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Structural features and high-temperature transport in $SrFe_{0.7}Mo_{0.3}O_{3-\delta}$

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ABSTRACT

The complex oxide $SrFe_{0.7}Mo_{0.3}O_{3-\delta}$ was obtained by combustion of the organometallic precursor in air followed by annealing in an argon flow at 1350 °C, and characterized with the help of X-ray and electron diffraction methods. Oxygen nonstoichiometry and electrical conductivity data were collected in the oxygen partial pressure range from 10^{-19} to 0.5 atm at temperatures 750–950 °C. The as-prepared single phase oxide $SrFe_{0.7}Mo_{0.3}O_{3-\delta}$ with the cubic double perovskite structure (SG *Fm*3*m*) is shown to undergo a structural transition to the tetragonal double perovskite phase (SG *I*4*mmm*) in the result of reducing treatment at $p_{O_2} = 10^{-12}$ atm and 950 °C. The ordered phases are characterized by a strong anti-site disordering of iron and molybdenum and nearly zero long-range ordering parameter. The maximal concentration of n-type carriers is about four times larger than of p-type carriers in the studied limits of oxygen pressure and temperature. The mobility of p-type carriers is found to vary within ~ 0.02–0.03 $cm^2\ V^{-1}\ s^{-1}$ with the migration energy of about 0.4 eV, while the n-type mobility being approximately twice higher does not practically depend on temperature. Such features as good electrical conductivity, which can rise up to 40 $S\ cm^{-1}$ in reducing conditions and a considerable amount of oxygen vacancies favorable for fast oxygen ion transport are beneficial for application of $SrFe_{0.7}Mo_{0.3}O_{3-\delta}$ as anode material in SOFCs and oxygen membrane for hydrogen generation by a water splitting.

1. Introduction

One of the important problems in the design of solid oxide fuel cells (SOFC) is the development of novel anode materials free of drawbacks typical for nickel-ceramic anodes such as poor stability under redox cycling, rapid degradation in the presence of sulfur compounds, and soot formation at dissociation of hydrocarbons on the nickel surface [1–4]. The possible alternative may be related to the use of oxide mixed conductors [5,6]. The important criteria of their applicability include high electron conductivity and stability in reducing atmospheres. In this relation, complex oxides $SrFe_{1-x}Mo_xO_{3-\delta}$ have attracted much attention in recent years. For instance, good electron conductivity and sufficient stability in harsh reducing conditions allowed successful testing of Sr_2FeMoO_6 as an anode material in dry hydrogen and methane [7,8]. However, Sr_2FeMoO_6 occurs unstable in oxidizing conditions; even when kept at room temperature in the air it tends to decompose with precipitation of strontium molybdate $SrMoO_4$ [9,10]. Therefore, the most intensive research activity has concentrated on the oxide with lower molybdenum content $SrFe_{0.75}Mo_{0.25}O_{3-\delta}$ that is quite stable in air. It is found that $SrFe_{0.75}Mo_{0.25}O_{3-\delta}$ does not display any signs of decomposition even after 24-h treatment in the 5% H_2 – 95% Ar flow at 1000 °C and in CO_2 atmosphere at 600 °C and 800 °C [11]. While being reactive in contact with yttria-stabilized zirconia (YSZ), $SrFe_{0.75}Mo_{0.25}O_{3-\delta}$ does not interact with $La_{1-x}Sr_xGa_{1-y}Mg_yO_{3-\delta}$ and $Ce_{1-x}Gd_xO_{2-\delta}$ solid electrolytes up to 1200 °C [11]. Moreover, $SrFe_{0.75}Mo_{0.25}O_{3-\delta}$ can tolerate sulfurous contaminants in fuel [12]. The advantageous features of $SrFe_{0.75}Mo_{0.25}O_{3-\delta}$ [13–16] suggest in-depth studies of the heavier doped compositions because increased molybdenum content is favorable for enhanced electron conductivity [17]. The highest solubility, $x = 0.3$, in air synthesized $SrFe_{1-x}Mo_xO_{3-\delta}$ is observed in work [18]. However, electron transport characteristics in $SrFe_{0.7}Mo_{0.3}O_{3-\delta}$ have never been reported. With this in mind, we synthesized $SrFe_{0.7}Mo_{0.3}O_{3-\delta}$ in order to obtain a material with maximal conductivity and good stability in reductive and oxidative conditions, and carried out an examination of its structural and transport properties.

2. Experimental

The oxide with nominal composition $SrFe_{0.7}Mo_{0.3}O_{3-\delta}$ was synthesized by means of the auto-combustion method. Carbonyl iron, high purity strontium carbonate $SrCO_3$, and molybdenum oxide MoO_3 were

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taken as starting materials. The iron and strontium carbonate in appropriate amounts were dissolved in some excess of nitric acid, while molybdenum oxide was dissolved in ammonia water. The obtained solutions were mixed in a beaker and added with glycine at continuous stirring. The resulting viscous gel was slowly heated on a hot plate until evaporation of water and self-ignition of the residue. The combustion product was calcined in air at 900 °C for 5 h. Then, the material was crushed in an agate mortar in alcohol media, dried, and formed into discs under 2 kbar of uniaxial pressure. Several discs were sintered in air at temperatures from 1200 to 1350 °C for 10 h. The other part of the pellets was fired in a stream of argon with $p_{O_2} \sim 10^{-4}$ atm at 1350 °C for 10 h. Rectangular bars $2 \times 2 \times 15$ mm^3 were cut from the obtained ceramics for conductivity measurements. Some amount of the ceramics was crushed into powder for X-ray examination and for the use in coulometric titration measurements. A part of the pulverized material was treated at 950 °C in the gas mixture CO /CO$_2$ /Ar with $p_{O_2} = 10^{-12}$ atm.

X-ray powder diffraction (XRD) data were collected at room temperature with a STADI-P (STOE) diffractometer in transmission geometry with a linear mini-PSD detector using CuKα1 radiation in the 2θ range from 10 to 120° with a step of 0.02°. Polycrystalline silicon (a = 5.43075(5) Å) was used as an external standard. Possible impurity phases were examined by comparison of the obtained XRD data with the PDF2 database (ICDD, USA, Release 2009). The phase composition and crystalline structure parameters were determined by the Rietveld method with the use of PCW 2.4 software package [19]. Thoroughly milled specimens were ultrasonically stirred in isobutyl alcohol bath and used to form sediments upon a carbon film. The film with deposited sediments was supported on a copper grid for the electron microscopy studies that were performed with the help of a JEM-200 CX (JEOL) microscope.

The oxygen content measurements in the oxide were carried out by means of a coulometric titration technique under variation of partial oxygen pressure in the interval between 10^{-19} and 0.5 atm at 750–950 °C. The basics of the method and experimental arrangements are described in work [20]. Electrical conductivity was measured by a four-probe dc technique in the range of oxygen partial pressure from 10^{-19} atm to 0.5 atm at 750–950 °C. The measuring electrochemical cell was made of YSZ ceramics and equipped with two pairs of Pt electrodes that served as oxygen pump and sensor in order to maintain and control partial pressure (activity) of oxygen over the sample. The measurements were carried out in isothermal runs starting from 950 °C in the mode of decreasing oxygen pressure. The equilibration criterion at given values of temperature and oxygen pressure was selected equal to variations in the logarithm of conductivity less than 0.0001 S cm^{-1} per minute. After the low-pressure limit of measurements was attained, the oxygen pressure in the cell was reversed back to the starting pressure (0.5 atm), the measuring temperature was decreased to 900 °C, and the experiment was continued in likewise mode. Additional experimental details can be found elsewhere [21].

3. Results and discussion

3.1. Phase composition and structural features

In contrast to the data [18], the air synthesized specimens contained admixtures of SrMoO$_4$ molybdate, which did not disappear at variations of the firing regime. On the contrary, annealing in argon flow ($p_{O_2} \sim 10^{-4}$ atm) resulted in the formation of single-phase samples with a double perovskite structure. Attempts to equilibrate the single-phase material in the air at 950 °C for 25 h resulted in the appearance of SrMoO$_4$ admixtures, Fig. 1. The refinement of respective XRD spectra confirmed the presence of about 1.8% mass. of strontium molybdate. Hence, it can be easily estimated that the separation of the second phase is to be accompanied by the change in the composition of the parent phase to SrFe$_{0.711}$Mo$_{0.289}$O$_{3-\delta}$. Taking this result in view the maximal solubility of molybdenum at a synthesis of SrFe$_{1-x}$Mo$_x$O$_{3-\delta}$ in the air can be evaluated as $x \sim 0.29$. The XRD pattern of the argon-prepared single-phase sample SrFe$_{0.7}$Mo$_{0.3}$O$_{3-\delta}$ is shown in Fig. 2. The cubic double perovskite structure (SG $Fm3m$) can be observed [22]. The grain size of about 135 nm and low lattice strain of 0.02% were estimated for cubic phase. It should be noted that the intensity of the superstructure reflections $(hkl)_{\text{cub}}$ with $h + k + l \neq 2n$, which depends on the degree of the Mo/Fe–site ordering, is close to zero. The best fitting results (R_p = 1.52, R_{wp} = 2.16) of the XRD data in Fig. 2 were obtained for the cubic double perovskite phase with the unit cell parameter a = 7.8750 Å. This value agrees well with the lattice parameter of cubic SrFe$_{0.7}$Mo$_{0.3}$O$_{3-\delta}$ obtained in previous works: a = 7.8776 Å [23] and a = 7.870(2) Å [18]. The long-range ordering parameter η for cubic SrFe$_{0.7}$Mo$_{0.3}$O$_{3-\delta}$ was found to be zero in our study. The supposition of a non-zero ordering parameter $\eta = P_{Mo}^{(1)} - P_{Mo}^{(2)} = P_{Fe}^{(2)} - P_{Fe}^{(1)}$, where $P_{Mo}^{(1)}$, $P_{Mo}^{(2)}$, $P_{Fe}^{(1)}$, $P_{Fe}^{(2)}$ stand for probabilities to find molybdenum and iron in the two possible sites 4a (0,0,0) and 4b (0.5,0.5,0.5), resulted in an appreciable divergence with the experimental data. As an example, the XRD profile calculated for the ordered double cubic perovskite phase near the (111) reflection is shown in Fig. 2 (inset). In the calculations, we used η = 0.4, which is smaller than the highest possible value η = 0.6 in the double perovskite SrFe$_{0.7}$Mo$_{0.3}$O$_{3-\delta}$ (S.G. $Fm3m$) and larger than the experimental value

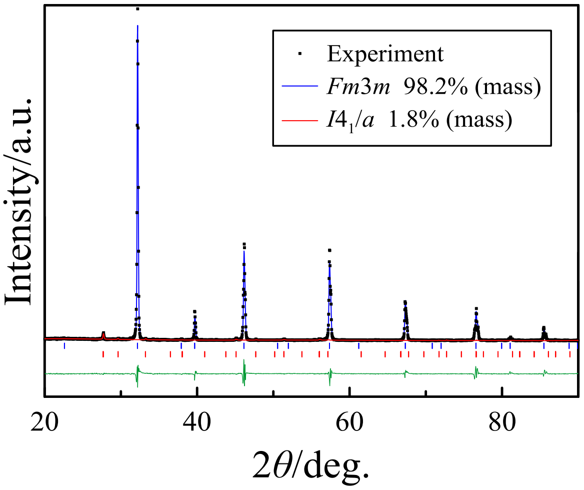

Fig. 1. XRD pattern of SrFe$_{0.7}$Mo$_{0.3}$O$_{3-\delta}$, annealed in air at 950 °C for 25 h. Oxide was synthesized in argon and has been single-phase before treatment in air.

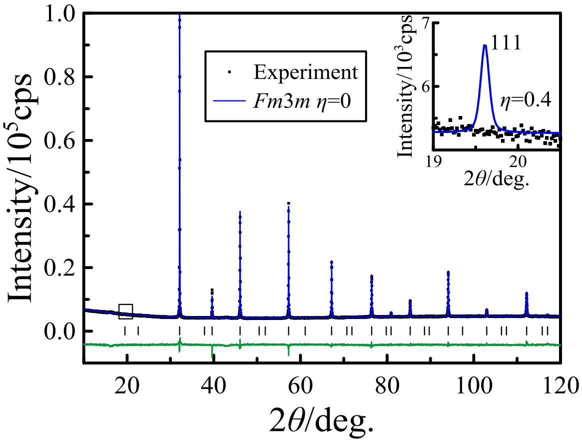

Fig. 2. Experimental XRD pattern of SrFe$_{0.7}$Mo$_{0.3}$O$_{3-\delta}$, equilibrated in argon, and calculated XRD profile for double perovskite phase ($Fm3m$) with long-range order parameter η = 0. The insert shows a fragment of XRD pattern and calculated XRD profile for double perovskite phase with η = 0.4 in the vicinity of the reflection $(111)_{\text{cub}}$.