

NANOCRYSTALLINE TITANATE POWDERS: SYNTHESIS AND MECHANISMS OF PEROVSKITE PARTICLES FORMATION

V. V. Srdić*, R. R. Djenadić

Department of Materials Engineering, Faculty of Technology,
University of Novi Sad, Bul. Cara Lazara 1, 21000 Novi Sad, Serbia and Montenegro,

Nanocrystalline titanate (SrTiO_3 , PbTiO_3 and $\text{La}_{2/3}\text{TiO}_3$) powders were synthesized by sol-gel and hydrothermal method in a two-step process, first by controlled hydrolysis of titanium-butoxide with distilled water, and then by further reaction of the formed amorphous titanium hydroxide gel particles with Sr^{2+} , Pb^{2+} or La^{3+} ions, carried out under different reaction conditions. Mechanisms and conditions for the formation of crystalline titanate nanoparticles in different systems were investigated. It is found that: (1) traces of strontium titanate nanoparticles with crystalline perovskite structure appear already at 20°C , but a complete crystalline nanopowder is synthesized at 80°C , (2) crystalline perovskite particles in PbTiO_3 and $\text{La}_{2/3}\text{TiO}_3$ system can be obtained only under the hydrothermal conditions at higher temperatures, and (3) the PbTiO_3 powders synthesized under the hydrothermal conditions are highly agglomerated and depending on processing conditions can have different morphology starting from spherical agglomerates, to platelet-like structure or even a complex structures involving titanate particles covered with one-dimensional nanostructured elements.

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1. Introduction

Ferroelectric titanates with perovskite structure have been widely used as functional ceramics in ferroelectric memories, sensors, actuators or electrooptical devices [1,2]. Advances toward nanoscale electronics have additionally increased interest in this field. Achievement of the improved properties of an electronic device is closely related to the processing, i.e. synthesis of superior titanate nanopowders and preparation of dense nanocrystalline ceramics with an appropriate sintering schedule. Synthesis of high-purity, ultra-fine and agglomerate-free powder with controlled particle size, morphology and stoichiometry is the first and perhaps the most important step in processing of perovskite ceramics with desirable properties.

Many different synthesis methods have been used for preparation of high quality titanate powders, but only techniques for the direct synthesis of crystalline particles are promising, as they enable to eliminate the calcination step usually responsible for the hard agglomerate formation. The techniques for direct synthesis of crystalline perovskite particles are based on the reaction between TiO_2 particles or titanium hydrous gels (produced by the controlled hydrolysis of titanium-chloride or titanium-alkoxides with water) and corresponding cations in a highly alkaline solution (see, for example, Refs. [3-10]). If TiO_2 particles are used for the formation of crystalline titanate particles, the reaction has to be carried out under the hydrothermal conditions [5,11]. It is proposed [11,12] that titanate is initially formed on the surface of the TiO_2 particles by a dissolution-precipitation mechanisms, i.e. by homogeneous nucleation of very small nanoparticles in solution, which then tend to cluster together. However, the titanium hydrous gels are more reactive than crystalline TiO_2 particles and hence the reaction with corresponding cations is much faster and could be carried out at lower temperature [3,6,13,14]. It is believed [3,4,13,15,16] that the amorphous titanium hydrous gel is infiltrated by aqueous solution containing metal ions Me^{n+} (such as strontium, barium, lead,

* Corresponding author: srdicvv@uns.ns.ac.yu

lanthanum etc.), which cover the entire surface of the porous titanium hydroxide gel and then could be incorporated into the gel structure causing the breaking of Ti-O-Ti and forming Ti-O-Me bonds. The reaction is very sensitive to different processing parameters. Although different formation mechanisms of crystalline titanate particles have been proposed, many fundamental aspects of the perovskite particle formation are not yet well defined. The aim of this work is to investigate mechanisms and conditions for the formation of crystalline titanate nanoparticles from titanium hydrous gel in different systems (SrTiO_3 , PbTiO_3 and $\text{La}_{2/3}\text{TiO}_3$).

2. Experimental procedure

Nanocrystalline titanate (SrTiO_3 , PbTiO_3 and $\text{La}_{2/3}\text{TiO}_3$) powders were synthesized by sol-gel and hydrothermal method in a two-step process: first by controlled hydrolysis of titanium-butoxide ($\text{Ti}(\text{OC}_4\text{H}_9)_4$, Fluka, Switzerland) with distilled water, and then by further reaction of the formed amorphous titanium hydroxide gel particles with Sr^{2+} , Pb^{2+} or La^{3+} ions under different reaction conditions in a strong alkaline solution ($\text{pH} > 13$). Strontium nitrate ($\text{Sr}(\text{NO}_3)_2$, Fluka, Switzerland), lead acetate ($\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$, Aldrich, USA) and lanthanum nitrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Riedel-de-Haen, Germany) were used as precursors for corresponding ions. The synthesis was conducted first by hydrolysis of $\text{Ti}(\text{OC}_4\text{H}_9)_4$ dissolved in anhydrous ethanol with distilled water (using the water/alkoxide molar ratio of 2 and the titania concentration of 0.5 mol/l). The obtained white titania sol was added to a 4 M NaOH aqueous solution under vigorous stirring to precipitate the titanium hydroxide gel. Then an aqueous solution containing Sr^{2+} , Pb^{2+} or La^{3+} ions was slowly added to the prepared slurry, and the reaction between titanium hydroxide particles and corresponding ions was carried out at different temperatures (over a period of 60 min): (i) up to 80°C at ambient pressure or (ii) up to 165°C under the hydrothermal conditions. The precipitated powders were collected with a centrifuge and washed several times with distilled water to expel sodium ions and then with absolute ethanol to decrease powder agglomeration by removing free water and replace the particle surface hydroxyl with ethoxy groups. The washed powders were dried at 120°C for 1 day in air. In the sample notation, beside two letters (ST, PT or LT) used to denote the specific ceramic system (SrTiO_3 , PbTiO_3 or $\text{La}_{2/3}\text{TiO}_3$ respectively), a number is used to indicate the synthesis temperature.

The specific surface area of the as-synthesized perovskite powders as well as the pore size distribution was measured by nitrogen adsorption according to the BET method using an ASAP 2000 instrument. The average particle size was calculated assuming spherically shaped particles. The X-ray diffraction measurements were performed with a Siemens D5000 instrument using Ni-filtered CuK_α radiation. The crystallite size of the perovskite powders was estimated from the full width at half maximum by the Scherrer equation, after correction for instrumental broadening. Thermal analysis (DTA and TG) was performed with a Bähr STA 503 equipment at a temperature up to 900°C with a heating rate of 10°C/min in static air atmosphere using alumina crucibles. The size and the morphology of the particles were examined using a scanning electron microscope (SEM JEOL, 6460LV, operating at 20 kV) and a high-resolution scanning electron microscope (HRSEM Philips XL 30 FEG, operating at 20 kV).

3. Results and discussion

Direct synthesis of crystalline titanate perovskite particles is based on the reaction between the hydrolyzed titanium alkoxide and different ions (such as strontium, barium, lead, lanthanum, etc.) in a highly alkaline solution, and the whole process is carried out in two steps. In the first step, the highly porous titanium hydrous gel, exhibiting a fine, porous network structure (Fig. 1) and a very high surface area, 260 m²/g, is formed. In the second step, the amorphous titanium hydrous gel is infiltrated by aqueous solution containing metal ions, and a reaction between them could be expected. The reaction is very sensitive to different processing parameters [3,13,16] such as: temperature, precursor concentrations, type of metal ions, type of mineralizer (e.g. NaOH, KOH or others), solution pH, etc.

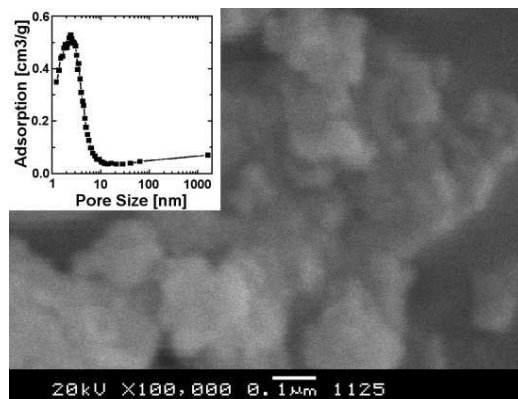


Fig. 1. SEM micrograph of pure titanium hydroxide gel dried at 120 °C together with its pore size distribution obtained by low temperature nitrogen adsorption.

3.1 Strontium titanate powders

Preparation of SrTiO_3 powders was carried out with an aqueous $\text{Sr}(\text{NO}_3)_2$ solution. According to Kiss et al. [17], the temperature of the reaction between the porous titanium hydroxide gel and Sr^{2+} ions in an alkaline solution is very low. Because of that, it was expected that soluble Sr^{2+} ions would be attached to the surface of the porous titanium hydroxide gel and then incorporated into the gel structure, forming perovskite SrTiO_3 phase. XRD results in Fig. 2 show that the powder ST-20 synthesized at 20 °C contains only traces of the perovskite phase, whereas sharp peaks of the crystalline cubic perovskite phase are present in the powder ST-80 synthesized at 80 °C. Both samples (ST-20 and ST-80, Fig. 2) contain SrCO_3 , as an impurity phase, which is normal unless great care is taken to ensure that the precursors and the reaction environment are CO_2 -free [3,8,13]. However, the intensity of the SrCO_3 peaks in the XRD pattern of the sample ST-20 is considerably higher than for the sample ST-80. Thermal analysis (Fig. 3) also indicates on a higher amount of SrCO_3 in the sample ST-20, as the mass loss, due to decomposition of SrCO_3 (at temperatures above 600 °C), is considerably higher for the sample ST-20 than ST-80. This could be explained by the fact that at 20 °C incorporation of Sr^{2+} ions into the porous gel structure is very slow, and they are mostly consumed in the much faster reaction with CO_2 . Thus, the as-synthesized ST-20 powder consists of an amorphous titania phase, small fraction of SrTiO_3 and considerable amount of extremely fine SrCO_3 crystallites. A similar work [13], examining the formation mechanisms of BaTiO_3 particles from hydrous titania gel, suggests that, if synthesis temperature is relatively low, only a small amount of the cubic BaTiO_3 crystallites of a few nanometers appears in the matrix of a Ti-rich amorphous phase (which contains some Ba^{2+} ions). On the other side, at higher synthesis temperature of 80 °C the favorable processes are incorporation of Sr^{2+} ions into the titanium hydrous gel structure, interaction with it and formation of the crystalline SrTiO_3 phase. As the reaction between Sr^{2+} and the titania gel is relatively fast at 80 °C, only a part of Sr^{2+} ions is spent in the reaction with CO_2 , and the nanopowder with dominant perovskite phase and a small amount of SrCO_3 is formed.

High resolution SEM micrographs, presented on Fig. 4, shows that the powders synthesized at 20 °C and 80 °C are agglomerated, with the primary particle size in nanometer range 32 nm and 37 nm, respectively. The amorphous nature of Ti-rich phase could be the reason for very high surface area (192 m^2/g) of the SrTiO_3 nanopowder synthesized at 20 °C. XRD patterns of the ST-20 powder calcined at different temperatures are presented in Fig. 5. After calcination at 500 °C for 1 h the transformation to the crystalline perovskite SrTiO_3 phase is negligible and becomes significant only at higher temperatures (≥ 600 °C) due to simultaneous decomposition of SrCO_3 . The crystallite size of the SrTiO_3 nanopowder synthesized at 80 °C (ST-80) of 35 nm, calculated by the Scherrer formula, is very close to the value estimated from HRSEM micrographs, but considerably higher than the value of 20 nm, estimated from the specific surface area (57 m^2/g). The reason could be still the presence of a small amount of the amorphous Ti-rich phase.

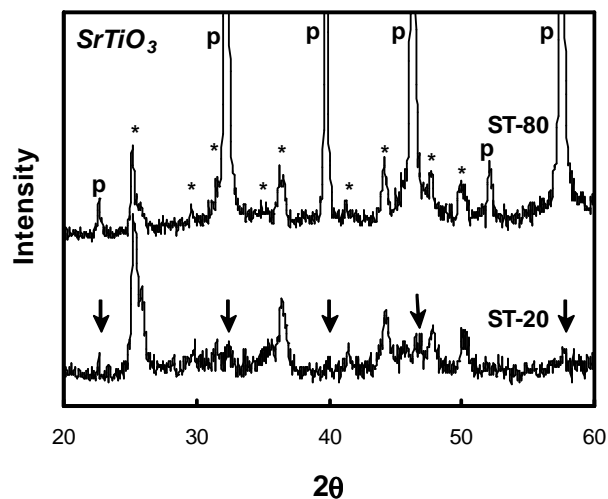


Fig. 2. XRD patterns of SrTiO₃ nanopowders synthesized at 20 °C and 80 °C (p – cubic SrTiO₃, * – SrCO₃).

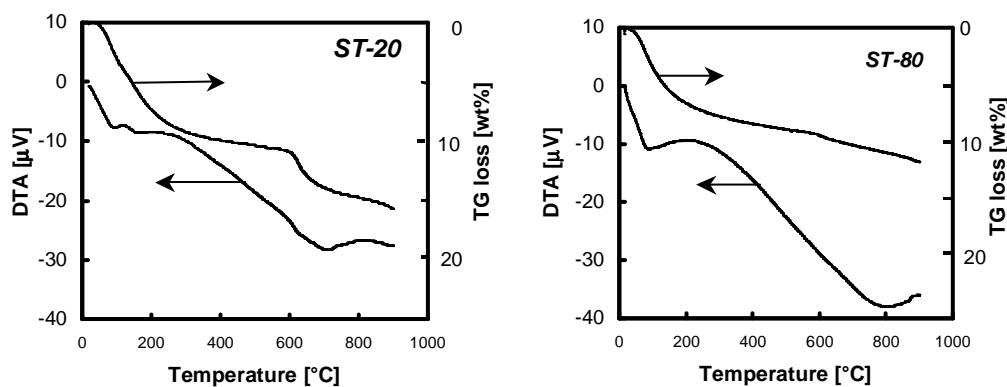


Fig. 3. Thermal analysis (DTA and TG) of SrTiO₃ nanopowders synthesized at: (a) 20°C and (b) 80°C

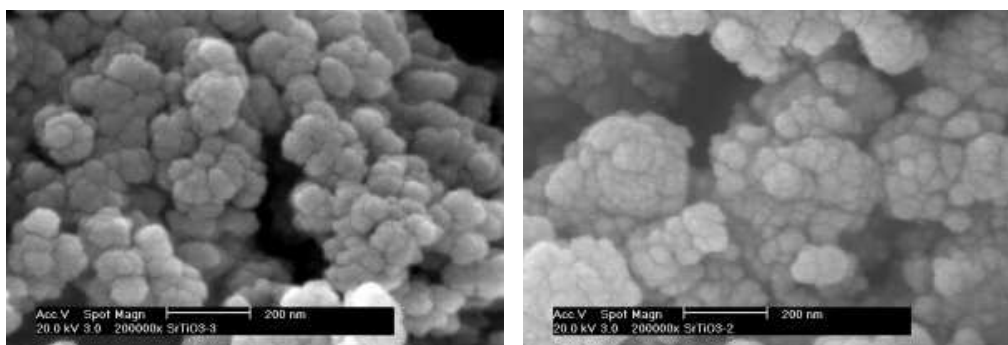


Fig. 4. HRSEM micrographs of SrTiO₃ nanopowders synthesized at: (a) 20°C and (b) 80°C. specific surface area (57 m²/g). The reason could be still the presence of a small quantity of the amorphous Ti-rich phase.

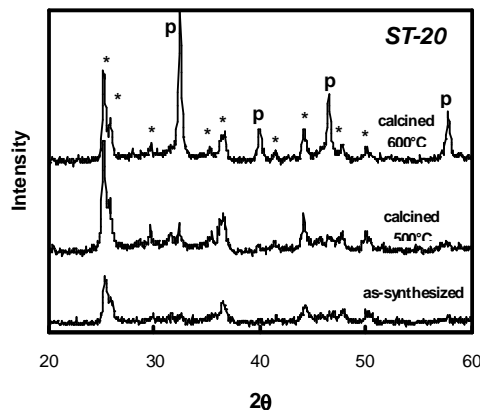


Fig. 5. XRD patterns of SrTiO_3 nanopowder synthesized at 20 °C (as-synthesized, calcined at 500 °C and calcined at 600 °C) (p – cubic SrTiO_3 , * – SrCO_3).

3.2 Lead titanate powders

Synthesis of PbTiO_3 powders was carried out with an aqueous $\text{Pb}(\text{CH}_3\text{COO})_2$ solution. Reaction of Pb^{2+} ions with the titanium hydrous gel in highly alkaline solution strongly depends on processing parameters, but it seems that reaction temperature and time are the most important [10,18-20]. If the reaction is carried out at 20 °C and even 80 °C, the as-synthesized powders (samples PT-20 and PT-80, respectively) are completely XRD amorphous (Fig. 6). It is believed that the relatively soluble Pb^{2+} ions cover the entire surface of the porous titanium hydroxide gel and then could be incorporated into the gel structure causing the rupture of Ti-O-Ti and the formation of Ti-O-Pb bonds. However, the reaction temperature $\leq 80^\circ\text{C}$ is too low for the nucleation of PbTiO_3 phase. Under the used reaction conditions no any other impurity phase is produced (Fig. 6). Small mass losses, less than 6 or 8 wt%, during heating up to 900 °C (Fig. 7) indicate an almost pure oxide structure of the as-synthesized amorphous powders. From the above, it is reasonable to assume that during particle consolidation separation does not appear in the precipitated phase and a very fine amorphous structure with intimate mixture of Ti and Pb ions is preserved in the as-synthesized powders.

Both as-synthesized powders (PT-20 and PT-80) consist of very fine amorphous particles with the average size of about 20 nm (Fig. 8a) and have very high surface areas (149 m^2/g and 147 m^2/g , respectively). DTA (Fig. 7) and XRD results show that the amorphous structure is transformed directly into the perovskite PbTiO_3 phase after calcination at around 500 °C. Rietveld analysis confirmed that the calcined powders (500 °C for 1 h) consist mainly of the pseudo-cubic PbTiO_3 , with the average crystallite size of about 20 nm, and a small fraction of tetragonal phase.

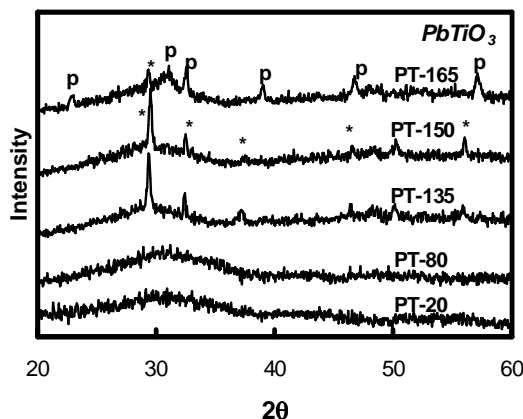


Fig. 6. XRD patterns of PbTiO_3 powders synthesized at different temperatures: 20 °C, 80 °C, 135 °C, 150 °C and 165 °C for 60 minutes (p – tetragonal PbTiO_3 , * – PbO-TiO_2 solid solution).

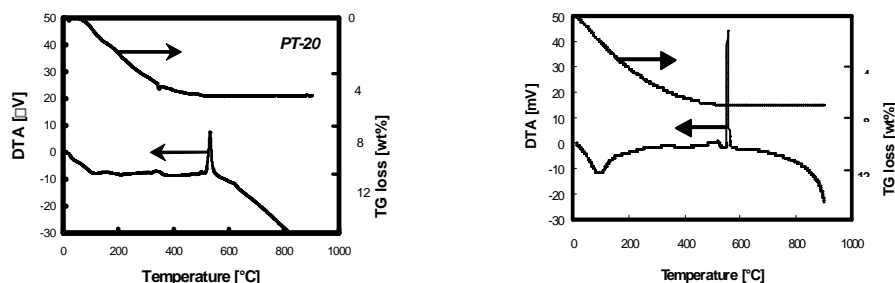


Fig. 7. Thermal analysis (DTA and TG) of PbTiO_3 nanopowders synthesized at: (a) 20 °C and (b) 80 °C.

In the PbTiO_3 system a crystalline product was directly synthesized in the reaction of Pb^{2+} ions with the titanium hydrous gel carried out under the hydrothermal conditions. Fig. 6 shows that an intermediate crystalline phase is obtained at lower temperatures (135°C and 150°C, samples PT-135 and PT-150, respectively) and somewhat higher temperature, 165°C (sample PT-165) is necessary for the formation of perovskite PbTiO_3 phase. Cheng et al. [20] suggested that the intermediate phase is PbO-TiO_2 solid solution with a tetragonal structure and the Pb/Ti ratio higher than 1. Differences in the observed temperature of the perovskite phase formation, as compared to the data found in literature [14,20], exist because of a strong influence of reaction time on the structure of obtained powder. Thus, pure perovskite PbTiO_3 phase is formed in the hydrothermal reaction conducted at 150°C, but for somewhat longer period of 180 minutes (Fig. 9). The obtained results confirm that only hydrothermal conditions provide enough energy, necessary not only for rearrangement of the titania gel structure by incorporating of Pb^{2+} ions initially adsorbed on its surfaces, but also for nucleation of crystalline lead titanate phases. It has been proposed [15,20] that the structure of titanium hydrous gel rearranges by dissolution with lead ions to form critical nuclei for an intermediate phase and further rapid precipitation of their primary particles. During the hydrothermal synthesis at higher temperatures the originally formed intermediate transforms to the perovskite phase. This is confirmed with the XRD pattern of the PT-165 powder (Fig. 6) consisting of both PbO-TiO_2 solid solution and perovskite PbTiO_3 phases.

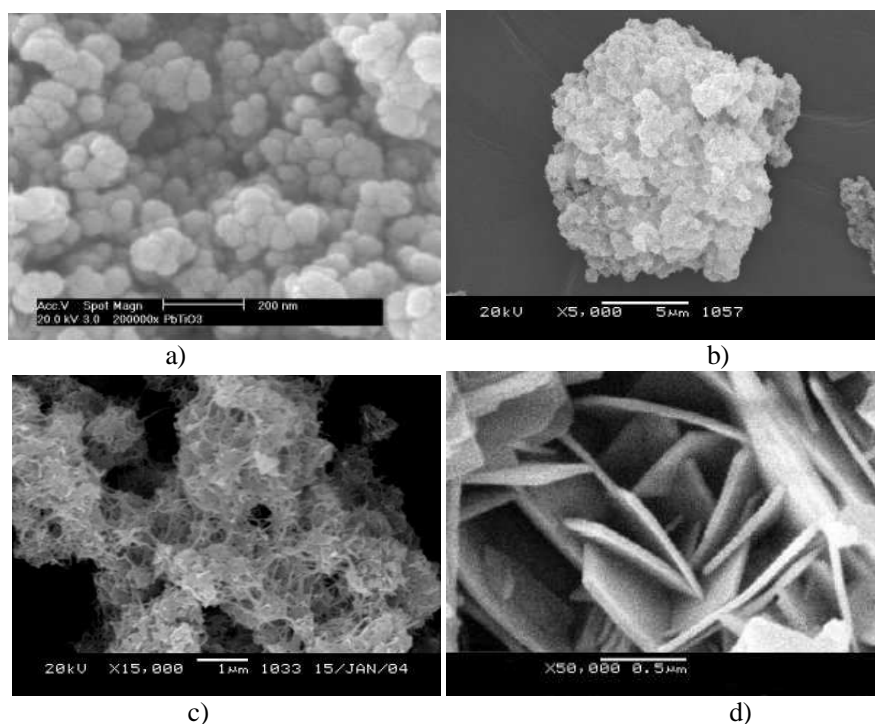


Fig. 8. SEM micrographs of PbTiO_3 powders synthesized at 20 °C (a) and 150 °C under different conditions (b, c and d).

The PbTiO_3 powders synthesized under the hydrothermal conditions cannot be considered as nanopowders. Depending on processing conditions as-synthesized powders can have different morphology, starting from spherical agglomerates with the size of few micrometers (Fig. 8b), to platelet-like structure (Fig. 8c) or even a complex structures involving titanate particles covered with one-dimensional nanostructured elements (Fig. 8d). It is important to note that even more attention has recently been paid to the complex structures, due to their novel physical properties and potential applications in the field of nanoscale electronics.

Different behavior between strontium and lead in the process of titanate formation may be found in the nature of these elements, because Sr, an alkaline earth metal, reacts easily with CO_2 and Sr-O bond does not possess a partial covalent character like Pb-O bond.

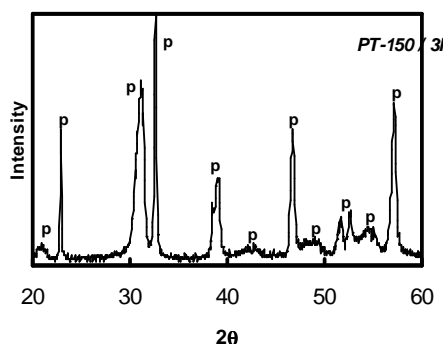


Fig. 9. XRD patterns of PbTiO_3 powders synthesized at 150°C for 180 minutes (p – tetragonal PbTiO_3).

3.3 Lanthanum titanate powders

Preparation of $\text{La}_{2/3}\text{TiO}_3$ powders were carried out using an aqueous $\text{La}(\text{NO}_3)_3$ solution as a precursor of lanthanum. It was expected that the incorporation of La^{3+} ions in titania hydrous gel structure would be even more complex in comparison to Sr^{2+} or Pb^{2+} . The reason is the well known “instability” of the pure $\text{La}_{2/3}\text{TiO}_3$ perovskite phase, due to the high amount of vacancies in the A cationic sublattice [21]. However, it is generally accepted that the lanthanum titanate structure may be stabilized by the presence of minute amounts of Ti^{3+} ions and by partial filling of A-site vacancies with M^+ (where M stands for Li, Na or K) [9,22]. XRD results, presented in Fig. 10, show that the powder synthesized at 20°C (LT-20) consists of almost pure $\text{La}(\text{OH})_3$ phase, as in the case of the lanthanum titanate powder prepared at 80°C . The formation of $\text{La}(\text{OH})_3$ phase is favorable even under the hydrothermal conditions, and at 110°C only a small amount of perovskite phase is obtained (indicated by arrows in Fig. 10). This means that, like the SrTiO_3 system, incorporation of La^{3+} ions in the titanium hydrous gel structure is impeded by the formation of an impurity phase. Microstructure observations made by scanning electron microscopy (Fig. 11) reveal that the as-synthesized powders are agglomerated with the primary particle size of about 30–40 nm.

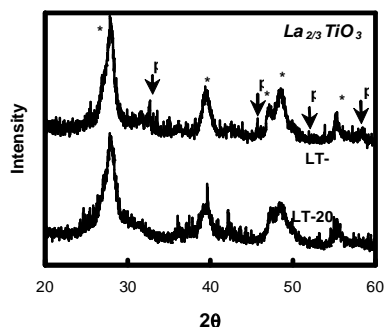


Fig. 10. XRD patterns of $\text{La}_{2/3}\text{TiO}_3$ powders synthesized at 20°C and 110°C (p – $\text{La}_{2/3}\text{TiO}_3$, * – $\text{La}(\text{OH})_3$).

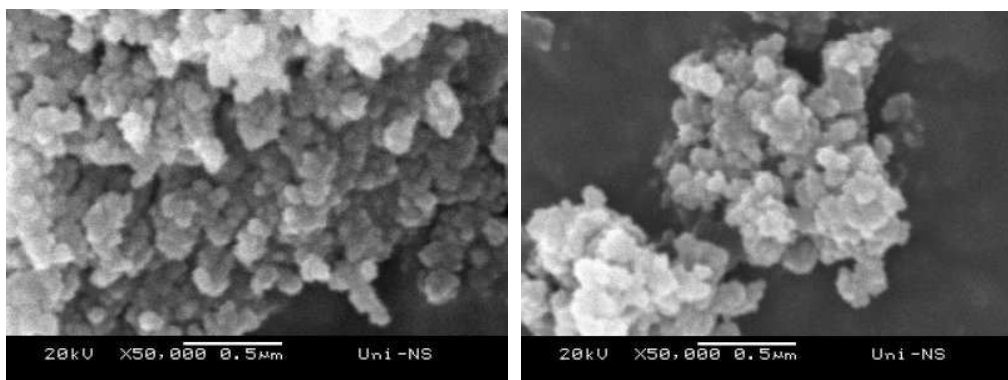


Fig. 11. SEM micrographs of $\text{La}_{2/3}\text{TiO}_3$ powders synthesized at: a) 20°C and b) 80°C.

4. Conclusions

Nanocrystalline titanate (SrTiO_3 , PbTiO_3 and $\text{La}_{2/3}\text{TiO}_3$) powders were synthesized by sol-gel and hydrothermal method in a two-step process: first by controlled hydrolysis of titanium-butoxide with distilled water, and, thereafter, by further reaction of the formed amorphous titanium hydroxide gel particles with Sr^{2+} , Pb^{2+} or La^{3+} ions, carried out at different reaction temperatures in highly alkaline solution. Traces of strontium titanate nanoparticles with crystalline perovskite structure appear already at 20 °C, but a complete crystalline nanopowder is synthesized at 80°C. However, crystalline perovskite particles in PbTiO_3 and $\text{La}_{2/3}\text{TiO}_3$ system can be obtained only under the hydrothermal conditions at higher temperatures. The PbTiO_3 powders synthesized under the hydrothermal conditions are highly agglomerated and are not nanosized, but have complex structures involving titanate particles covered with one-dimensional nanostructured elements.

Acknowledgment

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