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Oxygen Permeability of Mixed Conducting Perovskite Lanthanum Gallate – Based Ceramics

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Abstract. The structure, microstructure, electric transport and oxygen permeation properties of $(La,Sr)(Ga,Mg,Fe)O_{3-\delta}$ ceramics with perovskite or brownmillerite structures have been studied. Oxygen permeability values of ~0.1 $cm^3/cm^2 \cdot min$ has been revealed at 1000 K for the ceramics studied. The correlation of electroconducting properties of the $LaGaO_3$-based ceramics with perovskite and brownmillerite structures to their oxygen permeability characteristics has been proved.

Introduction

Anion-deficient perovskite $ABO_{3-\delta}$ and related structures are of technical interest as oxygen ion conductors in which conductivity occurs through vacancies hopping [1]. The perovskite-type structures provide good conditions for oxygen ion transport. It is also possible to create mixed-valence electronic conduction through the introduction of the transition elements into the B sublattice. The mixed ionic- and electronic conducting (MIEC) oxides attract much attention mostly due to prospects of their application as solid electrolyte membrane materials for oxygen separation or partial oxidation of hydrocarbons. As the oxygen diffusion process is facilitated by a large concentration of vacancies in the oxygen sublattice the introduction of the aliovalent ions ensures presence of oxygen vacancies in the perovskite structure. Lanthanum gallate-based perovskite oxides doped with strontium and magnesium cations were shown to possess the highest ionic conductivity in a wide range of the oxygen partial pressure while remaining stable in both oxidizing and reducing atmospheres [2-4]. The $LaGaO_3$-based perovskites are regarded as good candidates for the development of MIEC oxides providing additional doping of the compositions with the transition elements and intensively studied during last years [5-14]. In this work, changes in structure parameters, microstructure, electric transport and oxygen permeation properties of perovskite ceramics $(La_{0.9}Sr_{0.1})[(Ga_{1-x}Fe_x)_{0.8}Mg_{0.2}]O_{3-\delta}$ with $0 \le x \le 0.5$ (system I) and brownmillerite ceramics $(La_{0.2}Sr_{1.8})[Ga(Fe_{1-x}Mg_x)]O_{5.1+\delta}$ with $0 \le x \le 0.5$ (system II) have been studied. The electroconducting properties are shown to correlate well with the oxygen permeability characteristics.

Experimental

Ceramic samples were prepared by the solid state reaction method with intermediate regrindings at temperatures T_1=800-900°C (10 h); T_2=1000-1100°C (10 h); T_3=1400°C (3 h) [7, 11]. Densities of the ceramics were found to be ~93-95 % of theoretical values. Properties of the samples were

characterized by means of X-ray diffraction, electron microscopy, and DTA/TG methods. Dielectric spectroscopy measurements were performed in a frequency region 1 kHz - 100 kHz in the temperature range of 300-1200 K. The conductivity changes were analyzed under cycling atmospheres from nitrogen to oxygen ones. The oxygen permeation was measured in the temperature range of 1000-1400 K. The *ac*- and *dc*-conductivity measurements were carried out using bar-like ceramic samples with the dimensions typically about 1x1x10 mm with the small surfaces of the bars coated with Pt electrodes. Large surfaces of the bar-like samples were freely exposed to atmospheres that could be step-wise changed from oxidizing (air) to reducing (nitrogen). The oxygen permeability through membranes was measured in air/He gradients using a home-made set. The oxygen permeation experiments were performed in an alumina reactor composed from two coaxial alumina tubes covered with mutual cap. The analysis of the composition of the effluent stream was performed by the gas chromatography. Oxygen partial pressures were measured by the oxygen measuring set "Tsvet". The membrane was attached to the alumina tube with a glue and sealed at the temperature ~1000°C in air. Prior to sealing the cylindrical sides of the membrane were painted with a mixture of the glass and mullite powder. Helium gas was supplied to the inner permeate side of the membrane. The oxygen partial pressure in this compartment was varied by adjusting the total flow rate. The carrier gas supplied to the measuring chamber through the inner alumina tube flowed out through the outer alumina tube. The outer side of the membrane was exposed to air. The gas flow at the permeate side of the membrane was measured with a volumeter. The oxygen flux was calculated from the equation:

$$J_{O_2} = \frac{1}{G} \cdot \frac{Fc_{O_2}}{A}. \qquad (1)$$

Here, F is the flow rate at the outlet of the reactor, c_{O2} the oxygen concentration in the effluent stream and A the geometric surface area at the He side of the membrane. The dimensionless factor G (~1.1) was used to correct for the effect of non-axial oxygen diffusion due to the different areas of the membrane surfaces exposed to air and He, respectively. The gas tightness of the sealed membrane was checked by the detection of N_2 in the effluent side with the gas chromatograph. The contribution of molecular oxygen to the total oxygen flux through leakages was lower than 1 % at high temperatures.

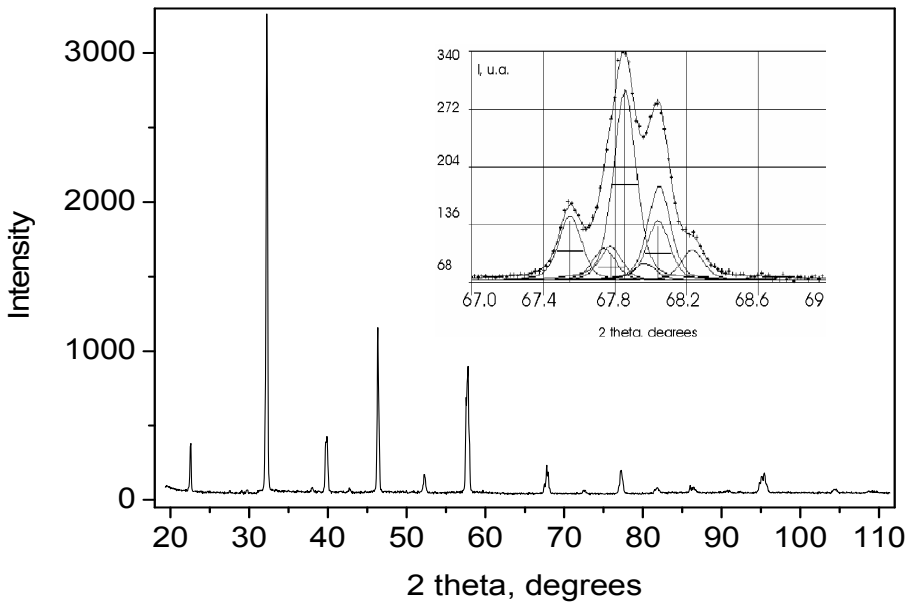

Fig. 1. The X-ray diffraction pattern of the sample $(La_{0.9}Sr_{0.1})(Ga_{0.64}Fe_{0.16}Mg_{0.2})O_{3-\delta}$. Insert: splitting of the 220 cubic lattice peak according to the monoclinic symmetry.

Results and discussion

The X-ray diffraction patterns confirmed the formation of pure perovskite structure solid solutions I (Fig.1). Additionally, the neutron diffraction experiments were carried out for the composition I with x=0.3 [15]. The monoclinic structure with the unit cell parameters a=7.811, b=5.508, c=5.51 A, and space group $I2/a$ was revealed at room temperature. The unit cell volume decreases along with Fe substitution for gallium up to x~0.4 in the system I, while it increases when magnesium substitutes for iron in the system II [10, 13]. Decreasing in the unit cell volume indicates a presence of Fe^{4+} cations in all compositions I with $x \leq 0.4$. Naturally, the number of oxygen vacancies in the perovskite lattice y must decrease depending on the Fe^{4+} cations content.

In contrast to this, practically a linear increase in the unit cell volume was observed for the compositions II with x<0.5. This determines decreasing in oxygen vacancies in the brownmillerite lattice δ for compositions II.

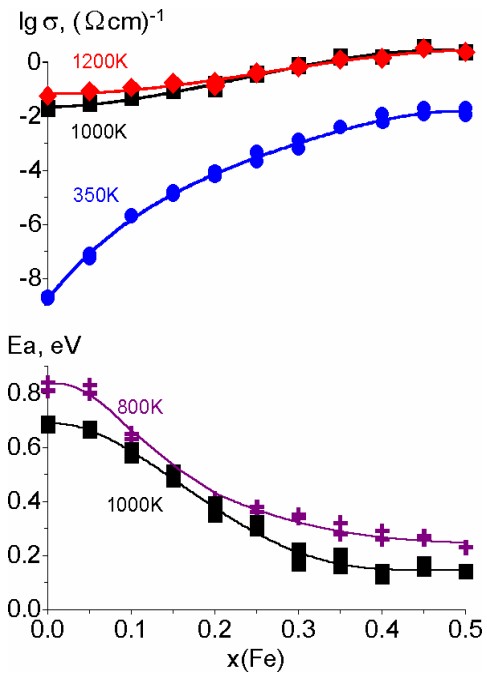

Fig. 2. Concentration dependences of total conductivity (upper curves) and activation energy (lower curves) for ceramics $(La_{0.9}Sr_{0.1})[(Ga_{1-x}Fe_x)_{0.8}Mg_{0.2}]O_{3-\delta}$.

Electron microscopy data confirmed a dense microstructure of the samples prepared, with the average size of isometric grains decreasing from 2-5 μm to 1-2 μm in samples I and from 10-30 μm to 3-5 μm in samples II when x increased from 0 to 0.5, respectively.

The *ac*-measurements of the total conductivity σ_t in a wide range of frequencies proved the almost pure ionic character of conductivity for the initial composition of ceramics I with x=0 though mixed ionic-electronic one for compositions with x>0 at high temperatures T≥1000 K (Fig. 2). Increasing σ_t values testifies to the increasing contribution of the electronic constituent of the conductivity σ_e both in low and high temperature ranges. The high ionic conductivity σ_i value of ~0.1 Sm/cm was observed in the samples with x=0 at T>1200 K. The *dc*-conductivity measurements revealed variation in the σ_e value from 0.01 to 1 Sm/cm in compositions I with $0.15 \leq x \leq 0.5$.

As it is shown in Fig. 2, the σ_t value increases to 2 orders in magnitude at high temperatures and more then 6-7 orders in magnitude at the room temperature with the iron addition. The effect is especially strongly pronounced at low iron concentrations. The activation energy E_a decreases with x increasing (lower curves in Fig.2). This corresponds to the change of dominating type of conductivity from almost pure ionic at smaller x<0.2 to mixed ionic - electronic at higher x>0.2.

On the contrary, in compositions II the σ_t value decreases along with x increasing. This evidently indicates decreasing of σ_e contribution along with the transition element substitution.

The mechanism of electronic conductivity was clarified through conductivity relaxation under cycling atmospheres from nitrogen to the oxygen one [14]. A growth of electrical conductivity was observed in all the samples I with x>0.15. This means that the p-type conductivity prevails normally

in the substances due to electron holes. The kinetic data obtained indicate more intensive mass transfer for the samples with x=0.3-0.4 in comparison with those with x<0.2. This may provide a significant increase in ionic conductivity in ceramics with x=0.3-0.4 in comparison with ceramics with lower x values.

This assumption was proved by the oxygen permeability measurements (Fig. 3). When the oxygen partial pressure gradient is applied across a membrane, oxygen diffuses from the high to the low partial pressure side. A joint flux of electrons or electron holes maintains local charge neutrality throughout the membrane. Under the conditions of small oxygen partial pressure gradients at relatively high oxygen pressures, the penetration properties of mixed ionic-electronic conducting membranes can be modeled by a diffusion mechanism. The activation energy of the process consists of two contributions, namely the enthalpy of oxygen vacancy formation and the activation energy for oxygen diffusion. The apparent activation energy has been shown to be almost completely determined by the diffusion [14].

The Arrhenius-type plots of oxygen permeability versus the reciprocal temperature are shown in Fig. 3. It is clear that the apparent activation energy for oxygen diffusion decreases when the iron content increases in the concentration range of x=0.3-0.4 (curves 1-3). In the samples with higher x, decreasing in the J_{O2} value was observed which is consistent with the decreasing concentration of mobile oxygen ions. Slightly higher J_{O2} values were observed for brownmillerite samples II (curve 6). This may be attributed to the higher oxygen vacancies concentration in samples II at least at temperatures higher than the temperature of the transition from the ordered brownmillerite phase to the perovskite phase with disordered oxygen vacancy sites.

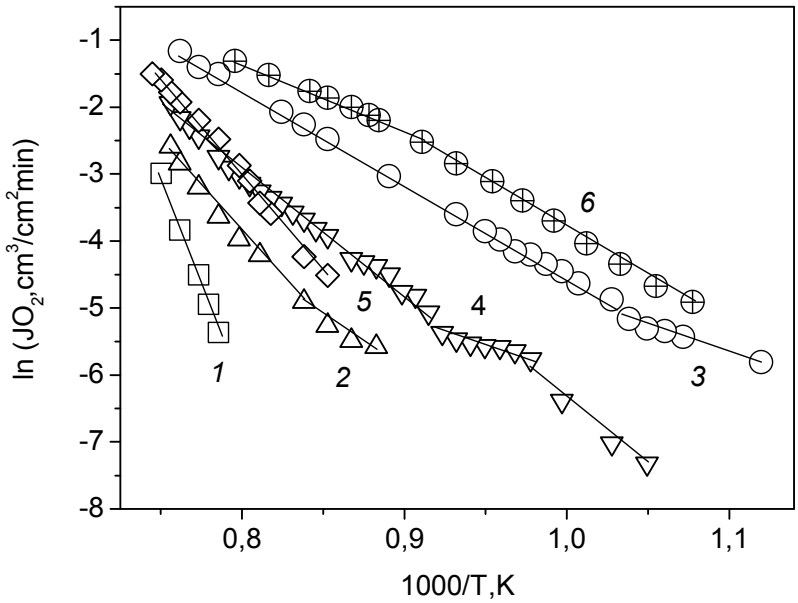

Fig. 3. The oxygen permeability of samples $(La_{0.9}Sr_{0.1})[(Ga_{1-x}Fe_x)_{0.8}Mg_{0.2}]O_{3-\delta}$ with x = 0.3 (*1*), 0.35 (*2*), 0.4 (*3*), 0.45 (*4*), 0.5 (*5*) and $(La_{0.2}Sr_{1.8})(GaFe)O_{5.1}$ (*6*) as a function of temperature.

The measured oxygen fluxes are nearly the same as measured in other $LaGaO_3$-based perovskites [16], though being an order in magnitude lower than the oxygen fluxes typical for Co-containing ceramics [17]. Nevertheless, the studied compositions can be promising in applications as thin membranes deposited on porous supports.

Conclusion

The results obtained confirmed the correlation of electroconducting properties of the $LaGaO_3$-based ceramics with perovskite and brownmillerite structures to their oxygen permeability characteristics.

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