SYNTHESIS OF NANOCRYSTALLINE COMPLEX OXIDES IN SUPERCritical ALCOHOLS

Abstract. An intensive search for solid electrolytes with high proton conductivity is being continued over the past few decades, which is primarily due to the high practical significance of these systems. Proton conductors are widely used as components of electrochemical devices such as gas sensors, electrolyzers, fuel cell membranes, etc. The variety of currently known solid proton conductors can be classified by operating temperature parameters, with the allocation of low, medium and high temperature regions. Each class, from the point of view of its practical use, has a number of advantages, but at the same time, specific disadvantages that hinder practical implementation. In this regard, the material science goal - the synthesis of new materials with functional properties, remains relevant.

For the first time, complex oxides - lanthanum niobates - were synthesized using alcohol solutions of salts of the corresponding metals by the solvothermal method in a flow reactor in a supercritical isopropanol medium. This method allows one to obtain single-phase lanthanum orthioniobate oxides, the phase composition, structure and morphology of which is characterized by X-ray phase analysis (XRD), Raman spectroscopy (Raman spectroscopy), scanning and transmission electron microscopy (SEM and TEM).

Key words: synthesis in supercritical alcohols, complex oxides, lanthanum orthioniobate.
Rare-earth metal orthoibates are a new class of high-temperature proton conductors with the ABO$_3$ perovskite structure [10,11], having proton conductivity of the order of $10^{-4}$ Ohm$^{-1}$ Sm$^{-1}$ at temperatures above 700°C and high stability in a humid and CO$_2$ enriched environment. However, LaNbO$_4$ has a rather low conductivity [12].

Since the presence of oxygen vacancies is the main factor responsible for the appearance of proton defects, the value of proton conductivity is directly related to the defectiveness of the complex oxide. Numerous efforts have been made to improve conductivity by single- or multi-element doping of perovskite sublattices with cations having a lower valency and a larger ionic radius, including monovalent (Na$^+$, K$^+$), divalent cations (Ca$^{2+}$, Sr$^{2+}$, Ba$^{2+}$) or trivalent cations (Fe$^{3+}$, Gd$^{3+}$, La$^{3+}$), as well as perovskite B-sublattices with cations having high valency with a small ionic radius, such as W$^{5+}$, Ce$^{4+}$, Zr$^{4+}$, Mn$^{3+}$, Co$^{3+}$, Yb$^{3+}$, and Y$^{3+}$ [13,14].

According to Hausgrund and Norby [11], when doping lanthanum niobate with calcium cations (La$_{0.99}$Ca$_{0.01}$NbO$_4$), the proton conductivity in wet hydrogen increases sharply and is about $10^{-3}$ C/cm at 900°C, while it is two orders of magnitude lower in the case of undoped material.

Various methods are used to synthesize rare-earth metal orthioibates: the preparation from salts melts [15, 16], solid-phase synthesis [11,15,16,17], the sol-gel method [18,19,20], spray pyrolysis (thermal decomposition of aerosol solutions) [12], coprecipitation [21] and mechanochemical synthesis [21,22]. Most of the above methods are multi-stage, time-consuming and require large time and energy spending. In contrast, synthesis using supercritical fluids (SCS) is characterized by simplicity and high productivity.

Aymonie [23] emphasizes that the supercritical fluid technology used to produce oxide materials makes it possible to control the synthesis process by varying the operating parameters and provides an understanding of how each parameter, affecting the synthesis process, allows controlling the material characteristics in terms of size, morphology, structure.

The aim of this work is to obtain proton-conducting materials using alcohol solutions of salts of the corresponding metals by the solvothermal method in a flow reactor in a supercritical isopropanol medium. During the study, the complex oxides LaNbO$_4$ and La$_{0.99}$Ca$_{0.01}$NbO$_4$ were synthesized and characterized by a complex of physicochemical methods.

**Experimental part.** Samples of complex oxides were synthesized by solvothermal synthesis using supercritical isopropanol in a flow-type reactor; installation scheme is shown in figure 1. Samples of lanthanum niobates were synthesized using alcohol solutions of salts of the corresponding metals. The precursors used were La(NO$_3$)$_3$·6H$_2$O (VECTON, 99.99%), Ca(NO$_3$)$_2$ (REAHIM, 99.5%), NbCl$_5$ (LLC NPP Methim, 99.90%). Precursor solutions were prepared by dissolving in isopropanol. The resulting mixture was injected into the mixer with a syringe pump at a rate of 5 ml/min. A preheated alcohol was injected continuously with a plunger pump in the same mixer at a rate of 9 ml/min. The synthesis was carried out at 400°C and 120-130 atm. After exiting the reactor and depressurizing the product was cooled in a heat exchanger and collected in a storage tank. The decantation method was used to separate the solid product from the mother liquor. The resulting precipitates were dried and calcined at 700-1300°C for 4 hours.

To obtain a dense ceramic based on a sample doped with calcium, the compressed tablet was calcined in air for 4 hours at 1300°C. Its density was estimated using data on its weight and geometric dimensions.

The phase composition of the samples was studied using a BrukerAdvance D8 diffractometer with CuKα radiation. Diffraction patterns were obtained by scanning in the angle range 15 - 90 (2θ) with a scan step of 0.05 (2θ). The obtained phases were identified using an ICDD X-ray file cabinet. The coherent scattering region (CSR) was determined by the diffraction reflection (004) for the tetragonal La$_{0.99}$Ca$_{0.01}$NbO$_4$ [PDF 50-0919] and (-121) for the monoclinic [PDF 22-1125] phases.

IR spectra of the samples were recorded on IR Fourier spectrometer Cary 660 FTIR spectrometer (Agilent Technologies) and PIKE Technologies Gladi ATR in the range of 4000-250 cm$^{-1}$, with a scanning step of 32. Electron microscopic studies were performed on a JSM-6460 LV scanning electron microscope (JEOL, Japan).
Results and discussion. According to the X-ray diffraction pattern (figure 2a), after supercritical synthesis, the initial lanthanum orthoniobate and the calcium doped sample are X-ray amorphous materials. After calcination at 700°C in both samples, lanthanum orthoniobate is formed in two phase modifications: low-temperature monoclinic [01-083-1911] and high-temperature tetragonal [00-050-0919].

According to the XRD data (figure 2b), La_{0.99}Ca_{0.01}NbO_{4} is a mixture of two phases — monoclinic and tetragonal, whose peaks are broadened, indicating that the sample obtained during the synthesis is an ultrafine material with a primary particle size of the nanometer range. With an increase of the calcination temperature (figure 3), the crystallization of both phases increases, and the phase ratio changes in the direction of increase of the monoclinic phase La_{0.99}Ca_{0.01}NbO_{4}. After calcination at 1300°C, the tetragonal phase is retained in very small quantities.
Table 1 - Characteristics of La<sub>0.99</sub>Ca<sub>0.01</sub>NbO<sub>4</sub> after calcination at 700-1300°C

<table>
<thead>
<tr>
<th>№</th>
<th>Calcination temperature, °C</th>
<th>Coherent scattering region, nm</th>
<th>S&lt;sub&gt;BET&lt;/sub&gt;, m&lt;sup&gt;2&lt;/sup&gt;/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>700</td>
<td>23.8</td>
<td>20</td>
</tr>
<tr>
<td>2</td>
<td>900</td>
<td>35.4</td>
<td>16</td>
</tr>
<tr>
<td>3</td>
<td>1100</td>
<td>52.9</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>1300</td>
<td>66.0</td>
<td>0.2</td>
</tr>
</tbody>
</table>

As follows from the data in Table 1, the domains of both phases remain in the nano-region even at high calcination temperatures. It should be noted that the size of the monoclinic phase domains decreases with an increase in the calcination temperature, which may be related to the specific dynamics of the transformation process of the tetragonal phase into the monoclinic one, which does not proceed to the end even at 1300°C. In this case, a decrease in the specific surface with increasing annealing temperature indicates an increase in the average particle size of the sample and, therefore, an increase in the density of domain walls with which the channel of rapid diffusion of oxygen ions and protons can be associated [19].

According to IR spectroscopy, the absorption bands in the range of 1500–1400 cm<sup>-1</sup> for the low-temperature sample correspond to carbonates (figure 4). The spectral absorption regions of Nb-O groups in the [Nb<sup>5+</sup> O<sub>4</sub>]<sup>3+</sup> tetrahedron are in the region of 600 cm<sup>-1</sup>. Oscillations in the regions of 800 and
430 cm⁻¹ correspond to the monoclinic phase La₀.₉₉Ca₀.₀₁NbO₄, which is in good agreement with the XRD data. The intensities of these peaks increase with annealing temperature.

The relative density of La₀.₉₉Ca₀.₀₁NbO₄ tablet calcined at 1300°C for 4 hours was ~ 90%, which indicates good sinter ability of the materials obtained by this method due to their disorder. Indeed, for samples obtained by the method of high-temperature solid-phase synthesis, such a density is achieved only at higher temperatures of ~ 1500°C [15-17]. The fine-grained structure of ceramics with the grain size 1-5 microns also should be noted (figure 5).

Figure 5 - SEM images taken from the surface (a) and from the cleavage (b) of the La₀.₉₉Ca₀.₀₁NbO₄ ceramic sample

Conclusions. Thus, in this work, the complex oxides LaNbO₄ and La₀.₉₉Ca₀.₀₁NbO₄ were obtained by solvothermal methods in a flow reactor in a supercritical isopropanol environment for the first time. According to XRD and IR spectroscopy of lattice vibrations, the structure of the samples is a mixture of monoclinic and tetragonal phases, the ratio of which varies with increasing calcination temperature. Preservation of nanocrystallinity even in the high-temperature La₀.₉₉Ca₀.₀₁NbO₄ sample can play a large role in its transport characteristics.

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НАНОКРИСТАЛДЫ КУРДЕЛІ ОКСИДТЕРДІ ЖОГАРЫ КРИТИКАЛЫҚ СПИРТТЕ СИНТЕЗДЕУ

Аннотация. Протон өткізгіші бар қатты электролиттерді интенсивті қаразыр әдеттері аркылы тұрғыданықты қызмет жасау үшін, екі электрод, мұндағы жүйелердің жоғары тәрізді, нормалды электролиттердің құрылымынан алынады. Газ датчикі, электродизератор, өткізгіш құрылым мембранасы және т.б. протон өткізгіш аудармалары және сілтілі жоғары температуралық құрылым жасау үшін, орташа із-шеп жоғары температура және нормалды протон өткізгіш құрылымдардың компоненті ретінде көмекші көзденілді. Қазір елдің бірінші протон өткізгішерінің жұмыс температурасына байланысты құрылымның қосындысы жоғары, орташа және құрылымға температура болып жатады. Бұрынғы кластерлер немесе құрылымдың бірінші негізгі мәніндегі функционалды қасиеттерді бар жаңа протон өткізгіш қасиеттері бәр нанокомпозиттердің синтездеу.
Протон откізіші касиеті бар электролиттерді 1980 жылдарында Ивахара және башқа галымдар зерттей бастады. Галымдар сирек кездесетін косылыс - ниобаттар мен танталақтардың гылыми қарым-қатыс, қолданылуының зерттеуі үшін қолданылады. Бұл керамикалық материал қасиетін зерттеу, олардың оптикалық қасиетін, және әрі тәжірибелерге негізделді. Лантан ортониобатының күрес кырылығы зерттелгенде 490-ден 525°С-қа дейінгі температуралық ауысуы байқалды.

Лантан ортониобаты – жоғары температуралы протон откізіші касиеті бар ABO₃ перовскит күресіндегі оксид, жоғары температуралық протон откізіші 10⁻⁴ Ω⁻¹·cm⁻¹, ал ылғалды және байытылған CO₂ өртінде тұрақты болып келеді.

Жалпы формуласы ABO₃ электролиттерінің күресіндегі касиеті, оптикалық қасиетін, және әрі тәжірибелерге негізделсіз. Лантан ортониобатының күресіндегі касиеті, олардың оптикалық қасиетін, әрі тәжірибелерге негізделсіз.

Сызған металлдар лантан ортониобатын синтездеу үшін келесілі эдістер колданылады: информатикалық және электролиттік электролиттер, сәріңізлік және электролиттік ріңкілік, спрей пиролиз (аэрозольдің термиялық ыдырау), бірге тұтқын және механохимиялық синтез. Жоғарыда аталған эдістердің кеңінен колданылады.

Синтез қосылымды перовскит күресіндегі оксидтердің касиеті, оптикалық қасиетін, сілтілік және әрі тәжірибелерге негізделсіз. Лантан ортониобатының күресіндегі касиеті, олардың оптикалық қасиетін, әрі тәжірибелерге негізделсіз.

Түйін сөзлер: жоғары температуралық протон откізіші касиеті бар нанокомпозиттер, күресіндегі касиеті, матеріалдардың жәнеқасиеттерінің зерттеуі.

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СИНЕЗ НАНОКРИСТАЛЛИЧЕСКИХ СЛОЖНЫХ ОКСИДОВ

В СВЕРХКРИТИЧЕСКИХ СПИРТАХ

Аннотация. Интенсивный поиск твердых электролитов с высокой протонной проводимостью продолжается на протяжении последних нескольких десятилетий, что обусловлено в первую очередь высокой практической значимостью данных систем. Протонные проводники находят широкое применение в качестве компонентов электрохимических устройств, таких как газовые сенсоры, электролизеры, мембраны топливных элементов и др. Многообразие известных в настоящее время твердых протонных проводников может классифицироваться по параметрам рабочих температур, выделяя низко-, средне- и высокотемпературные области. Каждый класс, с точки зрения их практического использования, обладает рядом достоинств и недостатков, сдерживающих их практическое применение. В этой связи, материаловедческая задача – синтез новых материалов с функциональными свойствами, остается актуальной.

Протонные проводники для H⁺-смотр были обнаружены Iwahara и соавт. в начале 1980-х годов. Они указали, что нанокомпозиты металлов представляют собой группу соединений с интересными свойствами как с научной, так и с практической точки зрения. Изучение свойств этих керамических материалов базировалось на исследовании их оптических свойств, и, в частности флуоресцентных. Структурные свойства этой керамики были изучены, и оказались, что нанокомпозит представляет собой интересное направление для дальнейших исследований.
temperature from 490 to 525°C promotes the phase transition (second order) from monoclinic to orthorhombic phase. The conductivity of La0.99Ca0.01NbO4 is two orders of magnitude lower than in the undoped material.

The synthesis of rare-metal niobates is an important task due to their unique properties. The key to improving the conductivity of these materials is the introduction of dopants that increase the proton conductivity.

The method of synthesis in supercritical solutions (SCS) differs from traditional methods in terms of simplicity and high productivity. The technology of Aymonie is based on the use of supercritical fluids to obtain oxide materials, which allows controlling the properties of the material in a single step.

**References**


