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Letter

Mechanochemical synthesis of $PbTiO_3$ from PbO and TiO_2

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Abstract

Data on mechanochemical synthesis of $PbTiO_3$ from PbO and TiO_2 without subsequent heating of activated mixtures are presented. Physical and chemical processes occurring during mechanical activation are followed by the X-ray diffraction (XRD) method, scanning electron microscope (SEM) analysis and measurement of BET specific surface area. It was shown that during vibro milling of 10 g oxide mixture, formation of $PbTiO_3$ was ended after 60 min. The progression of the chemical reaction was detected by the XRD method and chemical analysis.

Keywords: Mechanical activation; Synthesis; $PbTiO_3$

The synthesis of $PbTiO_3$ attracted great interest because of its ferroelectric and pyroelectric properties. The temperature of $PbTiO_3$ synthesis from starting oxide powders is above 800°C. However, at these temperatures the evaporation of PbO may cause considerable problems due to both its toxicity and the formation of non-stoichiometric compounds. Therefore, low temperature methods of $PbTiO_3$ synthesis have been developed such as chemical coprecipitation [1], the sol–gel procedure [2] the hydrothermal method from PbO and TiO_2 [3] and heating of previously activated oxide mixtures [4].

In this paper the results of the synthesis of an active $PbTiO_3$ powder are presented applying only mechanochemical treatment without subsequent heating. PbO (of 99% purity, Kemika Zagreb, Croatia) and TiO_2 (of 99% purity Merck, Germany) were used as starting components. X-ray diffraction (XRD) analysis was performed for characterization of starting powders. Siemens apparatus (type D 500) with Ni filtered Cu Kα radiation (35 kV and 20 A) was used at the continuous scan speed of 0.02 $2\Theta\ s^{-1}$. XRD analysis of starting powders showed that PbO was in the form of massicot, while TiO_2 was in the form of anatase. Morphological characteristics of starting oxides (Fig. 1) were observed under the scanning electron microscope (SEM), JEOL JSM 35. Powder samples for SEM analysis were covered with carbon and shadowed with Au–Pd alloy layers. Estimated average particle sizes were 4.2 and 0.1 μm for massicot and anatase, respectively.

Mechanochemical activation of equimolar mixtures of massicot and anatase was performed using a high energy vibro grinding set (Fritsch Pulverisett 9) with lining and grinding media made of hard metal. The useful volume of the set was 100 ml. Experiments were performed with 10-g batches. Activation time was raised up to 60 min. The mixtures obtained at different activation times were characterized using XRD, SEM and chemical analyses as well as by measuring of specific surface area (BET method).

Characteristic XRD patterns of activation products are given in Fig. 2. The dependence of BET specific surface area of activated mixtures on grinding time is given in Table 1.

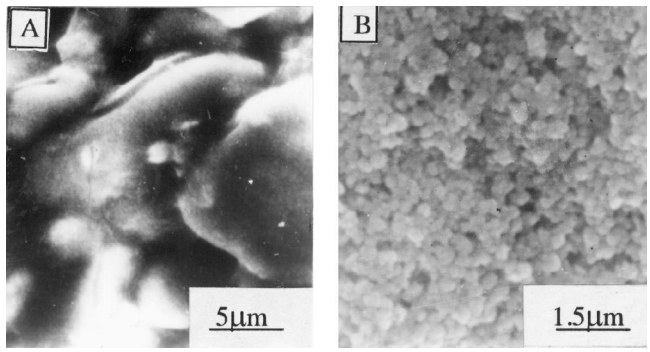

Fig. 1. Scanning electron micrographs of (A) massicot and (B) anatase.

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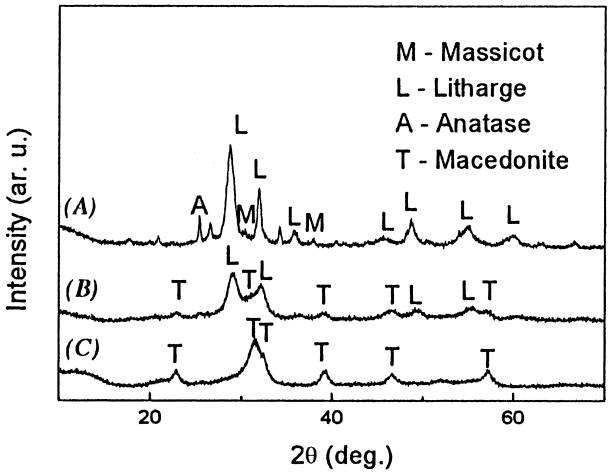

Fig. 2. XRD patterns of powder mixtures ground for (A) 3 min, (B) 30 min, (C) 60 min.

Table 1
Specific surface area of ground mixtures ($m^2 g^{-1}$)

Grinding time (min)									
0	1	3	5	10	15	20	30	45	60
3.2	2.9	3.0	2.7	4.1	5.8	3.1	2.0	1.7	1.6

The X-ray diagrams of activated mixtures show that the fraction of crystalline $PbTiO_3$ increased during prolonged grinding. Only the macedonite diffraction lines were detected after 60-min activation. Under the assumption that the activation product after 60-min grinding contains only crystalline $PbTiO_3$, a semiquantitative estimation of the chemical reaction advance as a function of activation time was performed. By comparing the integral intensity of the (111) diffraction line of $PbTiO_3$ which does not overlap with diffraction lines of other existing crystalline phases, the reaction degree in ground powder mixtures is calculated. The results obtained by the XRD method are presented in Table 2.

Data obtained by the XRD method were confirmed by performing chemical analysis of activated mixtures. This procedure is used on the basis of the difference in solubility of PbO and $PbTiO_3$ in 10% acetic acid. While unreacted PbO is completely soluble, Pb^{2+} ions were not detected in chemically treated $PbTiO_3$ under the same experimental conditions. The content of Pb^{2+} ions in the solution was determined by titration with 0.01 M EDTA [6,7]. PbO was not detected in the mixture that had been activated for 60 min. This result confirms our assumption that the reaction in which $PbTiO_3$ was formed was terminated after 60 min of intense grinding in the vibro mill. The dependence of the reaction degree on grinding time, obtained by the chemical analysis, is also given in Table 2.

The observed disagreement between the methods used could be a consequence of the semiquantitative estimation of the applied XRD procedure (without adequate standards because of the continuous change of crystallite size and lattice deformation of crystallites during mechanical treatment).

Applying the well-known procedure based on the Cauchy expression [8], the mean crystallite size and lattice strain of the $PbTiO_3$ crystallites formed were calculated. After 60 min of activation, the reaction product had a lattice deformation of 0.59% with an average crystallite size of 16.5 nm.

According to XRD data, starting reactants in ground mixtures undergo phase transformations (Fig. 2) before the start of the chemical reaction. After 5 min the massicot was transformed into litharge. The presence of the lead carbonate hydroxide hydrate (JSC Diffraction Card 9-0356) was also observed at a shorter grinding time. It should be outlined that products of anatase phase transformation in massicot–anatase mixtures were not detected, although the rutile, as an end product, was formed after intense mechanical activation of anatase [9,10]. However, the orthorhombic TiO_2 modification (JCP Diffraction Card 21-1236) was observed during grinding of pure anatase, as it can be seen in Fig. 3. This TiO_2 modification may be regarded as a transition phase during the anatase phase transition in these experiments. The orthorhombic phase probably appears in the activated mixtures of PbO–TiO_2 too, but it could not be detected because of overlapping of its strongest diffraction line with the diffraction lines of other crystalline phases that were present (Figs. 2 and 3). The faster disappearance of massicot'' compared to anatase'' diffraction lines points to slower phase transformation of TiO_2 compared to PbO during this experiment.

The specific surface area changes of activated mixtures could have many causes, such as reduction of the mean particle size, phase transformation, chemical reaction, agglomeration of powder particles. The increase in the specific surface area value up to 15 min activation (Table 1) is a consequence of the predominant influence of

Table 2
Fraction of $PbTiO_3$ (α) in ground mixtures (%)

Grinding time (min)	0	5	10	20	30	45	60
α obtained by EDTA titration	0	8.0	15.1	29.5	37.3	75.6	100
α obtained by XRD method	0	0	11.6	35.8	40.6	80.7	100

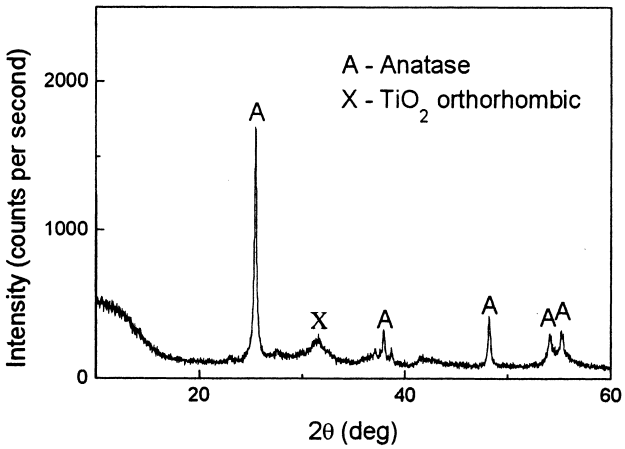

Fig. 3. XRD pattern of anatase ground for 5 min.

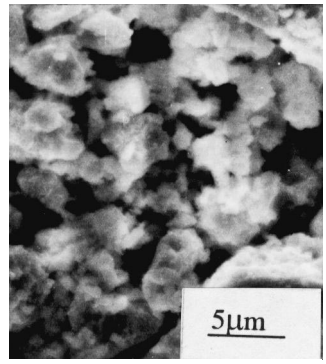

Fig. 4. Scanning electron micrograph of powder mixture ground for 45 min.

particle size reduction with activation time. Due to unreliable quantitative data on particle size change during grinding (SEM micrographs), XRD data of activated mixtures were used to calculate crystallite size reduction during grinding [5,8]. According to these data the highest degree of crystallite reduction and, at the same time, the decrease of particles, appears at shorter activation time. For instance, after 10 min, activation mean crystallite sizes of litharge and anatase were reduced down to 17 nm and 27 nm, respectively, while the initial mean crystallite size of TiO_2 was 106 nm and of PbO, 560 nm. The intense particle reduction is followed by both good homogenization of reactants and an increase in the contact area of the reactants. The latter change is a necessary condition for the intense development of the chemical reaction in the solid state. The decrease of specific surface after 15 min activation could be explained by the dominant chemical reaction and particle agglomeration. Data obtained prove that in this period of activation, $PbTiO_3$ formation progresses very fast (Table 2) as well as the appearance of particle agglomeration, Fig. 4.

This investigation demonstrated the possibility of synthesizing $PbTiO_3$ from PbO and TiO_2 during mechanical activation in a vibratory mill without a subsequent thermal treatment. Although the mechanism of $PbTiO_3$ formation was not elucidated, these results point to the creation of the new chemical compound from the finest particles of litharge and orthorhombic TiO_2 during grinding. The $PbTiO_3$ particles formed, due to crystallite lattice deformation and very fine crystallite size, are expected to be very active during subsequent processing at elevated temperatures, sintering for instance.

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