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The influence of Al dopant on the structure, densification behavior and electrical conductivity of heavily doped $Sm_2Ti_2O_7$

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ABSTRACT

Powders with compositions $Sm_2Ti_{2\text{-}x}Al_xO_{7\text{-}\delta}$ ($x = 0$, 0.1, 0.2) were synthesized using a modified Pechini method. Thermal treatment at 1173 K leads to the formation of pyrochlore structure, together with other secondary phases. A decrease in linear shrinkage and shrinkage rate after partial substitution of titanium with aluminum was evidenced by dilatometry. Mainly pyrochlore phase was obtained for $Sm_2Ti_2O_7$ and $Sm_2Ti_{1.9}Al_{0.1}O_{7\text{-}\delta}$ after thermal treatment at 1300 °C, while Al_2TiO_5 secondary phase was evidenced in $Sm_2Ti_{1.8}Al_{0.2}O_{7\text{-}\delta}$ pellet. Moreover, the addition of aluminum leads to the decrease in grain size and the presence of Al_2TiO_5 determine microcracks formation. The electrical conductivity of the single-phase samples was evaluated using EIS measurements. Al-doped sample exhibited higher conductivity and lower activation energy of conduction than undoped sample over the entire investigated temperature range for both bulk and grain boundaries components.

1. Introduction

The research in the field of Solid Oxide Fuel Cells (SOFCs) is currently focused on the decrease of their operation temperature down to intermediate range (773–973 K). Pyrochlore oxides with general formula $A_2B_2O_7$ have an ordered crystalline structure, where A^{3+} cations are octa-coordinated and B^{4+} cations are hexa-coordinated [1] (Fig. 1). A sites are usually occupied by trivalent lanthanides or actinides, while smaller cations such as Ti, Zr, Sn or Hf reside on B sites [2]. Due to their structural characteristics, this type of materials exhibits interesting physical and chemical properties leading to different applications, such as SOFC electrolyte [3].

Even if computing simulations of oxygen migration in A^{3+}/B^{4+} pyrochlores predicted a strong influence of the average B-site cation size [4], experimental studies do not support these predictions [5]. Doping was proved to be an effective way to tune the electrical, optical, thermal, catalytical properties of oxides with pyrochlore structure [6,7].

Al doping was successfully used to improve titania properties [8,9], the maximum Al content being about 15 at.%.

Fisher et al. [10] evidenced that alumina additions of less than 0.2 mol% in $BaTiO_3$ leads to the increase in nucleation and growth rates of abnormal grains More recently, Zhao et al. [11] revealed the positive effect of alumina chemical coating on the energy efficiency of fine-grain $BaTiO_3$-based ceramics.

For titanate pyrochlores, Al^{3+} is a suitable dopant as its ionic radius (0.535 Å) is close to the hexa-coordinated host Ti^{4+} (0.605 Å). The solubility limit of Al in titanate pyrochlore is still unknown [5].

Al_2O_3 was successfully used as sintering aid and to improve mechanical and electrical properties of SOFC electrolyte materials [12,13].

Ti^{4+} substitution with Al^{3+} generates oxygen vacancies according to the following equation written in Kröger-Vink notation:

$$Al_2O_3 \rightarrow 2Al'_{Ti} + 3O_O^x + V_O^{\cdot\cdot}$$

High concentration of defects and, consequently, high dopant concentrations are required to obtain an ionic conductivity suitable for SOFC electrolyte applications. Moreover, in this case the electrolyte has to be very dense.

Unlike traditional ceramic method, highly homogeneous nanocrystalline solid oxides with pyrochlore structure can be obtained

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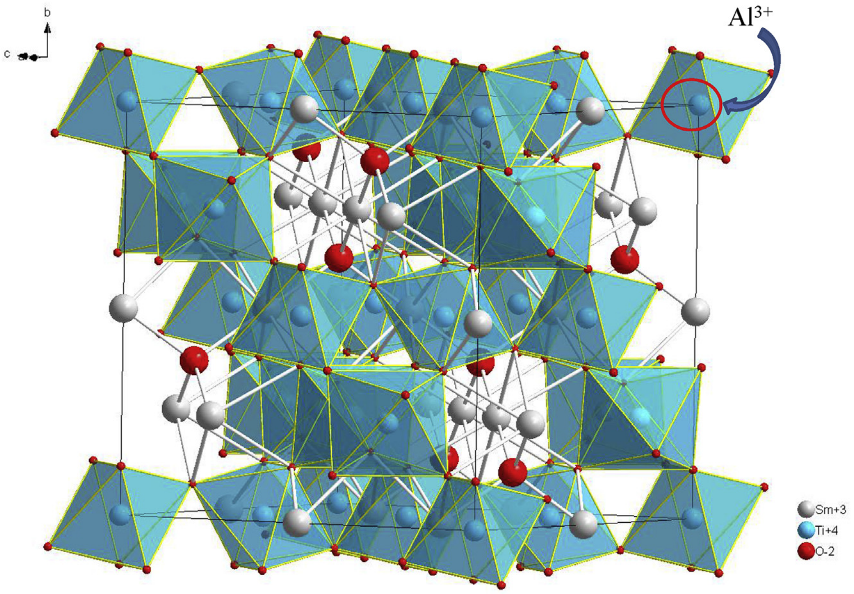

Fig. 1. Schematic presentation of $Sm_2Ti_2O_7$ pyrochlore unit cell.

by the sol-gel method [3] under mild conditions. Recently, the sol-gel technique was used to obtain an efficient $Sm_2Ti_2O_7$ photocatalyst [14] and to improve the optical properties of pyrochlore rare earth titanates [15]. In this context, in our study highly doped $Sm_2Ti_2O_7$ was synthesized using a modified Pechini method and the effect of aluminum addition on densification behavior was evaluated. It is worthmentioning that for the substitution of 5% Ti with Al in $Sm_2Ti_2O_7$, the ratio between the ionic radius of cations from A and B sites is similar with the one characteristic to the sample obtained by the substitution of 10% Sm with Ca ($r_A/r_B = 1.79$), this stoichiometry possessing high ionic conductivity [5].

2. Experiment

In our study, hydrated nitrate powders ($Sm(NO_3)_3 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$) and titanium (IV) isopropoxide (Sigma Aldrich) were used as precursors. Powders with stoichiometry $Sm_2Ti_{2-x}Al_xO_{7-\delta}$ ($x = 0, 0.1, 0.2$), designated ST, STA-1, and STA-2, respectively, were synthesized using a modified Pechini method. Citric acid was added in the reaction mixture as complexation agent and ethylene glycol was used as polymerization agent. The pH of the reaction mixture was adjusted to 5 with triethylamine in order to avoid the precipitation of components. The solution was heat-treated at 80 °C until a gel was obtained by the removal of excess solvent. The gel was dried at 180 °C over night and the as-obtained solid resin was further calcined at 900 °C for 5 h in air in a tube furnace.

Conventional sintering experiments were carried out on green pellets (5 mm diameter, 4–7 mm thickness) obtained by uniaxial pressing of the calcined powders. Measurements were performed in static air with a heating rate of 10 °C/min in the temperature range r.t. – 1673 K with a horizontal dilatometer DTA L75 PT from Linseis.

Powders calcined in air were further processed into pellets by uniaxial pressing in a 10 mm diameter stainless steel die. The as-obtained pellets were sintered at 1573 K for 5 h.

X-ray diffraction analysis of powders and sinters was carried out with a Rigaku SmartLab diffractometer in the range $2\theta = 20–120°$ with a 0.02° step using CuK_α radiation. ICSD database was used for phase identification and the unit cell parameters were refined by pattern matching using the FullProf software [16].

Raman spectra were recorded at room temperature with an inVia confocal Raman microscope (Renishaw) equipped with a diode DPSS visible laser source (532 nm) and a Peltier cooled CCD detector. The single beam power of the laser was 25 mW and the 50x objective of the microscope was used.

The morphology of calcined powders and sintered pellets was evidenced using a high resolution scanning electron microscope (Hitachi SU8010). The powders were dispersed onto a carbon tape, while the sintered pellets were polished using SiC tape with various grits followed by thermal etching at 1473 K for 1/2 h.

The electrical conductivity of the single-phase samples under air was evaluated using two-point probe impedance spectroscopy technique. The impedance measurements were performed with a Zahner IM6eX analyzer in the 3 MHz–0.10 Hz frequency range using gold electrodes. The amplitude of the AC perturbation signal was 50 mV and the mmeasurements were carried out in the temperature range 773–1073 K.

3. Results and discussion

The XRD patterns of the solid oxide powders obtained after calcination under air at 1173 K are shown in Fig. 2. The powders are crystalline and the diffraction peaks were indexed to several crystalline phases characteristic to ternary oxides, mainly $Sm_2Ti_2O_7$ (ICSD card 24208, space group *Fd*-3m - cubic) and Sm_2TiO_5 (ICSD card 191142, space group *Pnma* - orthorhombic). In addition, the most intense peaks of monoclinic $Al_2Ti_7O_{15}$ (ICSD card 202646, space group *C 1* 2/m *1*) were noticed in the diffraction pattern of STA-1 and STA-2 calcined powders.

Raman spectroscopy also evidenced the presence of orthorhombic and cubic pyrochlore phases (Fig. 3). The Raman spectrum of orthorhombic Sm_2TiO_5 phase is quite complex, having more than 20 active modes [17]. The spectral region below 200 cm^{-1} is characteristic mainly to lanthanide elements, while the Raman modes above 500 cm^{-1} represent the contributions of Ti–O bonds in the TiO_5 polyhedron, with a strong band centered at about 780 cm^{-1}.

There are seven observed bands in the Raman spectra of cubic pyrochlore titanate [18], with the strongest band from about 310 cm^{-1} ascribed to O–Sm–O bending mode.