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Dielectric and piezoelectric properties of the mechanochemically prepared PZT ceramics

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Mechanochemical synthesis was applied to obtain nanocrystalline powders of composition $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT). Milling was performed in a planetary ball mill using vials and balls made of zirconia or steel in order to investigate influence of milling media on the electrical properties of resulting ceramics. PZT ceramics showed high values for dielectric constant (ε_r), reaching 970 at room temperature, as well as low dielectric loss ($\tan\delta$) under the optimal processing conditions. High values of remanent polarization (P_r) indicate high internal polarizability. The best samples showed piezoelectric strain constant $d_{33} = 347$ pC/N and planar coupling factor $k_P = 0.44$. Milling in ZrO_2 medium prevents powder contamination and provides reproducibility of milling process. Also, PZT obtained from the powders milled in ZrO_2 exhibited lower values of dielectric loss, in comparison with the PTZ obtained from the powders milled in Fe. This suggests that contamination of the powder with Fe could result in an increase of conductivity in final product.

1. Introduction

Recently, mechanochemical synthesis was successfully used to synthesize PZT [1–5] ceramics. The basic idea was to apply intensive milling in solid state synthesis of PZT and to skip multiple steps of calcination at elevated temperatures and subsequent milling. Also, it was expected that the highly activated powder of PZT could be sintered at lower temperature, so the evaporation of PbO during sintering would be decreased or completely eliminated. On this way the stoichiometry of the powder would be maintained. All above mentioned authors investigated PZT with the composition near the morphotropic phase boundary ($Pb(Zr_{0.52}Ti_{0.48})O_3$), where the maximum in the dielectric and piezoelectric properties should be obtained. The piezoelectric properties of PZT obtained via mechanochemical synthesis are not published yet. As the electrical properties of PZT are very sensible on the presence of contamination, for example Fe from the milling vials and balls, it is very important to investigate influence of milling media on the properties of final ceramic product.

In this work we report about dielectric and piezoelectric properties of PZT prepared by mechanochemical synthesis in different milling media. The obtained ceramics showed good electric properties confirming the possibility of application of mechanochemisty in synthesis of ferroelectric materials with perovskite structure, such as PZT. Better results are obtained using ZrO_2 than stainless steel vials and balls, especially in reproducibility of preparation process.

2. Experimental procedure

The PZT composition selected for this study was $Pb(Zr_{0.52}Ti_{0.48})O_3$, which is near the morphotropic phase boundary. In powders milled in ZrO_2, about 1% of PbO was added in excess to maintain stoichiometry because ZrO_2 from balls and vials is entering the powder mixture during intensive milling. The starting materials were commercially available PbO (Budochemia), ZrO_2 (Carlo Erba) and TiO_2 (Vetec), all of >99.9% purity. According to the chemical formula of the desired PZT ceramics, appropriate amounts of starting oxides were weighted, mixed and further milled in planetary ball mill (Fritsch). Milling conditions were the following: stainless steel or ZrO_2 vials ($V = 500$ cm^3), stainless steel balls ($d = 13.4$ mm), ZrO_2 balls ($d = 9$ mm), ball-to-powder weight ratio was 40:1, powder quantity was 20 g, air atmosphere, basic disc rotation speed was 317 min^{-1}, rotation speed of discs with vials

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was 396 min^{-1}, milling time was 60 and 120 min. Obtained powder samples were characterized by the method of X-ray powder diffraction analysis (using a Siemens D-5000 1710 powder diffractometer with graphite-monochromatized Cu K_α radiation).

Synthesized powders were calcined at 500°C to remove carbonates and/or hydroxide, uniaxially pressed under the pressure of 800 MPa and sintered at 1150°C for 120 min. Heating and cooling rates were 5°C/min. Apparent densities of bulk samples were determined by the Archimedes method. The microstructure of the sintered samples was analyzed by scanning electron microscopy (SEM) (Topcon SM-300). Electrical characterization consisted in measuring dielectric and piezoelectric properties: dielectric constant (ε_r) and dielectric loss (tanδ) at frequency 1 kHz, determination of Curie temperature (HP9192A), hysteresis loops, remanent polarization (P_r (μC/cm^2)) and coercive field measurements (K_c (kV/cm)) (Radiant Technologies), as well as planar coupling factor (k_P) and piezoelectric strain constant (d_{33} (pC/N)).

3. Results and discussion

We already reported about properties of PZT synthesized in Fe medium [4, 5]. Here we will just summarize these results. After milling of the starting powders in Fe medium for 60 and 120 min almost the pure perovskite phase was registered by X-ray diffraction analysis. The X-ray diffraction patterns of powders milled in ZrO_2 vials for 60 min showed the presence of unreacted starting oxides (Fig. 1). Obviously, milling in ZrO_2 medium has lower efficiency. There are two possible reasons for that. First, ZrO_2 balls are of smaller diameter. The second reason is the lower density of ZrO_2 balls. Anyway, two hours of milling were demanded to obtain pure perovskite phase.

Although the electrical characteristics of the PZT milled in stainless steel media were very good [5], the low reproducibility was found. Repeated milling process showed spreading in values of density (95–99% of theoretical density) and also in electrical properties, especially in values of dielectric losses (tanδ = 0.04–0.07) and remanent polarization

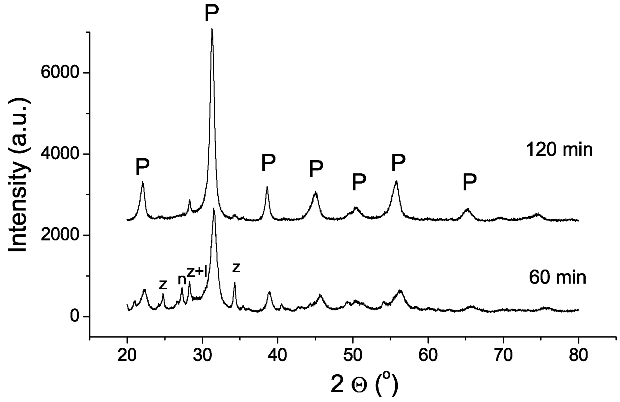


Figure 1 X-ray diffraction patterns of PZT powders mixtures milled in ZrO_2 media for 60 and 120 min (*n*-nonstoichiometric compounds of Zr and Ti, *z*-ZrO_2, *t*-TiO_2, *l*-PbO, *P*-perovskite).

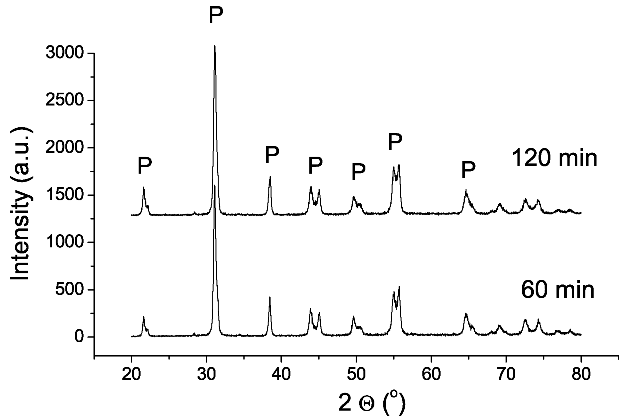


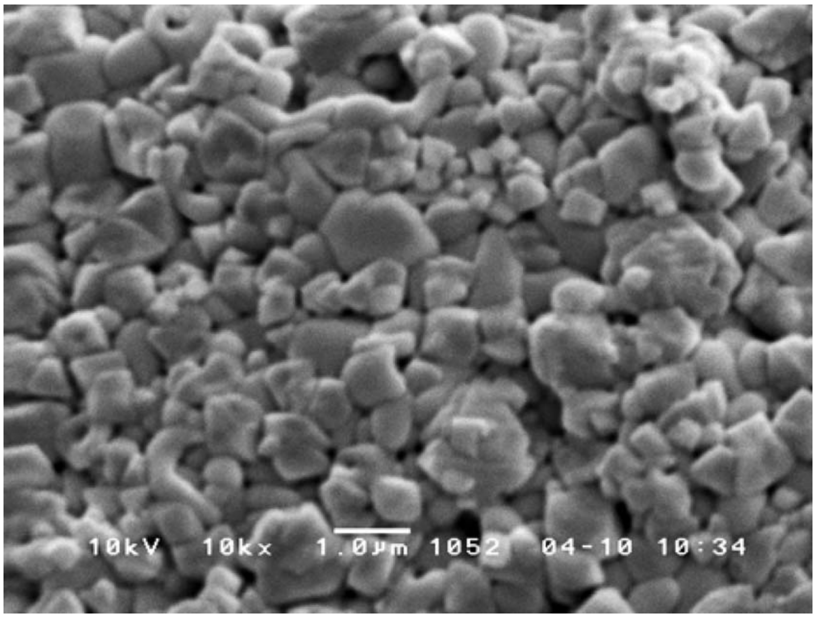
Figure 2 X-ray diffraction patterns of sintered samples milled in ZrO_2 media for 60 and 120 min (*P*-perovskite).

(P_r = 30–60 μC/cm^2). These parameters are especially sensible to the presence of foreign ions, such as Fe from vials and balls. Fe can significantly change the conductivity and its concentration in PZT powder can hardly be controlled. These were the main reasons to investigate PZT synthesis in different milling media, especially in ZrO_2.

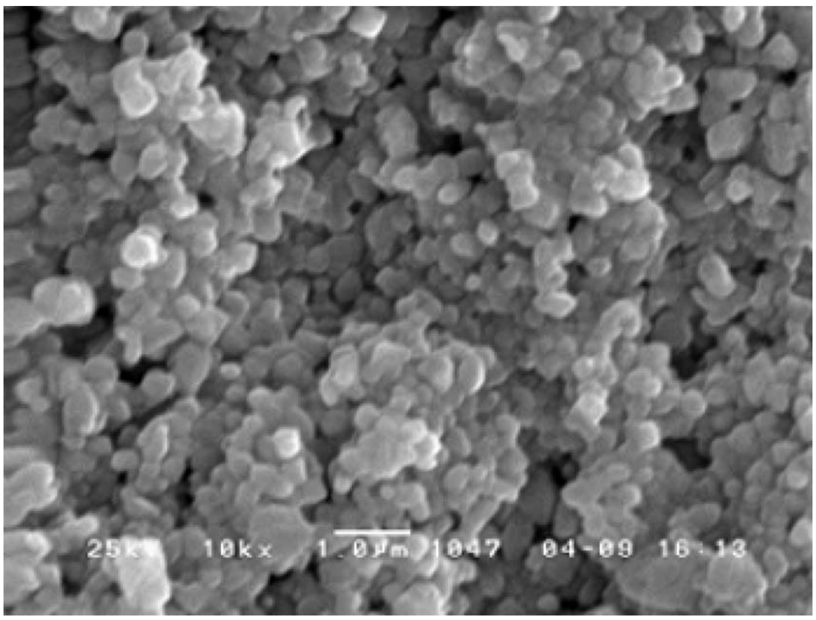
Sintered samples contained pure, well-crystallized perovskite phase in both milling media (Fig. 2 and [5]). Samples milled in ZrO_2 showed 95.8 and 94.8% of theoretical density for powders milled for 60 and 120 min, respectively. Although reaction was not completed in powders milled for 60 min, these powders were more activated for sintering and higher densities were reached. Moreover, reaction sintering can promote shrinkage and densification in these powders during thermal treatment. In accordance with this result, microstructural analysis showed larger grains in samples milled for 60 min (Fig. 3). Mean grain size was 0.82 μm in samples milled for 60 min and 0.39 μm in samples milled for 120 min. These values are similar to those obtained in samples milled in Fe media.

Dielectric properties of all investigated samples, measured at room temperature, are given in Table I. As it can be seen there is no significant difference in ε_r between samples milled in ZrO_2 or in Fe for 60 min, but sample milled for 120 min in Fe showed lower value of ε_r. On the other hand, samples milled in ZrO_2 medium showed more than 50% lower values of tan δ, which is important improvement. In comparison to the reported data in the literature for mechanochemically synthesized PZT [1, 3, 6, 7], slightly lower values of dielectric constants, but also lower values of dielectric loss are obtained in our investigation.

Values of remanent polarization (P_r) and coercive fields (K_c), obtained from the hysteresis loops (Fig. 4), are given in Table I. According to literature data, typical values of the lead-containing ferroelectrics vary from 30 to 40 μC/cm^2, whereas the values of K_c vary over a wide range, from ∼2 kV/cm to near electrical breakdown (∼125 kV/cm), depending on the type of dopants [8]. The best values were obtained in some samples milled in Fe and these values reached 60 μC/cm^2. Unfortunately, it was very difficult to reproduce these



(a)



(b)

Figure 3 SEM of the PZT powder mixtures milled in ZrO_2 media for: (a) 60 min and (b) 120 min.

results and a great spreading of values of P_r was registered. Samples milled in ZrO_2 for 120 min exhibited lower values of P_r with a better reproducibility. The hysteresis loop of samples milled for 60 min suggests high conductivity of sample.

Some of the samples milled in Fe medium were difficult to polarize and there were a lot of samples that could not be polarized for measurements of piezoelectric properties. Since these problems are "proportional to the milling time," they can be connected with the concentration of Fe inside the sample. High concentration of Fe in samples milled for longer time significantly change electrical conductivity and other properties of PZT. Values of characteristic piezoelectric parameters, planar coupling factor (k_P) and piezoelectric strain constant (d_{33}), are given in Table I. Samples milled in ZrO_2 for 120 min exhibited higher values of these parameters, confirming a bad influence of Fe incorporation on electric and piezoelectric properties. These values of d_{33} are similar to those measured for PZT prepared by other methods [8–10]. Otherwise, values of k_P are lower than that usually reported by other authors

TABLE I Room temperature values of dielectric constant (ε_r), dielectric loss ($\tan\delta$), remanent polarization (P_r), coercive field measurements (K_c), planar coupling factor (k_P) and piezoelectric strain constant (d_{33}) of the samples milled in Fe and ZrO_2 for 60 and 120 min

	in ZrO_2 medium		in Fe medium	
Time of milling (min)	60	120	60	120
ε_r	910.1	970.8	930.3	811.2
$\tan\delta$	0.022	0.019	0.04	0.06
K_c (kV/cm)	19.2	20.7	26.2	38.5
P_r ($\mu C/cm^2$)	27.1	33.9	60.4	57.3
d_{33} (pC/N)	185	347	–	140
k_P	0.08	0.44	–	0.30

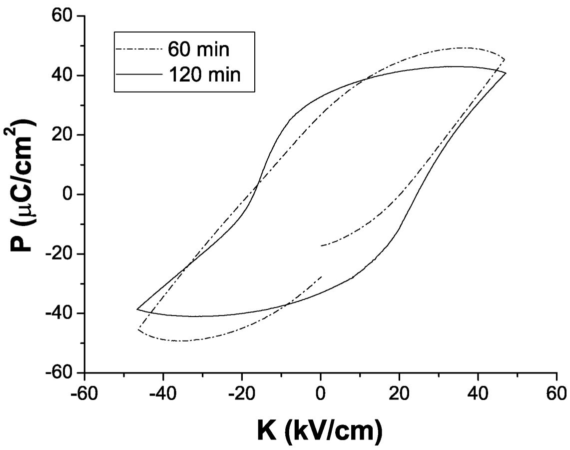


Figure 4 Hysteresis loops of the samples milled in ZrO_2 media for 60 and 120 min.

[8–10]. Samples milled for 60 min showed low values of piezoelectric parameters, confirming that these samples were not milled enough to finish reaction and to provide homogeneous microstructure and properties.

4. Conclusions

PZT ceramics with composition $Pb(Zr_{0.52}Ti_{0.48})O_3$ was obtained from the mechanochemically synthesized nanocrystalline powders. Milling was performed in planetary ball mill, using ZrO_2 or steel vials and balls. Electrical properties of the sintered samples showed that milling in Fe medium results in inferior properties in comparison with samples milled in ZrO_2, because of high concentration of Fe incorporated in powder mixture during milling. This process is very difficult to control, so these properties showed low reproducibility. Milling in ZrO_2 media can solve this problem.

PZT obtained from mechanochemically synthesized powders in ZrO_2 media showed good electrical properties: dielectric constants reaching 970 at room temperature, dielectric loss as low as 0.019, and remanent polarization up to 34. Values of d_{33} obtained for samples milled in ZrO_2 are as high as 350 pC/N, and similar to values measured in PZT prepared by some other methods.

Obtained results showed that mechanochemical synthesis could be applied in preparation of PZT ceramics, but use of ZrO_2 medium is recommended to avoid harmful powder contamination.

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