sup>16</sup> This is in agreement with a previous report on 0.65Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>–0.35PbTiO<sub>3</sub>.<sup>17</sup>

We report here results on nonrelaxor based MPB materials. The BiScO<sub>3</sub>–PbTiO<sub>3</sub> system was chosen because of its high Curie temperature as compared with Pb(Zr,Ti)O<sub>3</sub>,<sup>18</sup> and after the recent report of an increase of the piezoelectric coefficient for ceramics with grain size in the submicron range.<sup>19</sup> The (1–*x*)BiScO<sub>3</sub>–*x*PbTiO<sub>3</sub> solid solution has a wide MPB region between *x*=0.6 and 0.7, in which the monoclinic *Cm* and tetragonal *P4mm* polymorphs coexist.<sup>20</sup>

Nanocrystalline (1–*x*)BiScO<sub>3</sub>–*x*PbTiO<sub>3</sub> with 0.62 ≤ *x* ≤ 0.64 powders were obtained by mechanochemical activation.<sup>21</sup> An average particle size of 11 nm resulted, as measured by transmission electron microscopy. Nanostructured ceramics were processed by SPS of the powder (2080 Sumitomo apparatus). This technique allows high densification at moderate temperatures and short times, and thus, limited grain growth.<sup>22,23</sup> When applied to the nanocrystalline (1–*x*)BiScO<sub>3</sub>–*x*PbTiO<sub>3</sub> with 0.62 ≤ *x* ≤ 0.64, highly dense ( $\approx 7.6$  g cm<sup>–3</sup>; 99%) ceramic materials were obtained at a temperature as low as 923 K in only 3 min. Perovskite single phase was demonstrated by x-ray diffraction (XRD), as illustrated in Fig. 1. A transmission electron microscopy (TEM) image of a ceramic and the corresponding grain size distribution are also shown. The data fit well (*R*<sup>2</sup>=0.995) to a normal distribution with an average size of 80 nm.

Electrical characterization was carried out on ceramic disks on which Pt/Au electrodes were deposited by sputtering and annealed at 773 K.

The temperature dependence of the relative permittivity at 1 MHz for a nanostructured ceramic is shown in Fig. 2, along with results for a coarse grained material for comparison (7.4 g cm<sup>–3</sup>; 96%).<sup>21</sup> Measurements were carried out with a HP 4194A impedance/gain phase analyzer. The room temperature (RT) permittivity was higher, 1035, for the nanostructured material than for the coarse grained ceramic, 830. This might be due in part to the higher densification obtained, but also indicate that the grain boundaries in the material are not acting as a low relative permittivity layer in series with the grains.<sup>10,24</sup> RT losses at 1 MHz were 0.06,

<sup>a)</sup>Electronic mail: malguero@icmm.csic.es.

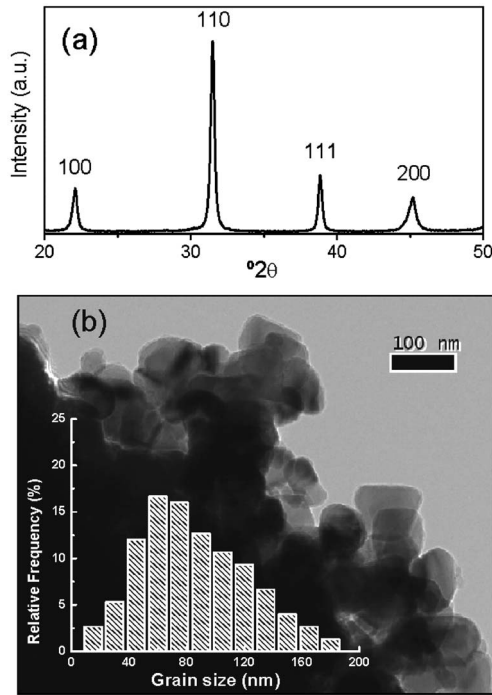


FIG. 1. (a) XRD pattern (perovskite peaks are labeled with the Miller indices assigned on the basis of a pseudocubic unit cell) and (b) TEM Image and grain size distribution of a  $0.37\text{BiScO}_3\text{-}0.63\text{PbTiO}_3$  ceramic obtained by SPS of nanocrystalline powder.

and decreased with frequency down to 0.02 at 1 kHz. The permittivity curve of the nanostructured MPB  $\text{BiScO}_3\text{-PbTiO}_3$  ceramic does present the dielectric anomaly associated with the paraelectric to ferroelectric transition at approximately the same temperature to that of the coarse grained material, 715 K, yet strongly flattened and broadened. This latter phenomenon has been widely reported before for  $\text{BaTiO}_3$  ceramics.<sup>9-11,24</sup>

The ferroelectric hysteresis loop at 0.1 Hz for the nanostructured ceramic with is shown in Fig. 3(a), along with results for a coarse grained material. Low frequency voltage (0.1–10 Hz), high voltage (up to 10 kV) sine waves were applied by the combination of a synthesizer/function generator (HP 3325B) and a high voltage amplifier (Trek model 10/40A), and charge was measured with homebuilt charge to voltage converter and software for loop acquisition and analysis. Loops are presented after compensation by sub-

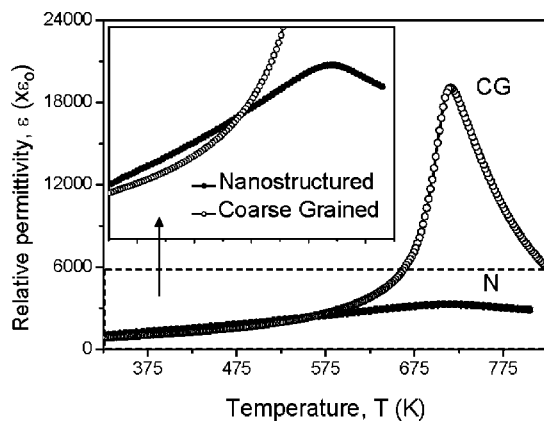


FIG. 2. Temperature dependence of the relative permittivity at 1 MHz for nanostructured (closed circles, N) and coarse grained (open circles, CG)  $0.375\text{BiScO}_3\text{-}0.625\text{PT}$  ceramics.

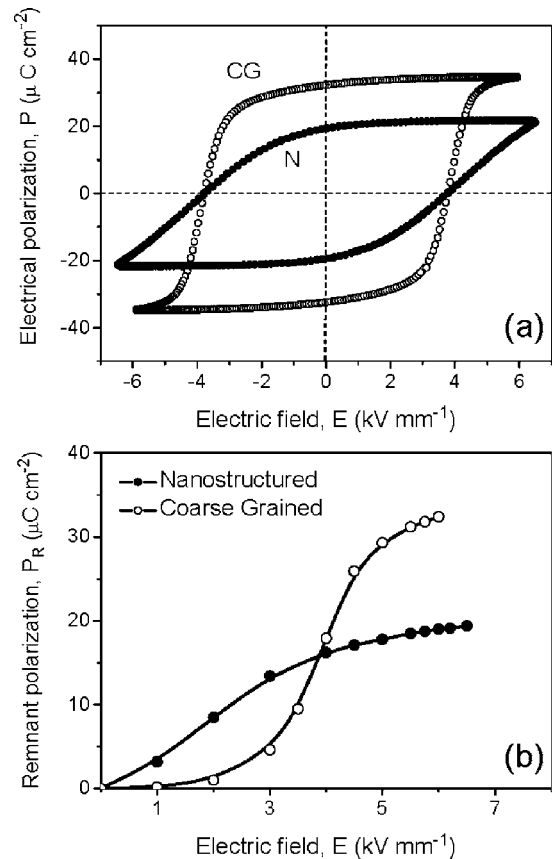


FIG. 3. (a) Ferroelectric hysteresis loops at 0.1 Hz and (b) remnant polarization of the ferroelectric loop as a function of the maximum electric field for nanostructured (closed circles, N) and coarse grained (open circles, CG)  $0.375\text{BiScO}_3\text{-}0.625\text{PT}$  ceramics.

tracting the linear polarization and conduction contributions. Macroscopic ferroelectricity is clearly demonstrated for this nanostructured material with a remnant polarization of  $19 \mu\text{C cm}^{-2}$ . Although this value is smaller than that of the coarse grained ceramic,  $32 \mu\text{C cm}^{-2}$ , and the loop is slightly lean, these results represent an unambiguous observation of macroscopic polarization switching in a nanostructured ferroelectric ceramic.

Remnant polarization as a function of field is shown in Fig. 3(b). Note that the field derivative of the remnant polarization continuously decreases above  $3 \text{ kV mm}^{-1}$  for the nanostructured material, which suggests that saturation is slowly approached. Therefore, the decrease in remnant polarization, from  $32$  to  $19 \mu\text{C cm}^{-2}$  for an average grain size of  $80 \text{ nm}$ , is most probably associated with a decrease of the spontaneous polarization with grain size. This is in agreement with a previous report of  $\text{PbTiO}_3$  nanoparticles.<sup>25</sup>

An issue worth discussing is the different behavior of ferroelectric switching with the decrease in grain size down to the nanoscale for  $\text{BaTiO}_3$  and MPB  $\text{BiScO}_3\text{-PbTiO}_3$  ceramics. The absence of macroscopic ferroelectric switching in nanostructured tetragonal  $\text{BaTiO}_3$  has been attributed to the pinning of transgranular ferroelectric  $180^\circ$  domains at the grain boundaries.<sup>10</sup> In contrast, the main phase of  $\text{BiScO}_3\text{-PbTiO}_3$  at its MPB is monoclinic  $C_m$ . In this phase, polarization is not restricted by symmetry rules to lie along any given direction, as it is the case for the tetragonal case, but to be contained in the (110) plane.<sup>26</sup> As a consequence more complex domain configurations can be expected, and have indeed been observed; a nanodomain configuration has

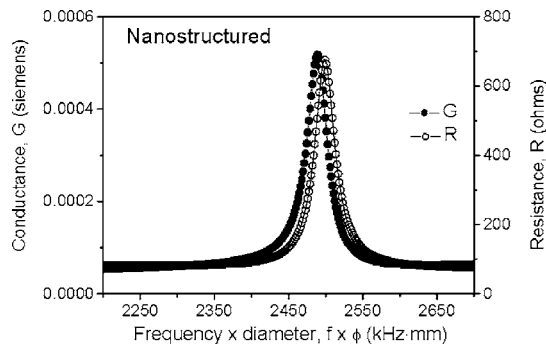


FIG. 4. Piezoelectric radial resonance for a nanostructured  $0.37\text{BiScO}_3-0.63\text{PT}$  ceramic.

been described for MPB  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ .<sup>27</sup> Furthermore, an evolution of the domains from a micron sized lamellar configuration to a submicron/nanometer sized crosshatched pattern has been described for MPB  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-\text{PbTiO}_3$  ceramics when the grain size was decreased down to  $0.15\ \mu\text{m}$ .<sup>28</sup> The ferroelectric switching observed here for MPB  $\text{BiScO}_3-\text{PbTiO}_3$  ceramics with an average grain size of  $80\ \text{nm}$  might be associated with the presence of such a nanoscale domain configuration within the grains, and could be a characteristic of MPB perovskites, not occurring in tetragonal  $\text{BaTiO}_3$ .

The observation of ferroelectric switching opens the possibility of poling the nanostructured ceramics and of studying their functional piezoelectric properties. The poling was carried out at  $423\ \text{K}$  with  $4\ \text{kV}\ \text{mm}^{-1}$ , which are standard conditions for coarse grained  $\text{BiScO}_3-\text{PbTiO}_3$  ceramic materials.<sup>18,21</sup> A  $d_{33}$  piezoelectric coefficient of  $\approx 40\ \text{pC}\ \text{N}^{-1}$  resulted. This has to be compared with values above  $150\ \text{pC}\ \text{N}^{-1}$  for the coarse grained materials.<sup>21</sup> Radial piezoelectric resonances were excited and analyzed to obtain the parameters relevant to the mode. A HP-4192A LF impedance analyzer and an automatic iterative procedure were used in the measurements. The resonance for a nanostructured material is shown in Fig. 4, from which a transverse piezoelectric coefficient of  $-14\ \text{pC}\ \text{N}^{-1}$ , a radial coupling factor of 9%, and a frequency number of  $2488\ \text{kHz}\ \text{mm}$  were obtained. Numbers of  $-66\ \text{pC}\ \text{N}^{-1}$ , 36%, and  $2350\ \text{kHz}\ \text{mm}$  are obtained for a coarse grained ceramic. The nanostructured material thus presents significant piezoelectricity, high enough to show resonant behavior. Piezoelectric resonances, or any other macroscopic piezoelectric response, had not previously been reported for a ceramic with an average grain size in the nanoscale.

In summary, the macroscopic electrical properties of highly dense ceramics of MPB  $\text{BiScO}_3-\text{PbTiO}_3$  with an average grain size of  $80\ \text{nm}$  have been characterized. The temperature dependence of the permittivity indicates that the material still presents the ferroelectric transition above  $700\ \text{K}$ . Macroscopic ferroelectric switching is clearly demonstrated in a nanostructured ceramic, with figures of remnant polarization as high as  $19\ \mu\text{C}\ \text{cm}^{-2}$ . Ceramic disks of the nanostructured material can be poled, and a  $d_{33}$  piezoelectric coefficient of  $40\ \text{pC}\ \text{N}^{-1}$  resulted. Their radial piezoelectric resonance was also excited and analyzed, and a  $d_{31}$

coefficient of  $-14\ \text{pC}\ \text{N}^{-1}$  and a coupling factor of 9% were obtained. The results suggest that nonrelaxor MPB perovskites with high Curie temperature present better down-scaling properties than relaxor based MPB systems and model tetragonal perovskites.

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