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Synthesis and piezoelectric properties of nanocrystalline PZT-based ceramics prepared by high energy ball milling process

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Nanocrystalline powders of a soft FeNbLi-doped PZT material have been prepared by a novel mechanochemical process consisting of mixing the stoichiometric oxides in a planetary ball mill for prolonged times up to 80 h. The constituent oxides were reacted in a tungsten carbide vial with balls of 5, 10 and 20 mm in diameter and a ball/powder ratio of 15/1. The chemical reaction between the component oxides was triggered after 20 h of energetic milling and was completed after 80 h. The XRD of the reacted nanopowder showed the well known perovskite structure. Compacted samples of this powder were sintered between 800–1300°C for 3 h and the main piezoelectric properties were determined. The density of the sintered samples reached nearly 99% of the theoretical density at 1100°C and showed good piezoelectric characteristics: planar coupling factor of 0.66, dielectric displacement constant d_{33} of 550 pm/V, mechanical quality factor of 85, and relative dielectric constant of 3800. The possible mechanisms for solid state reaction of mechanically activated nanopowders such as local heating and pressure at collision as well as defects diffusion are discussed.

1. Introduction

The importance of nanomaterials is now largely recognized due to the possibilities of improving the macroscopic properties of materials by varying their crystallite sizes. Among these materials, lead zirconate-titanate electroceramics play a major role in science engineering, electronic industry, space industry and medicine as well as domestic life [1–6]. Moreover, the recent advances in Micro Electro Mechanical Systems (MEMS) have created a strong interest in the fabrication of small piezoelectric transducers for various applications in the field of sensors and actuators for industrial applications [7].

The most usual, simple and cheap technology for making such materials is the well known ceramic technique, consisting of intimately mixing the stoichiometric oxides, followed by calcining this mixture at elevated temperatures. Calcination is an important step of this technique since, during it, the component oxides react by several mechanisms, among which diffusion plays an important role, and eventually, a rather homogeneous compound is formed.

Quite recently, novel mechanochemical processes have successfully synthesized a number of ceramic powders such as barium titanate [8], lithium and titanium oxides, and some niobates [9–11], bismuth vanadates [12], ferrites [13–17], composites [18, 20], and alloys (see for instance Ref. [21]) and complex perovskites [22, 23].

In this process the solid state reaction of oxides is activated by the combined effect of high mechanical energy and temperature produced during milling. Such process skips the high energy consuming calcination step, making the preparation process simpler than the conventional technique. Moreover, since it takes place at low temperature in a sealed container, the loss of lead is completely alleviated. Furthermore, the powder being in the nanometer range it exhibits a much higher degree of sinterability.

Several simple lead oxide-based ferroelectrics and piezoelectric with perovskite structure have already been synthesized by this new mechanically activated process, which involves nucleation and subsequent growth of perovskite nuclei into nanocrystallites as a

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result of continuous mechanical activation [22]. The piezoelectric materials processed by this technique were mixtures of the three basic oxides corresponding to classical PZT composition and there is not too much experimental evidence about the preparation of more complex PZT composition, containing more than three oxides. Therefore, the present investigation shows the results of the preparation by mechanochemical activation of a more complex composition, containing seven oxides, of a usual soft type piezoelectric composition. The sinterability behavior as well as the piezoelectric properties of the ceramic samples prepared by a mechanochemical process are compared with the properties of the same ceramic composition prepared by the conventional technique.

2. Experimental

The composition chosen for the present investigation was a soft type piezoelectric material with the following chemical formula: $Pb_{0.99}La_{0.01}(Fe_{0.01}Nb_{0.02}Li_{0.007}Ti_{0.453}Zr_{0.53})O_3$. Reagent grade oxides, commercially available with different grain sizes were used as starting materials. The stoichiometric amount of these oxides was firstly mixed for 2 h in acetone, using agate vials and balls of 10 mm diameter, in a planetary mill. After drying the mixed oxide powder showed a specific surface area of about 15 m^2/g corresponding to an average grain size of 62 nm. The mixture was then subjected to mechanical activation process by means of prolonged milling in a planetary ball mill using tungsten carbide vials and 3 tungsten carbide balls of 5, 10 and 20 mm diameter and a balls/powder weight ratio of 15/1. The mixed oxides were milled up to 80 h with an increment of 10 h, and were analyzed by X-ray diffraction technique using a Siemens Kristalloflex diffractometer provided with a copper target tube and a graphite monochromator. Electron microscopy was also used to evaluate the powder morphology after milling as well as after sintering. The same composition was also processed, for comparison, by the conventional technique where the mixed oxides were calcined at 880°C for 2 h, followed by the usual milling in acetone using agate vials and balls of 10 mm diameter, for 2 h.

3. Results and discussion

Fig. 1a displays the X-ray diffraction patterns for different milling times. The initially mixed oxide powder (0 h milling) shows the presence of lead oxides only. A milling time of 10 h was not enough to trigger the reaction between the component oxides but it seems to start after approximately 20 h of milling, where traces of the PZT perovskite structure appeared. After 40 h of milling, the formation of the perovskite is rather well defined and it is completely finished after 80 h of milling, where only the PZT perovskite phase is present, except for some insignificant traces of unreacted lead oxide. This last diffraction pattern was compared with the one obtained on the same composition prepared by the conventional mixed oxide route and calcined at 880°C for 2 h (Fig. 1b) where only PZT perovskite phase is present. One can easily see that from the point

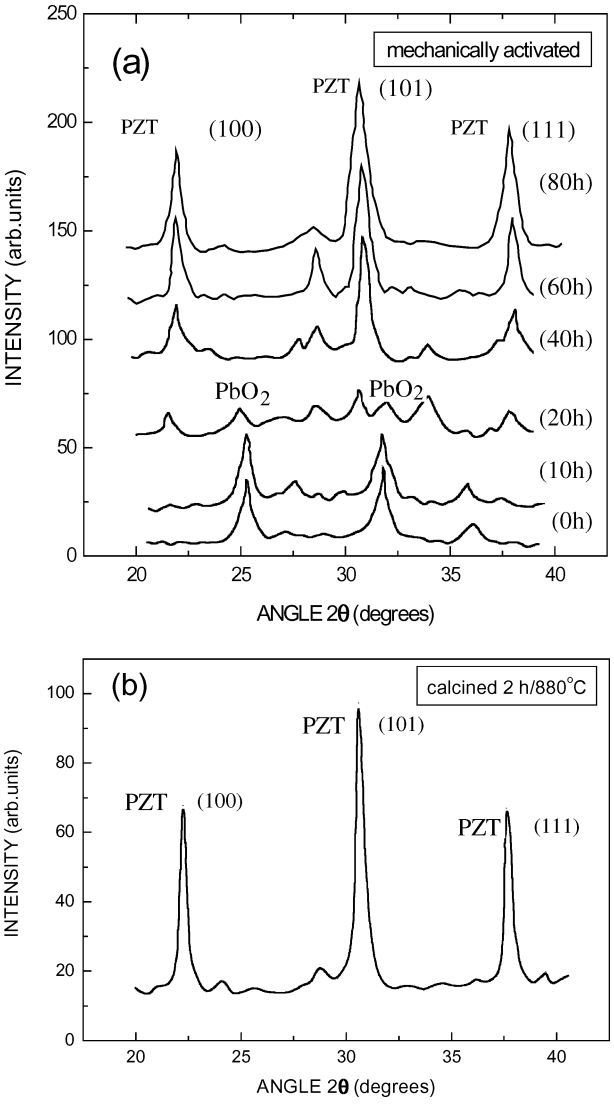

Figure 1 X-ray diffraction patterns of the PZT complex powders: (a) prepared by mechanochemical process, for different milling time and (b) prepared by conventional mixed oxide route and calcined at 880°C for 2 h.

of vie of phase composition there is no noticeable differences between them.

The micrograph of the powder prepared by mechanochemical process after 80 h of milling is shown in Fig. 2a. Its nanostructure appears obvious but the crystallites cannot be clearly identified. This fact can be assigned to the refinement of the particles together with a high degree of amorphization of the constituent oxides. In order to remove the residual stresses induced by prolonged milling we annealed this powder at 600°C for 2 h. The resulted powder is shown in Fig. 2b. Now, the crystallite shapes become more clearly defined but their sizes remain practically unchanged.

The micrograph of the powder prepared by conventional route is shown in Fig. 2c. Here, the crystallites are well defined, but they have large dimensions, up to few microns. If in the case of this powder the formation mechanism of the perovskite phase is rather well known, i.e., the thermally activated diffusion, in the case of mechanochemically processing, the formation mechanism seems to be more complicated and is not yet fully understood. Up to now the experimental evidence

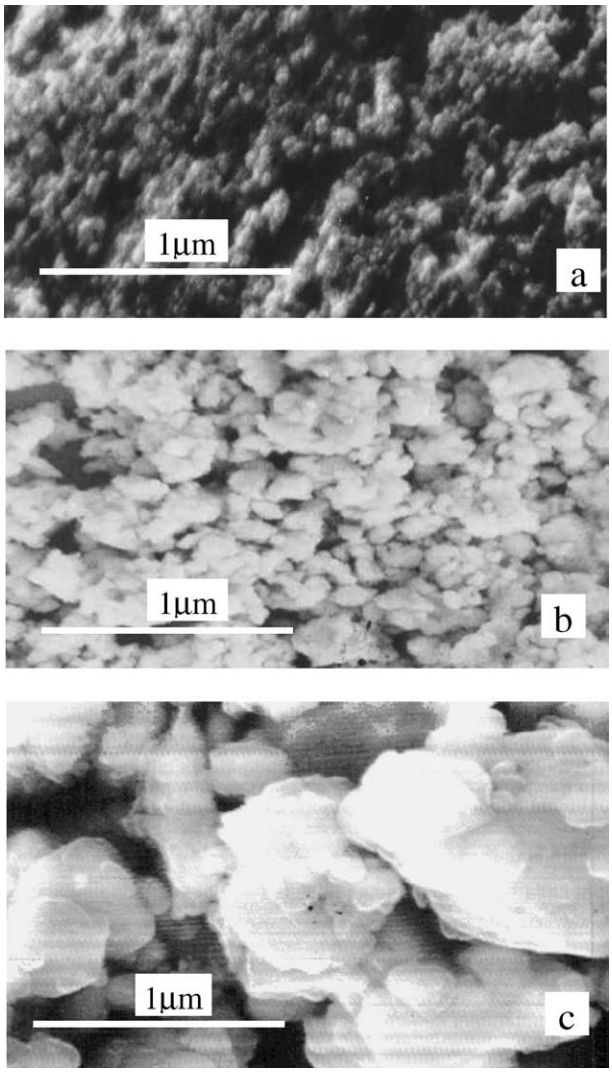

Figure 2 Micrographs of the PZT complex powders prepared by different routes: (a) mechanochemical process for 80 h, (b) the same powder after removing the residual stresses by annealing at 600°C for 2 h and (c) conventionally prepared by mixing and calcining at 880°C for 2 h.

indicates that in the first step of the process there is a significant refinement in particles and crystallite size. The increase of the surface area during this step is about ten times. This refinement is accompanied by a high degree of amorphization. At this level of particles refinement, some nuclei of the perovskite structure are initiated at the occurrence of the nanoparticles of the different constituent oxides by the local high temperatures and pressures created by collision of balls between them and/or the wall, when collisions take place at favorable angles. Next these perovskite nuclei are constantly distributed within the entire mass of the activated matrix powder and when they meet create the opportunity to grow, giving rise to a bigger crystallite with the same structure. There are indications [23] that local temperatures at the collision point may reach 500°C or more and the pressure reaches several kilobars [24]. Thus, the combined effect of local temperature and pressure created by collisions may initiate the reaction between the constituent oxides.

The sintering behavior of the nanoscale powder as well as the conventionally prepared powder is shown

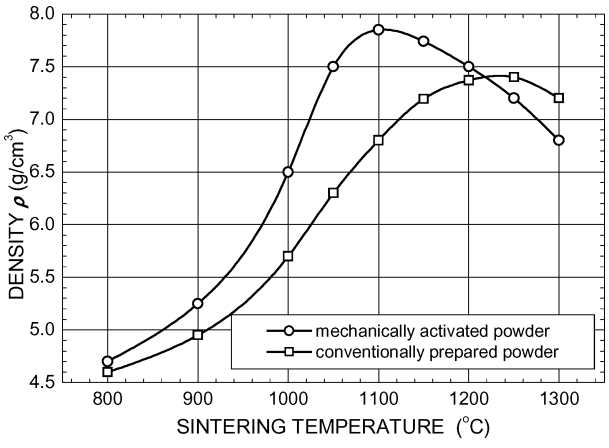

Figure 3 Sintering behaviour of the PZT complex powders, prepared by mechanochemical process and by conventional technique.

in Fig. 3. The sintering was carried out on disk shaped pressed samples of both powders. One can see that mechanically activated powder reaches its maximum density of about 7.85 g/cm^3 (about 99% of the theoretical density) at around 1100°C while the conventionally prepared one reaches its maximum density of about 7.4 g/cm^3 (about 94% of the theoretical density) at around 1250°C. One can notice that the temperature required for maximum densification of the nanopowder is about 150°C lower than that required by the conventionally prepared one. This fact may be attributed to the more reactive nanoparticles which can produce a dense ceramic at lower temperatures.

The microstructures of both sintered powders are shown in Fig. 4, for samples with maximum densities, in each case. One can see that both powders exhibit almost the same grain size growth behavior having similar morphology, except the fact that nanopowder produced by sintering is a more compact and rather poreless ceramic (Fig. 4a), while the conventionally prepared powder possess some pores and is less dense (Fig. 4b). This also explains the differences in the densities of the sintered samples.

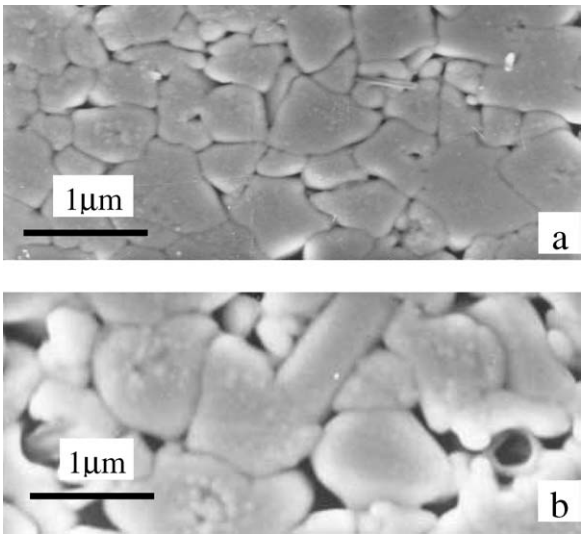

Figure 4 Microstructure of the sintered samples prepared by: (a) mechanochemical process and (b) conventional mixed oxide route and calcined at 880°C for 2 h.

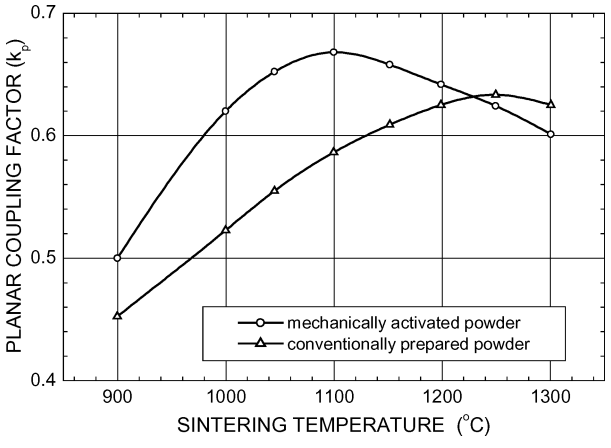

Figure 5 The behaviour of the planar coupling factor k_p for sintered samples, made from powders prepared by mechanochemical process and conventional technique.

Fig. 5 shows the dependence of the main piezoelectric electromechanical coupling factor k_p on the sintering temperature. As one can see the maximum values are centered around the same sintering temperatures as the densities. One may also note the slightly higher values of k_p for samples sintered from nanopowder compared with the samples sintered from conventionally prepared powder.

Dielectric constants measured at 1 kHz showed better values for nanopowder samples. Thus, the measurements for 6 samples gave values of ε of 3500–4000 compared with only 1800–2100 for samples sintered from conventionally prepared powder. This can actually be a grain size effect, since increasing grain size reduces the volume fraction of grain boundaries and consequently the coupling effect between the grain boundaries and the domain walls.

4. Summary

Powders of a soft PZT type piezoceramic material were synthesized both by conventional and mechanochemical activation techniques. The average grain size of the conventionally prepared powder was within the micrometric range, while that of the mechanochemically activated one within the nanometer range, as shown by X-ray and microscopic investigations.

Sintered bodies from both types of powders were produced at different temperatures from 800°C up to 1300°C and their properties were determined. Maximum densities and better piezoelectric properties were obtained for samples sintered from nanopowder at lower temperatures.

The mechanical activation technique has proven to be a reliable and simpler technique, able to produce high quality sintered ceramic bodies.

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