

Phase formations during mechanochemical synthesis of PbTiO_3

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Abstract Lead titanate nanopowders were fabricated by mechanochemical synthesis from lead oxide and titanium dioxide. The milling process has been carefully investigated by X-ray diffraction and X-ray excited photoelectron spectroscopy. The first traces of perovskite phase were detected after 5 h synthesis. It was found that intermediated phases ($\text{Ti}_{10}\text{O}_{18}$ and Pb_3O_4) have been formed at the early stage of synthesis. The 50 h milling results in single perovskite phase with average crystallite size of 20 nm.

Keywords Mechanochemical synthesis · Lead titanate · Perovskite structure

1 Introduction

Electroactive perovskites, the best materials for smart structures, sensors and actuators, are conventionally obtained by solid-state reactions or wet-chemistry. The methods are related to high production costs and have serious disadvantages: the calcination process that proceeds at several hundreds degrees Celsius, the chemistry-based routes use high purity chemicals that are usually expensive and difficult to handle (e.g. highly sensitive to moisture) and processing results in a coarsening and aggregation of the particles. A much less expensive alternative technique is a direct synthesis from respective oxides at room temperature via mechanically triggered chemical reaction. The method has been recently used to obtain nanocrystalline electroceramic materials of perovskite structure [1–6] and is especially appropriate for lead containing perovskites, which are known to exhibit high piezo- and pyroelectric-activity as well as high dielectric permittivity. The room temperature synthesis lowers the fabrication costs, eliminates the undesirable losses of volatile elements and enables the control of chemical and stoichiometry composition. Moreover, grains of nanometer size can be obtained, which enables the investigation of the ferroelectric phase stability in a volume with reduced spatial dimensions. The existence of the critical size, when ferroelectric behaviours vanish, is important both from fundamental and application point of view because it may be a technological limitation for miniaturization.

Lead titanate is considered as the ideal prototype ferroelectric since the phase transition is almost purely displacive with very high tetragonality and large value of spontaneous polarisation. It is also important because its solid solutions with lead zirconate (PZT, PLZT) are applied in almost all electronic devices (like miniature capacitors,

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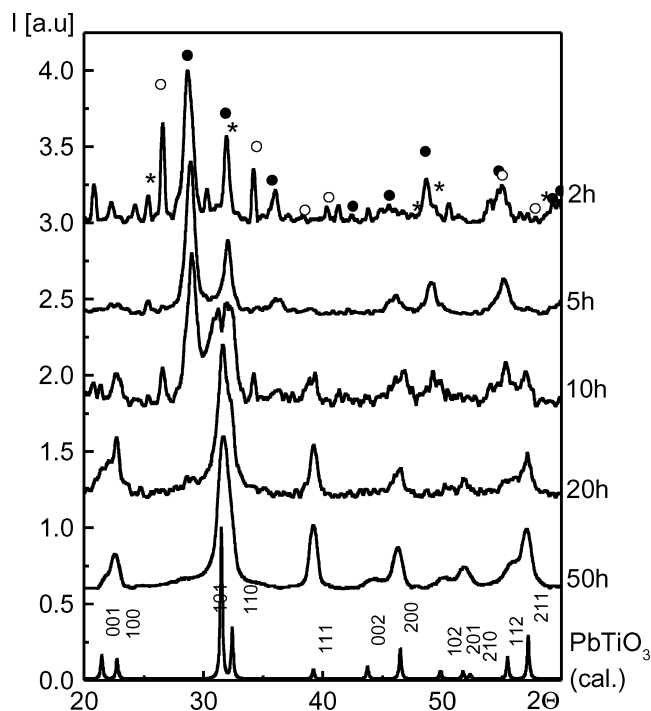


Fig. 1 XRD patterns of mechanically activated PbO and TiO₂ powder. Open circles indicate peaks originated from Ti₁₀O₁₈, solid circles—PbO and stars—Pb₃O₄. The calculated XRD spectra for tetragonal perovskite PbTiO₃ is showed on the bottom

transducers, actuators and electro-optic devices) [7]. We have obtained and characterized PbTiO₃ nanopowders by mechanical synthesis from PbO and TiO₂ at room temperature during 50 h milling in a SPEX 8000 Mixer Mill [8]. The transmission electron microscopy studies revealed a core-shell structure of the PbTiO₃ grains: the crystalline core was found to be surrounded by a disordered ~1 nm thick shell. Here we report the results of X-ray diffraction and X-ray excited photoelectron spectroscopy studies of various stages of the mechano-synthesis of lead titanate.

2 Experimental

PbTiO₃ was synthesized by mechanical activation from high purity PbO and TiO₂ (Aldrich). The mechanical

synthesis was carried out in a SPEX 8000 Mixer Mill for various milling times t_m at room temperature in the air atmosphere. Each batch contained ~6 g of the oxide powders in stoichiometric ratio. The weight ratio of the stainless steel balls to the oxides was 2:1. X-ray diffraction (XRD) and X-ray excited photoelectron spectroscopy (XPS) were used to study the development of the synthesis. We found it to be completed after $t_m=50$ h.

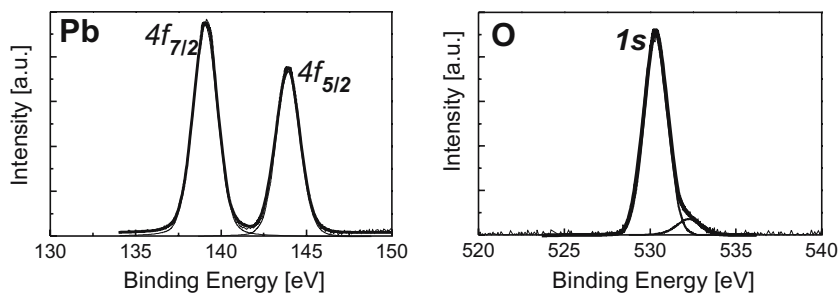
The synthesis of PbTiO₃ was controlled by X-ray powder diffraction studies at various time of mechanical activation. The diffractograms were recorded at room temperature using a STOE X-ray powder diffractometer with CuK α radiation. The diffractometer was equipped with a linear position-sensitive detector that allowed data collection within 2 θ angle in the range of 0–120°. Standard DHN-PDS reduction procedure was used to obtain final diffractograms of the PbTiO₃ powders.

XPS spectra of samples obtained after various times of mechanical activation of PbO and TiO₂ powders were recorded using a PHI 5700/660 Physical Electronics Photoelectron Spectrometer with monochromatized Al K α X-ray radiation (1,486.6 eV). The energy of the electrons was measured by means of a hemi-spherical mirror analyser 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 C 1s component set at the energy of 285 eV. The shapes of the bands were fitted after background subtraction, using the Gaussian–Lorentzian function.

3 Results and discussion

Figure 1 shows X-ray diffractograms for PbO and TiO₂ stoichiometric mixture after mechanical activation in a SPEX 8000 Mixer Mill for $t_m=2, 5, 10, 20$ and 50 h. For a comparison a simulated PbTiO₃ diffractogram (P4 mm space group) is presented at the bottom of the Fig. 1. One can observe that the diffraction pattern recorded for $t_m=2$ h contains the peaks, which belong to Ti₁₀O₁₈, PbO and Pb₃O₄ and are marked by open, solid circles and stars,

Fig. 2 XPS spectra of Pb4f and O1s from PbTiO₃ single crystal



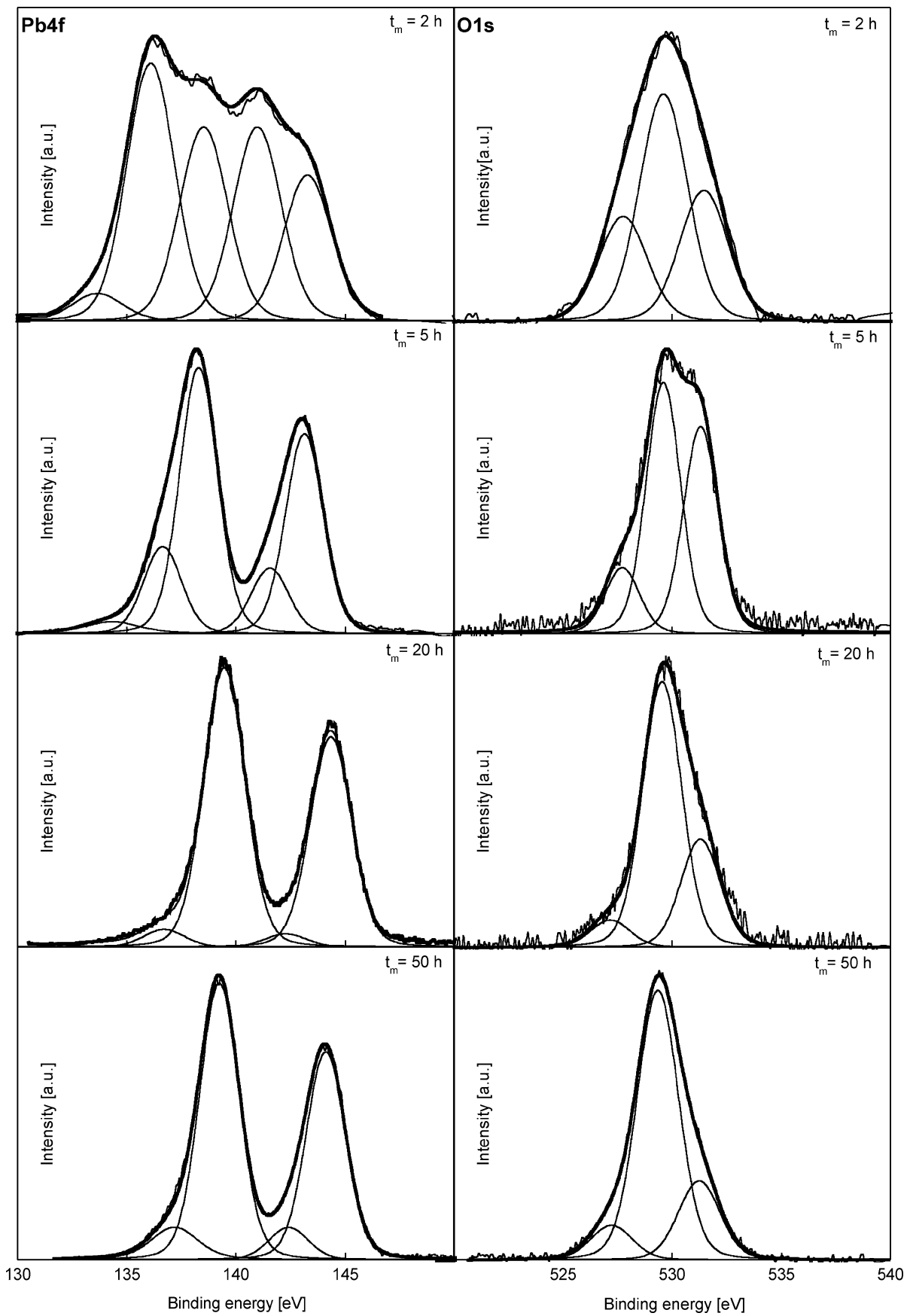


Fig. 3 XPS spectra of *Pb4f* and *O1s* from *PbO* and *TiO₂* mechanically activated for 2, 5, 20 and 50 h

Table 1 Binding energy E_B , full width at half maximum FWHM of the lines and relative intensities RI of the $Pb4f$ component lines for powders obtained at various times t_m of mechanical activation PbO and TiO_2 .

Pb4f											
t_m [h]	E_B /FWHM [eV]	RI	E_B /FWHM [eV]	RI	E_B /FWHM [eV]	RI	E_B /FWHM [eV]	RI	E_B /FWHM [eV]	RI	
2	133.6/2.7	0.11	136.1/2.6	1	138.5/2.4	0.70	141.0/2.6	0.75	143.3/2.5	0.58	
5	134.3/2.7	0.04	136.6/2.0	0.46	138.3/2.0	1	141.6/2.0	0.25	143.1/2.0	0.75	
10			136.3/2.3	0.26	138.5/2.4	1	141.6/2.2	0.11	143.3/2.2	0.75	
20			136.7/2.2	0.10	139.4/2.2	1	142.3/2.2	0.80	144.4/2.2	0.75	
40			137.2/2.1	0.12	139.5/2.1	1	142.6/2.1	0.10	144.4/2.1	0.75	
50			136.2/2.1	0.06	139.3/2.2	1	142.4/2.1	0.05	144.1/2.2	0.75	

respectively [9]. Longer milling results in a gradual evolution of the perovskite structure and the most intensive 101 reflection becomes visible even after 5 h mechanical activation. On further milling the intensity of the reflections characteristic of the initial oxides decreases and the pattern obtained for the powder after $t_m=50$ h can be assigned to the tetragonal perovskite structure apparent in a splitting of the 200 and 002 reflections. The lattice parameters calculated for $PbTiO_3$ powder after 50 h of mechanical synthesis are the following $a=0.3911(6)$ nm, $c=0.4114(9)$ nm. The reflections in the powder diffractogram are broad in comparison with those simulated. The broadening of the reflections is related to the decrease in the conventional XRD resolution due to the particle size. The mean size of the crystallites calculated for the powder from the increase in the full width at the half maximum of the base reflections by conventional procedure is ~ 20 nm which is good agreement with our previous HRTEM observations [8].

It should be also stressed that a size-driven tetragonal-cubic phase transition has been observed in ferroelectric perovskites ($BaTiO_3$ and $PbTiO_3$) [10–16]. It was found for particles below 200 nm the degree of tetragonality increases with increasing crystallite size. The critical size for $PbTiO_3$ particles has been estimated as ~ 15 nm [10–13]. For $PbTiO_3$ nanopowder produced by mechanical synthesis during 50 h the tetragonality of the lattice yields $c/a=1.052$. This value is smaller than that obtained for lead titanate single crystals from neutron diffraction studies $c/a=1.065$ [14], what confirms approaching the size driven transition limit. The tetragonality of the 50 h milled nanopowder seems to be slightly bigger than expected on the base of the paper [13]. This suggests that the critical value of $PbTiO_3$ particle size can be smaller the predicted in [13]; however, the accuracy of the lattice parameters determination for the nanograins is smaller due to the broadening of characteristic reflections and the c/a ratio can depend on the degree of imperfection of cationic and anionic sublattices of $PbTiO_3$ [15].

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. We used the X-ray photoelectron spectroscopy to characterize the formation of the $PbTiO_3$ powder in the process of mechanical activation of the respective oxides. The spectra of the powders after mechanical activation during different periods t_m were compared with the core levels of $Pb4f$ and $O1s$ in the $PbTiO_3$ single crystal. Figure 2 shows the main $O1s$ oxygen and $Pb4f$ lead peaks for $PbTiO_3$ single crystal and the same core levels of the powders produced by mechanical activation of PbO and TiO_2 during different periods t_m are presented in Fig. 3. 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 in $PbTiO_3$ single crystal are located at 143.9 eV (5/2) and 139.0 eV (7/2). The two lines have the same FWHM equal to 1.7 eV. The evolution of the $O1s$ and $Pb4f$ core lines in the powders in the process of mechanical activation of PbO and TiO_2 is summarized in Tables 1 and 2 where the binding energy E_B , full width at half maximum FWHM of the lines and relative intensities RI of the $Pb4f$ and $O1s$

Table 2 Binding energy E_B , full width at half maximum FWHM of the lines and relative intensities RI of the $O1s$ component lines for powders obtained at various times t_m of mechanical activation PbO and TiO_2 .

O1s							
t_m [h]	E_B /FWHM [eV]	RI	E_B /FWHM [eV]	RI	E_B /FWHM [eV]	RI	
2	527.8/2.6	0.46	529.6/2.6	1	531.4/2.6	0.58	
5	527.7/1.6	0.26	529.6/1.6	1	531.3/1.6	0.83	
10	527.7/2.2	0.31	529.5/2.2	1	531.3/2.2	0.64	
20	527.2/2.2	0.18	529.5/2.2	1	531.3/2.2	0.29	
40	527.7/2.3	0.14	529.3/2.2	1	531.3/2.2	0.27	
50	527.2/2.7	0.10	529.4/2.1	1	531.2/2.1	0.40	

lines are collected for different synthesis times t_m . 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 we would like to ascribe to the grain shells in which broken bonds and PbO are apparent. The broadening of the core level lines observed for $PbTiO_3$ perovskite nanopowders points to a disorder related to a distribution of the site potentials [16–18].

4 Conclusion

The mechanochemical synthesis is a promising route for perovskite materials preparation at room temperature. Lead titanate nanopowders can be synthesized in this way from lead oxide and titanium dioxide however, intermediated phases (lead-rich Pb_3O_4 , and $Ti_{10}O_{18}$) have been observed at the early stage of the process. The first traces of perovskite phase were detected after 5 h synthesis, longer milling time increases the amount of the perovskite phase resulting in the single phase $PbTiO_3$ nanograins after 50 h of mechanical activation.

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