Formation of complex phase LaLuO$_3$:Yb^{3+} nanopowders with perovskite type structure

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Precursors for obtaining nanopowders of a perovskite-type complex oxide phase LaLuO$_3$:Yb^{3+} were synthesized by the heterogeneous deposition method. The factors influencing the synthesis of precursors and the formation of the nanopowders derived from them have been established. These factors include temperature and pH of the solution, urea concentration, drying and thermal decomposition conditions. Adsorption and structural studies have shown that the synthesized precursors are mesoporous, nanodisperse powders. Depending on the synthesis conditions, the specific surface area of the synthesized precursors is 10 to 120 m^2/g. At the synthesis temperature of 40 and 60°C with 10 vol. % urea content in the solution, the specific surface area of the synthesized precursors is 14 to 9.7 m^2/g with an average diameter of priority range mesopores of 5.3–5.5 nm; at 80°C, the specific surface area of the precursor increases to 23.7 m^2/g, and the average diameter of mesopores up to 6 nm. It has been established that the synthesis temperature influences the formation of the precursor porous structure type, e.g. powders with different types of porous structure: corpuscular or layered. It was found that the amount of urea in the synthesis of the precursor affects only the general porosity characteristics; the range of mesopore size distribution remains the same. The highest porosity is observed during synthesis at a solution temperature of 80°C and urea content of 20 vol. %. In order to obtain and study nanopowders of complex oxide phase LaLuO$_3$:Yb^{3+} with a perovskite type structure, the synthesized precursors were thermally decomposed under nonisothermal conditions at a heating rate of 5 deg/min with gradual cooling; as a result, nanodisperse, mesoporous powders were formed with a specific surface area of 11–28 m^2/g and an average mesoporous diameter of 11–21 nm with the main phase of a perovskite-type structure in all samples.

Keywords: precursor, heterogeneous deposition, specific surface area, nanopowders, perovskite, sorption isotherms.

Формування нанопорошків складної фази LaLuO$_3$:Yb^{3+} зі структурою типу перовскиту. *О.В.Широков, О.В.Чудінович, Т.Ф.Лобунець, А.В.Рагуля*

Методом гетерогенного осадження синтезовано прекурсори для отримання нанопорошків складної оксидної фази LaLuO$_3$:Yb^{3+} типу перовскиту. Встановлено фактори, які впливають на синтез прекурсорів і формування отриманих з них нанопорошків. До них відносяться температура та рН розчину, концентрація сечовини, умови сушки та термічного розкладу. Адсорбційно-структурні дослідження показали, що синтезовані прекурсори є мезопористими, нанодисперсними порошками. В залежності від умов синтезу питома поверхня отриманих прекурсорів становить від 10 до 120 м^2/г. При температурі синтезу 40 і 60°C з 10 об.% вмістом сечовини у розчині питома поверхня синтезованих прекурсорів складає від 14 до 9,7 м^2/г при середньому діаметрі мезопор

пріоритетного діапазону 5,3–5,5 нм, а при 80°C питома поверхня прекурсору зростає до 23,7 м^2/г, а середній діаметр мезопор і до 6 нм. Встановлено, що температура синтезу впливає на формування типу пористої структури прекурсорів, зокрема утворюються порошки із різним типом пористої структури: корпускулярної чи пошарової. Встановлено, що кількість сечовини при синтезі прекурсору впливає тільки на загальні характеристики пористості при однаковому діапазоні розподілу мезопор за розмірами. Найбільша поруватість спостерігається в результаті синтезу з температурою розчину 80°C та 20 об. % вмістом сечовини. Для отримання та дослідження нанопорошків складної оксидної фази LaLuO$_3$:Yb^{3+} зі структурою типу перовскиту проводили термічний розклад синтезованих прекурсорів у неізотермічних умовах при швидкості нагріву 5 град/хв з поступовим охолодженням, внаслідок чого отримано нанодисперсні, мезопористі порошки з питомою поверхнею 11–28 м^2/г та середнім діаметром мезопор 11–21 нм і основною фазою зі структурою типу перовскиту, яка утворюється в усіх зразках.

Методом гетерогенного осаждения синтезированы прекурсоры для получения нанопорошков сложной оксидной фазы LaLuO$_3$:Yb^{3+} типа перовскита. Установлены факторы, влияющие на синтез прекурсоров и формирование полученных из них нанопорошков. К ним относятся температура и pH раствора, концентрация мочевины, условия сушки и термического разложения. Адсорбционно-структурные исследования показали, что синтезированные прекурсоры являются мезопористыми, нанодисперсными порошками. В зависимости от условий синтеза удельная поверхность полученных прекурсоров составляет от 10 до 120 м^2/г. При температуре синтеза 40 и 60°C с 10 об. % содержанием мочевины в растворе удельная поверхность синтезированных прекурсоров составляет от 14 до 9,7 м^2/г при среднем диаметре мезопор приоритетного диапазона 5,3–5,5 нм, а при 80°C удельная поверхность прекурсора возрастает до 23,7 м^2/г, а средний диаметр мезопор — до 6 нм. Установлено, что температура синтеза влияет на формирование типа пористой структуры прекурсоров, в частности образуются порошки с разным типом пористой структуры: корпускулярной или послойной. Установлено, что количество мочевины при синтезе прекурсора влияет только на общие характеристики пористости при одинаковом диапазоне распределения мезопор по размерам. Наибольшая пористость наблюдается в результате синтеза с температурой раствора 80°C и 20 об. % содержанием мочевины. Для получения и исследования нанопорошков сложной оксидной фазы LaLuO$_3$:Yb^{3+} со структурой типа перовскита проводили термическое разложение синтезированных прекурсоров в неизотермических условиях при скорости нагрева 5 град/мин с постепенным охлаждением, в результате чего получено нанодисперсные, мезопористые порошки с удельной поверхностью 11–28 м^2/г и средним диаметром мезопор 11–21 нм и основной фазой со структурой типа перовскита, которая образуется во всех образцах.

1. Introduction

The development of technologies for creating transparent functional ceramics is one of the promising areas of modern materials science [1–5]. In recent years, great practical interest has been shown in materials based on cubic solid solutions of rare earth elements (REE). Complex oxide phases LnLn′O$_3$ (Ln, Ln′ = REE) with a perovskite-type structure have not previously been regarded as optically transparent materials, although it is known that they have a variety of electrical (high dielectric permeability constant), magnetic and optical properties (anisotropic optics) [6, 7].

There are a number of general requirements for structural and morphological parameters of nanopowders that are important for creating transparent ceramics: morphological stability, geometric shape, high homogeneity in size, low agglomeration, high degree of crystallinity and phase composition stability. The distinctive feature of the technological process for producing nanopowders is the dependence of the structural-phase and granulometric state on the synthesis method.

To date, a number of methods have been applied for producing crystalline nanopowders based on REE: mechanosynthesis [8–10]; gas-phase method (plasma chemical synthesis) [11]; pyrolysis [10–13]; methods of chemical deposition from solutions [14–17]; hydrothermal method [18–20]; sol-gel method [20, 21]. Based on the analysis of literature data, it was found that, in contrast to other methods, the method of chemical deposition followed by heat treatment of the precursor to transform it into the crystalline phase makes it possible to obtain stable particles with a narrow size distribution. By varying the deposition parameters (type of precipitator, synthesis temperature, pH value, reagent concentration, order and speed of their mixing) it allows us to control the

phase and chemical composition of nanopowders, their crystallinity, particle size and a degree of agglomeration, as well as to achieve a uniform distribution of ions in the solution.

Literature contains information only on the synthesis of powders for producing isotropic ceramics based on cubic solid solutions of REE oxides. The synthesis of $(Lu_{0.95}Eu_{0.05})_2O_3$ by heterogeneous deposition from REE chlorides in ammonium bicarbonate is presented in [14]. The synthesis of $Er^{3+}:Lu_2O_3$ [15] and $Yb^{3+}:Lu_2O_3$ [16] was performed by deposition from REE nitrates, and ammonium hydroxide was used as a precipitator. The synthesis of transparent ceramics based on $Nd^{3+}:Lu_2O_3$ was carried out by deposition from REE nitrates in a mixture of solutions $NH_4OH + NH_4HCO_3$.

Due to the lack of technologically developed precursors for the production of nanopowders of complex oxide phases $LnLn'O_3$ (Ln, Ln' = REE) with a perovskite-type structure, our attention was primarily focused on the synthesis of precursors and the identification of factors affecting both the characteristics of the precursors and the powders of complex oxide phases with a perovskite-type structure derived from them. In previous studies we have established the area of thermodynamic stability of a perovskite-type phase on the basis of REE oxides state diagrams [22−24].

2. Experimental

The aim of this work is to obtain nanopowders of a complex oxide phase $LaLuO_3$ with a perovskite-type structure in the La_2O_3–Lu_2O_3 system with addition of Yb^{3+} ions. These ions, due to their magnetic moment, should facilitate the orientation of the obtained nanoparticles in the magnetic field to further produce transparent anisotropic ceramics. For this, we used the thermal decomposition of precursors synthesized by heterogeneous precipitation of nitrate solutions of a mixture of rare earth elements La^{3+} and Lu^{3+} with 3 vol. % of the fluorescent additive Yb^{3+}. As a precipitator, the 1 M ammonia solution with different percentage of urea was used. The obtained sediment of the precursor was separated by triple centrifugation with distilled water and a single centrifugation in the presence of ethyl alcohol, and dried at 120°C for 24 h. Thermal decomposition of the synthesized precursors was carried out by heating at a rate of 5 deg/min to a temperature of 720−840°C in air. The method of thermal decomposition of unstable precursors is one of the means to obtain nano-disperse powders. As a result of the removal of dissociation products, not only a strong framework is formed, but also a labyrinth of pore space, the parameters of which change during decomposition. Therefore, to elaborate the synthesis of nanopowders during thermal decomposition of precursors, the porous structure was studied.

The synthesized precursors and products of their thermal decomposition were studied by means of the adsorption-structural method and X-ray diffraction (XRD).

The porous structure of the obtained samples was studied by the adsorption-structural static volumetric method on the ASAP 2000M (Accelerated Surface Area and Porosimetry System) designed to obtain isotherms of adsorption of gases: nitrogen, argon, krypton and other non-aggressive gases, with their subsequent calculation. A DQ-1000 derivatograph was used for thermogravimetric analysis. For phase composition analysis, X-ray patterns were obtained on an X-ray diffractometer DRON-3M ($CuK\alpha$-radiation with a nickel filter).

The refinement of the precursor synthesis procedure was carried out at a Ln^{3+} concentration of 0.1 mol/l in nitrates under various conditions: temperature, urea concentration and pH of the solutions. The solution temperature under the precipitation of the mixture was changed in the range from 40 to 80°C, the urea concentration was from 5 to 20 vol. % while maintaining the pH of the solution.

3. Results and discussion

The effect of the solution temperature on the characteristics of synthesized precursors was studied on the samples obtained at the urea concentration of 10 vol. %. Structural adsorption studies have shown that an increase in the synthesis temperature from 40 to 80°C leads to the formation of precursors with higher porosity, as evidenced by the general characteristics of porosity: specific surface area, total pores volume in the investigation range (0.3−300 nm), volume and surface of mesopores (Table).

Nitrogen sorption isotherms for the samples of synthesized precursors belong to type IV isotherms according to the Brunauer, Deming, Deming and Teller (BDDT) classification, which characterizes the samples as mesoporous bodies (Fig. 1) [25]. The type of hysteresis loops on the isotherms of samples obtained at 40 and 60°C, according to IUPAC classification,

Table. General porosity characteristics of the synthesized samples

No	Urea concentration	T, solution	T, decomposition	V_{Σ}	BET		BJH		
					S_{BET}	$\overline{D}_{BET}$	V_{me}	S_{me}	$\overline{D}_{me}$
	vol. %	°C	°C	sm^3/g	m^2/g	nm	sm^3/g	m^2/g	nm
1	2	3	4	5	6	7	8	9	10
1	10	40	raw	0.0187	14.01	5.3	0.0175	13.1583	5.3
2	10	60	raw	0.0153	9. 72	6.3	0.0132	9. 5900	5.5
3	10	80	raw	0.0500	23.70	8.4	0.0499	33.4176	6.0
4	5	80	raw	0.1530	107.13	5.7	0.1573	140.1462	4.5
5	5	80	200	0.1684	97.81	6.9	0.1849	136.7447	5.4
6	5	80	720	0.0857	28.80	11.9	0.0864	39.8854	8.7
7	5	80	840	0.0650	16.20	16.1	0.0627	19.2282	13.1
8	10	80	raw	0.0325	21.24	6.1	0.0312	24.3556	5.1
9	10	80	840	0.0676	11.78	22.9	0.0700	13.4142	20.9
10	20	80	raw	0.2458	121.55	8.1	0.2486	173.7280	5.7
11	20	80	720	0.1046	28.64	14.6	0.1026	39.0989	10.4
12	20	80	820	0.1078	31.91	13.5	0.1115	40.9191	10.8
13	20	80	840	0.0973	27.09	14.4	0.1071	37.6228	11.4
14	20	80	raw	0.0809	39.82	8.1	0.0817	55.5372	5.9
15	20	80	200	0.1036	48.38	8.6	0.1048	66.9297	6.3
16	20	80	840	0.0924	18.74	19.7	0.0962	22.1964	17.3

where: V_{Σ} (sm^3/g) — total pore volume of the method range 0.3–300 nm, S_{BET} (m^2/g) — specific surface area calculated by the BET method (S.Brunauer, P.H.Emmett, E.Teller);
V_{me} (sm^3/g), S_{me} (m^2/g) — total mesopores volume and surface, calculated from the E.P.Barrett, L.S.Joyner, P.P.Halenda (BJH) theory; $\overline{D}_{BET}$ (nm) — mean equivalent pore diameter, calculated according to the BET and BJH theory.

most likely should be attributed to type H3, which is characteristic of materials with a layered structure or consisting of plane-parallel particles (Fig. 1a) [26]. In addition, the samples have similar structures, as evidenced by the differential size distributions of mesopore volumes and surfaces (Fig. 1b, c), as well as close values of the general characteristics of porosity – specific surface area (14–9.7 m^2/g) and average diameter of mesopores (5.3–5.5 nm) (Table). Raising the solution temperature up to 80°C during the synthesis of precursors leads to a significant increase in the values of their general porosity characteristics (Table). Thus, the specific surface area of the precursor increases to 23.7 m^2/g and the average mesopore diameter to 6 nm. At the solution temperature of 80°C, the samples with an indistinct hysteresis loop type (most likely H2) are formed, which is typical for corpuscular systems (Fig. 1a). So, at low solution temperatures during the synthesis, practically non-porous precursors are formed, which can be referred to the systems with a layered structure; but with an increase in the temperature of the solution in the process of synthesis, the porosity of the precursor increases, and its type becomes indistinct, most likely, the porous structure approaches the structure of corpuscular systems.

By means of X-ray phase analysis, it was established that the structure of powders of the synthesized precursors is mainly amorphous. On the X-ray spectra of the obtained precursor powders halos are observed in the intervals of angles $2\theta = 25–35°$ and $40–65°$, which indicates the amorphous nature of the samples. In addition to the amorphous phase, well-detectable lines characteristic of lanthanum hydroxide and subtle lines of lutetium hydroxide oxide are observed on the X-ray spectrum of the sample 3 obtained at a solution temperature of 80°C (Fig. 2). Thus, an increase in the temperature of the solution during the synthesis with a content of 10 vol. % urea contributes to the formation of a crystalline component in the amorphous structure of precursors.
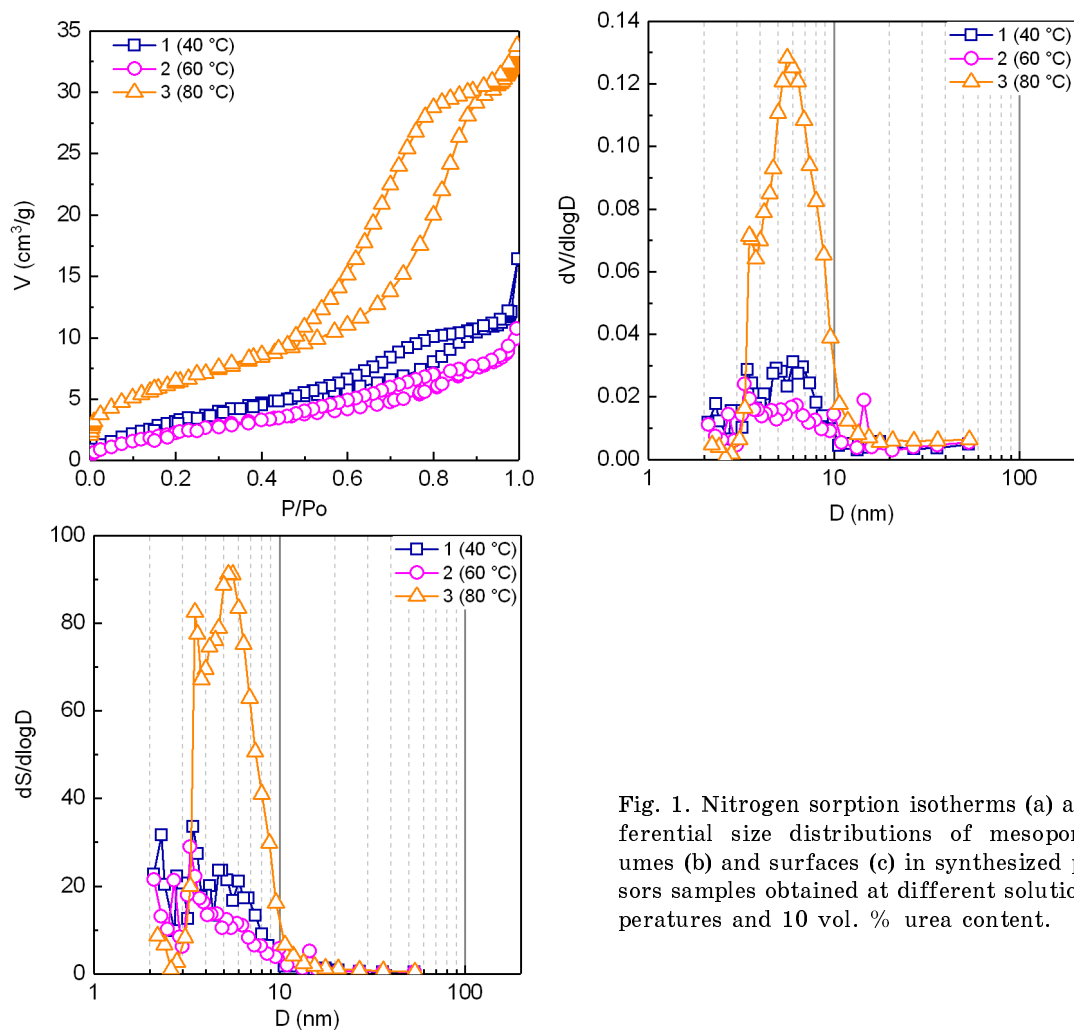
Fig. 1. Nitrogen sorption isotherms (a) and differential size distributions of mesopore volumes (b) and surfaces (c) in synthesized precursors samples obtained at different solution temperatures and 10 vol. % urea content.

The effect of urea percentage in the synthesis of precursors for the production of nanopowders of complex oxide phase $LaLuO_3$:Yb^{3+} with a perovskite-type structure was studied on the samples obtained at the solution temperature of 80°C. According to the results of adsorption-structural analysis, regardless of the percentage of urea in the solution at a synthesis temperature of 80°C, mesopores of the same range with a priority size of 5–6 nm are formed in the precursors. The highest porosity is observed during the synthesis with 20 vol. % urea content. Consequently, the amount of urea during the synthesis of the precursor does not affect the size distribution of mesopores, but only affects their amount, that is, the general characteristics of porosity (Table). X-ray phase studies have shown that the precursors obtained at a solution temperature of 80°C and a percentage of urea from 5 to 10 vol. % contain a compo-
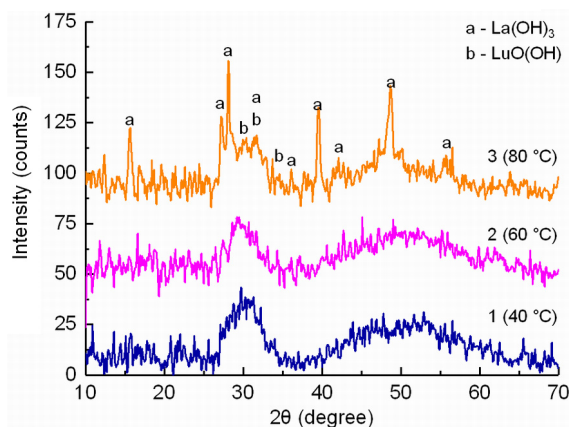

Fig. 2. X-ray patterns of precursor powders synthesized in ammonia solution with 10 vol. % urea content at temperature 40, 60 and 80°C.

nent of the crystal structure in addition to the amorphous component (Fig. 3). On the X-ray patterns of precursor samples synthesized at a solution temperature of 80°C and
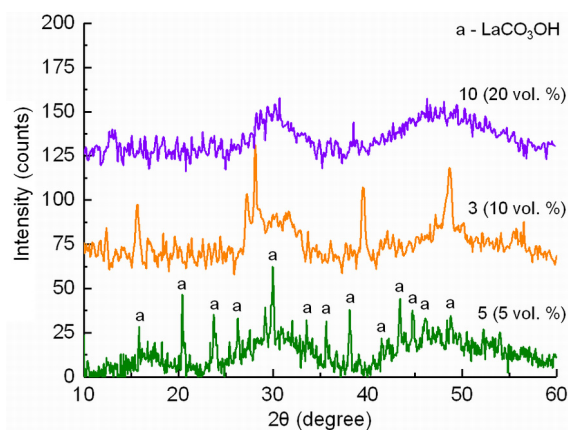
Fig. 3. X-ray patterns of synthesized precursor samples obtained at solution temperature of 80°C, depending on the urea percentage

an urea percentage of 5 vol. %, there are clear lines of LaCO$_3$OH; and at 10 vol. % urea, the lines of lanthanum hydroxide are observed. With a further increase in the percentage of urea (20 vol. %), the precursor becomes amorphous. Therefore, an increase in the temperature of the solution and an increase in the urea percentage contribute to the production of precursor powders, mainly consisting of an amorphous phase.

To obtain and study nanopowders of complex oxide phase LaLuO3:Yb3+ with a perovskite-type structure, the thermal decomposition of the synthesized precursors was performed under nonisothermal conditions at a heating rate of 5 deg/min with gradual cooling. According to derivatographic studies, the decomposition of the synthesized precursors is completed at temperatures of 790−900°C depending on the conditions of their synthesis, i.e., phase composition (amorphous or amorphous-crystalline), specific surface area and the priority mesopores size. Adsorption-structural studies have shown that nanodisperse, mesoporous nanopowders with a specific surface area SB$\underline{ET}$ of 11−28 m2/g and an average diameter D_{me} of 11−21 nm were obtained. Nitrogen sorption isotherms related to type IV isotherms according to the BDDT classification characterize the samples as mesoporous bodies (Table, Fig. 4). XRD data showed phases mainly with a perovskite-type structure (Fig. 5).

The type of hysteresis loops in the isotherms of the obtained samples, according to the IUPAC classification, should probably be classified as type H1, which is typical for agglomerates or homogeneously packed globules of similar size. In each case, however, the type of the hysteresis

loop in the nitrogen sorption isotherms of the final products of termally decompositioned precursors has its own differences. Thus, a clear type of hysteresis H1 is observed only in the nitrogen sorption isotherms of sample 13, the precursor of which was synthesized at a solution temperature of 80°C and the urea concentration of 20 vol. %. If we trace the process of its thermal decomposition from the synthesized precursor to crystalline powder, we can observe the evolution of the porous structure from the precursor (the hysteresis type of its isotherm is close to the hysteresis loop type H2) to the final product (hysteresis loop type H1). It should be noted that the porous structure of the intermediate and final products of thermal decomposition starting from the decomposition temperature of 720°C practically similar. The general characteristics of porosity, as well as volumes and surface differential size distributions of mesopores in the products of thermal decomposition are also almost identical (Table).

The XRD patterns of the intermediate products of termally decomposed amorphous precursor show, except for a perovskite-type phase formed in all samples, residues of the amorphous phase; in some samples, also lanthanum hydroxide, lutetium oxide phases are obsereved (Fig. 6). In addition, on the X-ray pattern of sample 12, the flat shoulders of perovskite lines at 2θ = 26−35 deg may indicate the presence of an additional nanosize powder fraction (< 15 nm). Thus, under these conditions, a mesoporous nanodispersed powder with a perovskite phase and residual amorphous phase with a specific surface area of 29 m^2/g and an average mesopore diameter of 11 nm was obtained. The particle size calculated from the specific surface area is about 25 nm (with a density of 8.2 g/cm^3).

It should be noted that even a slight deviation from the pH range during the precursor synthesis can result in very different values of the general porosity characteristics of the precursor with practically the same mesopore volume and surface distributions (Table, samples 10 and 14). Under the same conditions of the thermal decomposition of the synthesized precursor, a mesoporous nanodisperse powder with a specific surface area of 19 m^2/g and an average mesopore diameter of 17 nm was obtained. Its phase composition differs from the previous sample only quantitatively: it has a higher crystallinity, i.e. lower content of the amorphous phase. The size of the formed particles is about 40 nm, the crys-
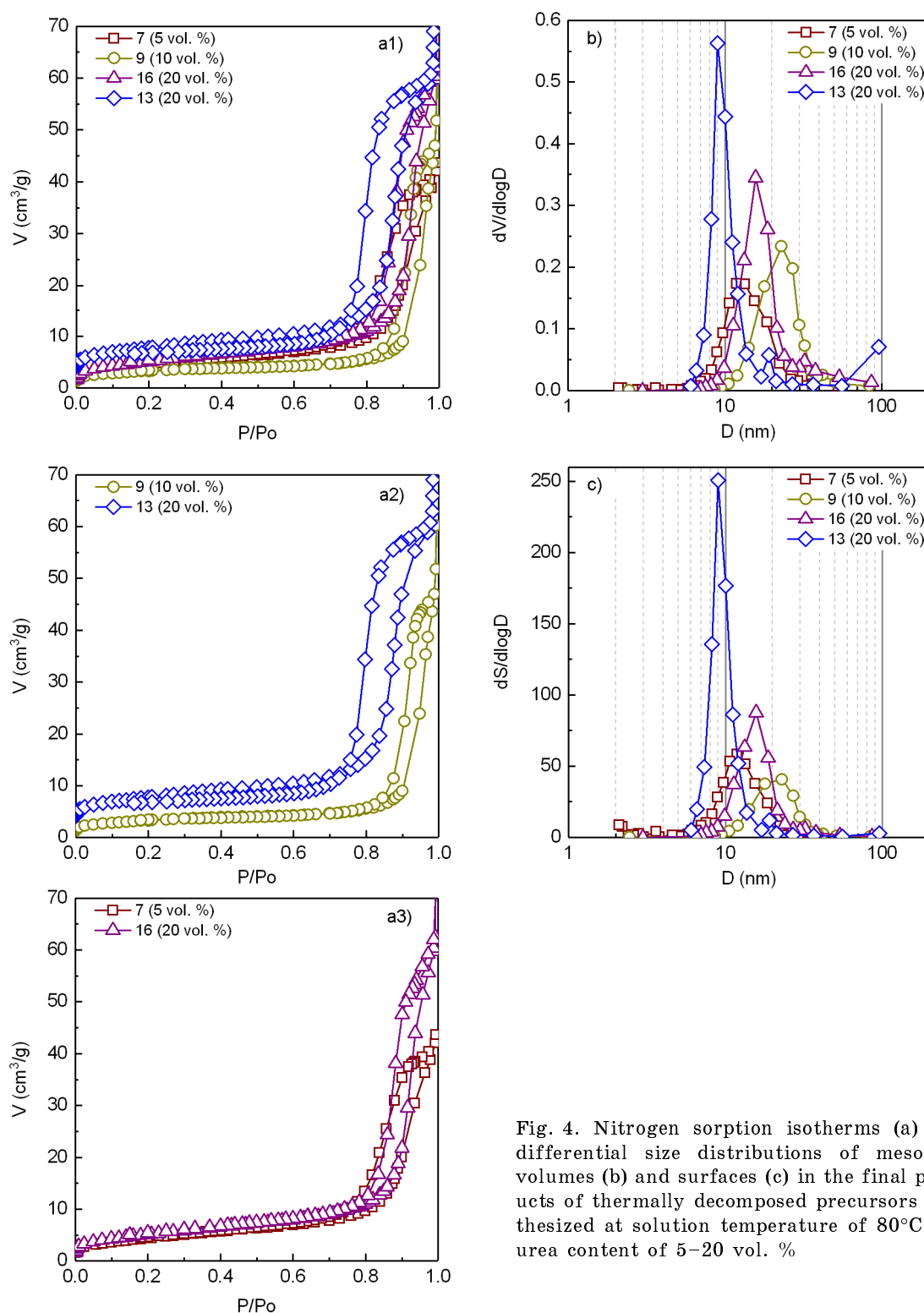
Fig. 4. Nitrogen sorption isotherms (a) and differential size distributions of mesopore volumes (b) and surfaces (c) in the final products of thermally decomposed precursors synthesized at solution temperature of 80°C and urea content of 5–20 vol. %

tallite size is 28 nm, and the lattice parameters are: $a = 0.6010$, $b = 0.8365$, $c = 0.5805$ nm. Thus, the precursors with the same sizes of mesopores but very different values of general porosity characteristics require different conditions for the decompo-sition of the precursor for the formation of the perovskite phase. It is likely that a higher temperature or heating rate is required for complete thermal decomposition of precursors with high general porosity characteristics. In addition, the use of the precur-
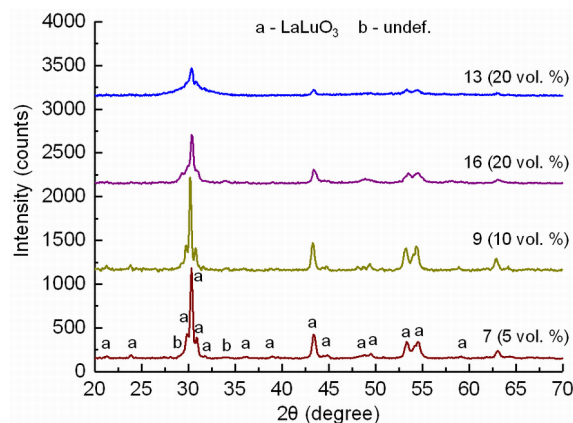
Fig. 5. X-ray patterns of the final products of thermally decomposed precursors synthesized at solution temperature of 80°C and urea content of 5–20 vol. %.

Fig. 6. X-ray patterns of products of thermally decomposed precursors synthesized at solution temperature 80°C and urea content 20 vol. %

sors of a complex oxide phase $LaLuO_3{:}Yb^{3+}$ with a perovskite-type structure for obtaining nanopowders with a small specific surface area and low porosity leads to almost single-phase powders, but with a larger particle size, a smaller specific surface area and larger average mesopores (for comparison, the lattice parameters in [27] $a = 0.6023$, $b = 0.8380$, $c = 0.5826$ nm, $\rho_{calc} = 8.175$ g/cm^3).

Thermal decomposition of the precursor synthesized under the same conditions with less urea concentration (10N vol. %), also produces mesoporous nanodisperse powder, but much coarser with a specific surface area of 12 m^2/g and an average mesopore diameter of 21 nm with a well crystallized perovskite phase and residues of an undefined phase (Table, Figs. 5 sample 9). The size of the synthesized particles is about 60 nm, the crystallite size is 48 nm and lattice parameters are: $a = 0.6011$, $b = 0.8370$, $c = 0.5811$ nm.

The application of the 5 vol. % urea solution for the precursor synthesis and subsequent thermal decomposition also results in the formation of mesoporous nanodisperse powder with a specific surface area of 16 m^2/g and an average mesopore diameter of 13 nm. At 720°C, the perovskite phase is mainly formed and the amorphous phase residues are observed. A further increase in temperature leads not only to the formation of the perovskite phase but also to the formation of impurities of the lanthanum hydroxide phase, possibly lutetium oxide and an indeterminate phase (Table, Fig. 5 sample 7).
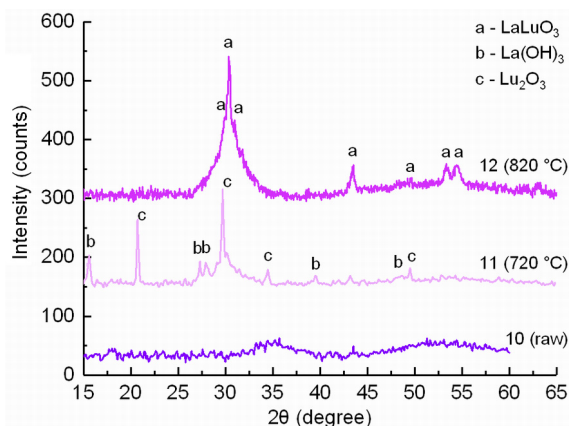
4. Conclusions

The factors influencing the synthesis of the precursors and the formation of nanopowders derived from them were established in this paper. These factors include temperature and pH of the solution, urea concentration, drying and thermal decomposition conditions.

Practically non-porous precursors are formed at low synthesis temperatures of 40–60°C with 10 vol. % urea content in the solutions; they can be classified as systems with a layered porous structure. At a solution temperature of 80°C, the porosity increases, and the porous structure, most likely, approaches corpuscular-type systems. An increase in the solution temperature during the precursor synthesis leads to the formation of more porous materials. The amount of urea of 5–20 vol. % in the solution at a precursor synthesis temperature of 80°C affects only the general characteristics of porosity and does not affect the size distribution of mesopores, which remains in the same range with a priority size of 4.5–6 nm. The highest values of the general porosity characteristics of the obtained precursors are observed during the synthesis with 20 vol. % urea content and solution temperature of 80°C. Depending on the synthesis conditions, the precursors have mainly amorphous or amorphous-crystalline structure.

Due to thermal decomposition of the synthesized precursors under nonisothermal conditions, nanodisperse, mesoporous powders with a specific surface area of 11–28 m^2/g, an average mesopore diameter of 11–21 nm and the main phase with a

perovskite-type structure were obtained, which is formed in all samples and has the same unit cell volume, but a different crystallite size. This indicates the formation of samples with different coordination number of packing during perovskite crystallization.

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