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Effect of oxygen partial pressure on the bulk and grain-boundary components of conductivity in $(Yb_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ ($x = 0$, 0.05, 0.1) solid solutions

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ABSTRACT

The electrical conductivity of $(Yb_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ ($x = 0$, 0.05, 0.1) pyrochlore solid solutions in a flowing mixture of oxygen and nitrogen has been determined as a function of oxygen/nitrogen ratio using impedance spectroscopy. The materials are shown to be oxygen ion conductors. The 700 °C conductivity of undoped $Yb_2Ti_2O_7$ is $\sim 1 \times 10^{-3}$ S/cm and that of $(Yb_{0.95}Ca_{0.05})_2Ti_2O_{7-\delta}$ and $(Yb_{0.9}Ca_{0.1})_2Ti_2O_{7-\delta}$ is $\sim 7 \times 10^{-3}$ S/cm. The increase in the bulk and grain boundary conductivity in the $(Yb_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ ($x = 0$, 0.05, 0.1) series is connected with a Ca doping effect, which ensures the high oxygen vacancy concentration in the grain interior and at grain boundaries.

1. Introduction

The ability to create new materials with the highest possible oxygen ion conductivity is a priority issue in modern materials research in the context of the development of advanced power sources capable of chemical-to-electrical energy conversion. Such materials could find a variety of electrochemical applications, including high-temperature solid oxide fuel cells (SOFCs), oxygen separation membranes, and gas sensors. Yttria-stabilized cubic zirconia (ZrO_2 – 9 mol% Y_2O_3) is the best known and most widely used solid electrolyte for state-of-the-art SOFCs. It is, however, of limited use at high temperatures, ~1000 °C, both as an electrolyte and as a component of the SOFC anode material Ni/ZrO_2–9 mol% Y_2O_3, because its oxygen ion conductivity drops considerably after 1000–2000 h of use. In connection with this, there is high current interest in advanced high-temperature solid electrolytes that would possess an oxygen ion conductivity of ~0.02–0.2 S/cm at lower temperatures, ~700 °C.

Potentially attractive solid electrolytes are $Ln_2M_2O_7$ pyrochlores in the Ln_2O_3 – MO_2 (Ln = Sm – Lu; M = Ti, Zr, Hf) systems, which possess intrinsic ionic conductivity. Intrinsic ionic conductors are known to be more stable to degradation than solid electrolytes with impurity conduction. Pyrochlore–defect fluorite (order–disorder) phase transitions [1] and the associated oxygen ion conductivity of the high-temperature phase [2], comparable to the conductivity of 9 mol% Y_2O_3-stabilized ZrO_2, were first found in the $Ln_2Zr_2O_7$ (Ln = Nd, Sm, Gd) zirconate pyrochlores. Among rare-earth titanates, ionic conduction was first found in $Y_2(Ti_{2-x}Y_x)O_{7-\delta}$, $Gd_2Ti_2O_7$, and the solid-solution systems $(Gd_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ and $Gd_2(Ti_{1-x}Zr_x)_2O_7$ [3–5]. In recent years, the family of oxygen ion conducting pyrochlores has been considerably extended: new oxygen ion conductors have been synthesized, $Ln_2Ti_2O_7$ (Ln = Dy – Lu) titanates and $Ln_2Hf_2O_7$ (Ln = Eu, Gd) hafnates, that have a disordered pyrochlore structure containing cation antistructure pairs and oxygen vacancies [6–10]. Through calcium doping of $Yb_2Ti_2O_7$, Shlyakhtina et al. [11] prepared for the first time the $(Yb_{0.9}Ca_{0.1})_2Ti_2O_{6.9}$ solid solution with high ionic conductivity, $\sim 2 \times 10^{-2}$ S/cm at 740 °C, the highest among the known pyrochlores. Later work [12] has confirmed that the oxygen transport in the $(Yb_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ ($x = 0$, 0.05, 0.1) ionic conductors follows a vacancy mechanism. Neutron diffraction studies of the $(Yb_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ ($x = 0.05$, 0.1) substitutional solid solutions revealed oxygen vacancies in positions 48f and 8b of the pyrochlore structure [12], which are basic to oxygen ion transport in pyrochlores [13]. Deng et al. [14] were the first to study the $(Yb_{0.98}Ca_{0.02})_2Ti_2O_{6.98}$ solid solution under reducing conditions. According to their results, the total conductivity of this material remains unchanged under reducing conditions, indicating that it possesses high stability under such conditions and, hence, can be used not only as an electrolyte but also as an SOFC anode material [15].

The purpose of this work was to study the relationship between the bulk and grain-boundary conductivities of $(Yb_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ ($x = 0$, 0.05, 0.1) as a function of oxygen partial pressure with the

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aim of confirming that the high-temperature conductivity of this pyrochlore-like solid solution has an ionic character.

2. Experimental

$(Yb_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ (x = 0, 0.05, 0.1) materials were synthesized from Yb_2O_3, CaO and TiO_2 powders mechanically activated in an eccentric vibratory mill with a 120 cm^3 vial volume [12]. The sample weight was 21 g, the ball-to-powder weight ratio was ~15, and the vibration amplitude and frequency were 0.5 cm and 50 Hz.

In conductivity measurements, we used disc-shaped samples 10 mm in diameter and 3–4 mm in thickness, prepared by pressing the milled powders at 950 MPa, followed by heat treatment at 1400 °C for 4 h ($(Yb_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ with x = 0.05 and 0.1) and at 1600 °C for 4 h (pure $Yb_2Ti_2O_7$). The ceramics were characterized by x-ray diffraction (XRD) on a DRON-3 M automatic diffractometer (Cu K $_\alpha$; 2Θ = 15–65°; 0.1° step).

The microstructure of the sintered ceramics was examined using scanning electron microscopy (JEOL JSM-6390LA). Prior to taking images the ceramic samples were manually ground, polished with diamond paste and finally thermally etched at 1250 or 1400 °C (pure $Yb_2Ti_2O_7$) for 0.5 h.

Conductivity was determined by impedance spectroscopy (Zahner IM6E bridge) at frequencies from 0.01 Hz to 10 MHz.

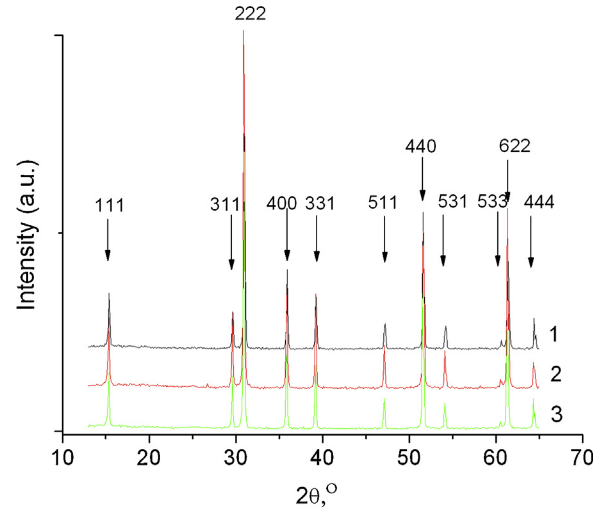

Fig. 1. XRD patterns of the $(Yb_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ (x = 0, 0.05, 0.1) solid solutions.

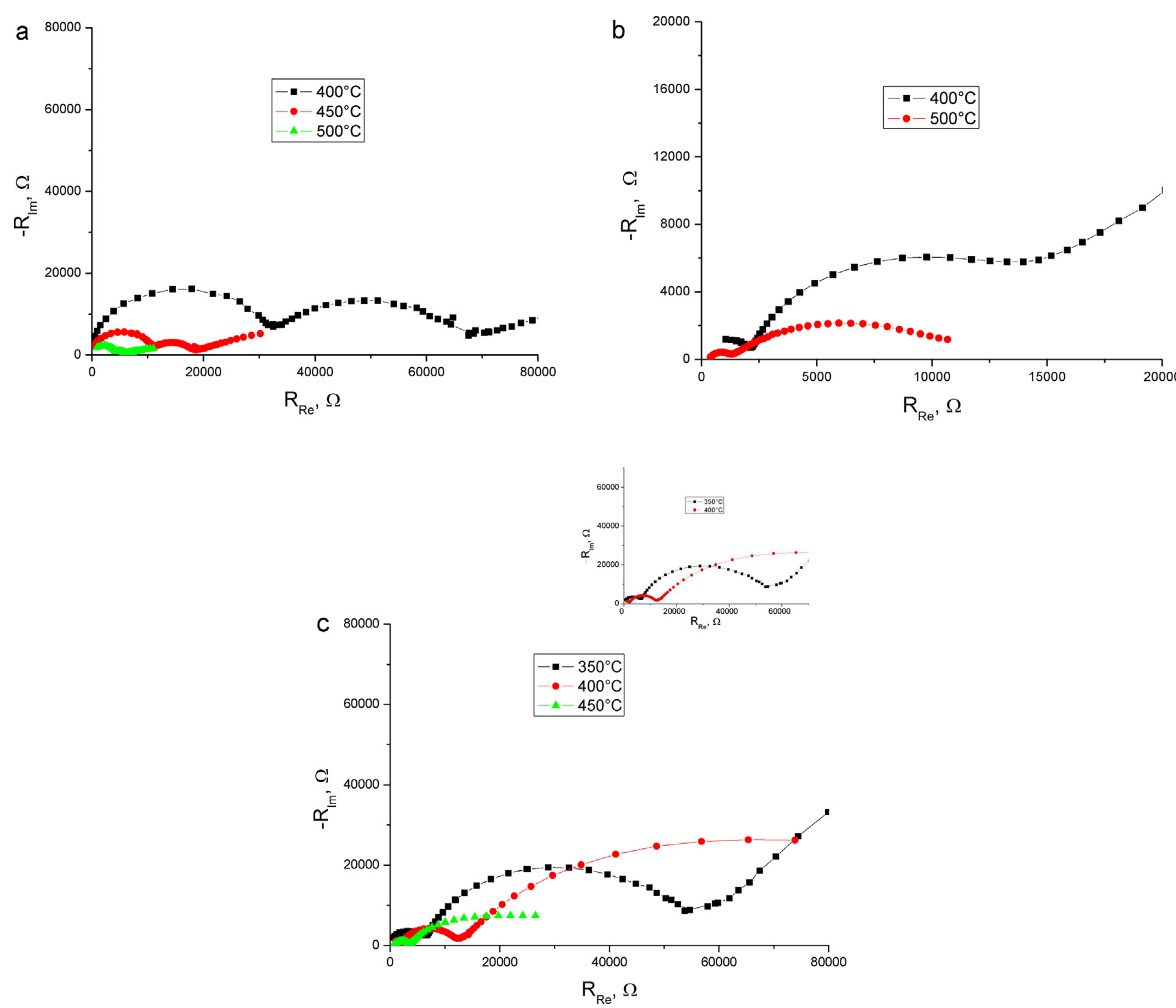

Fig. 2. Impedance spectra of the $(Yb_{1-x}Ca_x)_2Ti_2O_{7-\delta}$ (x = 0, 0.05, 0.1) solid solutions in air: (a) $Yb_2Ti_2O_7$ at 400, 450, and 500 °C; (b) $(Yb_{0.95}Ca_{0.05})_2Ti_2O_{7-\delta}$ at 400 and 500 °C; (c) $(Yb_{0.9}Ca_{0.1})_2Ti_2O_{7-\delta}$ at 350, 400, and 450 °C (inset: data obtained at 350 and 400 °C).