

SYNTHESIS AND CHARACTERIZATION OF $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ POWDERS FOR PROTON-CONDUCTING SOLID OXIDE FUEL CELLS

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This work reports on the preparation and characterization of Sr^{2+} -doped $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$ powders prepared by a solid-state synthesis as promising materials for solid oxide fuel cells. The influence of synthesis parameters and strontium content ($x = 0; 0.05; 0.10; 0.15; 0.20$) on the phase composition and properties of $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ powders was studied. The results of the phase analysis show that $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ ($x = 0; 0.05; 0.10$) powders with a minimum amount of secondary phases can be obtained after at least three repeated synthesis cycles at 1060–1080 °C for 10 h. According to the laser diffraction analysis, the synthesized powders comprise particles with a polydisperse size distribution spreading from 0.05 μm to 12 μm and average particle size of 2.1 μm . Electron microscopy observations support these findings and demonstrate that the particles and their aggregates have rounded irregular shape. Moreover, it was found that the morphology and particle size of the powder does not depend on the strontium content. Doping $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ with 15 mol.% and 20 mol.% Sr^{2+} leads to the formation of a significant amount of secondary phases due to exceeding the solubility limit of strontium, thus making these compositions unsuitable for use in solid oxide fuel cells.

Keywords: solid-state synthesis, perovskite, $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$, powder, electrolyte.

INTRODUCTION

In recent years, the world is increasingly focused on hydrogen energy as one of the clean energy sources [1, 2]. The use of hydrogen will have a positive impact on environmental, energy security and economic development issues [3]. Hydrogen can be obtained by electrolysis

of water using electricity produced from excess renewable energy [4, 5]. The produced hydrogen can be burned to generate electricity and heat using fuel cells, which are more efficient than combustion engines [6, 7].

Fuel cells (FCs) are electrochemical devices that can convert the chemical energy

of a fuel directly into electrical and thermal energy [8]. The main advantages of FCs are high efficiency (up to 50%) [9], low level of pollutants and noise emissions, modularity and compact design, which allows easy and quick assemble of power plants with different capacities within one technology [8]. Among many types of FCs, the most promising for electrochemical oxidation of hydrogen are solid oxide fuel cells (SOFCs) with a ceramic oxide electrolyte. SOFCs can be divided into two types with respect to the charge transfer mechanism through a dense electrolyte: oxygen-ion-conducting (O^{2-} -SOFCs) and proton-conducting (H^+ -SOFCs). The main advantage of O^{2-} -SOFCs is their flexibility in terms of using different types of gaseous fuel that is oxidized at the anode [10]. While H^+ -SOFCs have higher energy conversion efficiency (up to 60%) due to lower activation energy of proton conductivity (0.3–0.6 eV) compared to that of ionic conductivity (0.8–1.1 eV) [11]. In addition, water is formed at the cathode during the operation of H^+ -SOFCs, and therefore the fuel does not mix with the products of its oxidation leading to more efficient fuel utilization. High efficiency at low temperatures (500–600 °C) reduces the requirements for other SOFCs components and significantly decreases the rate of their degradation. These advantages provide 27–37% lower cost for production of H^+ -SOFC stacks with an operating temperature of 550 °C compared to O^{2-} -SOFCs operating at 800 °C [12].

Solid solutions of BaZrO_3 and BaCeO_3 with the perovskite-type ABO_3 structure are the most widely used electrolytes for H^+ -SOFCs [13–16]. However, the need for high sintering temperatures (up to 1600 °C) [17] and alloying with rare earth oxides encourage the search for

new, more technological and cheaper materials with better functional properties.

High proton and oxide ion conductivity in $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$ compound with a disordered hexagonal perovskite structure has recently been discovered [18, 19]. This perovskite has high oxide ion conductivity in dry oxygen environment and proton conductivity in a humidified or reducing atmosphere. For example, the bulk conductivity in humidified air at 510 °C is about twice as high (4 mS/cm) compared to the conductivity in dry air (1.9 mS/cm). Note that the bulk conductivity of $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$ in dry oxygen is significantly higher than that for 8YSZ and is comparable with that of $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{2.815}$, whereas in humidified air ($\text{pH}_2\text{O} \sim 0.021$ atm) the proton conductivity of $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$ is close to that of barium cerates. Fop et al. [20] also demonstrated that the positional oxide ion disorder generated by the close proximity of available oxygen sites due to the particular topology of the palmierite layers in hydrated $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$ contributes to the creation of a frustrated proton sublattice with high proton mobility and low energy diffusion pathways. $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$ also has low sintering temperature (up to 1200 °C) and relatively high chemical resistance to CO_2 [18].

Two recent papers [18, 19] have noted that the properties of $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$ can be improved by doping, in this regard we proposed the synthesis of $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ ($x = 0.05; 0.10; 0.15; 0.20$), where part of Ba atoms is replaced by Sr atoms. The choice of strontium as an alloying additive is due to its similar chemical properties and ionic radius (1.39 Å for Sr^{2+}) to barium (1.49 Å for Ba^{2+}) [21] that will provide partial replacement of barium atoms without destroying the crystal lattice of the perovskite.

Regarding the synthesis of $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$, it should be noted that this issue is almost not studied in the available literature. The first report on the synthesis and crystal structure of $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$ was made by Garcia-Gonzalez et al. [22], who synthesized it by solid-state reaction of BaCO_3 , Nb_2O_5 , and MoO_3 at 1300 °C for 72 hours. Fop et al. [18] reported that a single-phase powder can be obtained after repeated annealing at 1050 °C, while the synthesis at 1100–1150 °C leads to the formation of phases other than $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$. Whereas in the paper [19], repeated annealing at 900 °C for 10–12 hours was carried out to synthesize $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$ -based materials. Taking into account the discrepancies noted above, as well as the fact that strontium carbonate has a higher melting point ($t_m = 1497$ °C) than barium carbonate ($t_m = 811$ °C) [23], we tailored the synthesis parameters and then synthesized $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ with various strontium content ($x = 0; 0.05; 0.10; 0.15; 0.20$). The phase composition, particles size and morphology of the obtained powders were studied.

EXPERIMENT AND DISCUSSION OF THE RESULTS

Solid-state synthesis was used to obtain powders with nominal compositions of $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$, $x = 0.05; 0.10; 0.15; 0.20$. Barium carbonate (BaCO_3 , $\geq 99\%$, Carl Roth GmbH + Co. KG), strontium carbonate (SrCO_3 , 99%, Alfa Aesar), niobium(V) oxide (Nb_2O_5 , 99.5%, ChemPur Feinchemikalien und Forschungsbedarf GmbH), and molybdenum(VI) oxide (MoO_3 , $\geq 99.8\%$, Carl Roth GmbH + Co. KG) were used as starting materials. The required amount of materials was mixed and ground in a porcelain mortar. The

resulting mechanical mixture was sieved and packed down tightly into the crucible by tamping with a glass rod. The solid-state synthesis of $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ powders was performed in an air muffle furnace at temperatures of 1000–1100 °C (step 20 °C) to determine the best reaction conditions for obtaining powders with the maximum concentration of the required phase. The duration of each synthesis was 10 h, and the number of repeated synthesis operations under the same conditions was varied from two to four in order to optimize the synthesis process as well. The heating rate to the dwell temperature was 8 °C/min, while cooling was allowed to take place naturally. After each annealing the powders were additionally grinded and mixed.

The effect of synthesis temperature and strontium content on the phase composition of powders was investigated by X-ray diffraction method using Rigaku Ultima IV diffractometer (Rigaku Co. Ltd., Japan). The diffractograms were recorded using continuous scanning with a step of 0.05° or with a counting time of 4 s per step at $U = 30$ kV, $I = 30$ mA with monochromatic Cu K α radiation. Phase analysis was performed using the JCPDS database and PDXL2 v. 2.0.3.0 software.

The average crystallite size was calculated using the Scherrer formula [24] from the two most intense diffraction peaks at $\sim 27.8^\circ$ and $\sim 30.5^\circ$ corresponding to (014) and (110) planes of $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$ structure, respectively:

$$D = 0.89\lambda/\beta\cos\theta, \quad (1)$$

where D is the crystallite size, λ is the X-ray wavelength of 1.5406 Å, θ is Bragg diffraction angle, and β is the full wide of half maximum of the XRD peak.

Dislocation density was defined by relation [25]:

$$\delta = 1/D^2. \quad (2)$$

where δ is the dislocation density and D is the crystallite size.

Lattice strain was calculated by using the following equation [25]:

$$\varepsilon = \beta/4\tan\theta, \quad (3)$$

where ε is the strain and β is the full wide of half maximum of the XRD peak.

The particle size distribution of the powders was measured by Bettersizer S3 Plus (Bettersize Instruments Ltd., China), which determine the angular variation in intensity of light scattered as a laser beam passes through a dispersed particulate sample. Distilled water was used as the dispersing medium. An ultrasonic actuator built into the device was used to destroy weak agglomerates. The Fraunhofer evaluation model was applied to process the raw data using associated software.

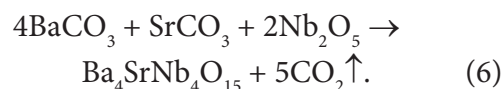
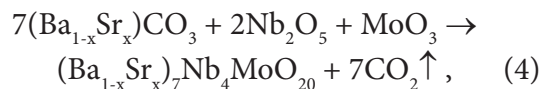
Electron microscopic studies of the obtained powders were performed on a scanning electron microscope (SEM) Axia ChemiSEM (Thermo Fisher Scientific Inc., USA).

The synthesized $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ powders with a nominal content of Sr^{2+} equal to 5 mol.%, 10 mol.%, 15 mol.%, and 20 mol.% are denoted as BS5NMO, BS10NMO, BS15NMO, and BS20NMO, respectively for convenience.

Chemical reactions between carbonates and metal oxides take place during the heating and holding processes at the annealing temperature of the powder mixture. Due to the low melting point of barium carbonate ($t_m = 811^\circ\text{C}$) and molybdenum oxide ($t_m = 802^\circ\text{C}$) [23], the synthesis occurs through the formation of a liquid phase, which accelerates the processes of homogenization and phase formation. After

some period of time, the synthesis proceeds in the solid phase due to the formation of more refractory oxides [18], which finally form $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$ perovskite at optimal solid-state reaction conditions.

To determine the optimal temperature for solid-state reaction, a powder mixture with a nominal composition of $(\text{Ba}_{0.9}\text{Sr}_{0.1})_7\text{Nb}_4\text{MoO}_{20}$ was selected as a representative sample, the phase composition of which was investigated within a 2θ range of $23\text{--}33^\circ$, where the main peaks of the formed phases are located [18, 19]. **Fig. 1** shows XRD patterns of BS10NMO powder after three annealing cycles for 10 h at 1000°C , 1020°C , 1040°C , 1060°C , 1080°C , and 1100°C . According to **Fig. 1a**, the main phase of the powder after synthesis at 1000°C is a solid solution of strontium in $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$ (ICDD No. 00-051-0484), there are also two secondary phases, namely, BaMoO_4 (ICDD No. 00-029-0193) and $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$ (ICDD No. 00-054-1174). The relative intensity of $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$ phase is high, indicating its high concentration possibly due to the incomplete chemical reaction at low synthesis temperature. While the amount of BaMoO_4 phase is very low as indicated by the intensity of the main peak (**Fig. 1a**). The formation of these phases is possible by the following chemical reactions (4) – (6):



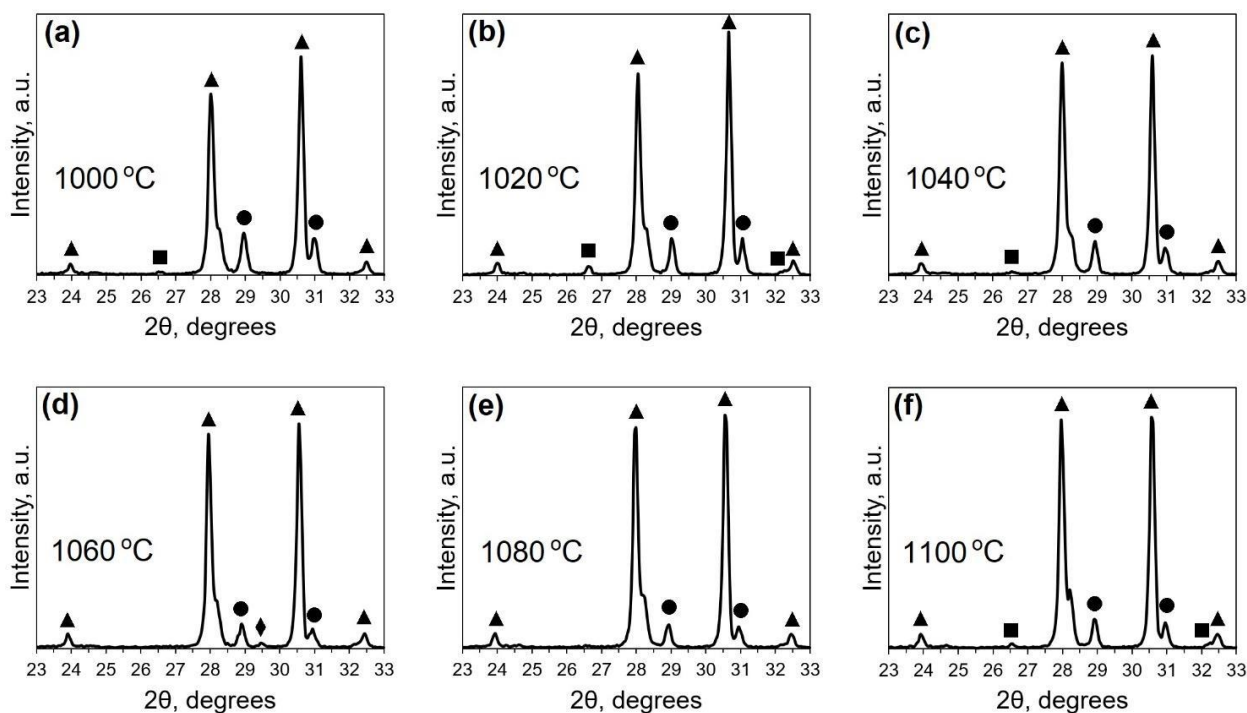


Fig. 1. XRD patterns of BS10NMO powder after synthesis at (a) 1000 °C, (b) 1020 °C, (c) 1040 °C, (d) 1060 °C, (e) 1080 °C, and (f) 1100 °C. Marked peaks: $\blacktriangle$ – $(\text{Ba}_{0.9}\text{Sr}_{0.1})_7\text{Nb}_4\text{Mo}_{20}$; $\blacksquare$ – BaMoO_4 ; $\bullet$ – $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$; $\blacklozenge$ – $\text{Ba}_6\text{Nb}_3\text{O}_{13.5}$.

When the synthesis temperature was increased to 1020 °C (**Fig. 1b**), the phase composition of the powder did not change qualitatively, but the diffraction pattern showed a slight increase in the intensity of BaMoO_4 peaks and the opposite for $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$ peaks. This indicates that the amount of BaMoO_4 and $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$ is slightly increased and decreased, respectively. A further increase in the synthesis temperature to 1040 °C (**Fig. 1c**) led to an increase in the intensity of the main phase peaks, while the intensities of BaMoO_4 and $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$ peaks decreased, which is accompanied by the disappearance of less intense BaMoO_4 peak at $2\theta \approx 32.1^\circ$. These results indicate that the chemical reaction (4) proceeds

more quickly with increasing synthesis temperature.

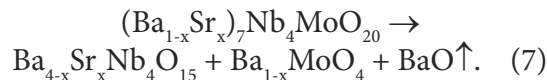
At the synthesis temperature of 1060 °C (**Fig. 1d**), the tendency of reducing the intensities of secondary phases still continues. As a result, the BaMoO_4 phase disappeared completely, and the intensity of $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$ peaks decreased by about a quarter. However, the diffraction pattern shows a peak at $2\theta = 29.5^\circ$, which most likely belongs to $\text{Ba}_6\text{Nb}_3\text{O}_{13.5}$ (ICDD No. 00-035-0933). This phase has two main most intense peaks, which are located at $2\theta = 27.51^\circ$ and 29.55° . The peak at 27.51° is not observed, apparently due to its lower intensity in this case. The formation of $\text{Ba}_6\text{Nb}_3\text{O}_{13.5}$ is most likely due to the inhomogeneous distribution

of the starting materials in the mixture and/or incomplete solid-state synthesis reactions [18]. It should be noted that the content of $\text{Ba}_6\text{Nb}_3\text{O}_{13.5}$ phase in the obtained powder is insignificant.

Increasing the synthesis temperature to 1080 °C under other identical conditions (triple annealing for 10 h) resulted in the powder that in addition to the main phase, contains only one secondary phase, namely $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$ (see Fig. 1e). As could be suggested from the relative intensity of $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$ peaks (Fig. 1e), the amount of this phase is low in comparison with the samples obtained at 1000–1040 °C and remains almost the same as after synthesis at 1060 °C (Fig. 1d).

When the synthesis temperature was increased further to 1100 °C (Fig. 1f), BaMoO_4 formed and the relative intensity of $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$ phase increased, indicating its higher content in the synthesized powder. The most probable reason for this is the decomposition of $(\text{Ba}_{0.9}\text{Sr}_{0.1})_7\text{Nb}_4\text{MoO}_{20}$ to $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$ and BaMoO_4 due to the low thermal stability

of $(\text{Ba}_{0.9}\text{Sr}_{0.1})_7\text{Nb}_4\text{MoO}_{20}$ at high temperatures [18] and the evaporation of barium oxide [26, 27], according to the chemical reaction (7):



Thus, according to the obtained XRD results, the optimal temperature interval for solid-state synthesis of $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ is 1060–1080 °C that provides a minimum concentration of secondary phases in the powder.

In the case of solid-state synthesis, it is common that the intermediates of the reaction can be located in different parts of the volume of the powder mixture and have different reactivity, as a result the efficiency of further interaction in the system is significantly reduced. Therefore, in order to achieve homogeneous phase chemistry, it is necessary to further activate the reactivity in the system, which can be done by repeated procedures of grinding and mixing the reaction products, followed by prolonged annealing [18, 19, 28, 29].

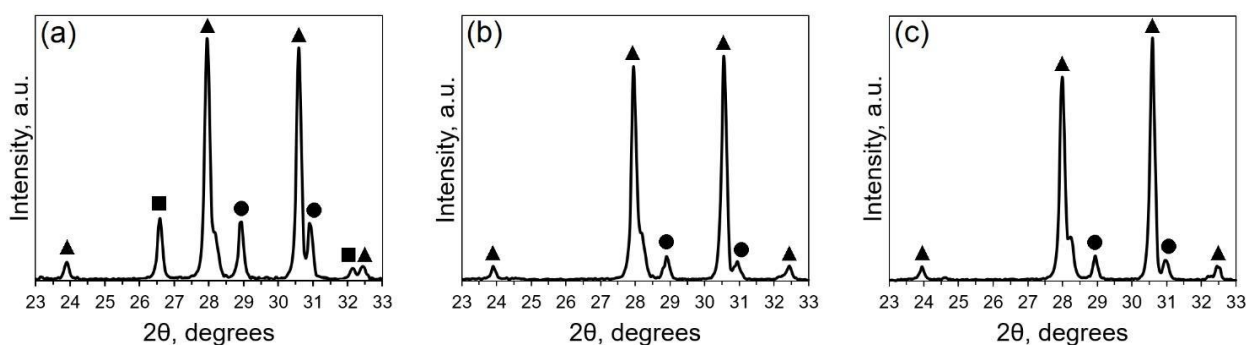


Fig. 2. XRD patterns of BS10NMO powder after (a) two, (b) three, and (c) four repeated synthesis cycles at 1080 °C for 10 h. Marked peaks: $\blacktriangle$ – $(\text{Ba}_{0.9}\text{Sr}_{0.1})_7\text{Nb}_4\text{MoO}_{20}$; $\blacksquare$ – BaMoO_4 ; $\bullet$ – $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$.

The XRD pattern in **Fig. 2a** indicates that double annealing at 1080 °C for 10 h is not enough to obtain pure BS10NMO powder. Although the main phase is $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$, there are still significant amounts of residual phases such as BaMoO_4 and $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$. After triple synthesis processes, the concentration of $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$ notably reduced, while BaMoO_4 phase disappeared (**Fig. 2b**). The obtained powder was then additionally subjected to the synthesis procedure in order to eliminate unwanted phases. However, as can be seen from **Fig. 2c**, the phase composition and intensity of the peaks remained much the same indicating that the reaction closely approached its thermodynamic equilibrium and further repeated annealing can be considered as ineffective [29]. Thus, under the applied synthesis conditions, the solid-state synthesis process should be repeated not less than three times in order to obtain $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ perovskite with a small amount of secondary phases.

Using the above-established optimized synthesis parameters we carried out solid-state synthesis of a series of $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ ($x = 0; 0.05; 0.10; 0.15; 0.20$) powders and studied their XRD structural parameters.

According to the XRD pattern shown in **Fig. 3a**, the powder without the strontium additive contains two phases, namely $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$ and $\text{Ba}_5\text{Nb}_4\text{O}_{15}$, after triple annealing at 1060 °C for 10 h. From the ratio of peaks' intensity in **Fig. 3a**, it can be suggested that the amount of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ phase is small.

In the case of BS5NMO powder (**Fig. 3b**), it can be seen that except the peaks of the main phase (solid solution of Sr in $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$), there are other peaks which belong to $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$ and $\text{Ba}_6\text{Nb}_3\text{O}_{13.5}$ phases. The small intensity of the peaks of $\text{Ba}_6\text{Nb}_3\text{O}_{13.5}$ indicates

that the amount of this phase is very small, while the amount of $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$ remained almost the same compared to that of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ phase in the powder without strontium additive.

To synthesize $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ with 10–20 mol.% Sr^{2+} , the temperature of multiple annealing was increased to 1080 °C in order to accelerate the diffusion processes due to the increase in the powder mixture of more refractory SrCO_3 ($t_m = 1497$ °C) compared to BaCO_3 ($t_m = 811$ °C) [23]. The XRD pattern of BS10NMO powder in **Fig. 3c** shows that in addition to the main peaks of $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$ -based oxide, there are peaks that belong to $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$, while $\text{Ba}_6\text{Nb}_3\text{O}_{13.5}$ or BaMoO_4 phases were not detected. It should be noted that the amount of $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$ phase in BS10NMO powder is slightly higher compared to that of BS5NMO powder as indicated by the increased intensity of the respective peaks.

According to the XRD pattern of BS15NMO powder in **Fig. 3d**, an increase in strontium content to 15 mol.% resulted in the formation of BaMoO_4 and $\text{Ba}_3\text{Nb}_6\text{O}_{13.5}$ phases, which have relatively high intensity of XRD peaks. There is also a significant increase in the intensity and number of $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$ peaks indicating an increase in the amount of this phase in the powder. However, the solid solution of Sr in $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$ remains as the main phase in the synthesized powder. The most probable reason for such a significant increase in the amount of secondary phases is that Sr reached its solubility limit in $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$, and as a result the excess amount of Sr leads to redistribution of elements and formation of secondary phases. It should be noted that the crystal lattice parameters of $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ phase in BS10NMO and BS15NMO powders remained unchanged.

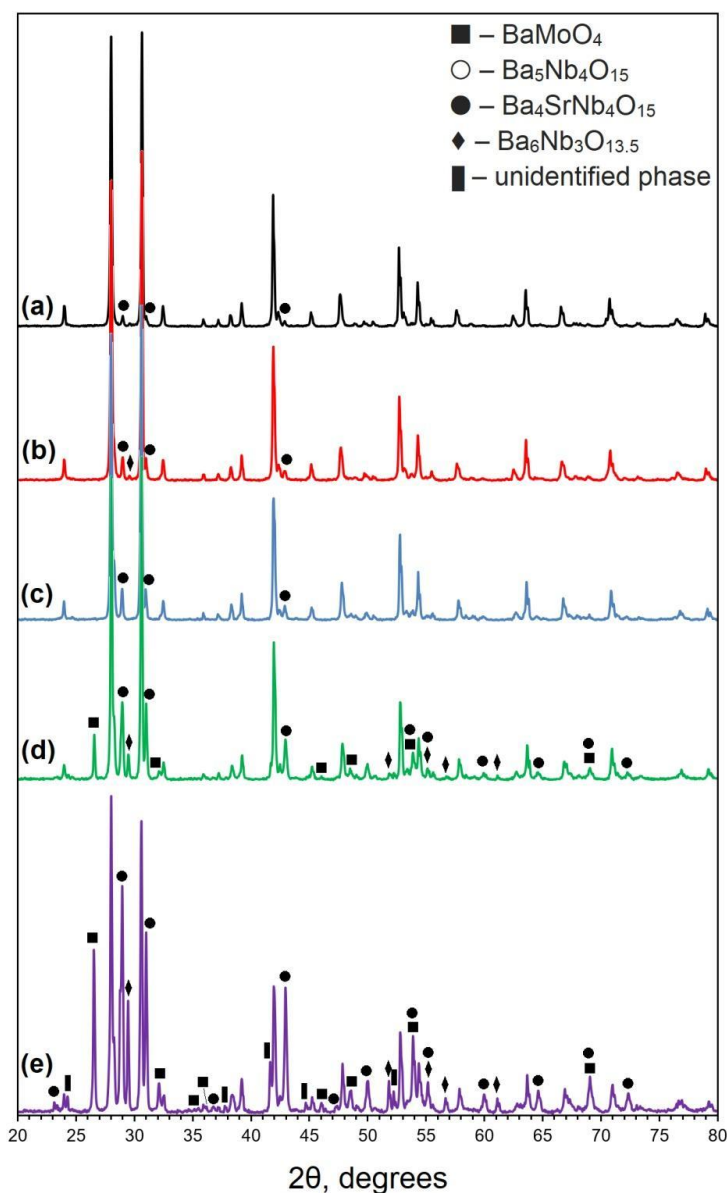


Fig. 3. XRD patterns of (a) $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$, (b) BS5NMO, (c) BS10NMO, (d) BS15NMO, and (e) BS20NMO powders. All unmarked peaks correspond to the main $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ phase.

As can be seen from **Fig. 3e**, when barium is partially replaced by 20 mol.% Sr^{2+} , there is a further remarkable increase in the intensity of the diffraction peaks of BaMoO_4 , $\text{Ba}_3\text{Nb}_6\text{O}_{13.5}$, $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$, and unidentified phase with a si-

multaneous decrease in the intensity of $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ phase, leading to a significant difference in phase composition from the expected one. Thus, BS15NMO and BS20NMO materials cannot be used as an electrolyte for

H⁺-SOFCs because they contain a significant amount of BaMoO₄, Ba₄SrNb₄O₁₅, Ba₃Nb₆O_{13.5} phases, which do not possess high ionic or proton conductivities [30–32].

It should be noted that Sr-based impurity phases were not detected in the synthesized powders (**Fig. 3**). The reason for this lies in the following facts: (a) Ba and Sr have similar chemical properties; (b) strontium has smaller ionic radius than that of barium [21]; (c) the used concentration of Sr²⁺ to dope Ba₇Nb₄MoO₂₀ was low (5–20 mol.%). Therefore, strontium would rather substitute part of barium atoms in Ba-based compounds than form separate Sr-based phases.

The crystal lattice parameters of (Ba_{1-x}Sr_x)₇Nb₄MoO₂₀ (x = 0; 0.05, 0.10, 0.15, 0.20) perovskites are given in **Table 1**. It can be seen that the crystal lattice parameters of the synthesized perovskites have a tendency to decrease with increase Sr content due to the smaller ionic radius of Sr²⁺ (1.32 Å) compared to that of Ba²⁺ (1.49 Å) [21]. The volume of the crystal lattice of Ba₇Nb₄MoO₂₀ decreases by ~ 0.57% and ~ 0.71% with the addition of 5 mol.% Sr²⁺ and 10 mol.% Sr²⁺, respectively. The variations in the crystal lattice parameters and unit cell vo-

lume indicated that the strontium ion is entering in the lattice of Ba₇Nb₄MoO₂₀ perovskite.

The crystallite size of (Ba_{1-x}Sr_x)₇Nb₄MoO₂₀ (x = 0; 0.05, and 0.10) powders was found to be in the range of 45–53 nm (**Table 1**). It follows the same trend of decreasing values with increasing strontium content reaching a minimum at 10 mol.%. This can be due to the increase in lattice strains because of ionic size mismatch as ionic size of Sr²⁺ is lower than that of Ba²⁺. The strain increases with the increase in strontium content due to the distortion of the lattice. The incorporation of Sr into (Ba_{1-x}Sr_x)₇Nb₄MoO₂₀ not only produced lattice distortion but lattice defects and nucleation centers which inhibits the growth of the perovskite crystals. With increasing the Sr doping content to 15 mol.% and 20 mol.%, some fluctuations in the width and intensity of the two main diffraction peaks of the main phase are observed (**Fig. 3**). Although the lattice parameters remain unchanged (**Table 1**), the other structural parameters of BS15NMO and BS20NMO powders most likely to be affected by significant amount of impurity phases and chemical inhomogeneity [25].

Table 1

Structural parameters of (Ba_{1-x}Sr_x)₇Nb₄MoO₂₀ perovskites.

Powder	Lattice parameters			Unit cell volume, Å ³	Crystallite size, nm	Lattice strain, %	Dislocation density, m ⁻²
	a, Å	b, Å	c, Å				
Ba ₇ Nb ₄ MoO ₂₀	5.861	5.861	16.518	491.4	53	0.264	3.63·10 ¹⁷
BS5NMO	5.852	5.852	16.473	488.6	48	0.299	4.53·10 ¹⁷
BS10NMO	5.842	5.842	16.409	485.1	45	0.308	4.94·10 ¹⁷
BS15NMO	5.842	5.842	16.409	485.1	51	0.267	3.84·10 ¹⁷
BS20NMO	5.842	5.842	16.409	485.1	43	0.317	5.41·10 ¹⁷

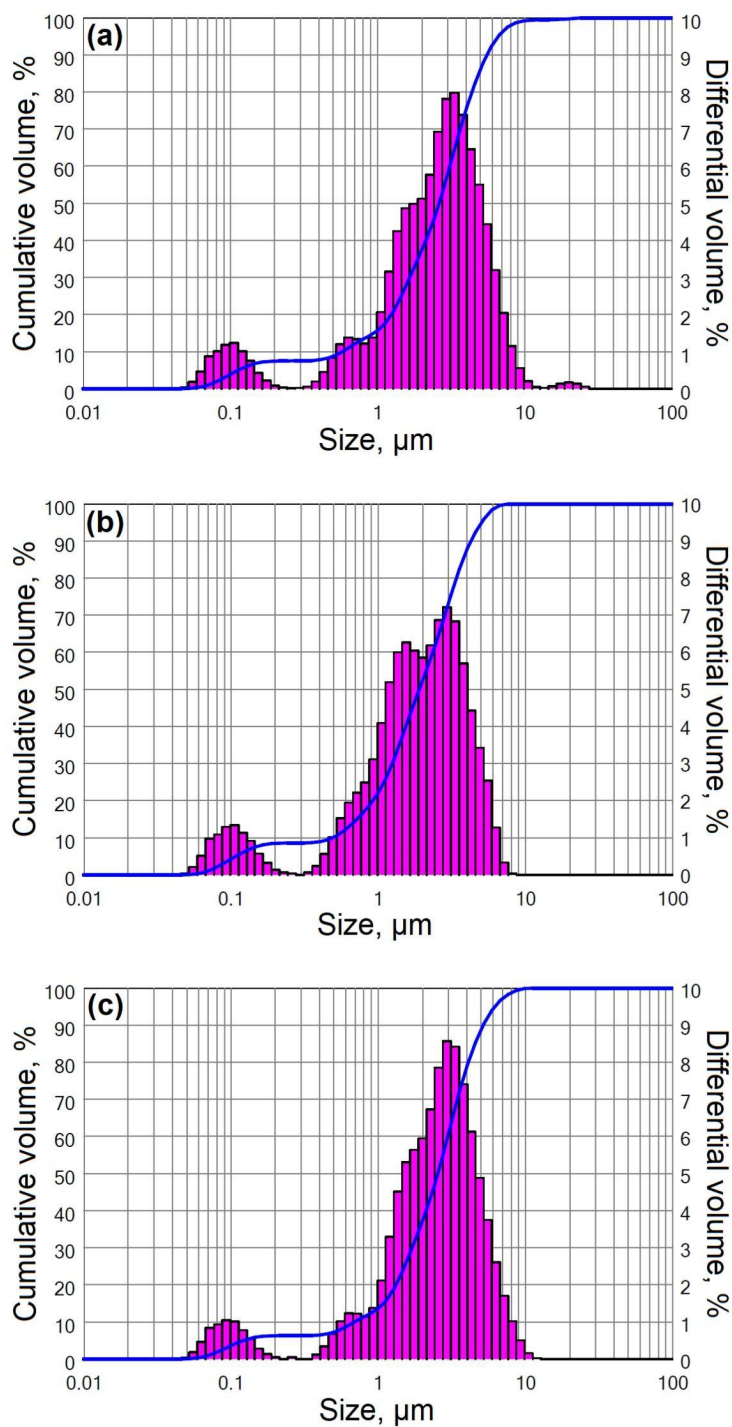


Fig. 4. Particle size distribution of (a) $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$, (b) BS5NMO, and (c) BS10NMO powders.

Particle size distribution is an important characteristic of powders that influences their physical and chemical properties, and, accordingly, their technological properties as well as the feasibility of their practical use [33]. For example, the particle size of the powder affects its behavior during compaction and sintering, as well as such characteristics of the sintered products as microstructure, physical and mechanical properties [34–38].

In **Fig. 4** and **Table 2** is presented the results of the particle size analysis of the powders with different strontium content in $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ perovskite.

It should be noted that the particle size distribution and morphology of BS15NMO and BS20NMO powders was not studied here due to the significant amount of the secondary phases that can affect the results. A comparison of the particle size distribution of $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$, BS5NMO, and BS10NMO powders suggests that their size distribution is approximately the same and does not depend on the phase and chemical composition of the powders. The particle size of the synthesized powders is in the range of 0.05–12 μm , and their average size is about 2.1 μm .

Table 2

Particle size distribution of $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ powders.

Powder	Size (d_n) below which n-percent of the particles is contained, μm										Span
	d_3	d_6	d_{10}	d_{16}	d_{25}	d_{50}	d_{75}	d_{84}	d_{90}	d_{97}	
$\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$	0.09	0.12	0.50	0.76	1.10	1.90	3.10	3.68	4.28	5.53	1.98
BS5NMO	0.09	0.12	0.49	0.76	1.10	1.90	3.09	3.69	4.27	5.53	1.99
BS10NMO	0.09	0.16	0.69	1.15	1.51	2.54	3.75	4.45	5.16	6.91	1.76

The obtained powders are polydisperse and show a weak bimodal distribution with a relatively small fraction of fine particles of ~50–110 nm in size and coarse particles with sizes from ~0.4 μm to 12 μm . The volume contribution of the fine fraction does not exceed 12%. The majority of the particles are within the 1.5–5 μm size range and the span of the particle size distribution is 1.76–1.99. The formation of the coarse powder fraction is due to the sintering of small particles into dense aggregates during synthesis at high temperatures. While the formed aggregates cannot be effectively destroyed by the applied methods in this study. The relatively small

particle size of the powders was obtained as the result of using starting powder materials with particles less than 5 μm in size, as well as due to the fast nucleation and slow growth of $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ phase [39].

Electron microscopic studies were performed to investigate the morphology and size of $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ particles after solid-state synthesis. According to **Fig. 5**, particles and their aggregates are characterized mainly by a rounded irregular shape, which is the result of formation of new phase, sintering of nano- and submicron particles, and disintegration of large agglomerates during grinding of synthesis products. Particles and their

aggregates are characterized by a relatively wide size distribution, which is in the range of 0.3–10 μm . The size of most particles does not exceed 5 μm , while the fraction of particles/aggregates with sizes between about 5 μm and 10 μm is relatively small. According to SEM analysis of $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ powders, it can be concluded that the morphology and particle size of the powder does not depend on the strontium content. Thus, the effect of

particle size on the powder compaction behavior will be the same for powders with different strontium content [38]. It should be noted that the results obtained by SEM and laser diffraction measurements are in good agreement indicating the correctness of the applied research methods. Our future efforts will be focused on the preparation of the electrolyte and anode from the synthesized powders and their characterization for SOFC application.

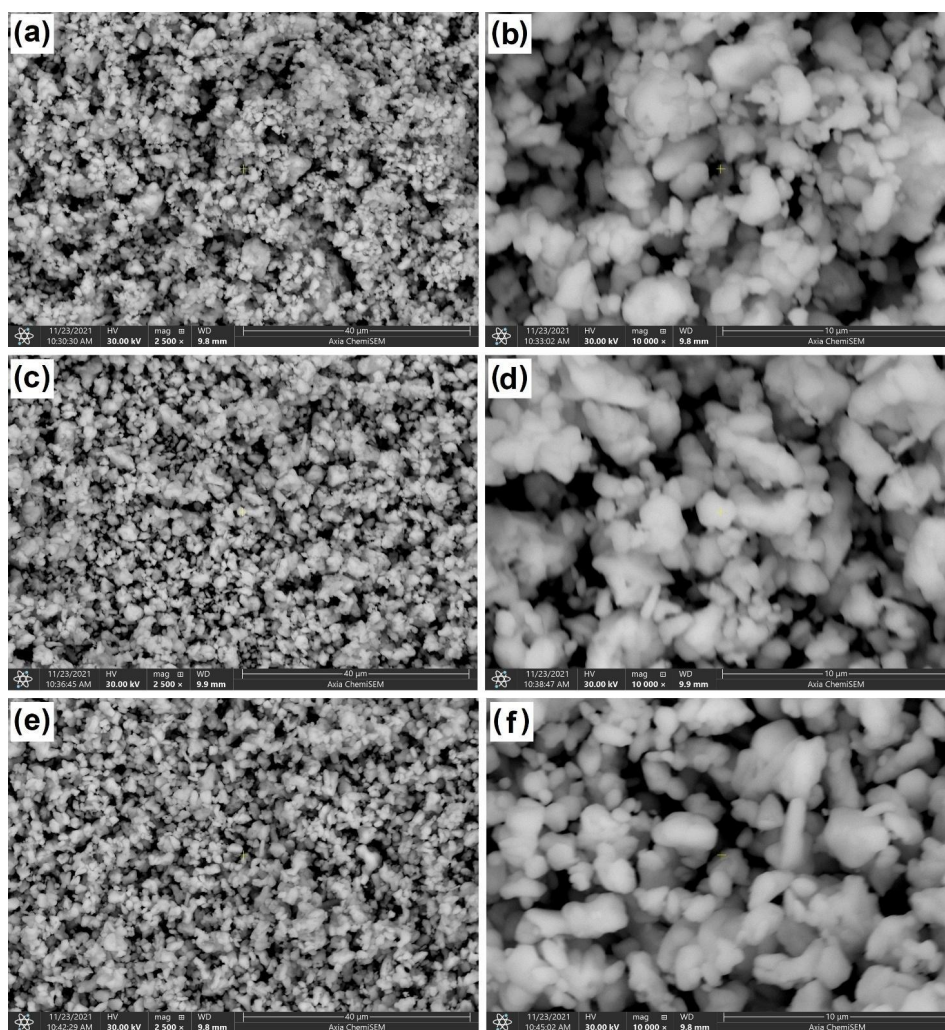


Fig. 5. SEM images of (a, b) $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$, (c, d) BS5NMO, and (e, f) BS10NMO powders at magnification of 2500 $\times$ (a, c, e) and 10000 $\times$ (b, d, f).

CONCLUSIONS

The effect of solid-state synthesis conditions and strontium content on the phase composition and properties of $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ powders was studied. It was found that the optimal temperature interval for solid-state synthesis of $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ ($x = 0; 0.05; 0.10$) powders with a minimum content of secondary phases is 1060–1080 °C. Moreover, under the applied synthesis temperatures, the solid-state synthesis process should be repeated not less than three times. The X-ray diffraction patterns reveal the formation of $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ perovskites with an average crystallite size in the range of 45–53 nm. The crystallite size decreases with the increase of Sr^{2+} content due to the increase in lattice strains which suppress the growth of the crystals. It was observed that an increase in the strontium content in $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ above 10 mol.% leads to redistribution of elements and formation of significant amount of BaMoO_4 , $\text{Ba}_3\text{Nb}_6\text{O}_{13.5}$, and $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$. According to the laser diffraction method, the synthesized $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ powders had particle size in the range of 0.05–12 μm with an average size of about 2.1 μm . Moreover, the size of the particles was found not to depend on the strontium content and was mainly influenced by synthesis parameters, size of starting powders, and grinding efficiency after repeated annealing operations. These results correlate with the results obtained by electron microscopy, according to which the particles and their aggregates have rounded irregular shape. The study findings indicate that 15 mol.% and 20 mol.% Sr^{2+} -doped $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$ cannot be used as an electrolyte for H^+ -SOFCs due to the significant amount of second phases.



ACKNOWLEDGMENTS. This study was performed under the project 2020.02/0301 “Development of new functional materials for the needs of hydrogen energy” funded by the National Research Foundation of Ukraine.

СИНТЕЗ ТА ВЛАСТИВОСТІ ПОРОШКІВ $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ ДЛЯ ПРОТОН-ПРОВІДНИХ ТВЕРДООКСИДНИХ ПАЛИВНИХ КОМІРОК

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Одним із перспективних напрямів вироблення та споживання електричної енергії є воднева енергетика. Для вироблення електроенергії з водню найефективніше використовувати електрогенеруючі установки на основі твердооксидних паливних комірок (ТОПК) із протонною провідністю електроліту завдяки їхній високій ефективності за робочих температур 500–600 °C. Для використання в ролі електроліту перспективними вважають матеріали на основі гексагонального перовськіту $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$, властивості якого можуть бути покращені шляхом його легування. У зв'язку з цим

нами було запропоновано здійснити синтез перовськіту $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$, в якому частина атомів барію була б замінена атомами стронцію, та відпрацювати умови його синтезу. Отже, в цій роботі досліджено вплив параметрів твердофазного синтезу та вмісту стронцію на фазовий склад та властивості порошків із номінальним складом $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ ($x = 0; 0,05; 0,10; 0,15; 0,20$). Для цього використані такі методи дослідження, як рентгенівська дифракція, скануюча електронна мікроскопія та лазерна дифракція. Відповідно до результатів рентгенофазового аналізу порошків, синтезованих за 1000–1100 °C, встановлено, що оптимальним температурним інтервалом для одержання перовськітів $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ ($x = 0; 0,05; 0,10$) із мінімальним вмістом вторинних фаз є 1060–1080 °C. Тоді як необхідна кількість повторних відпалів по 10 год має бути не менше трьох. При вмісті стронцію 15 мол.% та 20 мол.% спостерігаємо суттєве зростання вмісту вторинних фаз (BaMoO_4 , $\text{Ba}_4\text{SrNb}_4\text{O}_{15}$, $\text{Ba}_6\text{Nb}_3\text{O}_{13,5}$) внаслідок досягнення границі розчинності Sr в $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$, що виключає можливість використання зазначених перовськітів як електроліту ТОПК. Дослідження гранулометричного складу порошків $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ ($x = 0; 0,05; 0,10$) показало, що дисперсність порошків не залежить від їхнього хімічного складу та визначається в основному дисперсністю вихідних речовин, умовами синтезу та ефективністю подрібнення порошку після повторних операцій відпалу. Встановлено, що розмір частинок порошків $(\text{Ba}_{1-x}\text{Sr}_x)_7\text{Nb}_4\text{MoO}_{20}$ знаходиться в діапазоні 0,05–12 мкм, тоді як їхній середній розмір складає 2,1 мкм. Ці результати співпадають із результатами

електронної мікроскопії, відповідно до якої частинки порошку мають неправильну округлу форму, яка зумовлена процесами формоутворення, що відбуваються під час утворення нової фази з вихідних речовин, руйнування/агломерації частинок під час подрібнення продуктів синтезу та спікання малих частинок під дією температури.

Ключові слова: твердофазний синтез, перовскіт, порошок, $\text{Ba}_7\text{Nb}_4\text{MoO}_{20}$, електроліт.

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Стаття надійшла 16.04.2022.