

Changes in structure and electrical conductivity of rare-earth titanate pyrochlores under highly reducing atmosphere

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Abstract

M₂Ti₂O₇ (M = Y, Gd, Sm) pyrochlore materials are synthesized by a Pechini method. The pyrochlore phase evolution with temperature under air and under highly reducing conditions (2% H₂ in Ar) is investigated using high-temperature X-ray diffraction. The decomposition of pyrochlore oxides into their component single oxides is evidenced when they are exposed to a hydrogen atmosphere. Sm₂Ti₂O₇ pyrochlore is the most stable compound, while Gd₂Ti₂O₇ undergoes a strong reduction even at RT. The bulk electrical conductivity of the samples is evaluated by electrochemical impedance spectroscopy. The greatest increase in conductivity is evidenced for Gd₂Ti₂O₇, while Sm₂Ti₂O₇ is the most stable among the investigated compounds. Besides oxygen ions and electrons, the contribution of hydrogen defects to the bulk conductivity must be considered in such reducing atmosphere.

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1. Introduction

The wide range of applications for solid oxides with pyrochlore structure is mainly determined by their great diversity in composition [1,2]. Thus, pyrochlores with general formula A₂B₂O₇ exhibited interesting properties for applications such as catalysts, host matrices for nuclear wastes, thermal barrier coatings, oxygen sensors, etc. [3–5]. Due to their high structural flexibility, materials with appropriate electrical properties for SOFC electrolyte or mixed ionic–electronic conducting anode can be developed. From structural point of view, A₂B₂O₇ pyrochlore oxides possess cubic symmetry (space group *Fd-3m*), the hexa-coordinated B⁴⁺ cation (16*d* site) being smaller than the octa-coordinated A³⁺ cation (16*c* site) [6]. This structure is a derivative of AX₂

fluorite structure, half of the A cations being substituted with B cations and 1/8 of the anion sites being vacant.

In the pyrochlore structure there are chains of BO₆ distorted octahedra, with six oxygen ions (O₁) placed at equal distances from B cation, and A₂O distorted cubes (scalenoedra) with two of the eight oxygen anions (O₂) placed at smaller distance from A cation [7]. The BO₆ octahedra chains are the backbone of pyrochlore structure, with A sites filling the interstices.

There are three types of oxygen sites in the A₂B₂O₇ pyrochlore structure, with different environment (Fig. 1). Thus, 48*f* sites-with two B⁴⁺ and two A³⁺ neighbors (O₁ anions), 8*a* sites-with four A³⁺ neighbors (O₂ anions), 8*b* sites (O₃ anions)-with four B⁴⁺ neighbors. The 8*b* sites are systematically vacant, each B⁴⁺ cation being coordinated with two 8*b* sites [8]. Previous studies regarding the stability of A₂B₂O₇-type pyrochlore structure revealed a strong dependence on the cation radius ratio r_A/r_B and on the electronic configurations of A and B cations.

Rare-earth titanate pyrochlores have been investigated as potential nuclear waste storage materials, as well as mixed

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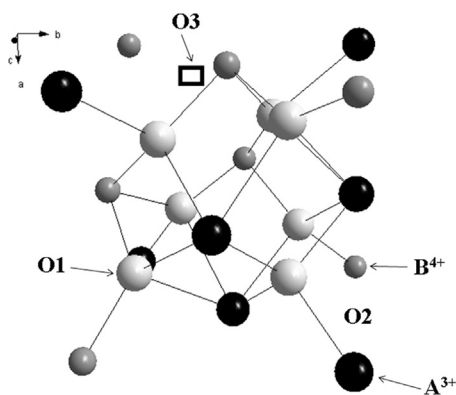


Fig. 1. $\frac{1}{4}$ unit cell of $A_2B_2O_7$ pyrochlore structure.

ionic–electronic conductors for oxygen ion sensors and solid oxide fuel cells (SOFCs) [9]. The shape of TiO_6 octahedra is sensitive to the positional parameter of oxygen 48*f* site [10]. $Gd_2Ti_2O_7$ has the smallest positional parameter of 48*f* oxygen compared with other rare-earth titanate pyrochlores [11], leading to a distortion of TiO_6 octahedra. There are two factors contributing to the lowest value of positional parameter of 48*f* oxygen in $Gd_2Ti_2O_7$: (i) the highest overlap of Ti 3*d* and O_2 p orbitals, confirmed by the shortest $Ti-O_{48f}$ bond distance; (ii) displacement of oxygen atoms toward titanium cations due to strong ionic character of gadolinium–oxygen bonds [12].

An increase in ionic conductivity of pyrochlore materials can be attained by inducing structural disorder. The rigorous selection of the cations occupying the A and B sites may lead to different disorder degrees in the pyrochlore lattice and consequently, an improvement in their electrical conduction behavior can be achieved.

This work aims to give an insight into the structural and electrical conductivity changes in $M_2Ti_2O_7$ pyrochlores (with $M=Y, Gd, Sm$) under hydrogen containing atmosphere such the one typical to anode side of SOFCs. High temperature X-ray diffraction (HT-XRD) under different atmospheres, X-ray photoelectron spectroscopy (XPS) and electrochemical impedance spectroscopy (EIS) were the tools used to fulfill this goal.

2. Experiments

$M_2Ti_2O_7$ ($M=Y, Gd, Sm$) powders were synthesized by a Pechini method using $Y(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar, $\geq 99.9\%$), $Gd(NO_3)_3 \cdot 6H_2O$ (Sigma-Aldrich, $\geq 99.9\%$), $Sm(NO_3)_3 \cdot 6H_2O$ (Sigma-Aldrich, $\geq 99.9\%$), and titanium (IV) isopropoxide (Sigma-Aldrich, $\geq 97\%$) as precursors. After excess solvent removal, the obtained gels were dried at $120^\circ C$ overnight. TG/DSC analysis of the resulted precursor resins was performed in order to establish the optimal thermal treatment which can lead to solid oxides. Simultaneous TG/DSC analysis was carried out using a Diamond (Perkin-Elmer) analyzer in air. Investigations were performed in the temperature range r.t. – $1100^\circ C$, using a heating rate of $10^\circ C/min$. According to TG/DSC results, the precursor resins of

$Gd_2Ti_2O_7$ were calcined in air at $850^\circ C$. Higher temperature was necessary to get $Sm_2Ti_2O_7$ single phase pyrochlore. X-ray diffraction (XRD) data were recorded using a D8 Bruker diffractometer in the range of $2\theta=20-80^\circ$ with a 0.02° step and a 1.5 s/step counting time using $CuK\alpha$ radiation. Rietveld refinement of crystal structure was carried out using FullProf software to determine de lattice parameters.

High-temperature X-ray diffraction (HT-XRD) in air and H_2 (2%)-Ar mixture was also performed on calcined powders. Diffraction data were collected at RT and in the temperature range $50-800^\circ C$ during heating/cooling cycles with a $50^\circ C$ step and a heating/cooling rate of $1^\circ C/min$. Before XRD data collection, the sample was kept at the temperature of interest for 5 min.

Surface analysis performed by X-ray photoelectron spectroscopy (XPS) was carried out on PHI Quantera equipment with a base pressure in the analysis chamber of 10^{-9} Torr. The X-ray source was monochromatized Al $K\alpha$ radiation (1486.6 eV) and the overall energy resolution is estimated at 0.65 eV by the full width at half-maximum (FWHM) of the Au4*f*7/2 photoelectron line (84 eV). Although the charging effect was minimized by using a dual beam (electrons and Ar ions) as neutralizer, the spectra were calibrated using the C1*s* line ($BE=284.8$ eV) of the adsorbed hydrocarbon on the sample surface (C–C or (CH) n bondings). As this spectrum was recorded at the start and the end of each experiment the energy calibration during experiments was quite reliable.

For the electrochemical characterization, the powders were shaped into pellets by uniaxially pressing in a 10 mm diameter stainless steel die and further isostatically pressed under 180 MPa to obtain green pellets. These pellets were sintered at $1200^\circ C$ for 24 h using a heating rate of $2^\circ C/min$. Densities of all sintered pellets were estimated to be higher than 90% of their theoretical density. Gold was used as electrode. The AC impedance spectroscopy measurements were performed on sintered pellets in air and Ar/hydrogen (2 vol%) mixture, in the temperature range $300-800^\circ C$, using a SI 1266 Solartron Impedance/Gain-Phase Analyzer in the 30 MHz–0.10 Hz frequency range. The amplitude of the AC perturbation signal was 50 mV.

3. Results and discussion

From TG/DSC analysis several steps can be identified in the thermal decomposition process of precursor solid resins (Fig. 2). The first broad endothermic step (up to about $200^\circ C$) can be ascribed to the removal of residual solvent, while the subsequent exothermic steps (between $200^\circ C$ and $450^\circ C$) can be attributed to the oxidation of the organic components. The last broad exothermic step (up to about $850^\circ C$) is ascribed to the removal of organic residues and to the formation of crystalline phase. The total weight loss in the investigated temperature range was $\sim 79\%$.

XRD patterns of calcined powders and Rietveld refinement for $Sm_2Ti_2O_7$ powder are shown in Fig. 3. The XRD patterns of the investigated powders exhibited only the characteristic reflexions of pyrochlore structure. However, it should be

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