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Electrical conductivity of $Ca_{1-x}Sr_xTi_{0.65}Fe_{0.35}O_{3-\delta}$, $x = 0$, 0.5 and 1, polycrystalline compounds in the 300–500 K range

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ABSTRACT

Bulk and grain boundary electrical conductivity of oxygen deficient $Ca_xSr_{1-x}Ti_{0.65}Fe_{0.35}O_{3-\delta}$, $x = 0$, 0.5 and 1.0, polycrystalline specimens were evaluated by impedance spectroscopy measurements in the 5 Hz–13 MHz frequency range from 300 to 500 K. The ceramic powders were synthesized by solid state reaction and by a chemical route, the polymeric precursor technique. The X-ray diffraction of the samples at room temperature shows the following perovskite crystalline structures: cubic for $x = 0$ and orthorhombic for $x = 0.5$ and 1.0. The impedance plots are composed of two semicircles ascribed to grains (bulk) and interfaces (grain boundaries) contributions. The impedance data show that sintered pellets using powders prepared by solid state synthesis present higher intergranular and intragranular resistivity values than pellets prepared by the chemical route. Observations of scanning probe microscopy topographic images of the surfaces of the sintered pellets show evident differences between the grain morphology of the pellets prepared with powders synthesized by the two routes.

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1. Introduction

Many studies are focused in the $SrTiO_3$ (STO) compound mainly for its thermoelectric behavior. STO-based oxides are a promising group of *n*-type thermoelectric materials because they exhibit excellent electronic transport properties and are basically stable at high temperatures [1]. Successful aliovalent doping yields compounds with different interesting properties either in bulk ceramic or thin/thick film specimens.

More recently, several studies on $SrTi_{1-x}Fe_xO_{3-\delta}$ (STFO) compounds were undertaken looking for suitable compositions for use in temperature independent oxygen automotive lambda sensors [2–9]. The main reported conclusions are that these compounds exhibit mixed ionic–electronic conductivity at elevated temperatures (>550 °C), predominant *n*-type electronic conductivity at low oxygen pressures, ionic conductivity at intermediate oxygen pressures, and *p*-type electronic conductivity at high oxygen pressures, and that the oxygen vacancy concentration is independent on the partial pressure of oxygen [5]. The electrical resistance of these compounds was studied in the 700–1000 °C in the oxygen partial pressure range from 10^{-4} to 1 bar [4]. Fe ions are considered to be one of the main constituents of the $SrTi_{0.65}Fe_{0.35}O_{3-\delta}$ compound and not just an acceptor impurity dopant with such a high level [5]. Moreover, the composition $SrTi_{0.65}Fe_{0.35}O_{3-\delta}$, in which 0.35 mol of Ti is replaced by Fe, shows a zero temperature coefficient of resistance (zero-TCR), i.e., the electrical response depends only on the partial pressure of oxygen in a certain temperature range, being consequently the optimized composition for a temperature independent oxygen sensor [2,3]. For this reason, electrical measurements on compositions with 0.35 mol Fe are here reported.

An interesting approach to the study of the electrical behavior of polycrystalline compounds is the electrochemical impedance spectroscopy technique. There are several complex formalisms to analyze the impedance spectroscopy data. Here we expose the data using two plots: the impedance plot, $[Z''(\omega) \times Z'(\omega)]$, and the Bode reactance plot, $[Z''(\omega) \times \log f]$. The former highlights the resistive components and the latter allows for visualizing better the frequency dependence [10]. The impedance plot is composed of one or more overlapped semicircles, which may be assigned to different contributions to the electrical resistivity due to bulk (grains) and to interfaces (mainly grain boundaries) when the compound is a polycrystalline ceramic [11]. Bode plots are either $|Z(\omega)|$ or $Z''(\omega)$ as a function of the logarithm of the frequency. Depending on the temperature and on the frequency range the experiment is performed, the impedance plot $[-Z''(\omega) \times Z'(\omega)]$ usually presents in the complex plane two visually separated semicircles [10,12], each one being represented by an equivalent circuit composed of a resistor in parallel with a capacitance ($R//C$). The high-frequency semicircle is due to the electrical response of the bulk of the polycrystalline specimen, whereas the low frequency one is assigned to the electrical properties of the grain

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boundaries, which may act as blockers to charge carriers. The capacitance may be represented by a constant phase element, CPE, when the center of the semicircle lies below the Z' axis. The impedance of a CPE is given by $Z_{CPE} = Q^{-1}(j\omega)^{-\alpha}$, $0 \leq \alpha \leq 1$, $\alpha = 1$ representing a pure capacitance, given by $Z_C = 1/(j\omega C)$ [13]. For the estimation of capacitances associated with impedance arcs, the equation $Cps = (RQ)^{1/\alpha}/R$ is used [14,15]. R is the resistance determined at the intersection of the impedance arc with the real axis. The impedance spectroscopy technique allows, at least to a first approximation, the separation of impedance contributions from grain interior (bulk) and grain boundaries [16].

Detailed impedance analysis of bulk conductivity of Ni-doped $SrTiO_3$ and of grain boundaries in acceptor (Ni, Fe and Al) doped $SrTiO_3$ has been given by Waser [17,18]. Oxygen vacancies were suggested as the mobile species for the electric conduction [17], and the high resistive grain boundary layer was ascribed to a space charge depletion layer [18]. The behavior of the electrical conduction at grain boundaries in polycrystalline $SrTiO_3$ is usually considered to be due to space-charge layers in the bulk regions adjacent to the interfaces [19]. Charge and mass may be blocked at these interfaces. For single crystalline $SrTiO_3$ specimens, oxygen vacancies at the grain boundaries are considered responsible for the intrinsic correlation between microstructure and impedance [20]. Impedance spectroscopy experiments were already performed in $SrTiO_3$ polycrystalline specimens with different amounts of Fe_2O_3, 1%, 2% and 3% [21] and with 0.05, 0.07, 0.10, 0.15, 0.2, 0.4 and 0.5 mol [22]. The electrical behavior of grain boundaries as well as the grain growth was found to strongly depend on the Fe content. A detailed experimental work was also reported concerning the electronic structure, the defect chemistry and the transport properties of $SrTiFe_xO_{3-y}$ solid solutions, oxide ion conductivity being proposed to be predominant at intermediate oxygen partial pressures [5].

Recent applications of strontium titanate based materials have been reported on anode for Solid Oxide Fuel Cells due to their electrical behavior and mechanical compatibility with the yttria-stabilized zirconia solid electrolyte [23,24].

Many research works have also been carried out in $CaTiO_3$ (CTO), which has a distorted perovskite structure with orthorhombic symmetry at room temperature. CTO shows the ability of forming solid solutions with a large number of oxides and, therefore, many compounds have been synthesized for different applications [25–31]. Bulk and grain boundary conductivity of $Ca_{0.97}Ti_{1-x}Fe_xO_{3-\delta}$ (x = 0, 0.01, 0.035, 0.07 and 0.15) materials show that the electrical conductivity increases with Fe addition with a behavior similar to Fe-doped strontium titanate [32].

Here a careful examination was pursued on the analysis of impedance data of $SrTi_{0.65}Fe_{0.35}O_{3-\delta}$, $CaTi_{0.65}Fe_{0.35}O_{3-\delta}$ and $Ca_{0.5}Sr_{0.5}Ti_{0.65}Fe_{0.35}O_{3-\delta}$ synthesized by two techniques, namely, the polymeric precursor (chemical route) and the solid state reaction (ceramic route) techniques. The ionic radii of Ca^{2+} and Sr^{2+} are 1.48 and 1.58 Å, respectively, suggesting a favorable accommodation of the Ca^{2+} ion for Sr^{2+}in the ABO_3 structure of the perovskite lattice. The large content of Fe substitution for Ti in $SrTiO_3$ and in $CaTiO_3$ creates oxygen vacancies, enhancing their ionic conductivity relatively to the undoped titanates. Impedance, Bode and Arrhenius plots are presented.

2. Experimental

$Ca_{1-x}Sr_xTi_{0.65}Fe_{0.35}O_{3-\delta}$, x = 0, 0.5 and 1 (hereafter CTFO, CSTFO and STFO), powders were prepared according to two techniques: (1) solid state reaction, consisting in mixing stoichiometric amounts of $CaCO_3$, $SrCO_3$, TiO_2 and Fe_2O_3 (all from Alfa Aesar) for 2 h in alcoholic medium in a turbula mixer, drying the mixture, and promoting solid solution formation by calcination in air at 1250 °C for 15 h [33]. Simultaneous thermogravimetry and differential thermal analyses, not reported here, were carried out in a Netzsch STA409E equipment in the room temperature – 1550 °C-room temperature cycle under flowing synthetic air, to be sure that the heat treatment at 1250 °C completely reduces both carbonates; (2) polymeric precursor technique, consisting of mixing under stirring at 100 °C stoichiometric amounts of calcium carbonate ($CaCO_3$), strontium carbonate ($SrCO_3$), iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) and titanium isopropoxide ($C_{12}H_{28}O_4Ti$) (all from Alfa Aesar), in an acid solution (H_2O/HNO_3 = 20/1); after stirring for 20 min, citric acid and ethylene glycol were added stepwise to the solution under stirring for 30 min, yielding a highly viscous resin, which had the organics burnt out after calcination at 200, 250 and 300 °C for 2 h and at 800 °C for 5 h. These temperature profiles were chosen after evaluating the thermogravimetric analysis of the resins.

X-ray diffraction experiments were carried out in all compositions in a Bruker-AXS D8 Advance X-ray diffractometer with θ–2θ Bragg–Brentano configuration with Cukα radiation with Ni filter, 40 kV–40 mA, in the 10–90° 2θ range, 0.05° step size, and 5 s counting time per step.

The powders of each composition, namely, STFO, CTFO and CSTFO, prepared by both the solid state synthesis (hereafter SS) and the polymeric precursor (PP) technique, were pressed to 12 mm diameter disks (uniaxially at 96 MPa, followed by isostatically at 210 MPa). Sintering was performed in air in a programmable Lindberg-BlueM furnace at 1300 °C for 2 h, 5 °C/min heating and cooling rates.

For the impedance measurements, thin silver layers were deposited in the parallel surfaces of the sintered pellets. These electrodes are known to give rise to negligible electrode polarization contribution in the impedance plot and, consequently, do not produce overlapping with the grain boundary arc in the low frequency region. The impedance response of the polycrystalline specimens was determined with a 4192A Hewlett Packard LF Impedance Analyzer connected to a series 360 Hewlett Packard Controller over the frequency range of 5 Hz–13 MHz, with signal amplitude of 100 mV. Some measurements were performed with 50, 100, 200 and 500 mV to determine the linear response region and the lowest input signal that gives rise to the less noisy electrical responses. Measurements were made in the temperature range $300 < T(\mathrm{K}) < 500$ at atmospheric air pressure. For each impedance measurement, the temperature was expected to be constant within 0.5 °C. The $[-Z''(\omega) \times Z'(\omega)]$ impedance plots were deconvoluted using a special software to obtain the intergranular (grain boundary – gb) and intragranular (bulk or grain – g) electrical resistances, frequencies and decentralization angles [34].

The polished surfaces of the sintered pellets were observed in a scanning probe microscope (Jeol JSPM-5200, contact mode, dynamic force topography images, 10 μm × 10 μm scanning area). Polishing was done sequentially with silicon carbide powders and 30, 15, 6, 3 and 1 μm diamond pastes, with further ultrasonic cleaning with isopropanol. The polished specimens were thermally etched at 1200 °C/20 min to reveal the surface grain boundaries.

3. Results and discussion

Fig. 1 shows the results of the X-ray diffraction experiments on STFO, CTFO and CSTFO powders prepared by the solid state synthesis and by the polymeric precursor technique.

Rietveld analyses performed with the GSAS software [35] of X-ray diffraction data of the compounds synthesized by the polymeric precursor technique give the following values for the lattice parameters: perovskite orthorhombic with a = 5.41309 (0.00004) Å, b = 7.65496 (0.00006) Å and c = 5.41091 (0.00008) Å

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