

## Obtaining the Nanosize Powders and Epitaxial Films of Complex Oxides of Rare Elements of IV–V Groups from Aqueous Peroxide Solutions\*

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### Abstract

The process to obtain lithium metatantalate, lithium and sodium metaniobates and their solid solutions, lithium-conducting phosphate solid electrolytes, epitaxial films of lithium metatantalate and metaniobate, and  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  solid electrolyte on various substrates with the use of their precursor peroxide solutions has been studied.

### INTRODUCTION

The most widespread method to produce lithium niobate and tantalate is solid-phase interaction of niobium or tantalum pentoxide with lithium carbonate at heating to a temperature  $>1200\text{ }^\circ\text{C}$  [1]. Completeness of the reaction and a degree of single-phase nature of the termination product depend on the grain size, the mixture uniformity, and on passivation of particles by the reaction products. Uncontrollable change in composition of the termination product also occurs, which is caused both by metrological problems (by sophisticated determination of the main substance content in starting materials used for synthesis) and by loss of components of the reaction mixture during high-temperature synthesis. In addition, high-temperature sintering produces an agglomeration of the products, which precludes obtaining fine-grained powders, an interest to which is currently growing.

The high requirements, which are placed on the quality of oxide materials, have led to necessity of developing radically new methods for their production. Among the promising methods is the sol-gel method that additionally allows obtaining epitaxial films of these compounds. However, the use of alkoxides as precursors considerably complicates its realization [2].

This work reports the development of a procedure to obtain lithium metatantalate, lithium and sodium metaniobates and their solid solutions, lithium-conducting phosphate solid electrolytes, epitaxial films of lithium metatantalate and metaniobate, and  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  solid electrolyte on various substrates using peroxide solutions of their precursors.

### EXPERIMENTAL

#### *Obtaining of lithium metaniobate and metatantalate*

The method we worked out to produce high-purity lithium metaniobate and metatantalate is based on relatively good dissolving of a freshly deposited niobium or tantalum hydroxide

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in 35 % hydrogen peroxide. To synthesise stoichiometric lithium tantalate and niobate, we need to know first of all the exact content of tantalum or niobium oxide in the freshly deposited hydroxide. Therefore, tantalum or niobium pentachlorides of qualification “extra pure” (os. ch.) were applied as mother substances. A batch of the appropriate pentachloride was loaded in small portions under stirring into 25 % water solution of ammonia of qualification “extra pure” (os. ch.) taken according to the ratio solid : liquid = 1 : 4. The produced deposit of niobium or tantalum hydroxide was separated from a mother solution and subjected to triple repulping in 5 % water solution of ammonia to clear the chlorine ions. A content of chlorine ions was controlled by the potentiometric method with the use of the Cl-selective electrode of KhS-Cl-001 specification. Their content in washing water from the last repulping was  $\leq 10$  mg/l.

## RESULTS AND DISCUSSION

When dissolving the freshly deposited tantalum or niobium hydroxide in  $H_2O_2$  at ambient temperature, a sharp warming and foaming of the solution occurs after an inertial period (15–20 min). To prevent this effect, the dissolving process should be performed with hydrogen peroxide precooling to 0 °C. Complete dissolving of the deposit is achieved for 35–40 min.

It was found that dissolving of a freshly deposited tantalum or niobium hydroxide in  $H_2O_2$  proceeds more smoothly in the presence of lithium hydroxide. In this connection, a stoichiometric quantity of one-aqueous lithium hydroxide of qualification “extra pure” (os. ch.) was added to freshly deposited tantalum or niobium hydroxide and stirred. Hydrogen peroxide of 35 % concentration of qualification “extra pure” (os. ch.) was poured in portions into the mixture under intensive stirring until complete dissolving of reagents and thus a transparent solution of  $LiMeO_4$  precursor was obtained with a content of 90–110 g/l. This solution was subjected to evaporation until a dry deposit of  $LiMeO_4 \cdot nH_2O$  precursor was formed.

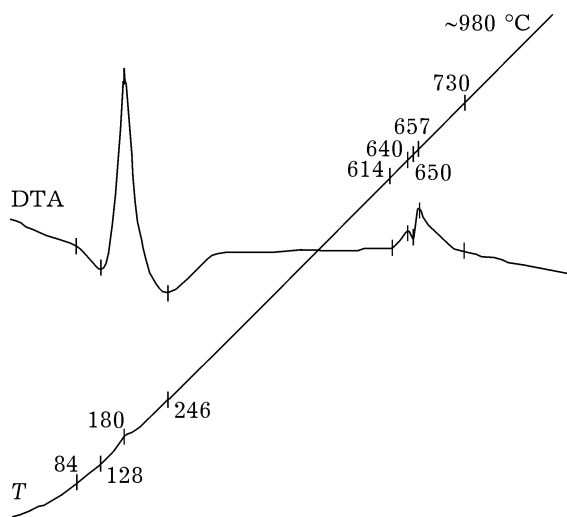


Fig. 1. DTA curve of  $LiNbO_3$  precursor, which has been dried at 100 °C.

Presented in Fig. 1 is the DTA curve of lithium niobate precursor that was dried up at 100 °C. The small endoeffect at 84–128 °C is due to removal of crystal water. The exoeffect with a maximum at 180 °C is caused by  $LiNbO_4$  decomposition with the evolving of active oxygen [3]. The subsequent endoeffect with a minimum at 246 °C may be related to interaction of residual hydroxides of niobium and lithium with elimination of water. The exoeffect in an interval 640–730 °C is associated with crystallization of  $LiNbO_3$ .

From this it is inferred that the calcination temperature for  $LiMeO_4 \cdot nH_2O$  precursor must comprise 750–800 °C. The termination product represents crystalline nanodispersed powder of single-phase  $LiMeO_3$  stoichiometric in composition. The dispersity of powders has been found by means of digital scanning electronic microscope SEM LEO-420 (the resolution of 7.5 nm) and it comprises 80–100 nm. Single-phase nature is confirmed by the Raman spectroscopy method in the Ramanor-1000 spectrometer at excitation by the 514.5 nm line of ILA-120 Ar-laser at ambient temperature: Raman spectrum of ceramic samples for the synthesized and reference  $LiMeO_3$  are in perfect agreement. The compliance of composition of the synthesized lithium niobate and tantalate with stoichiometry is confirmed by chemical analysis:  $LiNbO_3$  contains 10.07 mass %  $Li_2O$  and 89.93 mass %  $Nb_2O_5$  (theoretical content: 10.1 mass %  $Li_2O$  and 89.9 mass %  $Nb_2O_5$ );

$\text{LiTaO}_3$  contains 6.31 mass %  $\text{Li}_2\text{O}$  and 93.69 mass %  $\text{Ta}_2\text{O}_5$  (theoretical content: 6.33 mass %  $\text{Li}_2\text{O}$  and 93.67 mass %  $\text{Ta}_2\text{O}_5$ ). The content of specified impurities in both products are the following (mass %): Ca  $6 \cdot 10^{-4}$ , Mg  $6 \cdot 10^{-4}$ , V  $< 5 \cdot 10^{-4}$ , Fe  $< 3 \cdot 10^{-4}$ , Co  $< 5 \cdot 10^{-4}$ , Mn  $2 \cdot 10^{-4}$ , Cu  $< 5 \cdot 10^{-4}$ , Ni  $5 \cdot 10^{-4}$ , Cr  $5 \cdot 10^{-4}$ , Si  $6 \cdot 10^{-4}$ , and Cl less than 0.01.

#### Obtaining of $\text{Li}_x\text{Na}_{1-x}\text{NbO}_3$ solid solutions

Application of the procedure, which was worked out for synthesis of lithium niobate and tantalate, turned out to be the most promising to yield solid solutions of the  $\text{Li}_x\text{Na}_{1-x}\text{NbO}_3$  type. The stoichiometric quantities of one-aqueous lithium hydroxide of qualification "extra pure" (os. ch.) and of sodium hydroxide of the same qualification in the form of water solution with concentration of 16.5 M (660 g/l) were added to a freshly deposited niobium hydroxide and stirred. 35 % solution of hydrogen peroxide of qualification "extra pure" (os. ch.) was poured into the mixture by portions under intensive stirring until complete dissolving of the reagents. The transparent peroxide solution was evaporated in a drying chamber at 140 °C; the dry product was calcined at 800 °C. Solid solutions with  $x = 0.125, 0.17, 0.25,$  and 0.5 have been produced. Studying phase composition of the synthesized products was performed by X-ray diffraction analysis with

the use of DRON-2 diffractometer with  $\text{CuK}\alpha$  radiation and with graphite monochromator. Only  $\text{NaNbO}_3$  reflexes are present in the diffractogram (Fig. 2, curve 1) of  $\text{Li}_{0.125}\text{Na}_{0.875}\text{NbO}_3$  solid solution that allows us to assume that solid solutions around  $\text{NaNbO}_3$  exist in an interval  $0 < x \leq 0.125$ . At higher values of  $x$ , the reflexes of both  $\text{NaNbO}_3$  and  $\text{LiNbO}_3$  are observed in the diffractograms, which can be seen more distinctly in the diffractogram of the material of composition  $\text{Li}_{0.5}\text{Na}_{0.5}\text{NbO}_3$  (see Fig. 2, curve 2). By this is meant that the synthesized products constitute a mixture of two solid solutions around  $\text{NaNbO}_3$  and  $\text{LiNbO}_3$ .

#### Obtaining of $\text{LiTaO}_3$ and $\text{LiNbO}_3$ epitaxial films

Peroxide solutions of  $\text{LiNbO}_4$  and  $\text{LiTaO}_4$  precursors, which are formed as intermediate products, can be useful for obtaining the  $\text{LiNbO}_3$  and  $\text{LiTaO}_3$  epitaxial films on various substrates.

Solutions of  $\text{LiNbO}_4$  and  $\text{LiTaO}_4$  precursors are unstable, because after 1–2 h, their pH rises from an initial value of 6 up to 8–9 and the deposit precipitates from them. It has been found that stability of solutions sharply increases upon addition of glycerine as a film-former: at a content of glycerine  $> 5$  vol. %, the initial pH value is preserved for 5–10 days. To produce films, the peroxide solutions containing 1–5 mass %  $\text{LiMeO}_3$  and 3–6 vol. % glycerine were used.

The layers of precursor solution were applied onto substrates either by the centrifugal way, or by slow pooling of a substrate dipped into a peroxide solution out of it (by the dipping method). After applying a solution layer, the sample was air-dried for 10–15 min, placed in a vacuum drying chamber preheated up to 140 °C, and then let to stand in it during 15–30 min. Then the sample was annealed at 450 °C for 15–20 min, cooled slowly to ambient temperature, and the following solution layer was applied onto it with the temperature treatment repeated. A final stage represented the annealing of the sample at 900 °C for 1 h.

Presented in Fig. 3 are the diffractograms of films with three, six, and nine layers of  $\text{LiTaO}_3$ , which have been obtained on a

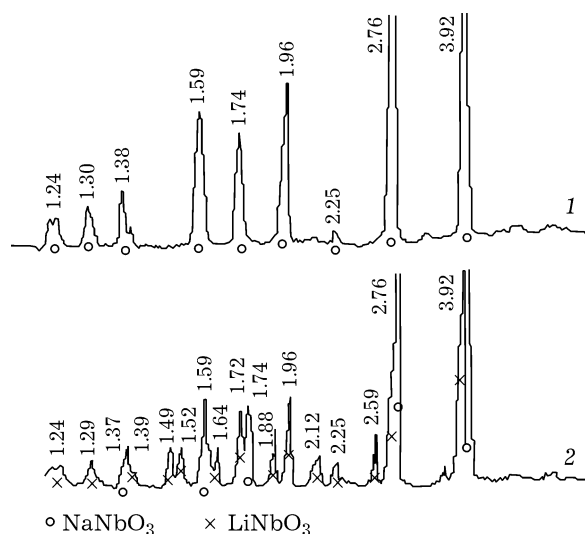


Fig. 2. Diffractograms of  $\text{Li}_{0.125}\text{Na}_{0.875}\text{NbO}_3$  (1) and  $\text{Li}_{0.5}\text{Na}_{0.5}\text{NbO}_3$  solid solutions (2).

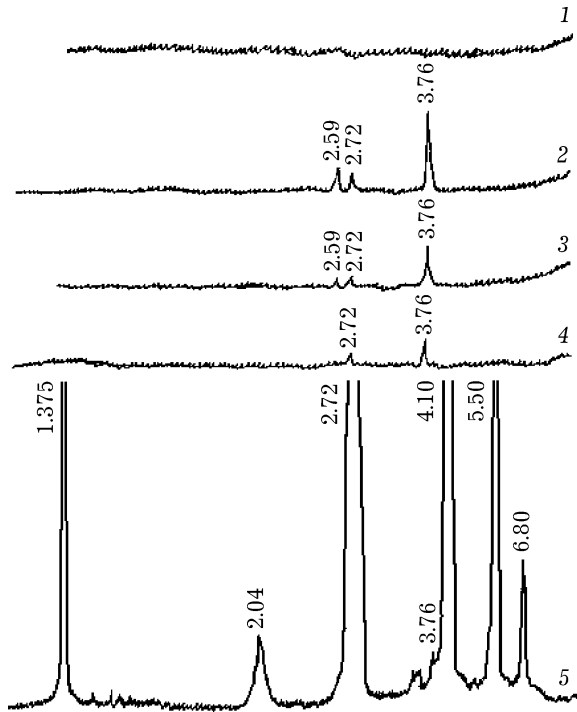


Fig. 3. Diffractograms of  $\text{LiTaO}_3$  films that were applied onto corundum substrate. See designations in the text.

corundum substrate by the centrifugal way using 3 % peroxide solution of  $\text{LiTaO}_4$  precursor with 4 vol. % of glycerine. Figure 3, curve 1 presents the diffractogram of the corundum substrate. It is evident that after application of three layers, three weak reflexes (3.76, 2.74, and 2.59 E) are present in the diffractogram (see Fig. 3, curve 2), these reflexes being characteristic of powdered  $\text{LiTaO}_3$ . Upon application of six layers, the intensity of these reflexes in the diffractogram (see Fig. 3, curve 3) decreased almost by a factor of two, and upon application of nine layers, the reflex with  $d = 2.59$  E disappeared in the diffractogram (see Fig. 3, curve 4) and the intensity of two other reflexes decreased additionally 2 times. This is an indirect evidence for the fact that the proportion of the oriented layer of lithium metatantalate increases with an increase in the film thickness. To register the reflections from  $\text{LiTaO}_3$  oriented layer, the counter of DRON-2 device was mounted at an angle of  $2\theta = 32.7^\circ$  and the sample with a nine-layer coating was turned manually until the intensive reflections from 104 plane ( $d = 2.739$  E) had been obtained. In this position, the recording of the diffractogram (see Fig. 3, curve 5) has been made, where seven

reflexes are present. The reflexes with  $d = 1.375$  and 2.72 E are characteristic of single-crystal  $\text{LiTaO}_3$ , and the reflexes with  $d = 2.04$ , 3.76, 4.10, 5.50, and 6.80 E appeared supposedly as a consequence of defectiveness in structure of the  $\text{LiTaO}_3$  film.

Analogous results have been produced with the use of peroxide solution of  $\text{LiNbO}_4$  precursor.

Essential advantage of the dipping method is a sharp decrease in the consumption of peroxide solution, since with the centrifugal way, 95 % of the solution is removed from the substrate surface and this part needs for regeneration. To produce multiple coating of  $\text{LiTaO}_3$  on a substrate from single-crystal

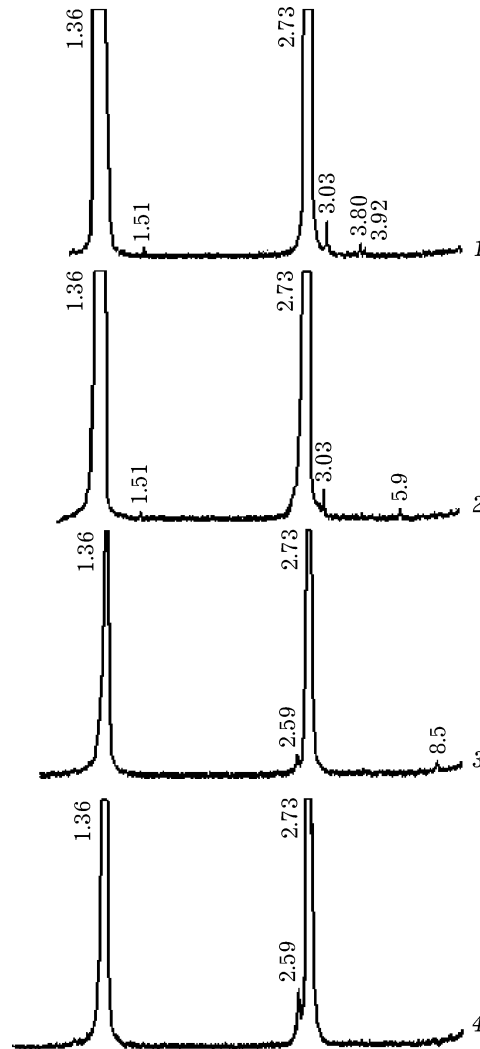


Fig. 4. Diffractograms of  $\text{LiTaO}_3$  films, which have been obtained on a substrate from  $\text{LiNbO}_3$  by the dipping method. See designations in the text.

LiNbO<sub>3</sub> plate 1.5 mm in thickness by this method, the solutions containing 1.5–2.5 mass % LiTaO<sub>4</sub> and 2–3 vol. % glycerine were applied. The solution was heated up to 30 °C prior to application; the substrate was pulled out of the solution at a rate of 0.6 cm/min.

As Fig. 4, curve 1, suggests, along with the intensive reflexes of 2.73 and 1.36 E that are characteristic of single-crystal LiNbO<sub>3</sub>, four weak additional reflexes (3.92, 3.80, 3.03, and 1.51 E) are present in the diffractogram of the substrate. Their emergence points to the defectiveness of the substrate surface. Upon application of two layers LiTaO<sub>3</sub>, the reflexes 3.92 and 3.80 E disappear from the diffractogram (see Fig. 4, curve 2), the intensity of the reflex 3.03 E decreases by 1/3, but there appears a weak reflex of 5.90 E. Upon application of three layers of LiTaO<sub>3</sub>, the reflexes 5.90, 3.03, and 1.51 E disappear from the diffractogram (see Fig. 4, curve 3) and there appear the weak reflexes 2.59 and 8.50 E. With a four-layer coating, only one additional reflex 2.59 E remains in the diffractogram (see Fig. 4, curve 4), this reflex being characteristic of powdered LiTaO<sub>3</sub>. Based on this, a conclusion is drawn that a three-layered coating by the dipping method is enough to obtain a highly oriented film of LiTaO<sub>3</sub> on the LiNbO<sub>3</sub> single-crystal substrate. The film produced after a four-layer coating is transparent, about 0.3 μm in thickness (the thickness of a single layer comprises on the average 75 nm).

The sample with the four-layer coating has been studied at ambient temperature by method of Raman spectroscopy with the Ramanor U-1000 spectrometer using the optical microscope Microraman with a locality of 1.5–10.0 μm. The reflection scattering geometry has been used. It was found that the substrate is evenly covered by a layer of lithium metatantalate. Scanning over the coating surface revealed no essential differences (within the experimental error) in Raman spectra in different points of the surface. Figure 5 presents the typical Raman spectra of ceramic samples of lithium tantalate and niobate with non-polarized radiation, which have been produced following an ordinary procedure of high-temperature synthesis, and the spectra of film coating and substrate are presented in Fig. 6.

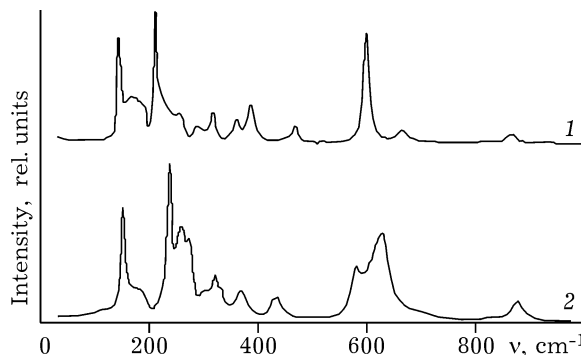


Fig. 5. Raman spectra of LiTaO<sub>3</sub> (1) and LiNbO<sub>3</sub> (2) ceramic samples.

The spectra consist of three line groups separated by an energy gap: the ranges 100–450, 550–650, and 850–900 cm<sup>-1</sup> contain the lines, which correspond to vibrations of B ions (Nb or Ta) located in oxygen octahedra, to vibrations of BO<sub>6</sub> oxygen octahedra, and to bridging stretching vibrations of oxygen ions within BO<sub>6</sub> octahedron respectively.

Presented in Fig. 6, curve 3 is the difference Raman spectrum of the substrate and the coating. It gives clear evidence that the spectrum of the coating contains the pronounced lines in the region of vibrations of oxygen octahedra (500–700 cm<sup>-1</sup>) and the lines in the region of vibrations of the ions located within the octahedral voids (0–500 cm<sup>-1</sup>). There is a “hint” to the availability of a line in the region of stretching B–O–B bridging vibrations (850–900 cm<sup>-1</sup>). It is significant that the distribution of intensities and frequencies in the spectrum of the produced film coatings perfectly fits the distribution of frequencies and intensities in the

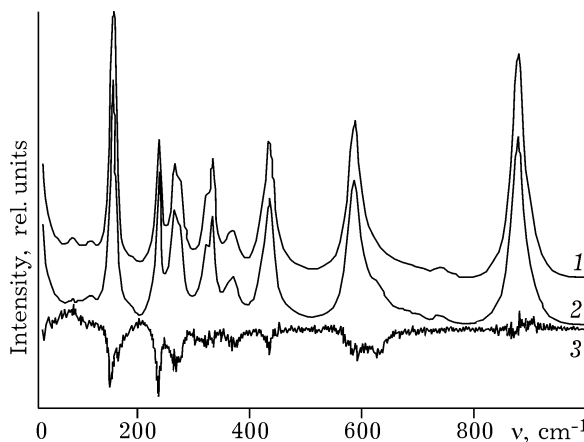


Fig. 6. Raman spectra of film coating (1), of substrate (2) and the difference Raman spectrum of the substrate and the film coating (3).

spectrum of substrate with a specified orientation.

The appearance of the difference Raman spectrum permits the following statements. Formation of an oriented film occurs on the substrate surface; it is possible that the film is even single-crystal, but significantly more disordered in structure than the structure of ceramic samples of lithium niobate or tantalate obtained by the ordinary high-temperature synthesis. It can be assumed that the coating constitutes strongly disordered (possibly, nanostructured) oriented near-surface solid solution of lithium niobate-tantalate that resembles a single-crystal solution. In Raman spectrum, so strong disordering of structure typically shows as some merged groups of lines forming wide diffuse bands, but not as a broadening of particular lines, that is exactly the case observed in Fig. 6. However, we cannot rule out that the obtained film coatings constitute well-oriented polycrystalline lithium tantalate with strongly disordered cationic and anionic sublattices, the material being close to nanostructures. All these variations of coating structure (solid solution, polycrystalline lithium tantalate with disordered structure, as well as their nanostructure variations) correlate with the obtained Raman spectra. It can be inferred that the observed disordering of the coating from lithium metatantalate on the surface of lithium metaniobate is attributable to a strong disordering of thin superficial layer of the substrate. This disordering appears during mechanical polishing of the surface with abrasive powders.

#### *Obtaining of $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ solid electrolyte*

When synthesising the solid electrolytes like  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  by ceramic method, a problem of reproducibility of the properties for termination product arises, which is caused by the mechanism of solid-phase reactions. The most promising method to produce solid electrolytes of this type with stable properties must be a prior transfer of all initial components into solution followed by its evaporation. In so doing, the most difficult is the transfer of titanium into solution. It has been found that a freshly deposited titanium hydroxide is

satisfactorily dissolvable in the form of a peroxide complex in acidic medium. The freshly deposited titanium hydroxide was obtained by dissolving a batch of titanium oxide of the anatase form in etching acid. The obtained acidic fluoride solution was heated to a temperature of 50–60 °C and poured in the small portions under stirring into 25 % ammonia solution. The precipitated amorphous deposit of titanium hydroxide was washed from fluorine ions with 5 % ammonia solution through repulping. The content of fluorine ions was monitored by the potentiometric method with the use of F-selective electrode of KhS-F-001 type. The content in washing water of the last repulping was  $\leq 10$  mg/l.

Synthesis of  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  solid electrolyte was performed with the use of a freshly deposited titanium hydroxide, water solutions of 1 M  $\text{LiNO}_3$  and  $\text{Al}(\text{NO}_3)_3$ ,  $\text{HNO}_3$  (65 mass %),  $\text{H}_3\text{PO}_4$  (85 mass %), and  $\text{H}_2\text{O}_2$  (35 mass %). Titanium hydroxide was dissolved in the mixture containing 70 vol. %  $\text{HNO}_3$  and 30 vol. %  $\text{H}_2\text{O}_2$ . The obtained solution was used to add solutions of  $\text{LiNO}_3$ ,  $\text{Al}(\text{NO}_3)_3$ , and  $\text{H}_3\text{PO}_4$  under stirring in compliance with stoichiometry. The resulting was that a transparent aqueous peroxide solution ruby in colour was produced that contained 160–170 g/l of the termination product. A white-coloured powder, which was obtained after evaporation of the solution, was calcined at a temperature of 900 °C for 1 h; then the tablets were pressed from it, which were sintered at 1000 °C for 1 h. The ionic conductivity of the sintered tablets was equal to  $6 \cdot 10^{-4}$  Sm/cm at ambient temperature that coincides with the value of conductivity for  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  samples produced through solid-phase synthesis.

#### **CONCLUSIONS**

The main advantage of the developed procedure to produce the stable peroxide solutions in the  $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{P}_2\text{O}_5-\text{H}_2\text{O}-\text{H}_2\text{O}_2$  system consists in the possibility of their application to produce the thin films of  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  solid electrolyte on a substrate by the dipping method with addition of glycerine as a film-former. A disk from

single-crystal sapphire was used as a substrate. The solution, which contains 12 g of precursor of  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  solid electrolyte in 100 and 5 ml of glycerine, is stable during 7 days. To apply a film, a substrate was dipped into solution and then pulled out at a rate of 0.6 cm/min, air-dried, annealed at 450 °C for 15 min, and cooled to room temperature. The process of application of the solution onto the substrate was repeated, but annealing of the sample was conducted at 850 °C for 30 min. Filming on the substrate has been confirmed by means of Neophot-2 microscope (magn. 200). X-ray diffraction analysis has demonstrated that four reflexes are present in the diffractogram of the produced film, these reflexes being characteristic of powdered  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  electrolyte. Hence it follows that the dipping method can be employed to obtain the films of lithium-conducting titanophosphate solid

electrolytes on the appropriate substrates. These films hold promise for production of thin-film chemical current sources.

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