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Properties of Nb-doped $SrCo_{0.8}Fe_{0.2}O_{3-d}$ perovskites in oxidizing and reducing environments

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ABSTRACT

The phase stability of $SrCo_{0.8}Fe_{0.2}O_{3-d}$ perovskite doped with niobium was studied by in situ high-temperature X-ray diffraction in the temperature range of 30–1000 °C and oxygen partial pressure 0.2–10^{-5} atm. The stability of the cubic perovskite structure in a wide range of oxygen partial pressures is the main advantage of $SrCo_{0.8-x}Fe_{0.2}Nb_xO_{3-d}$ ($x = 0.1$–0.3) system in comparison with $SrCo_{0.8}Fe_{0.2}O_{3-d}$. It is suggested that equilibrium of the thermal expansion with changes of the oxygen non-stoichiometry leading to the same lattice parameters in the oxidizing and reducing environments at the catalytic temperatures is a necessary requirement for stable operation of perovskite as an oxygen-conducting membrane. In the case of $SrCo_{0.8-x}Fe_{0.2}Nb_xO_{3-d}$ perovskite this condition is met at $x = 0.2$. This makes the $SrCo_{0.6}Fe_{0.2}Nb_{0.2}O_{3-d}$ composition promising for application as oxygen-conducting membrane.

1. Introduction

Dense oxygen-permeable membranes with mixed electronic–ionic conductivity based on perovskite-like oxides are of increasing interest during past years for novel separation of oxygen from air inside a reactor. Pure oxygen then can be used in different catalytic oxidation processes such as partial oxidation of methane [1–5] or ethane [6], oxidative coupling of methane [7,8], etc. During the process one side of the membrane where the air is fed contacts with atmosphere with high oxygen partial pressure. Meanwhile, the other side of the membrane where the catalytic reaction takes place is subjected to the environment with low oxygen pressure and the oxygen gradient across the membrane can reach extremely high values. Oxygen mobility in oxygen-conducting perovskites at elevated temperatures and the presence of an oxygen gradient across the membrane can result in its structural transformation, e.g. change of the oxygen non-stoichiometry or phase transformations. Consequently, to sustain stable catalytic oxidation process an oxygen-conducting membrane must possess structural stability under conditions with large oxygen gradients at the temperatures of the catalytic reaction.

The application of perovskite-type oxides as oxygen-conducting membranes was first demonstrated in 1985 [9], and $SrCo_{0.8}Fe_{0.2}O_{3-d}$ was shown to have the highest oxygen flux. This composition was later studied in detail by many researchers. It was found that at low oxygen pressures this material undergoes a perovskite–brownmillerite structural transformation and as a result destruction of the membrane during the process was observed [10,11]. To improve the stability of strontium cobaltite in a wide oxygen pressure range it was suggested to substitute the main cation in the initial structure by another cation. For example, a cycle of studies was devoted to $SrCo_{0.8}Fe_{0.2}O_{3-d}$ modification with barium [4,6,12]. It was shown that the barium introduction to the system improves the stability of the perovskite phase $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-d}$ at oxygen partial pressures range 1–10^{-5} atm [12]. However, a detailed study revealed that during operation the oxygen rich membrane side was subjected to segregation of Sr and Ba, whereas the oxygen lean side of the membrane was enriched with cobalt [4,6]. A significant change of the component ratio on different membrane sides during operation resulting in the membrane destruction was also observed for the material where strontium was partially substituted with lanthanum $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d}$ [13]. Complete strontium substitution for other elements, e.g. Sm in $Sm_{0.4}Ba_{0.6}Fe_{0.8}Co_{0.2}O_{3-d}$, did not yield a stable composition. In this case the air side of the membrane was enriched with Ba and Co, whereas the catalytic side was enriched with Fe and depleted with Ba [14]. Other attempts to improve the stability of the $SrCo_{0.8}Fe_{0.2}O_{3-d}$ system included substitution of B-cation in

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perovskite, e.g. cobalt substitution for zirconium or cerium [15,16]. Such substitution led to improvement of the system stability in the reducing environment. Unfortunately, in this case the oxygen conductivity was much lower.

In this paper the physicochemical properties of strontium cobaltide $SrCo_{0.8}Fe_{0.2}O_{3-d}$ doped with niobium were investigated. We studied its structure, phase transformations in the oxidizing and reducing environments in the temperature range of 30–1000 °C and under conditions of partial methane oxidation. The choice of niobium as the modifying element was based on the two main factors. Niobium cations can stabilize the cubic structure after introduction into the perovskite lattice in wide range of oxygen non-stoichiometry $3-d$ [17]. Also doping with niobium makes it possible to improve the reduction stability of system containing transition metals [18]. The structural stability of perovskites was studied by in situ high-temperature X-ray diffraction, which is successfully used for investigation of phase transformations as a function of temperature and gas phase [12,19].

2. Experimental

The $SrCo_{0.8-x}Fe_{0.2}Nb_xO_{3-d}$ ($x = 0$–0.3) samples were synthesized by ceramic method [17] using $SrCO_3$, Fe_2O_3, Co_3O_4 and Nb_2O_5 as precursors. Depending on the composition, the final calcination temperature was varied from 1100 to 1250 °C.

In situ high-temperature X-ray diffraction was carried out using a Bruker D8Advance diffractometer and an Anton Paar HTK-16 high temperature chamber in oxygen partial pressure window 0.2–10^{-5} atm. It was shown in [20] that major perovskite changes, i.e. chemical expansion, initially increases faster in this oxygen pressure window and then plateaus at lower oxygen pressure 10^{-5}–10^{-15}. A sample was deposited on the platinum heater plate and heated at 1 °C/s rate from 30 to 1000 °C in air or in vacuum (10^{-5} atm). The cooling rate was equal to 1 °C/s. When the desired temperature was reached, the sample was maintained at this temperature for 20 min followed by registration of diffraction pattern in 2θ range 20–70° with 0.05° step and 5 s accumulation at each point.

The microstructure of the samples was studied using a JEM 2010 transmission electron microscope with an attachment for elemental analysis.

Temperature-programmed reduction (TPR) was carried out in 10% H_2 in Ar mixture at 40 ml/min flow rate and 10 °C/min heating rate from ambient temperature to 900 °C.

To study the stability of perovskites in partial methane oxidation, the samples (0.5–1 mm fraction) were placed in a tubular reactor fed with the reaction mixture containing 70 vol.% Ar, 20 vol.% CH_4 and 10 vol.% O_2 at 50,000 h^{-1} flow rate. The composition of the reaction mixture and the products was analyzed by gas chromatography using a TCD detector.

3. Results

The chemical, phase and mechanical stability of the membrane in the oxidizing and reducing environments at temperatures of catalytic processes (700–1000 °C) is an important factor for choice of the optimal perovskite composition for application as an oxygen-conducting membrane. To evaluate these factors we studied the stability of $SrCo_{0.8-x}Fe_{0.2}Nb_xO_{3-d}$ ($x = 0$–0.3) samples during heating in the air and in vacuum up to the 1000 °C.

When $SrCo_{0.8}Fe_{0.2}O_{3-d}$ was heated in air from 30 to 1000 °C the perovskite structure was registered in the whole temperature range. The XRD pattern of the sample cooled from 1000 °C to ambient temperature practically matched that of the initial sample (Fig. 1a). On the contrary, when the sample was heated under vacuum (Fig. 1b) a significant structural transformation was observed at 800 °C. This transformation resulted in the formation of a phase corresponding to brownmillerite structural type that was formed due to the ordering of oxygen vacancies. When the sample was cooled down under vacuum the brownmillerite structure with *Pnma* space group and lattice parameters $a = 5603$ Å, $b = 15{,}776$ Å, $c = 5479$ Å was preserved. These parameters are close to those of $Sr_2Fe_2O_5$ and $Sr_2Co_2O_5$ with brownmillerite structural type. The obtained results are in good agreement with the literature data showing that $SrCo_{0.8}Fe_{0.2}O_{3-d}$ perovskite is stable in the oxidizing atmosphere and is subjected to perovskite–brownmillerite structural transformation in the reducing environment [10–12].

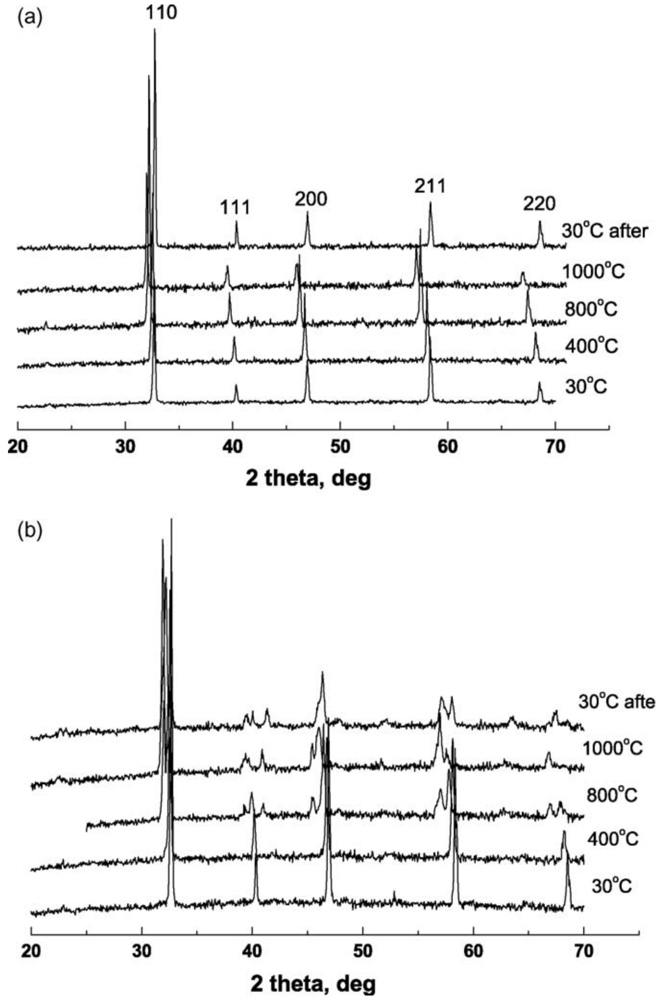

Fig. 1. XRD patterns of $SrCo_{0.8}Fe_{0.2}O_{3-d}$ recorded at different temperatures in air (a) and under vacuum (b).

The structure of $SrCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-d}$ sample looses stability during heating in air starting from 800 °C (Fig. 2a). The cubic structure of the initial perovskite with *Pm*3*m* symmetry is distorted resulting in the splitting of 1 1 0, 2 0 0 and 2 1 1 reflexes and change of their relative intensities. When the sample was heated under vacuum (Fig. 2b) the splitting of the individual reflexes at 800 °C was more evident. At 1000 °C all the observed reflexes were split. When the sample was cooled down under vacuum the structural distortion was preserved resulting in the reflex splitting untypical for the cubic phase. It is important to note that in the high temperature interval the lattice parameters in the air and in vacuum differed by 0.02 Å (Fig. 3a).

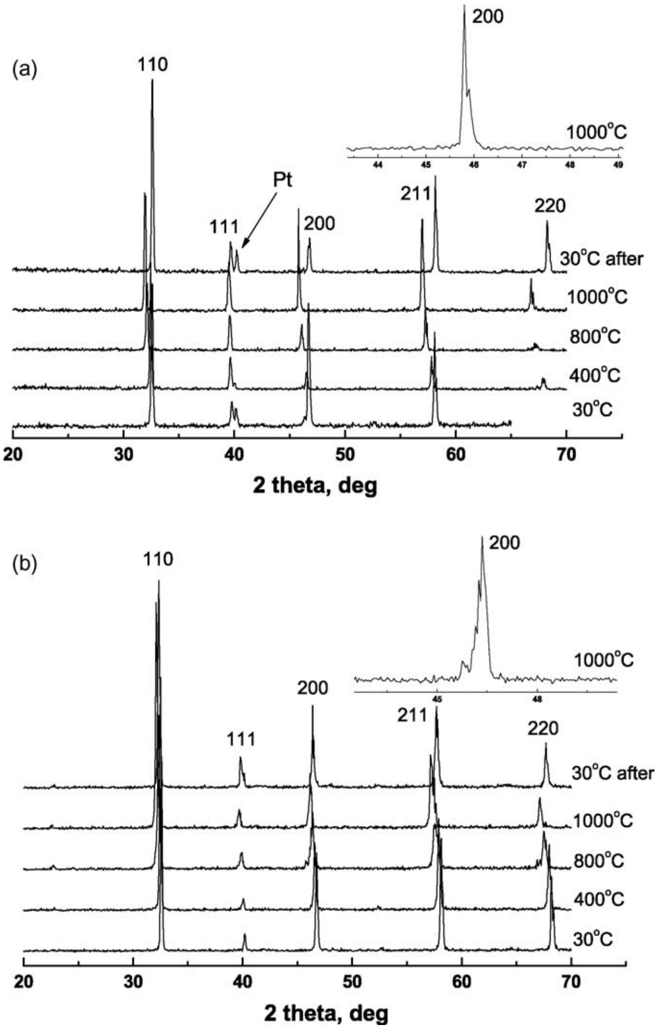

Fig. 2. XRD patterns of $SrCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-d}$ recorded at different temperatures in air (a) and under vacuum (b). The splitting of 2 0 0 reflex at 1000 °C is shown as an example.

The $SrCo_{0.6}Fe_{0.2}Nb_{0.2}O_{3-d}$ sample preserved the cubic perovskite structure in the whole temperature range studied both in the air and in vacuum (Fig. 4). This fact indicates that this system is very stable in the oxidizing and reducing environments. The changes observed during heating in the air were reversible, so that the lattice parameters before and after heating were identical. It is very important that the lattice parameters of this sample in the air and in vacuum at temperatures above 700 °C are the same within the experimental error (Fig. 3b).

The structure of $SrCo_{0.5}Fe_{0.2}Nb_{0.3}O_{3-d}$ sample was more stable with respect to temperature than that of $SrCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-d}$ but less stable than that of $SrCo_{0.6}Fe_{0.2}Nb_{0.2}O_{3-d}$ (Fig. 5). No peak splitting was observed during heating in air. Only their relative intensities at different temperatures changed, most likely, due to variation of the oxygen concentration in the sample. The changes observed during heating under vacuum were more significant. The splitting of the 2 2 0 peak was observed starting from 400 °C and the 2 0 0 peak was split starting from 800 °C. In the 800–1000 °C temperature range the lattice parameters in air and in vacuum differed by ~0.015 Å (Fig. 3c).

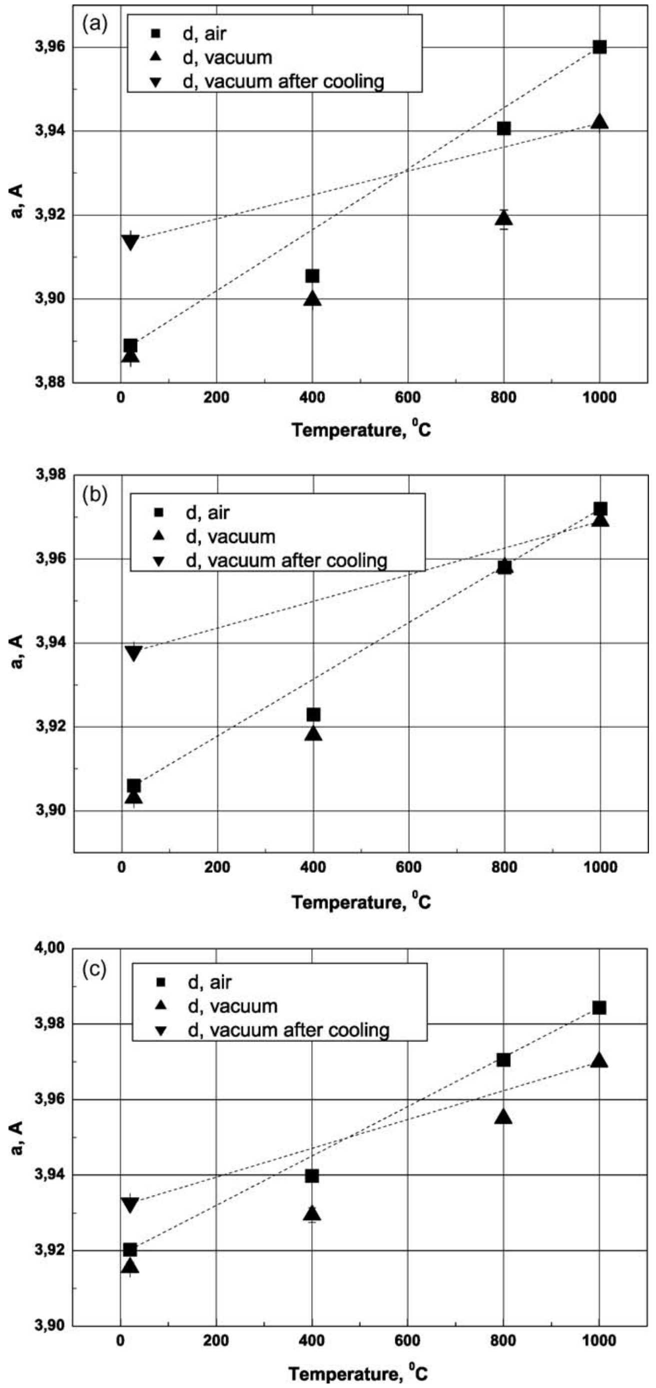

Fig. 3. Temperature dependence of the lattice parameters of $SrCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-d}$ (a), $SrCo_{0.6}Fe_{0.2}Nb_{0.2}O_{3-d}$ (b) and $SrCo_{0.5}Fe_{0.2}Nb_{0.3}O_{3-d}$ (c).

The niobium introduction into $SrCo_{0.8-x}Fe_{0.2}Nb_xO_{3-d}$ resulted in a continuous growth of the initial perovskite lattice parameter at room temperature in air from 3.871 Å at $x = 0$ to 3.920 Å at $x = 0.3$. For all three samples $SrCo_{0.8-x}Fe_{0.2}Nb_xO_{3-d}$ ($x = 0.1–0.3$) cooling in air returned the lattice parameters to the initial values. However, when the samples were cooled down in vacuum, their lattice parameters were increased by ~0.025, 0.035 and 0.013 Å, respectively (Fig. 3). The TEM with elemental analysis showed that initial composition of perovskite particle $SrCo_{0.6}Fe_{0.2}Nb_{0.2}O_{3-d}$ at the surface and in the bulk were identical Fe:Co:Sr:Nb = 11:25:53:11 (at.%). After the sample was heated under vacuum to 1000 °C and cooled down, the distribution of the elements across the particle did not change beyond the experimental error. Consequently, the observed increase of the sample lattice parameters after cooling under vacuum can be related only to changes in the perovskite oxygen non-stoichiometry. It is important that the perovskite–brownmillerite structural transformation observed for $SrCo_{0.8}Fe_{0.2}O_{3-d}$

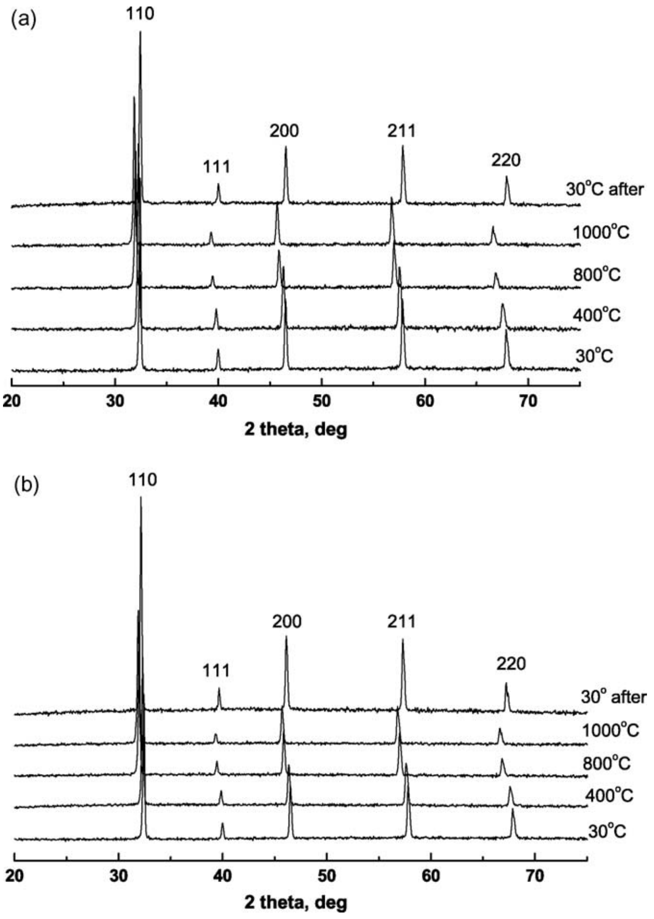

Fig. 4. XRD patterns of $SrCo_{0.6}Fe_{0.2}Nb_{0.2}O_{3-d}$ recorded at different temperatures in air (a) and under vacuum (b).

in reducing environment was not found for Nb-doped samples during heating under vacuum. This proves that Nb plays an important role in stabilization of the perovskite cubic structure.

The reduction stability of $SrCo_{0.8}Fe_{0.2}O_{3-d}$ and $SrCo_{0.6}Fe_{0.2}Nb_{0.2}O_{3-d}$ samples was also studied by TPR. The TPR profile of $SrCo_{0.8}Fe_{0.2}O_{3-d}$ has three major peaks at $T_1 = 545$ °C, $T_2 = 634$ °C, and $T_3 = 751$ °C (Fig. 6). Doping with niobium altered the TPR profile. The low-temperature peak shifted to lower temperatures by 35 °C and its relative area increased. The maximum positions of the other two peaks did not change whereas their relative peak areas decreased. The amounts of hydrogen consumed in the 25–900 °C temperature range were 0.00643 mol/g for $SrCo_{0.8}Fe_{0.2}O_{3-d}$ and 0.00428 mol/g for $SrCo_{0.6}Fe_{0.2}Nb_{0.2}O_{3-d}$. This indicates that the Nb-doped perovskite is more stable to reduction.

The investigation of $SrCo_{0.6}Fe_{0.2}Nb_{0.2}O_{3-d}$ sample in partial oxidation of methane showed that this sample was not active by itself. The methane conversion was 3.5%, with CO and H_2 selectivities equal to 40% and 30%, respectively. The phase composition of $SrCo_{0.6}Fe_{0.2}Nb_{0.2}O_{3-d}$ was preserved during the reaction but the perovskite lattice parameter increased by 0.019 Å. This proves that the oxygen non-stoichiometry was changed during reaction and is in agreement with the data obtained in the XRD chamber (Fig. 7).

4. Discussion

In this study the structural stability of Nb-doped $SrCo_{0.8}Fe_{0.2}O_{3-d}$ system in the oxidizing and reducing environments was studied by in situ high-temperature XRD. Its stability is an important factor determining the applicability of this material as an oxygen-conducting membrane. The main advantage of $SrCo_{0.8-x}Fe_{0.2}Nb_xO_{3-d}$ $(x = 0.1–0.3)$ in comparison with $SrCo_{0.8}Fe_{0.2}O_{3-d}$ is the preservation of the perovskite cubic structure both in the oxidizing and reducing environments and, consequently, the absence of the perovskite–brownmillerite structural transformation.

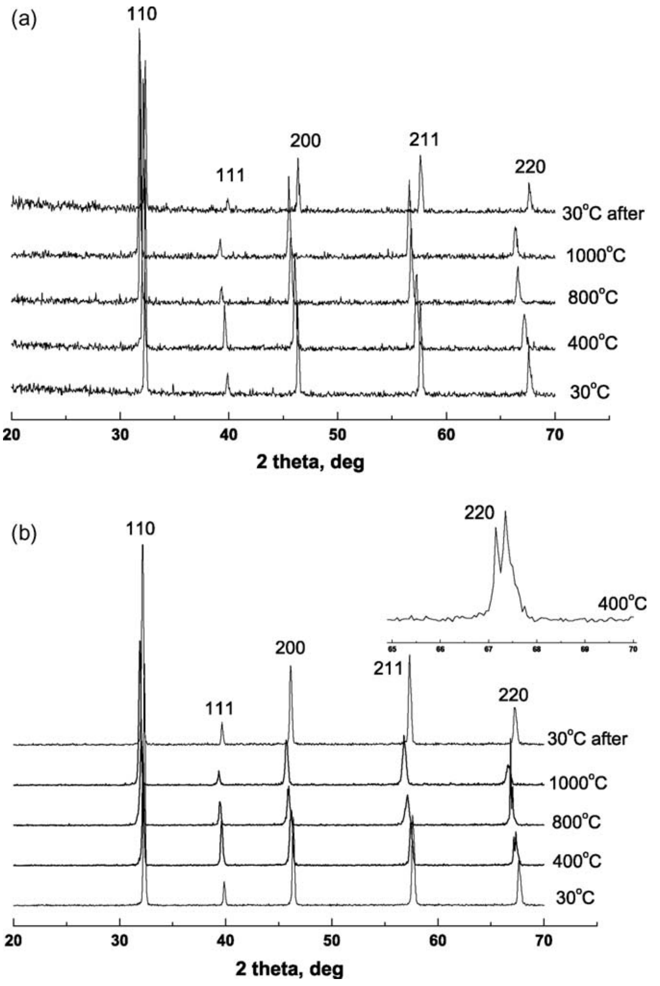

Fig. 5. XRD patterns of $SrCo_{0.5}Fe_{0.2}Nb_{0.3}O_{3-d}$ recorded at different temperatures in air (a) and under vacuum (b). The splitting of 2 2 0 reflex at 400 °C is shown as an example.

The analysis of the perovskite lattice parameters in the oxidizing and reducing environments in the high temperature

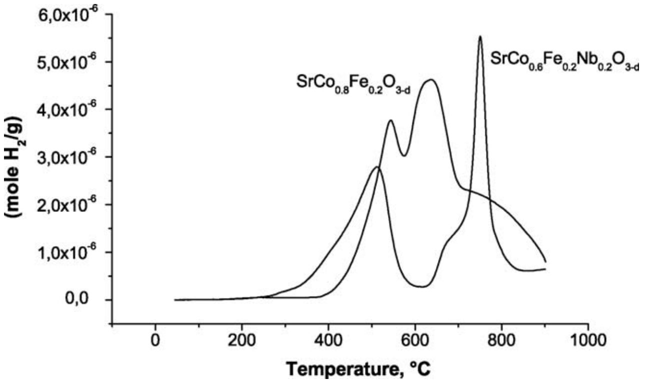

Fig. 6. TPR profiles of $SrCo_{0.8}Fe_{0.2}O_{3-d}$ and $SrCo_{0.6}Fe_{0.2}Nb_{0.2}O_{3-d}$.

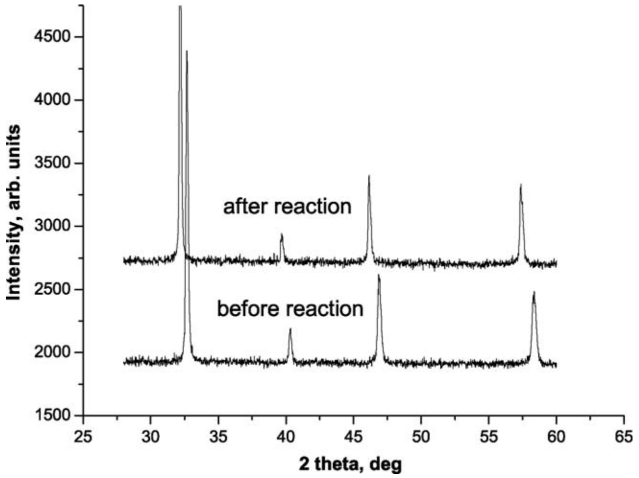

Fig. 7. XRD patterns of $SrCo_{0.6}Fe_{0.2}Nb_{0.2}O_{3-d}$ before and after methane partial oxidation reaction.

region ($T > 700\,^{\circ}C$) is crucial during the investigation of the structural and mechanical stability of the membrane material. The presented data indicate that the perovskite lattice parameters of all three samples depend on temperature in a non-linear way. The temperature dependence of the lattice parameters of the studied samples is determined by two processes: perovskite thermal expansion and change of the oxygen non-stoichiometry $3 - d$ due to the loss of a part of oxygen upon heating and reoxidation during cooling in the oxygen-containing environment. The conclusion on a significant dependence of the oxygen non-stoichiometry on the lattice parameter was made on the basis of our high-temperature experiments carried out under vacuum. When the sample was heated under vacuum to 1000 °C followed by cooling to room temperature, the perovskite lattice parameter was increased in comparison with the initial value by 0.025 Å for $x = 0.1$, 0.035 Å for $x = 0.2$ and 0.013 Å for $x = 0.3$. As transmission electron microscopy coupled by elemental analysis showed that the Fe:Co:Sr:Nb ratio in the cooled samples was constant, the lattice parameter growth can be attributed only to the change of the oxygen non-stoichiometry, namely, an increased concentration of oxygen vacancies. Indeed, it was measured by iodometric titration [21] that the oxygen concentration in the initial $SrCo_{0.6}Fe_{0.2}Nb_{0.2}O_{3-d}$ sample was 2.7 and it decreased after heating under vacuum to 2.6.

Two processes proceeding in perovskite system upon heating, i.e. loss of oxygen and thermal expansion, result in the lattice parameter growth. However, these processes are not completely independent because the change of the oxygen concentration in the sample seems accompanied by a significant decrease of the thermal expansion coefficient. Indeed, the straight lines connecting the values of the lattice parameters at room temperature and at 1000 °C for samples cooled under vacuum have substantially lower slope than the corresponding lines drawn for samples cooled in air (Fig. 3). Although the linear expansion law does not seem to hold in this case, this fact appears to indicate that the thermal expansion coefficient decreases when the concentration of oxygen vacancies increases.

Thus, the concentration of oxygen vacancies grows with temperature. This results in an increase of the lattice parameter but simultaneously decreases the thermal expansion coefficient. Therefore, it can be concluded that stable perovskite operation in the oxidizing and reducing environments requires equilibrium of these two processes, leading to the same lattice parameters in both environments in the temperature range of the catalytic process ($T > 700\,^{\circ}C$). The chemical composition of the samples is a regulated parameter that can be varied to achieve the desired result—equal lattice parameters in the oxidizing and reducing environments. The change of the chemical composition after introduction of Nb^{5+} cations with large charge appears to result in a change of the oxygen non-stoichiometry both at low and high temperatures, which eventually determines the lattice parameter. For samples $SrCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-d}$ and $SrCo_{0.5}Fe_{0.2}Nb_{0.3}O_{3-d}$ the differences of the lattice parameters at high temperatures are significant (0.02 and 0.015 Å, correspondingly). Consequently, they would lead to tensions during operation of these materials as membranes and would result in destruction under conditions with different oxygen partial pressure on the two sides of the membrane. On the contrary, the lattice parameters of $SrCo_{0.6}Fe_{0.2}Nb_{0.2}O_{3-d}$ are the same in the oxidizing and reducing environments. Hence, it is natural to expect that no mechanical tensions will appear during operation of a membrane with this chemical composition.

5. Conclusions

A series of samples $SrCo_{0.8}Fe_{0.2}O_{3-d}$, $SrCo_{0.7}Fe_{0.2}Nb_{0.1}O_{3-d}$, $SrCo_{0.6}Fe_{0.2}Nb_{0.2}O_{3-d}$, $SrCo_{0.5}Fe_{0.2}Nb_{0.3}O_{3-d}$ were studied by in situ high-temperature XRD in a wide oxygen partial pressure range (0.2–10^{-5} atm). Perovskite with $SrCo_{0.6}Fe_{0.2}Nb_{0.2}O_{3-d}$ composition demonstrated the highest stability, apparently, due to equilibrium between the thermal expansion process and changes of the oxygen non-stoichiometry at temperatures above 700 °C. Consequently, perovskite with this composition is the most stable both from the phase composition and from the mechanical strength viewpoints. It preserves the ideal perovskite cubic structure and has about the same values of lattice parameters in air and under vacuum at high temperatures. The latter property makes $SrCo_{0.6}Fe_{0.2}Nb_{0.2}O_{3-d}$ perovskite the most promising among listed materials for further study. The final conclusion on possibility of the use of Nb-doped perovskites as oxygen-conducting membranes will be made based on the oxygen transport performance and stability of membrane during operation in real catalytic process, these experiments are in progress.

Acknowledgements

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