

Composit structures $Ba_{0.5}Sr_{0.5}Co_{1-x}Fe_xO_{3-z}$, synthesized on the big solar furnace

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ABSTRACT: Anion-deficient structures based on the composition $Sr_{0.5}Ba_{0.5}Co_{1-x}Fe_xO_{3-z}$ synthesized from a melt in a solar furnace in a stream of concentrated solar radiation with a density of 100–200 W/cm² have been studied. Briquettes of the form of tablets based on a stoichiometric mixture of carbonates and oxides of the corresponding metals ($SrCO_3 + BaCO_3 + Co_1O_3 + Fe_2O_3$) were melted on the focal spot of the big solar furnace. Drops of the melt flowed into the water, cooling at a rate of 10³ deg/s. Drops of the melt flowed into the water, cooling at a rate of 10³ deg/s. The castings were crushed to a fineness of 63 μm, dried at 400 °C, molded into tablets (samples) (20 mm in diameter and 10 mm high). Samples of the material were sintered in the temperature range 1050 °C–1250 °C. The structure, water absorption and degradation in a carbon dioxide medium were studied on the samples. The crystal lattice of the material had a perovskite structure with a unit cell parameter $a = 4.04 \text{ \AA}$. The material samples showed increasing water absorption with increasing sintering temperature. There is also a dependence of the resistance of the material structure to the effects of carbon dioxide and water vapor on the sintering temperature. The observed values of structural parameters indicate that the material based on the perovskite $Sr_{0.5}Ba_{0.5}Co_{1-x}Fe_xO_{3-z}$ structures can be used as a catalyst in the production of hydrogen and synthesis gas by reforming and methane oxidation. Preliminary experiments on obtaining synthesis gas showed that the perovskite structures of the composition are not inferior to phosphogypsum in terms of efficiency. However, the implementation of such approaches requires the development and creation of special equipment that makes it possible to control the flows of gases and water into the reaction chamber irradiated by a concentrated flux of high density solar radiation.

KEYWORDS: synthesis from a melt; concentrated flow; hydrogen production; synthesis gas; perovskite catalytic structures

1. Introduction

In the fundamental triad “composition-structure-properties”, one can trace the manifestation of unique properties (high-temperature superconductivity, magnetoresistance, ferroelectricity, catalytic activity) of materials with the ABO_3 perovskite structure^[1–6]. Because of this, such materials are widely used in various promising areas^[7–9]. For example, in obtaining synthesis gas^[10,11].

Anion-deficient $\text{ABO}_{3-\delta}$ structures with transition metals in B positions (Mn, Fe, Co, Ni, Cu) can be distinguished from the class of perovskites. A feature of such structures, for example, $\text{SrBaCo}_{1-x}\text{Fe}_x\text{O}_{3-z}$, is mixed oxygen-electronic conductivity, which makes it possible to use them as oxygen-reversible ($\text{ABO}_{3-\delta} + 1/2\delta\text{O}_2 \leftrightarrow \text{ABO}_3$) electrode materials replacing expensive platinum in solid oxide fuel cells (SOFC).

Oxygen-permeable membranes, reducing the cost of producing synthesis gas and sorbents with 100% oxygen selectivity^[12-16]. Interest in materials of this class is especially growing under the conditions of rapidly developing hydrogen energy^[17,18]. However, this material interacts well with carbon dioxide and decomposes into carbonates and oxides, which limits its applicability^[19]. Perovskites are used in solid oxide fuel cells to convert chemical energy into electricity. At the same time, such devices have high efficiency (more than 80%) and very low emissions of harmful gases. with high efficiency, low emissions and fuel flexibility. In addition, perovskites are successfully used in membrane reactors based on oxygen-conducting membranes (OTMs). Such devices combine separation and chemical reactions in one unit^[20].

It was shown in the study of Pan et al.^[21] that oxygen-conducting materials based on phosphogypsum significantly increase the efficiency of producing hydrogen-enriched synthesis gas (72.51% was established) at a reaction temperature of about 1023 K.

In this work, the material of the perovskite structure of the composition $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-z}$, was studied. The purpose of the work was to show the possibility of synthesizing perovskite structures on a solar furnace.

2. Methodology of experiments

A concentrated flux of solar radiation through mirror concentrating systems is widely used for heating, processing and melting a wide range of materials. For example, the large solar furnace (BSP) with a thermal power of 1 MW was recently used to extract metals from industrial waste^[22], hydrogen from water^[23]. The technological capabilities of BSP were also used to synthesize high-temperature materials^[24].

From mixtures of iron and cobalt oxides with barium and strontium carbonates $\text{BaCO}_3 + \text{SrCO}_3 + \text{Fe}_2\text{O}_3 + \text{Co}_2\text{O}_3$. in a stoichiometric ratio after grinding (63 μm) and molding by semi-dry pressing (100 MPa), samples were made in the form of a cylinder \varnothing 20 mm, which were installed on a water-cooled melting unit located on the focal plane of the solar furnace. A concentrated flux of solar radiation with a density of the order of $Q = 150 \text{ W/cm}^2$ was directed to the sample. This value of the flux density according to Stefan Boltzmann's law.

$$T = \sqrt[4]{\frac{Q}{\varepsilon\sigma}}$$

where Q is the flux density of the concentrated flux of solar radiation, 250 W/cm^2 , ε is the emissivity, $\sigma = 5.67 \times 10^{-8} \text{ W/m}^2\text{K}$ is the Stefan Boltzmann constant, corresponds to the temperature of the heated body of 2200 K. At this temperature, the sample melts and melt drops fall into the water and cooled at a rate of 10^3 deg/s . Such cooling conditions made it possible to fix the high-temperature structural states of the material.

Drops of the melt, loaded into the water, cracked into small glass-like particles of arbitrary shape. The melt quenched into water was crushed to a fineness of 60 μm and molded into cylinders 8 mm in diameter and 2 mm high. Cylindrical samples were sintered at different temperatures.

X-ray phase analysis of samples of the obtained materials was performed on a Panalytical Empyrean diffractometer with software in the Bragg-Brentano reflection geometry with CuK α radiation ($\lambda = 1.5418$ Å). Data was taken between 10° and 64° in 0.5° increments.

Studies of the morphology and microstructural features of the material samples were used by scanning electron microscopy (SEM).

Thermogravimetric (TG) curves were obtained on a TG50 instrument either running in air at a heating rate of 10 °C/min using about 50 mg of sample.

The temperature coefficient of thermal expansion was measured on a cathetometer in the temperature range 300–1250 K. The electrical resistance was measured by the four-contact method in the temperature range of 300–1300 K.

The relative density of the samples was determined as the ratio of the density of the material sample was 4.87 g/cm³.

3. Results and discussion

We have studied perovskite structures Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} synthesized from a melt in a solar furnace.

Figure 1 shows a Panalytical Empyrean X-ray diffractometer with CuK α radiation of a sintered sample at 1100 °C.

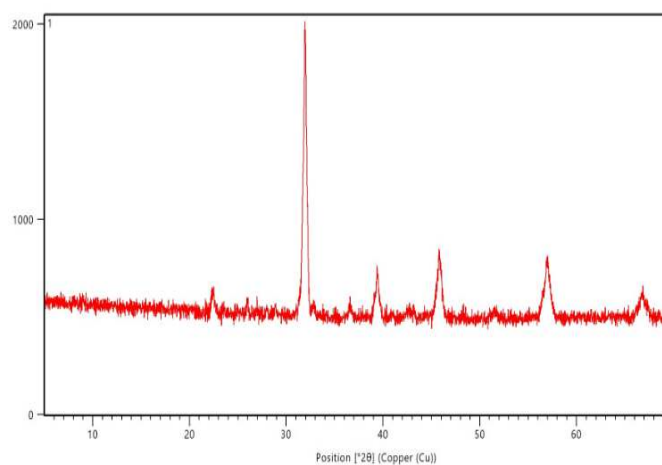


Figure 1. X-ray pattern of a material sample obtained by synthesis from a melt in a solar furnace of composition Sr_{0.5}Ba_{0.5}Co_{0.8}Fe_{0.2}O_{2.78}.

An analysis of the X-ray diffraction patterns showed that the obtained oxides have a cubic perovskite-like structure with a lattice parameter $a = 4.04$ Å of the Pm3m space group. It was also found that such structures are characterized by a significant nonstoichiometry in oxygen. The estimated region of homogeneity of the resulting complex compositions Sr_{0.5}Ba_{0.5}Fe_{1- x} Co _{x} O_{3- δ} lies in the range from $x = 0.0$ to $x = 0.7$.

Figure 2 shows the dependence of shrinkage on the sintering temperature, and **Figure 3** shows the dependence of density on the sintering temperature.

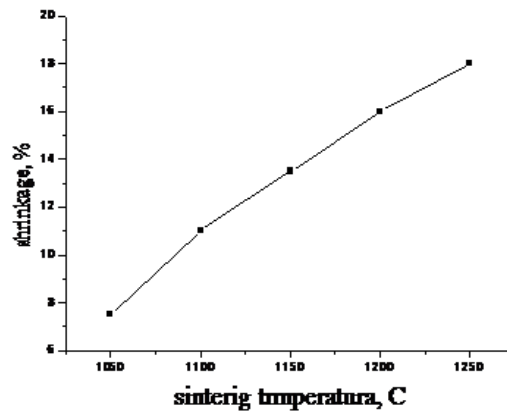


Figure 2. Dependence of shrinkage on sintering temperature.

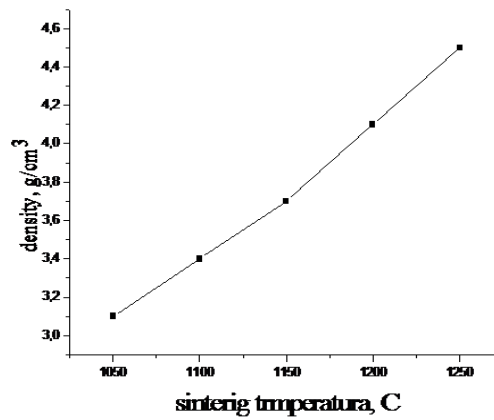


Figure 3. Dependence of density on sintering temperature.

As can be seen from **Figures 2 and 3**, with an increase in the sintering temperature of ceramics, an increase in shrinkage and density is observed. At the same time, a decrease in the porosity of the material is observed.

Figure 4 shows the dependence of electrical resistance on the sintering temperature of material samples. As can be seen in **Figure 4**, with increasing temperature, an increase in electrical resistance is observed, i.e., samples of the material show a metallic character of conductivity.

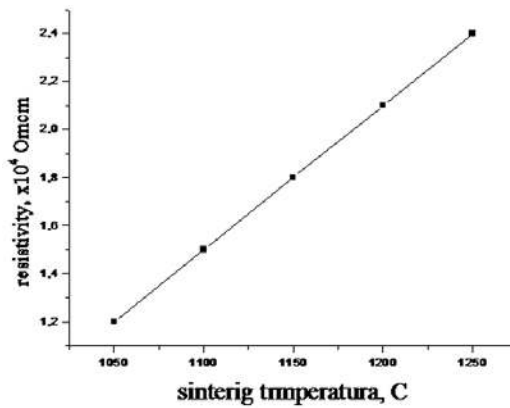


Figure 4. Dependence of electrical resistance on sintering temperature.

Figure 5 shows the dependence of the water absorption of the material sample on the sintering temperature. As can be seen from **Figure 5**, an increase in the ceramic sintering temperature to 1200 °C

causes a decrease in water absorption. Thus, by the method of synthesis from a melt in a solar furnace, it is possible to obtain a material resistant to carbon dioxide and water vapor, with low water absorption.

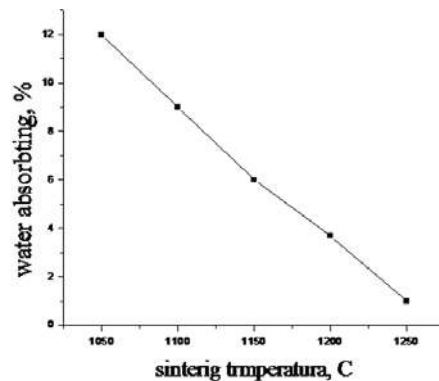
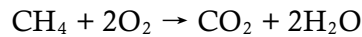
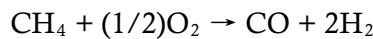
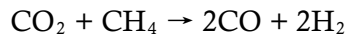
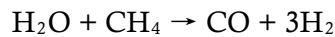


Figure 5. Dependence of water absorption on sintering temperature.

From the above, we can conclude that the material based on $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{2.78}$ perovskite structures can be used as a catalyst in the production of hydrogen and synthesis gas by reforming and oxidizing methane:



Preliminary experiments on obtaining synthesis gas showed that the perovskite structures of the composition are not inferior to phosphogypsum in terms of efficiency.

However, the implementation of such approaches requires the development and creation of special equipment that makes it possible to control the flows of gases and water into the reaction chamber irradiated by a concentrated flux of high density solar radiation.

4. Conclusion

Perovskite structures $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Co}_{1-x}\text{Fe}_x\text{O}_{3-z}$ were synthesized from a melt in a solar furnace in a stream of concentrated solar radiation with a density of 100–200 W/cm².

The material had a cubic structure with a unit cell parameter $a = 4.04 \text{ \AA}$ and showed resistance to carbon dioxide and water vapor and low water absorption.

The material can be used as a catalyst in the production of hydrogen and synthesis gas by reforming and oxidizing methane.

Author contributions

Conceptualization, MSP; methodology MSP; software, FE and OR; validation, FE, OR, NK and AH; supervision, MSP; project administration, MSP. All authors have read and agreed to the published version of the manuscript.

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Conflict of interest

The authors declare no conflict of interest.

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