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Single phase materials based on Co-doped $SrTiO_3$ for mixed ionic-electronic conductors applications

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ABSTRACT

In the present work the effect of cobalt oxide addition on the structural and electrical properties of strontium titanate is examined. The $SrTi_{1-x}Co_xO_{3-\delta}$ ($0 \leq x \leq 0.4$) samples were synthesized according to solid state reaction method at 1150 °C and sintered at 1400 °C. The samples are single phase and crystallize in the cubic perovskite-type structure. With the increase of cobalt content the lattice parameter of the cubic cell is reduced, due to dimensional factor. The most dense sample is obtained for $x = 0.2$. The electrical conductivity is examined by 4-probe dc-technique in the range of 600–1000 °C in air atmosphere, as well as in a wide range of oxygen partial pressures ($pO_2 = 1 \times 10^{-19}$–0.21 atm) at 900 °C. The conductivity dependence on pO_2 can be explained by using the formalism of quasi-chemical reactions. The single-phase materials exhibit poor stability in reducing atmosphere (hydrogen) and good stability in salt-forming (carbon dioxide) components. In the oxidative region, the samples are characterized by mixed ionic-type conduction, and therefore can be used as membranes in high-temperature electrochemical devices; as for example, for oxygen production. The oxygen permeability and the thermal expansion measurements confirm that the specific materials can be used in electrochemical devices.

1. Introduction

Specific oxides that are characterized by mixed ionic–electronic conductivity (MIEC) are promising materials for membranes used for the electrochemical production of oxygen from gas mixtures. Among the investigated oxides, perovskite-like materials based on titanates of alkaline earth elements have attracted considerable attention, due to their satisfying stability in severe environment [1]. Titanates of alkaline earth elements that present mixed ionic–electronic conductivity can be used in electrochemical devices for hydrogen or oxygen production [2]. However, this kind of applications requires also high values of ambipolar conductivity and stability in severe environment (high gradient of pO_2, high temperatures and thermocycling). Therefore, the development of novel materials that will maintain optimal properties during long term operation is requisite. The properties of oxide systems can be varied in a wide range by doping with an acceptor or donor agent in a sublattice of rare earth elements or/and in the sublattice of titanium [3–8]. For pure and acceptor doped $SrTiO_3$, there is a transition from n- to p-type regions with increasing the oxygen partial pressure (pO_2) [5]. The onset of the p-type conduction at the conductivity minimum depends on the type and the amount of the acceptor impurity added to $SrTiO_3$ [5].

As far as it concerns $SrFe_{0.2-x}Ti_{0.8}Co_xO_{3-\delta}$ materials, a significant increase of the grain size was observed with the increase of cobalt's concentration in the samples [9]. Additionally, the lattice of these samples was compressed due to the formation of oxygen vacancies and the electrical conductivity increased. It was found that in the case of $SrFe_{0.2-x}Ti_{0.8}Co_xO_{3-\delta}$ ($x = 0.05$–0.2) samples, the iron rich and completely cobalt substituted samples exhibit good change in electrical conductivity between 21% O_2 and 10 ppm O_2 in argon [9]. In the case of $SrCo_{1-x}Ti_xO_{3-\delta}$ system, in the work of Kharton et al. it was found that the oxygen permeability increases with the increase of titanium concentration [10]. The present work aims at the investigation of the structural, electrical and thermomechanical properties of Co-doped $SrTiO_3$ in a wide range of operation conditions, in order to determine the suitability of the prepared materials for applications in electrochemical devices.

2. Experimental

The $SrTi_{1-x}Co_xO_{3-\delta}$ ($x = 0$–0.4, $\Delta x = 0.05$) samples were synthesized according to the standard ceramic technology. In order to eliminate hydration effects, the powders were heated beforehand in air ($SrCO_3$, Co_3O_4 at 200 °C, TiO_2 at 800 °C). The stoichiometric mixture was synthesized at 1150 °C in air for 5 h (heating/cooling

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rate of 300 °C h^{-1}). After preliminary calcinations, these powders were ground in an agate mortar in acetone for 30 min and then a 4% solution of SKN26-M (Omsky Caoutchouc Company, Russia) in a mixture of acetone and gasoline at a ratio of 3:2 was added to the powder. The resulting mixture was poured onto a fluoroplastic substrate. The dried film was rolled to 1 mm thick plates using a roller machine and then 20 mm × 5 mm × 1 mm bars were cut from the plates. The bars were heated to 600 °C in air for 5 h with heating/cooling rate of 1 °C min^{-1}. Then the samples were heated to 1400 °C at 5 °C min^{-1} for 5 h in air. The density of the sintered ceramic samples determined by the hydrostatic weighting method in kerosene was no less than 96% of the density calculated from the XRD data.

The XRD analyses were carried out by using a DMAX-2500, Rigaku Co. Ltd., Japan device in CuKα radiation in $15° \le 2\theta \le 85°$. The unit cell parameters were defined using XRD data. The morphology and the structure of the ceramic membranes' surface were determined with the aid of scanning electron microscopy (JSM-5500 LV JEOL microscope). The conductivity of the as-prepared samples was investigated by using the standard four probe dc-method, in a wide range of temperatures, as well as in a wide range of oxygen partial pressures (1×10^{-19}–0.21 atm) at 900 °C. The experimental details of the oxygen permeability measurements were presented in a previous work [11]. Finally, the thermal expansion was measured in air during heating from room temperature to 900 °C using a quartz dilatometer, with a heating/cooling rate of 200 °C h^{-1}. The bar-shaped ceramic samples were prepared in the same way as those for the electrical conductivity measurements.

3. Results and discussion

In Fig. 1 typical XRD patterns of the $SrTi_{1-x}Co_xO_{3-\delta}$ samples are presented ($SrTiO_3$ – JCPDS No. 73-0661). Solid solutions with perovskite cubic structure (space group *Pm*3*m*) based on strontium titanate are formed. The obtained results are consistent with already published data. More precisely, in the case of $SrTiO_3$ the lattice parameter of the unit cell has been reported to be equal to 3.905 Å [12], whereas in the case of $SrTi_{0.8}Co_{0.2}O_{3-\delta}$ 3.895 Å [9], which are in good agreement with the data of the present work. The volume of a cubic unit cell decreases with the increase of the cobalt content. The observed behavior can be attributed to the fact that the ionic radius of Co^{4+} (r = 0.530 Å) is smaller in comparison to the radius of Ti^{4+} (r = 0.605 Å). In the work of Souza et al. where the system $Sr_{1-x}Co_xTiO_3$ was investigated, it was found that the lattice parameters decrease when the amount of cobalt increases, due to its smaller ionic radius [13]. However, the slow decrease of the unit cubic cell along with the increase of x is probably connected with the mixed valence state of cobalt Co^{+3}—Co^{+4} [12]. Therefore, the average effective radius of cobalt increases (Co^{3+}, r = 0.610 Å). As shown in Fig. 2, the lattice parameters' dependence as a function of Co-content in $SrTi_{1-x}Co_xO_{3-\delta}$ does not obey Vegard' s principle. The sharp curve is observed in the concentration range of x = 0.25–0.30. The non-linear dependence may derive from the existence of an isostructural phase of strontium cobaltite, which has characteristic peaks at the same angles as the phase of strontium titanate, and therefore they are not detectable by XRD. The formation of isostructural phases were also observed by other authors [14,15]. In the work of Kharton et al. it was found that in the oxide system $SrCoO_{3-\delta}$—$SrTiO_3$, in air and at temperatures below 1277 °C, two concentration ranges exist in which isostructural solid solutions with perovskite-like cubic crystal lattice form. The concentration range, in which both isostructural phases coexisted in $SrCo_{1-x}Ti_xO_{3-\delta}$, corresponded to $0.3 \le x \le 0.7$ [14]. According to the results of Pascanut et al. the homogeneity of the solution on the basis of cobaltite extends to 50 mol.% [15].

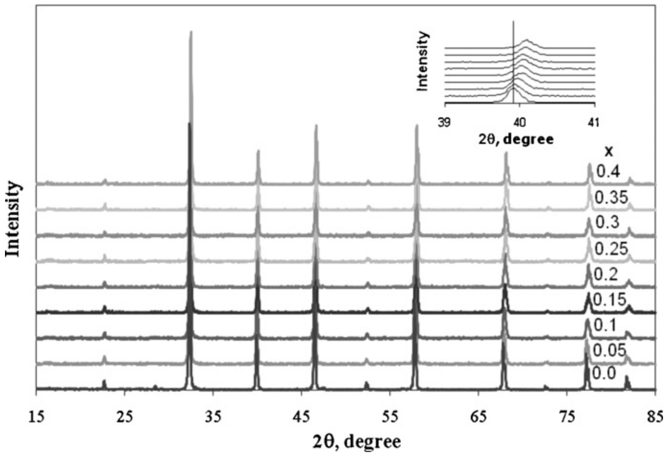

Fig. 1. Room temperature XRD data for the samples of $SrTi_{1-x}Co_xO_{3-\delta}$.

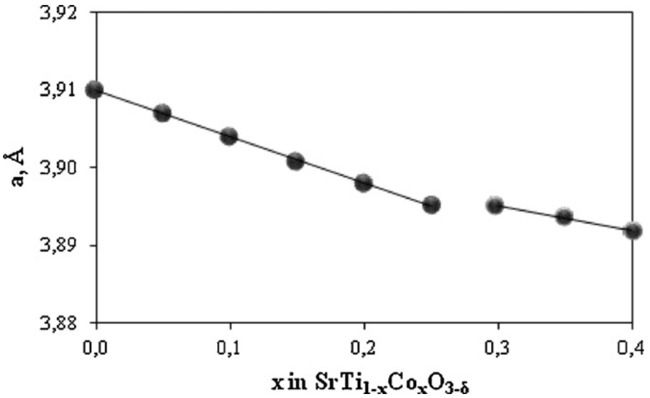

Fig. 2. Lattice parameters as a function of Co-content in $SrTi_{1-x}Co_xO_{3-\delta}$.

In Fig. 3, the SEM images of the as-sintered $SrTi_{1-x}Co_xO_{3-\delta}$ (x = 0.0, 0.1, 0.2 and 0.3) samples are presented. It can be observed that fine micro-structure with good connected grains and small amount of pores is observed for $SrTi_{1-x}Co_xO_{3-\delta}$ sintered at 1400 °C. At the same time, the Co addition results in a slight increase of relative densities of the ceramics with non-porous structure. In the case of $SrTiO_3$ and $SrTi_{0.9}Co_{0.1}O_{3-\delta}$, several fractions are distinguished: the fraction of grains with size less than 1 μm and the fraction of grains with an average size of approximately 6 μm. If the sintering process for these samples was incomplete, the presence of smaller and large grains, as well as porosity may have been observed. Moreover, pores with diameter of 10 μm exist on the surface of $SrTiO_3$ and $SrTi_{0.9}Co_{0.1}O_{3-\delta}$ samples. The $SrTi_{0.8}Co_{0.2}O_{3-\delta}$ sample's surface is nonporous and consists of grains with size of ~5–7 μm. Finally, in the case of $SrTi_{0.7}Co_{0.3}O_{3-\delta}$ the grain size corresponds to 3–8 μm and practically has no pores.

In Fig. 4 the temperature dependence of the electrical conductivity in air of the $SrTi_{1-x}Co_xO_{3-\delta}$ system is presented in Arrhenius coordinates. These materials have a semiconducting type of conductivity in the temperature range of 600–1000 °C. The conductivity increases with the increase of cobalt concentration. The maximum value for single-phase samples (x = 0.25) is 303.1 mS cm^{-1} at 1000 °C.

Fig. 5 shows the dependence of the electrical conductivity on the oxygen partial pressure at 900 °C. The SrTiO3 sample presents p-type of conductivity at oxidizing atmosphere and n-type of conductivity at reducing atmosphere. As seen in the graph, the increase of cobalt concentration leads to the increase of the electrical conductivity throughout the range of the oxygen partial pressure, which is maximized in the case of x = 0.25. This change of