



Ferroelectric perovskite nanopowders obtained by mechanochemical synthesis

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Abstract

Simple perovskite nanopowders were fabricated by mechanochemical synthesis. High-energy milling process of respective oxides, leading to production of ferroelectric perovskites, was carefully investigated and characterized by X-ray diffraction, electron microscopy and X-ray excited photoelectron spectroscopy. It has been found that: (i) the powder consists of loosely packed grains with a broad distribution of sizes between a few nm and 45 nm, (ii) the grains possess core/shell structure, (iii) the grain core of sizes larger than about 20 nm exhibits well developed crystalline structure, (iv) the grains are coated by structurally disordered (amorphous) shell. Intermediate phases have been found in the process of PbTiO_3 mechanosynthesis only. The obtained nanopowders were used for preparation of dense ceramics.

Keywords: mechanochemical synthesis, perovskites, nanopowders, core-shell structure

I. Introduction

Electroactive perovskites, the best materials for smart structures, sensors and actuators, are conventionally obtained by solid-state reactions or wet-chemistry. The methods usually need the high temperature treatment (even several hundreds degrees Celsius) in order to obtain the proper crystallographic structure. During last decades a big effort has been done on lowering temperature requires for perovskite preparation and high-energy mechanical milling has been successfully used to synthesize various nano-sized powders of ferroelectrics [1–26]. Nanostructure materials, with grain size of few nanometers, are produced due to repeated deformation caused by high-energy compressive impact forces. The technique can be used to induce chemical reactions in powder mixtures at room temperature, or at much lower temperatures than normally required to synthe-

size, because the large volume fraction of atoms in the grain boundaries enhances the diffusion. The processing of the materials is far from the equilibrium conditions and the constitution of the synthesized powder depends not only on the type of the mill and milling container but also on the milling time, milling speed and the ball-to-powder weight ratio. The most important parameter of the mechanosynthesis is the time of milling which has to be optimized for the type of mill used and the particular powders as well as the intensity of milling and the ball-to-powder ratio. From technological point of view mechanochemical synthesis seems to be very attractive also because simple oxides can be used as starting materials for oxide perovskites, the method enables strict control of stoichiometry and eliminates undesirable losses of volatile elements. Moreover, mechanochemical synthesis is a low-temperature solid-state processing technique and therefore limitations imposed by phase diagrams do not apply here. It is especially appropriate for synthesis of lead-based complex perovskites

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with relaxor properties for which the synthesis by mechanical activation is different from thermally-induced solid state reaction [1–9]. Though there are numerous papers related to mechanochemical synthesis of ferroelectric perovskites [8–18] the information on the structure of the nanograins are rather poor. There are however few papers related to the structure of nanograins of nickel ferrite and solid solution of nitrogen in ferrite produced by mechanochemical synthesis [28,29]. Here we would like to present our last achievements related to the characterization of nanosized BaTiO_3 , PbTiO_3 and PZT powder prepared by mechanochemical synthesis.

II. Experimental

Commercially available oxides (BaO , PbO , TiO_2 -anatase and ZrO_2 purchased from Aldrich, 99% purity or higher) were used as starting materials. Mechanochemical synthesis was performed under normal atmospheric conditions using a SPEX 8000 Mixer Mill. The composition of the starting powder mixture corresponded to the stoichiometry reaction. Each batch contained about 6 g of powders. The round bottom stainless vials were used for the mechanical treatment. The weight ratio of hard steel balls to mixed powder was 2 : 1. The mill was run for various periods t_m ranging from 2–120 h.

The obtained powders were characterized by X-ray diffraction, electron microscopy and X-ray excited photoelectron spectroscopy (XPS). XRD were performed using an X-ray powder diffractometer with $\text{Co}_{K\alpha}$ or $\text{Cu}_{K\alpha}$ radiation at the various stages of milling. The structure of the powder was studied by high resolution transmission electron microscopy (HRTEM) with Philips CM-20 TEM working at the accelerating voltage of 200 kV. XPS spectra were recorded using a PHI 5700/660 Physical Electronics Photoelectron Spectrometer with monochromatized $\text{Al}_{K\alpha}$ X-ray radiation (1486.6 eV). The energy of the electrons was measured by means of a hemi-spherical mirror analyzer with an energy resolution of about 0.3 eV. In every case the neutraliser was used due to a charging effect that occurs for non-conducting samples. The binding energy was determined by reference to the C1s component set at the energy of 285 eV. The shapes of the bands were fitted after background subtraction, using the Gaussian-Lorentzian function.

III. Results and discussion

Figs. 1–3 show the XRD patterns of the starting oxides and their stoichiometric mixtures after various time of milling. The mechanochemical syntheses of BaTiO_3 , PbTiO_3 and $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ proceed similarly for all investigated compounds. At the first step of high energy milling all XRD peaks of the starting materials have disappeared. This stage has taken between 2 and 10 hours depending on the compositions. After 10–15 h of synthesis several relatively sharp diffraction peaks,

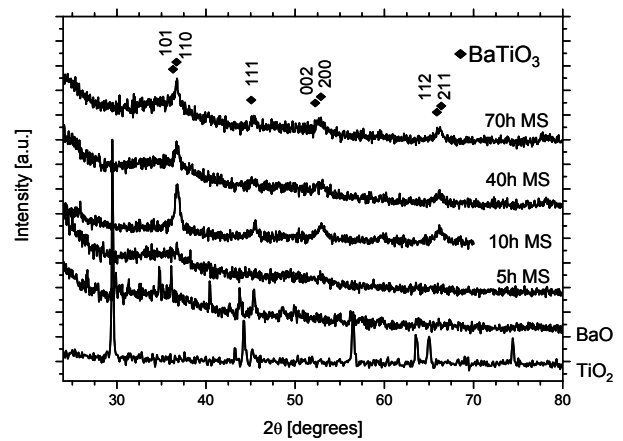
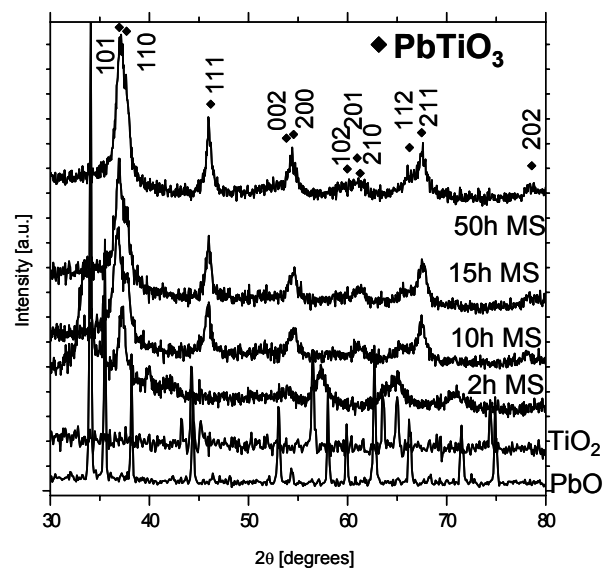
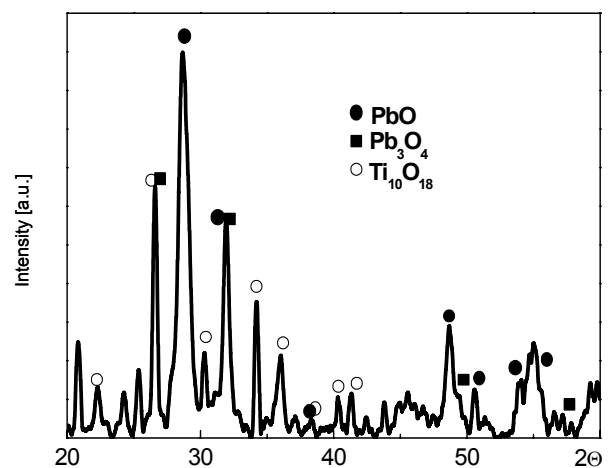


Figure 1. XRD patterns of starting oxides and BaTiO_3 after different milling periods (squares indicate peaks related to the perovskite phase)



a)



b)

Figure 2. XRD patterns recorded with $\text{Co}_{K\alpha}$ of starting oxides and PbTiO_3 : a) after various durations of high energy milling and b) traces of additional phases formed at the early stage of synthesis (diffractogram recorded with $\text{Cu}_{K\alpha}$ after 2 h of high-energy milling)

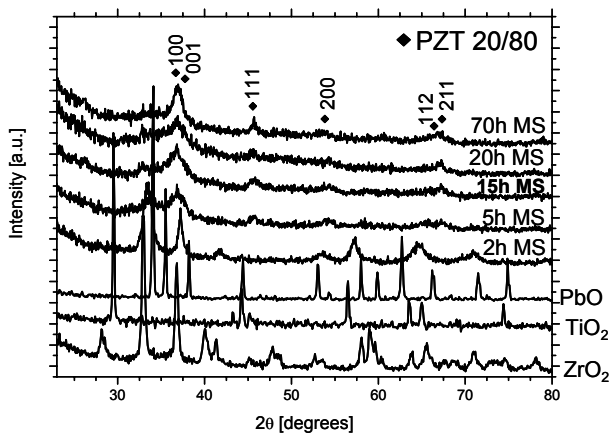


Figure 3. XRD patterns of starting oxides and $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ at different stage of mechanochemical reaction

characteristic of the perovskite structure, appear. Longer duration of mechanochemical synthesis (20–30 h milling) produced material with sharper peaks on diffraction patterns. However, for still longer milling periods (more than 30 h) the peaks become broader. This broadening suggests a significant refinement in the crystalline size. The appearance of these diffraction peaks prove that nanocrystalline perovskite can be obtained at room temperature without any additional crystallization steps.

During preparation of nanopowder sometimes intermediated phases have been observed on in the early stage of mechanochemical synthesis. This was a case for the PbTiO_3 formation when the traces of $\text{Ti}_{10}\text{O}_{18}$ and Pb_3O_4 were apparent (see Fig. 2b).

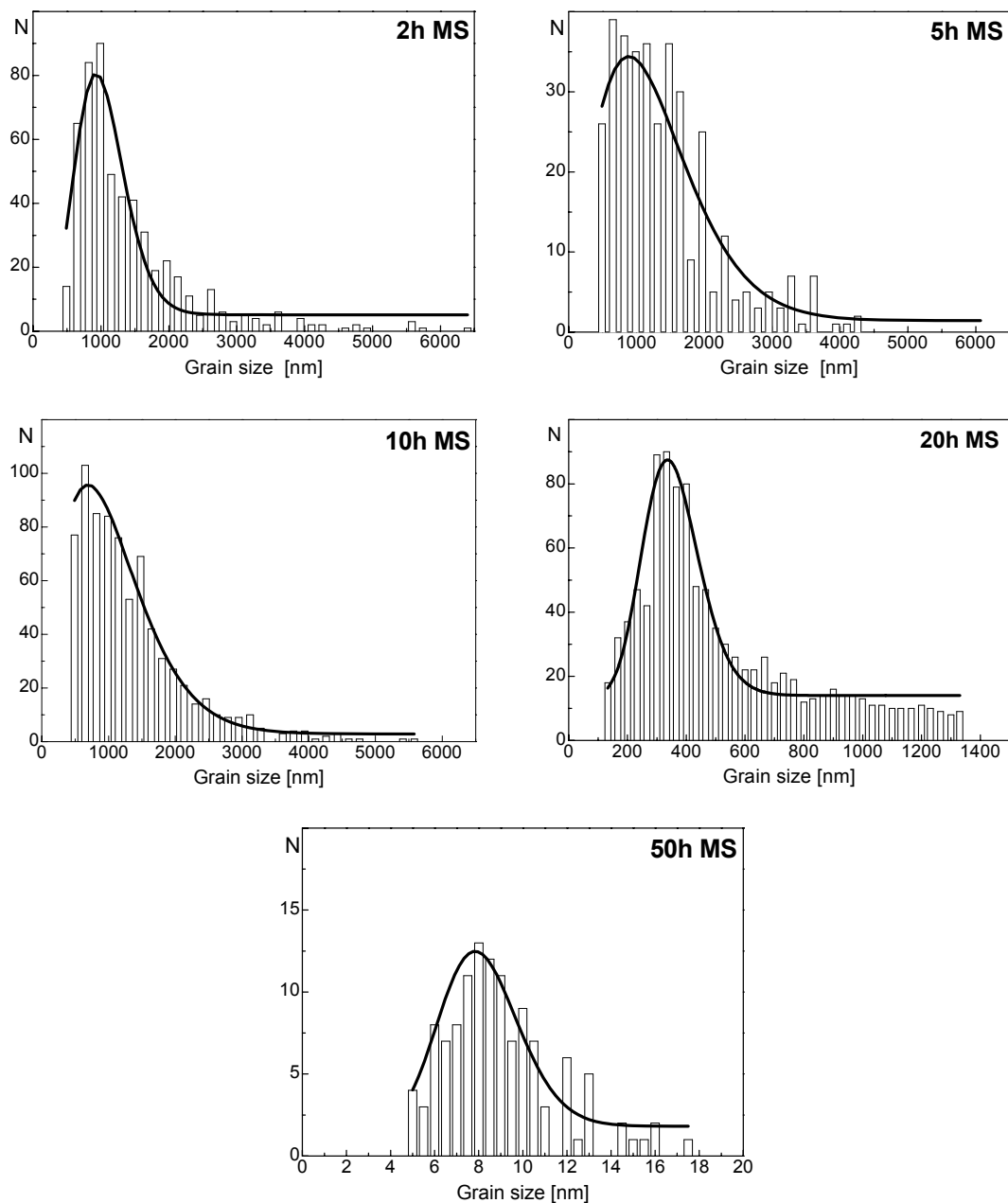


Figure 4. Distribution of grain sizes of PbO and TiO_2 powder at different stage of mechanochemical reaction

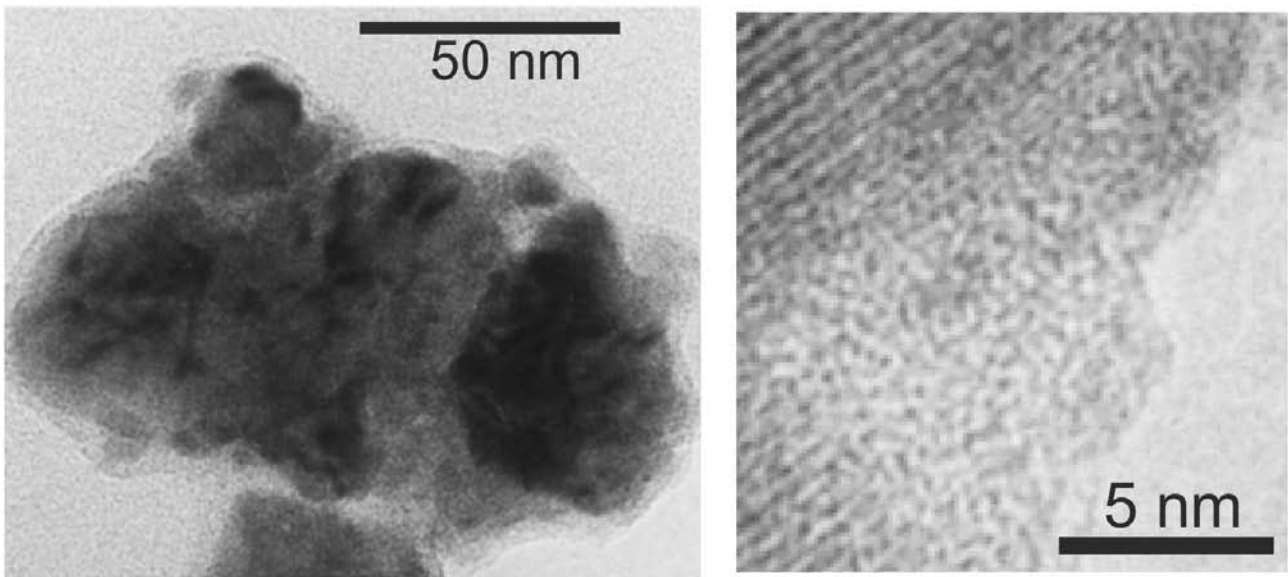


Figure 5. TEM images of PbTiO_3 powder after 50 h of mechanochemical synthesis

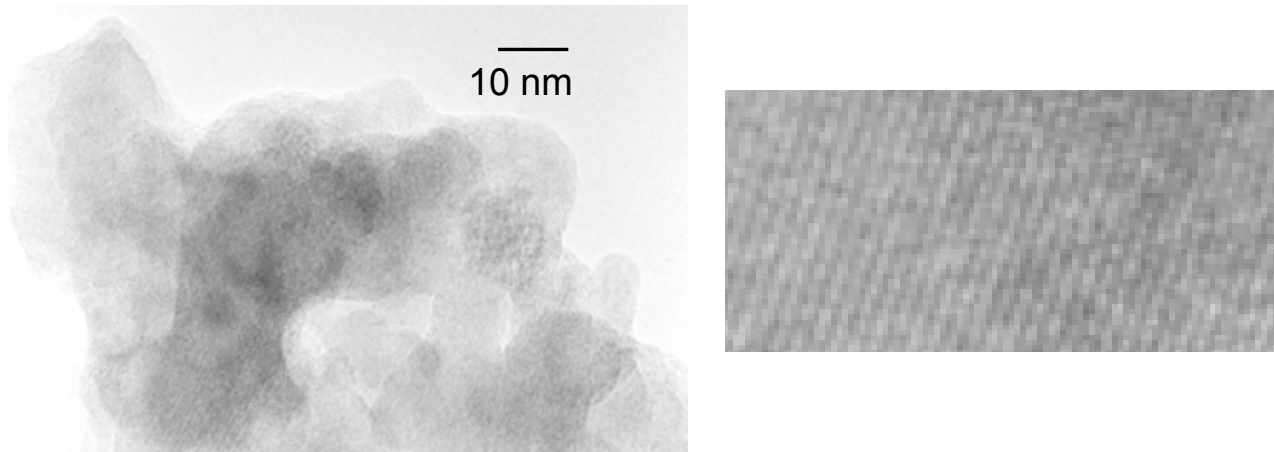


Figure 6. TEM images of BaTiO_3 powder after 120 h of mechanochemical synthesis

Based on XRD results the average sizes of crystallites have been determined as ~ 20 nm for 50 h milled PbTiO_3 and PZT. Based on electron microscopy images performed after different milling time the grain size distribution analysis was made and the results for milled powder of PbO and TiO_2 are shown in Fig. 4.

Fig. 5 presents TEM images of the 50 h milled PbTiO_3 sample and Fig. 6 shows high resolution structure of the 120 h milled BaTiO_3 . The crystallites form grains that are irregular loose-packed aggregates with lateral size of 70–150 nm. Detailed analysis made at high resolution showed that the grains are built by nanocrystallites. The size of the crystallites has broad distribution between a few nm and 50 nm. Grains larger than 20 nm have well-developed crystallographic structure (see Fig. 6b). All nanocrystallites are surrounded by thin disordered/amorphous 1–2 nm thick layer. In case of nanopowder with the smallest crystallites this amorphous phase can have even $\sim 40\%$ of the total volume. Because the ferroelectric properties

are closely related to the proper crystallographic (polar) structure the presence of core/shell structure may have a big impact.

The binding energies of the electrons, characteristic of a given element, are modified due to the valence electron distribution when the element is involved in a compound and moreover the atoms at the surface are in a different potential than the bulk atoms due to the reduced coordination number. The last effect that results in a core-level shift is considerably apparent for the nano-size particles. The X-ray photoelectron spectroscopy was used to characterize the formation of nanopowder from the respective oxides. Fig. 7 shows the main $O1s$ oxygen and $Pb4f$ lead peaks for PbTiO_3 single crystal and nanopowder after different periods of high-energy milling. The binding energy of $1s$ oxygen electrons in PbTiO_3 single crystal is equal to 530.3 eV and the full width at half maximum (FWHM) of the core $O1s$ line amounts to 1.7 eV. The $Pb4f$ core line exhibits two maxima due to spin-orbital splitting, which

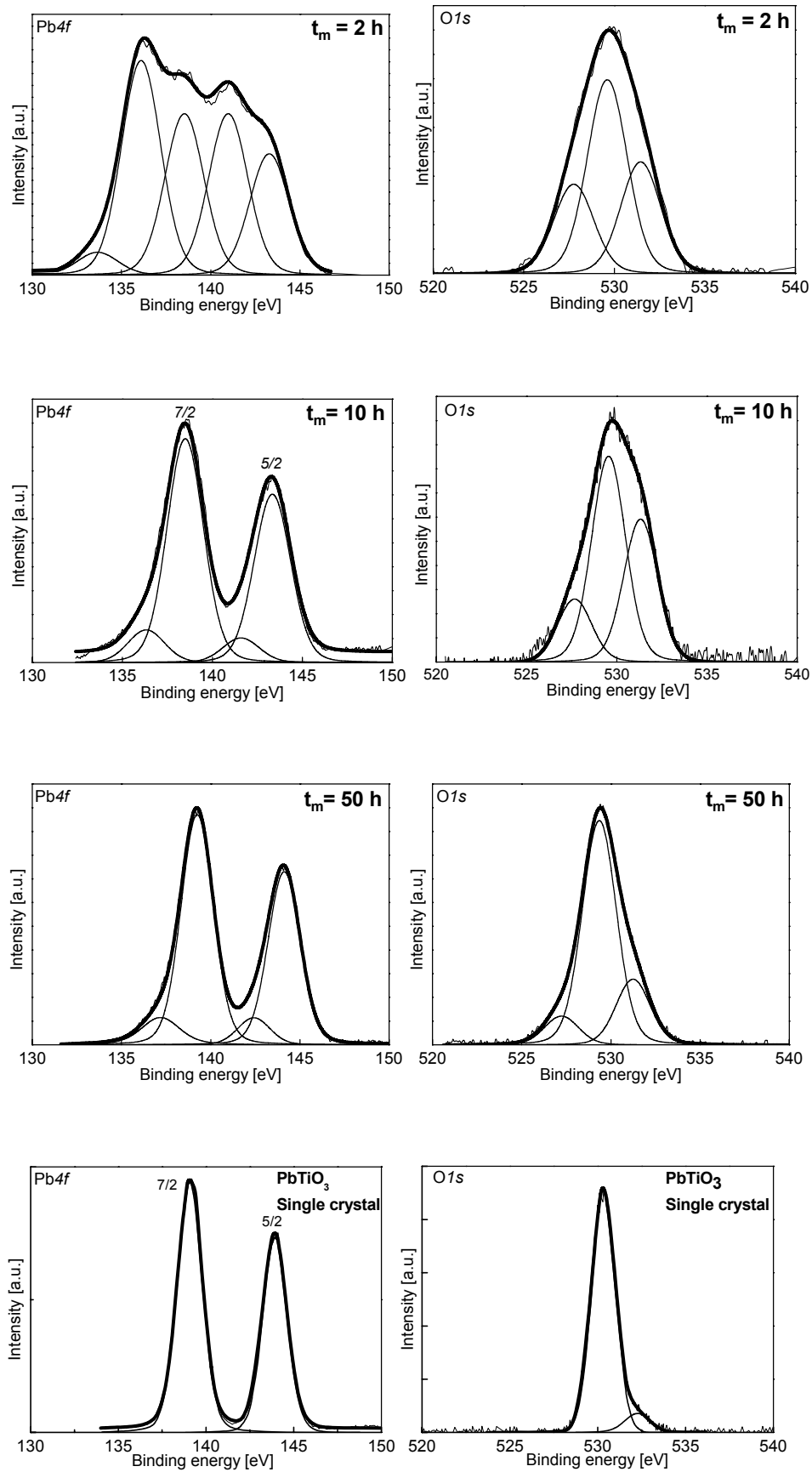


Figure 7. XPS spectra of $Pb4f$ and $O1s$ from PbO and TiO_2 after different milling periods (2, 10 and 50 h) and from $PbTiO_3$ single crystal

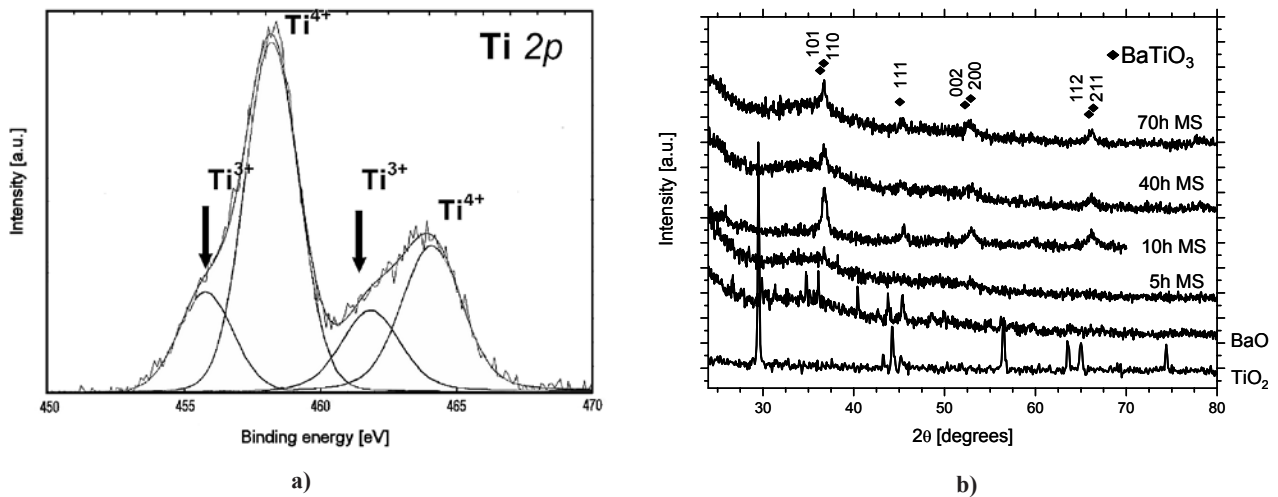


Figure 8. XPS spectra of $Ti2p$ from: a) BaO and TiO_2 high energy milled for 70 h and b) $BaTiO_3$ single crystal

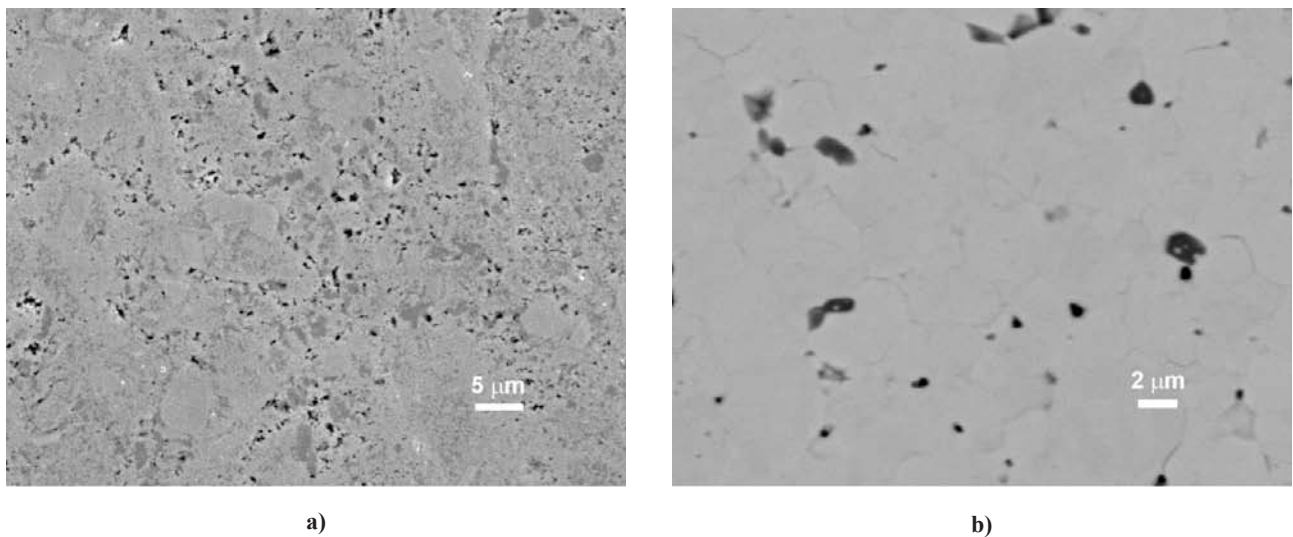


Figure 9. Microstructure of: a) $BaTiO_3$ and b) $PbTiO_3$ hot pressed ceramic

in $PbTiO_3$ single crystal are located at 143.9 eV (5/2) and 139.0 eV (7/2). In the beginning of the mechanical synthesis the spectra are complex and point to the presence a lead-rich phase, besides the starting compound PbO . As indicated by XRD, Pb_3O_4 is present in the activated powder in the early stage of the mechanical synthesis. For the powders activated for $t_m \geq 20$ h the core lines resemble those of $PbTiO_3$ single crystal but are broader and accompanied on their low-energy side by small components. The additional bands disappear after recrystallization. We ascribe the additional bands at the low energy side to the grain shells since the atoms at the surface are in different potential than that of the bulk atoms due to broken bonds and different mean electron densities at the ions. The spin-orbita splitting of $Ti2p$ peak into at 464.5 eV (1/2) and 458.7 eV (3/2) has been also observed for $BaTiO_3$ nanopowder (Fig. 8). The nanopowders obtained by mechanochemical synthesis were used for preparation of electroceramics.

The ceramics was fabricated by hot-pressing method appropriate for producing high density ceramics. $BaTiO_3$ nanopowder was pressed at 20 MPa and 1250°C for 2 h. The microstructure was investigated by scanning electron microscopy (Fig. 9a). The hot-pressing conditions for $PbTiO_3$ nanopowder were found as 20 MPa for 1150°C and 2 h (Fig. 9b). In both cases dense ceramics have been successfully obtained.

IV. Conclusions

Nanostructure materials, with grain size of few nanometers, are produced due to repeated deformation caused by high-energy compressive impact forces. During mechanochemical synthesis high energy milling reduces the particle sizes (increases in the contact area of reactant particles) and the reaction can proceed without thermally-induced diffusion through the product layer, i.e. during mechanochemical synthesis the solid state reaction occurs at lower temperatures. As a result of milling oxides pure perovskite phase nanopowder is

formed. The powder consists of loosely packed grains with a broad distribution of sizes between a few nm and 45 nm. All grains have a shell of thin disordered/amorphous layer the crystalline core that may have impact on final properties.

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