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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 orthoniobate.

Proton-conducting electrolytes for H^+ - SOFC were discovered by Iwahara et al. [1,2] in the early 1980s. They indicated that niobates and tantalates of rare earth metal are a group of compounds with interesting properties, both from scientific and practical point of view. The study of the properties of these ceramic materials was based on the study of their optical and, in particular, fluorescent properties [3-4].

The structural properties of this ceramic were studied in [5,6]; It turned out that lanthanum niobate at 490 to 525°C undergoes a phase transition (of the second kind) from a monoclinic phase with a fergusonite structure to a tetragonal one with scheelite structure. This phase transition is accompanied by a large thermal expansion, and in turn, it was determined that the high-temperature phase has a higher proton conductivity.

A number of works were devoted to the search for doping cations capable of stabilizing the high-temperature phase. It was shown that in the case of introduction of cations into the lanthanum sublattice, the transition temperature changes only slightly, whereas in the case of substitution of niobium into the sublattices, it changes appreciably (up to room temperature in the case of doping with antimony or vanadium) [7, 8].

The introduction of lanthanides with a smaller ionic radius into the lanthanum position does not affect significantly the phase transition temperature, but strongly changes the optical and electrical properties of rare-earth niobates, in particular, enhances the luminescent properties [9].

Rare-earth metal orthiobates 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 orthioiobates: 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 $La(NO_3)_3*6H_2O$ (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 400^0C 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 700-1300^0C 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).

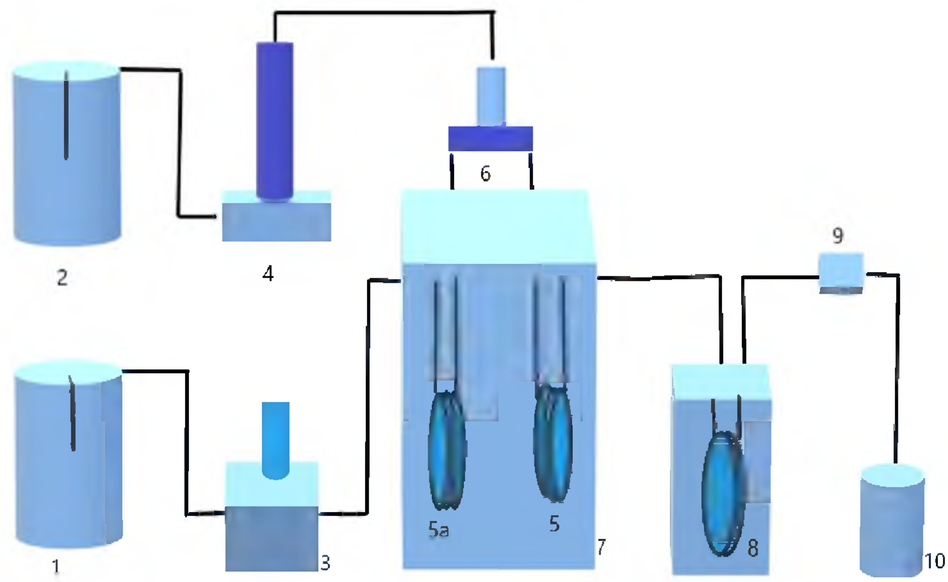

Figure 1 - Laboratory installation for supercritical synthesis 1 - a tank with alcohol, 2 - a tank with a solution of metal salts, 3 - a plunger pump, 4 - a syringe pump, 5 - a reactor, 5a - a flow heater for alcohol, 6 - a mixer, 7 - a furnace, 8 - a heat exchanger, 9 - back pressure valve, 10 - storage tank

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]

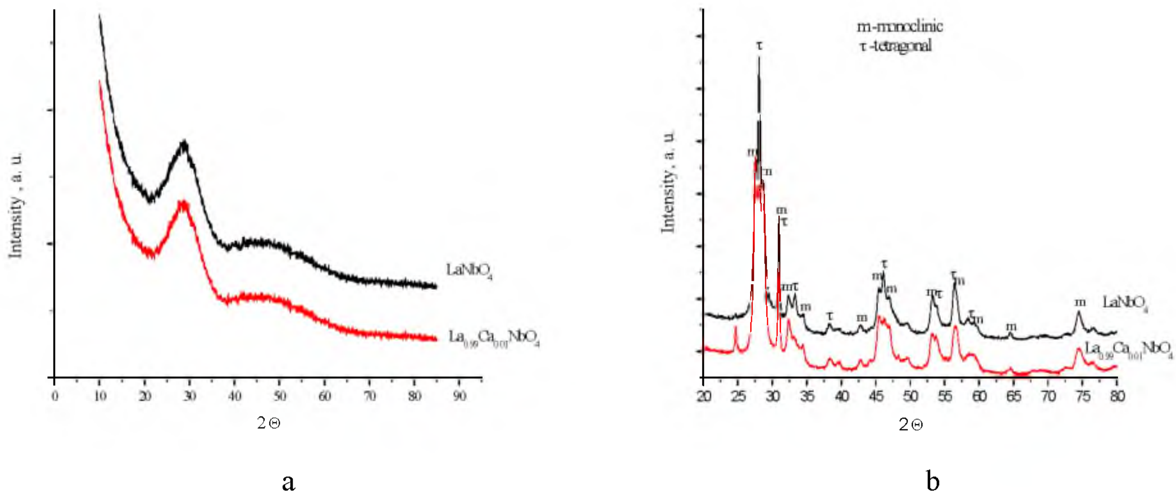

Figure 2 - X-ray diffraction patterns of lanthanum orthoniobate samples a) after SCA and b) after calcination at 700°C

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.

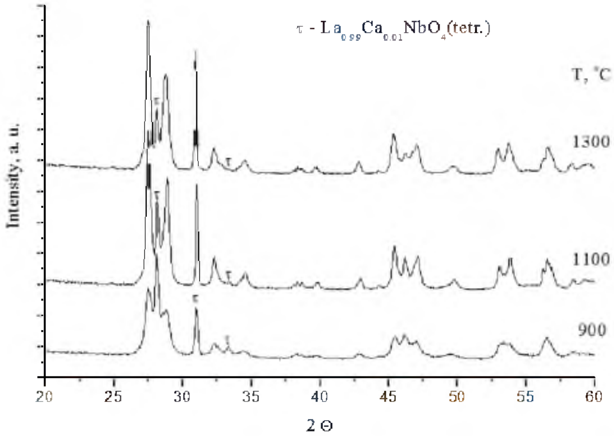

Figure 3 - Diffraction patterns of $La_{0.99}Ca_{0.01}NbO_4$ after calcination at 900–1300°C

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].

Table 1 - Characteristics of $La_{0.99}Ca_{0.01}NbO_4$ after calcination at 700-1300℃

№	Calcination temperature, ^{0}C	Coherent scattering region, nm		S_{BET}, m^2/g
		Tetragonal phase	Monoclinic phase	
1	700	23.8	-	20
2	900	35.4	42.3	16
3	1100	52.9	27.9	4
4	1300	66.0	27.5	0.2

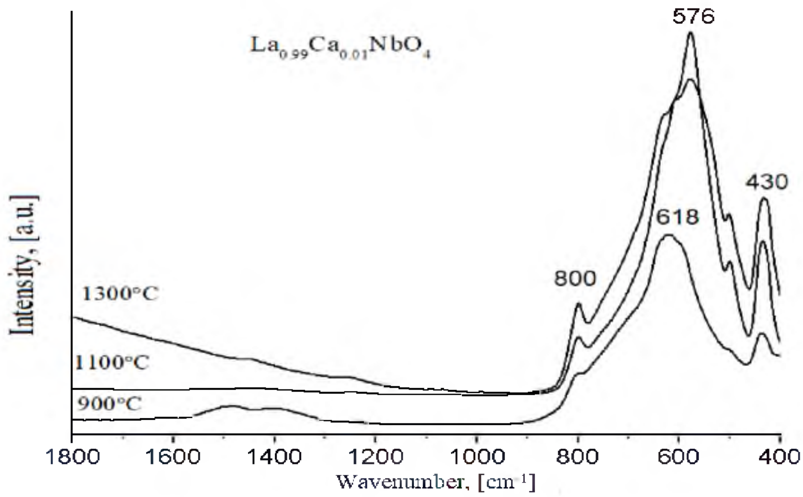

Figure 4 - IR spectra of lanthanum orthoniobates after calcination at 900–1300°C

According to IR spectroscopy, the absorption bands in the range of 1500–1400 cm^{-1} for the low-temperature sample correspond to carbonates (figure 4). The spectral absorption regions of Nb-O groups in the $[Nb^{5+} O_4]^{3+}$ tetrahedron are in the region of 600 cm^{-1}. Oscillations in the regions of 800 and

430 cm^{-1} correspond to the monoclinic phase $La_{0.99}Ca_{0.01}NbO_4$, which is in good agreement with the XRD data. The intensities of these peaks increase with annealing temperature.

The relative density of $La_{0.99}Ca_{0.01}NbO_4$ 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).

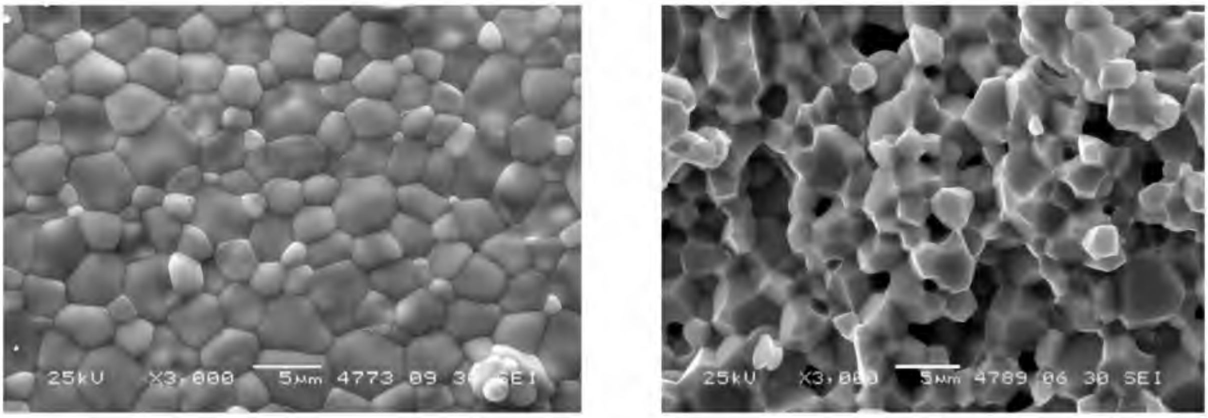

Figure 5 - SEM images taken from the surface (a) and from the cleavage (b) of the $La_{0.99}Ca_{0.01}NbO_4$ ceramic sample

Conclusions. Thus, in this work, the complex oxides $LaNbO_4$ and $La_{0.99}Ca_{0.01}NbO_4$ 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 $La_{0.99}Ca_{0.01}NbO_4$ sample can play a large role in its transport characteristics.

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НАНОКРИСТАЛДЫ КҮРДЕЛІ ОКСИДТЕРДІ ЖОҒАРЫ КРИТИКАЛЫҚ СПИРТТЕ СИНТЕЗДЕУ

Аннотация. Протон өткізгіші бар қатты электролиттерді интенсивті қарастыру жұмысы бірнеше ондаған жылдар бойы жалғасуда және бұл, ең алдымен, мұндай жүйелердің жоғары практикалық маңыздылығына байланысты. Газ датчигі, электролизатор, отынның жасушалық мембранасы және т.б. протон өткізгіші электрохимиялық құрылғылардың компоненті ретінде кеңінен қолданылады. Қазіргі уақытта белгілі протон өткізгіштерінің жұмыс температурасына байланысты төмен, орташа және жоғары температуралы протон өткізгіштер болып жіктеледі. Әрбір кластың практикалық қолдану тұрғысынан алғанда, бірқатар артықшылығы бар, сонымен бірге олардың сәтті коммерцияллануына кедергі болатын нақты кемшіліктері де кездеседі. Осыған байланысты материалтану ғылымының негізгі міндеті – функционалды қасиеттері бар жаңа протон өткізгіш қасиеті бар нанокомпозиттерді синтездеу.

Протон өткізгіш қасиеті бар электролиттерді 1980 жылдардың басында Ивахара және басқа да ғалымдар зерттей бастады. Ғалымдар сирек кездесетін қосылыс – ниобаттар мен танталдардың ғылыми тұрғыдан да, практикалық тұрғыдан да маңызды қасиеттері бар қосылыстар тобы екенін көрсетті. Бұл керамикалық материал қасиетін зерттеу, олардың оптикалық қасиетін, атап айтқанда, люминесцентті зерттеуге негізделді. Лантан ортониобатының құрылымдық қасиетін зерттегенде 490-ден 525°С-қа дейінгі температурада фергусонит құрылымы бар моноклиндік фазадан, шеелит құрылымы бар тетрагональды фазаға ауысуы байқалады.

Лантан ортониобаты – жоғары температуралы протон өткізгіш қасиеті бар ABO_3 перовскит құрылымды күрделі оксид, жоғары температурада 700°С протон өткізгіші $10^{-4}Ом^{-1}см^{-1}$, ал ылғалды және байытылған CO_2 ортасында тұрақты болып келеді.

Жалпы формуласы ABO_3 перовскит құрылымды күрделі оксидтер тұрақтылығына байланысты электролиттің ең қолайлы материалы. А перовскит катионына төмен валентті сілтілік металдар (Na^+, K^+), еківалентті сілтілік жерметалдар (Ca^{2+}, Sr^{2+}, Ba^{2+}) және үшвалентті (Fe^{3+}, Gd^{3+}, La^{3+}) катиондар орналасуы мүмкін. Керісінше, перовскит В катионы W^{5+}, Ce^{4+}, Zr^{4+}, Mn^{3+}, Co^{3+}, Yb^{3+} және Y^{3+} сияқты кішкентай иондық радиусы бар жоғары валентті катиондармен қамтамасыз етіледі. Көптеген перовскит құрылымды күрделі оксидтердің протон өткізгіштік қасиеті бар.

Сирек кездесетін металдар лантан ортониоттарды синтездеу үшін келесідей түрлі әдістер қолданылады: балқытпалардан тұз дайындау, қатты фазалы синтез, золь-гель әдісі, спрей пиролизі (аэрозольдің термиялық ыдырау), бірге тұну және механохимиялық синтез. Жоғарыда аталған әдістердің көпшілігі көпсатылы, ұзақ уақыт пен энергияны қажет етеді. Керісінше, жоғары критикалық сұйықтықты қолдана отырып синтездеу әдісі қарапайым және жоғары өнімді болып келеді. Aymonie еңбектерінде оксидті материалды өндіруде қолданылатын жоғары критикалық сұйықтық технологиясы зерттелетін материал морфологиясы, құрылымы жағынан параметрлерін өзгертіп, синтез үдерісін бақылауға және синтез үдерісіне әсер ететін әрбір параметрдің мөлшері мен материалдық сипаттамаларын басқаруға болатындығын айтты.

Сондықтан, бұл жұмыста алғаш рет жоғары критикалық ортада изопропанол қатысында $LaNbO_4$ мен $La_{0.99}Ca_{0.01}NbO_4$ күрделі оксидтер синтезделінін алынды. Алынған $LaNbO_4$ мен $La_{0.99}Ca_{0.01}NbO_4$ күрделі оксидтердің күйдіру температурасына байланысты физико-химиялық қасиеттері зерттелді.

Жұмыс нәтижесінде алынған $LaNbO_4$ мен $La_{0.99}Ca_{0.01}NbO_4$ құрамды күрделі оксидтер қазіргі уақытта сутегі энергия саласында қарқынды зерттеуге байланысты үлкен сұранысқа ие. Сондықтан протон өткізгіш қасиеті бар нанокомкомпозиттер әлі де үлкен зерттеулерді талап етеді.

Түйін сөздер: жоғары критикалық спиртте синтездеу, күрделі оксидтер, лантан ортониобаты, құрылымдық сипаттамалар.

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СИНТЕЗ НАНОКРИСТАЛЛИЧЕСКИХ СЛОЖНЫХ ОКСИДОВ В СВЕРХКРИТИЧЕСКИХ СПИРТАХ

Аннотация. Интенсивный поиск твердых электролитов с высокой протонной проводимостью продолжается на протяжении последний 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, но и в то же время специфическими недостатками, сдерживающими их практическое внедрение. В этой связи, материаловедческая задача − синтез новых материалов с функциональными свойствами, остается актуальной.

Протонпроводящие электролиты для Н + -ТОТЭ были обнаружены Iwahara и соавт. в начале 1980-х годов. Они указали, что ниобаты и танталаты редкоземельных 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 оказалось, что ниобат лантана при

температуре от 490 до 525°С претерпевает фазовый переход (второго рода) из моноклинной фазы со структурой фергусонита в тетрагональную со структурой шеелита. Ортониобаты редкоземельных металлов являются новым классом высокотемпературных протонных проводников со структурой перовскита ABO_3, имеют протонную проводимость порядка 10^{-4} $Ом^{-1}$ $См^{-1}$ при температурах выше 700 °С и высокую устойчивость во влажной и обогащенной CO_2 среде. Однако $LaNbO_4$ обладает достаточно низкой проводимостью. Поскольку наличие вакансий кислорода является основным фактором, ответственным за появление протонных дефектов, то величина протонной проводимости напрямую связана с дефектностью сложного оксида. Многочисленные усилия были предприняты для улучшения проводимости путем одно- или многоэлементного допирования как А-подрешетки перовскита катионами, имеющими более низкую валентность и больший ионный радиус, включая одновалентные (Na^+, K^+), двухвалентные катионы (Ca^{2+}, Sr^{2+}, Ba^{2+}) или трехвалентные катионы (Fe^{3+}, Gd^{3+}, La^{3+}), так и В-подрешетки перовскита катионами, имеющих высокую валентность с небольшим ионным радиусом, таким как W^{5+}, Ce^{4+}, Zr^{4+}, Mn^{3+}, Co^{3+}, Yb^{3+} и Y^{3+}. Согласно Hausgrund и Norby, при допировании ниобата лантана катионами кальция ($La_{0.99}Ca_{0.01}NbO_4$) протонная проводимость во влажном водороде резко увеличивается и составляет около 10^{-3} С/см при 900°С, в то время как в случае недопированного материала проводимость на два порядка ниже.

Для синтеза ортониобатов редкоземельных металлов используют различные методы: получение из расплавов солей, твердофазный синтез, золь-гель метод, спрей-пиролиз (термическое разложение аэрозоля растворов), соосаждение и механохимический синтез. Большинство из перечисленных выше методов являются многостадийными, трудоемкими и требуют больших временных и энергетических затрат. В отличие от них синтез с использованием сверхкритических флюидов (СКС) характеризуется простотой и высокой производительностью. В работе Aymonie подчеркивается, что технология сверхкритических флюидов, применяемая для получения оксидных материалов, дает возможность управлять процессом синтеза путем варьирования рабочих параметров и дает понимание того, как каждый параметр, влияющий на процесс синтеза, позволяет контролировать характеристики материала с точки зрения размера, морфологии, структуры.

Целью данной работы является получение протонпроводящих материалов с использованием спиртовых растворов солей соответствующих металлов сольвотермальным методом в проточном реакторе в сверхкритической среде изопропанола. В ходе работы были синтезированы сложные оксиды $LaNbO_4$ и $La_{0.99}Ca_{0.01}NbO_4$ и охарактеризованы комплексом физико-химических методов.

Таким образом, в данной работе впервые получены сложные оксиды $LaNbO_4$ и $La_{0.99}Ca_{0.01}NbO_4$ сольвотермальном методам в проточном реакторе в среде сверхкритического изопропанола. По данным РФА и ИК-спектроскопии колебаний решетки, структура образцов представляет собой смесь моноклинной и тетрагональной фаз, соотношение которых изменяется с ростом температуры прокаливания. Сохранение нанокристалличности даже у высокотемпературного образца $La_{0.99}Ca_{0.01}NbO_4$ может играть большую роль в его транспортных характеристиках.

Ключевые слова: синтез в сверхкритических спиртах, сложные оксиды, ортониобат лантан.

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