

# Two mechanisms of thermal expansion in perovskite $\text{SrCo}_{0.6}\text{Fe}_{0.2}\text{Nb}_{0.2}\text{O}_{3-z}$

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**Abstract** Perovskite  $\text{SrCo}_{0.6}\text{Fe}_{0.2}\text{Nb}_{0.2}\text{O}_{3-z}$  attracts attention as a promising material with high oxygen conductivity. The sample was investigated by means of high-temperature X-ray powder diffraction and thermogravimetry. Phase transition was detected near 400 °C and accompanied with significant mass loss. The phase transition affects oxygen mobility, important for the synthesis of oxygen permeable membranes. The unit cell parameters are proved to change with temperature after two effects (1) reversible conventional thermal expansion and (2) irreversible contraction-expansion due to the changes in the oxygen content. In situ high-temperature X-ray diffraction experiments allowed us to separate the contributions and to measure them as a function of temperature.

**Keywords** Oxygen membrane · Perovskite · Thermogravimetry · XRPD

## Introduction

Amongst the modern methods for obtaining pure oxygen for different applications, the membranes with mixed

ionic-electronic conductivity (MIEC) seem to be the most promising materials [1–3]. The membrane should have mixed electronic-ionic (oxygen) conductivity and be oxygen selective. Wide group of solids that have MIEC belongs to the class of perovskite-like oxides  $\text{ABO}_{3-z}$ , with structural and calorimetric properties being thoroughly investigated [4–12]. Nowadays the development of oxygen permeable membranes for catalytic membrane reactors of spontaneous natural gas oxidation faces a problem difficult to overcome: there is no appropriate chemical composition for a membrane that has high enough oxygen conductivity, structural and mechanical stability up to 1,000 °C in oxidizing and reducing environments. To provide mechanical strength of the membrane, its material must fit the requirement of proximity of lattice parameters in environments with high and low oxygen partial pressures. Therefore, it is essential to have complete information about thermal expansion processes in these compounds.

The lattice parameter in perovskite-type oxide was supposed to depend on two factors: (1) conventional thermal expansion  $\alpha$  and (2) changes in oxygen stoichiometry  $\gamma$ , specific for the materials with high ionic conductivity [13]. Coefficients  $\alpha$  and  $\gamma$  are defined as

$$\alpha = \frac{d \ln a}{dT}; \quad \gamma = \frac{d \ln a}{dz}$$

where  $z$  is the oxygen non-stoichiometry. The change in the interaction between ions changes the lattice parameter of perovskite.

In this work we investigated thermal properties of strontium cobaltite doped with Fe and Nb  $\text{SrCo}_{0.6}\text{Fe}_{0.2}\text{Nb}_{0.2}\text{O}_{3-z}$  in order to confirm experimentally the correlation between oxygen stoichiometry of the perovskite and its lattice parameter.

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## Experimental

### Preparation of the sample

Sample  $\text{SrCo}_{0.6}\text{Fe}_{0.2}\text{Nb}_{0.2}\text{O}_{3-z}$  was synthesized from initial oxides  $\text{SrCO}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4$  and  $\text{Nb}_2\text{O}_5$  that were thoroughly mixed in AGO-2 ball mill for 30 s. After drying and calcination at 950 °C for 8 h, the mixture was retreated in the ball-mill for 30 s. The pellets prepared from the oxide mixture were placed into a furnace at 1,250 °C and kept there for 12 h [14, 15].

### In situ high-temperature X-ray diffraction

High-temperature X-ray diffraction experiments were conducted using diffractometer Bruker D8 Advance with vacuum chamber HTK-16 Anton Paar which allows one to carry out experiments in air and vacuum ( $\sim 5 \cdot 10^{-3}$  torr). The radiation  $\text{CuK}\alpha$  with a wavelength of 1.5418 Å was used. The sample in a form of a powder was placed on a Pt heater, the heating rate was of 1 °C s<sup>-1</sup>. When the desired temperature was reached, the sample was held at constant temperature for 30 minutes. Then the diffraction pattern in parallel beam geometry with Göbel mirror and angle range  $2\theta = 30\text{--}70^\circ$  with a step of 0.05° and the time of exposure of 5 s per point was collected. The parallel beam geometry was used in order to avoid the affect of shifting of the sample from reflecting boundary, which can occur while heating because of inflation of a sample. Peak position was determined using non-linear approximation of analytical functions software “fityk” (<http://www.unipress.waw.pl/fityk/>). The lattice constants were refined by least-squares method.

### Thermogravimetry

Thermogravimetric experiments were carried out using Netzsch TG-209 in temperature range from ambient to 850 °C in argon, heating rate of 15 °C min<sup>-1</sup>. Gold crucible was used, sample mass was 75 mg. One experiment was arranged in two stages: first, the sample was heated up to 850 °C and then cooled down to 25 °C; second, the sample was heated again using the same experimental conditions.

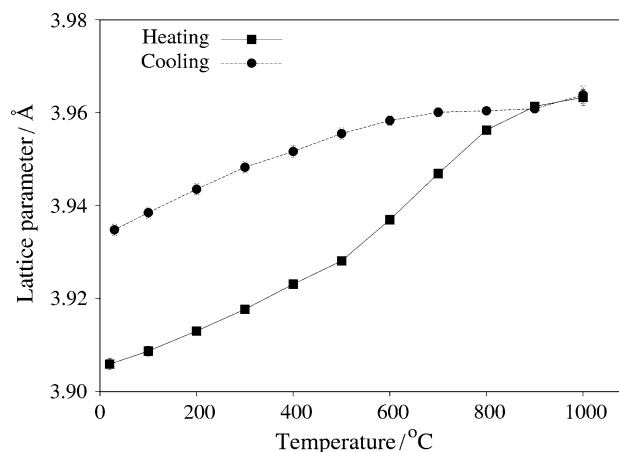
## Results and discussion

### X-ray diffraction experiments in vacuum

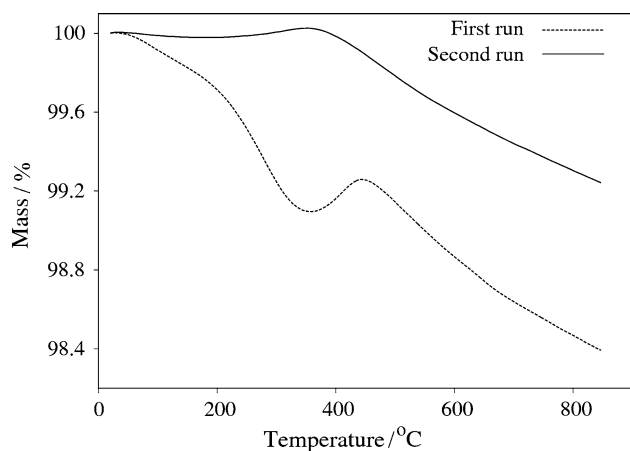
Over the whole temperature range of experiments in air and vacuum the sample remains cubic perovskite phase. Lattice parameters in vacuum on heating and cooling are shown in

Fig. 1 as a function of temperature. There are two lines in the Figure, one for the heating and one for the cooling. The sample loses oxygen at heating up to 1,000 °C. When cooled in vacuum, the oxygen content in the sample decreases also at very high temperatures but remains constant at low temperatures because of the lack of oxygen atoms in the experimental cell. If heated and cooled in oxygen atmosphere, the sample changes its oxygen content reversibly, but the vacuum does not allow it to restore initial oxygen content. This consideration is supported with the TG results shown in Fig. 2. Sample loses its mass over the whole temperature range at the first heating, but only above 400 °C at the second one. The sample loses the mass below 400 °C at the first run because its stoichiometry was equilibrated in air with quite significant oxygen content. It does not lose mass below 400 °C at the second heating because it did not restore its oxygen content while cooled down after the first heating in argon and its oxygen content is less than the starting one. It is surprising that the sample mass increases slightly near 400 °C at the second heating. Probably, the sample absorbs the traces of oxygen in argon, trying to equilibrate (increase) its oxygen content near 400 °C. As the heating continues, the sample starts to lose its mass again.

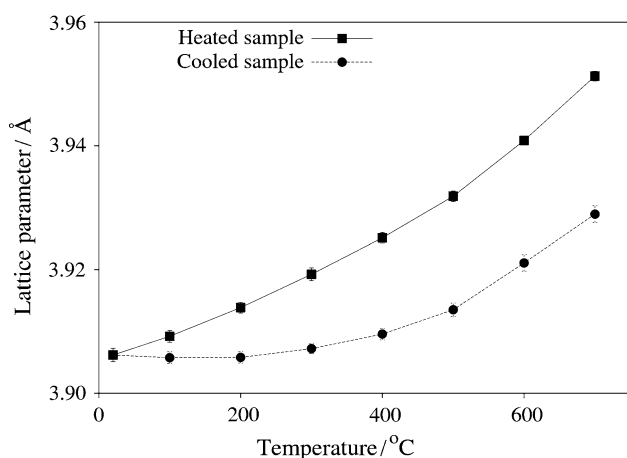
The lattice parameter of the sample after the experiment differs from the starting one by  $0.029 \pm 0.002$  Å (see Fig. 1). As the sample was synthesized at 1,250 °C, it is evident that the difference by 0.03 Å arises from the change in the oxygen content. The total change in the lattice parameter at heating from room temperature to 1,000 °C is about 0.06 Å, and we may conclude that the effect of the oxygen depletion on the change in the lattice parameter is nearly equal to the conventional thermal expansion. Below 400 °C, the total thermal expansion coefficients  $1/a \, da/dT$  are very similar for both stages in Fig. 1, their values being about  $11.6 \cdot 10^{-6} \text{ K}^{-1}$ . They are



**Fig. 1** Lattice parameters of the sample while heating and cooling in vacuum



**Fig. 2** Thermogravimetric data at both stages of heating up



**Fig. 3** Two contributions to the thermal expansion of perovskite

similar to those of perovskite-like oxides presented in [16]. We may assume that the contribution from the vacancy factor  $\gamma$  is negligible in this temperature range and only conventional thermal expansion factor  $\alpha$  at constant oxygen vacancy concentration is essential.

#### Separation between two contributions

To separate the two contributions in the thermal expansion, we can use the results of the experiments shown in Fig. 3. While the sample is heated up to temperature  $T$ , definite concentration of oxygen vacancies is formed in it. When the sample is cooled down in vacuum to room temperature, oxygen content stays the same but the lattice parameter appears to be enlarged as has been shown in previous experiment:

$$\Delta a = a \int_{T_0}^T \gamma \frac{dz}{dT} dT$$

**Table 1** Values of the two thermal expansion coefficients before and after the phase transition

Temperature (°C)	$\alpha/10^{-6} \text{ K}^{-1}$	$\gamma \frac{dz}{dT} / 10^{-6} \text{ K}^{-1}$
20–400	10.5	0
400–700	5.5	19.7

The heating up to temperature  $T$  and cooling down to room temperature with the diffraction patterns detection at these temperature points allows us to obtain the values of lattice parameters at different oxygen vacancies concentration. This is the way to obtain only vacancy factor  $\gamma$ , excluding the effect of conventional thermal expansion of the lattice. In these experiments, the sample was heated up to 100 °C with consequent diffraction pattern registration, then it was cooled down also with diffraction pattern registration. The same procedure was conducted for temperatures 200, 300, ..., 700 °C with the step of 100 °C. Difference between the lattice parameters after these experiments is shown in Fig. 3. The lattice parameter of the sample at room temperature practically stays the same if the temperature of heating up in vacuum is below 300 °C. After heating up to 400 °C, the cooled sample has a bit enlarged lattice constant. The change of lattice constant increases with the temperature of heating. These results allow us to detect the oxygen outlet from the structure during the heating. Below 400 °C oxygen atoms stay within the structure, their stream outside is negligible to change the stoichiometry. At 400 °C and above, the sample loses oxygen, which causes the lattice parameter increment at room temperature. The point 400 °C is supposed to be the phase transition temperature after the high-precise X-ray powder diffraction using synchrotron radiation (to be published). Table 1 represents the two contributions to the thermal expansion below and above the phase transition temperature, 400 °C.

#### Conclusion

In this work we have made the complementary analysis of X-ray powder diffraction and thermogravimetric data and proved that the oxygen vacancies do make the contribution in the thermal expansion of perovskite-type oxides. We separated the contribution of structural vacancies from that of conventional thermal expansion using in situ high temperature X-ray powder diffraction.

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