



ELSEVIER

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Structure, thermal and electrical properties of calcium doped pyrochlore type praseodymium zirconate

K. Vasundhara, S.N. Achary*, A.K. Tyagi

Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400085, India

ARTICLE INFO

Article history:

Received 17 July 2014

Received in revised form

19 January 2015

Accepted 24 January 2015

Available online xxx

Keywords:

Pyrochlore

Crystal structure

X-ray diffraction

Mixed conduction

Thermal expansion

ABSTRACT

Herein we report the structure, thermal and electrical properties of pyrochlore type $\text{Pr}_{2-x}\text{Ca}_x\text{Zr}_2\text{O}_7$ ($x = 0.00, 0.10$ and 0.20) compositions. These compounds have been prepared by gel combustion method followed by heating in reducing (Argon/Hydrogen) atmosphere and characterized by powder X-ray diffraction, Raman spectroscopy and ac-impedance studies. The powder XRD and Raman spectroscopic studies revealed the retention of the parent cubic pyrochlore type structure up to the compositions with $x = 0.10$. The thermal stabilities of the compositions have been investigated by *in situ* high temperature powder XRD and thermogravimetric studies. A maximum of about 1.25% weight gain due to oxidation of Pr^{3+} is observed in all the samples. The typical axial thermal expansion coefficients (α_a) for the compositions with $x = 0.00, 0.10$ and 0.20 are 8.40×10^{-6} , 11.29×10^{-6} and $11.67 \times 10^{-6} \text{ K}^{-1}$, respectively. The analyses of impedance and admittance spectra revealed maximum conductivity at $x = 0.10$, while the activation energy increases with Ca^{2+} content. At around 770 K, the conductivities of the compositions with $x = 0.00, 0.10$ and 0.20 are $2.26 \times 10^{-5} \text{ S/cm}$, $1.88 \times 10^{-4} \text{ S/cm}$ and $1.23 \times 10^{-4} \text{ S/cm}$, respectively. The activation energy for electronic conductivity for the composition with $x = 0.00$ and 0.10 are 0.42 and 0.63 eV, respectively. The temperature dependent conductivity of the composition with $x = 0.20$ composition revealed a deviation around 700 K where the activation energy decreased from 0.97 eV to 0.38 eV. The electrical properties $\text{Pr}_{2-x}\text{Ca}_x\text{Zr}_2\text{O}_7$ have been correlated with structural parameters and explained by the coexisting electronic and ionic conductivities.

Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

The oxides with high ionic or electron mobility have significant importance in fuel cell either as electrolyte or electrode. Because of several technological challenges, like high cost,

unwanted chemical reaction between cathode and electrolyte and less compatibility between electrode and inter connect material due to thermal expansion mismatch etc, tremendous research efforts are being carried out to decrease the operation temperature of the solid oxide fuel cell. In this context, electrolytes with better ionic conductivity at relatively lower

* Corresponding author. Tel.: +91 22 2559 2328; fax: +91 22 2550 5151.

E-mail address: sachary@barc.gov.in (S.N. Achary).

<http://dx.doi.org/10.1016/j.ijhydene.2015.01.148>

0360-3199/Copyright © 2015, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

temperature are desired. Pyrochlore type oxides, in particular rare-earth zirconates have been considered as promising materials for such intermediate or low temperature fuel cells as they exhibit oxide or proton conduction properties at relatively lower temperature [1–7]. The structure of pyrochlore is closely related to fluorite structure except the cations and vacancies are ordered and formed only with cations of appropriate ionic radii ($r_A/r_B = 1.46–1.80$) and charges [8].

The pyrochlore type structures have been reported for $\text{Ln}_2\text{Zr}_2\text{O}_7$ (Ln = Rare-earth) type zirconates [6–14]. Since the oxygen stoichiometry and hence ionic conductivity of such pyrochlore type $\text{A}_2\text{B}_2\text{O}_7$ materials can be controlled by aliovalent substitution at A or B sites, a number studies on substituted pyrochlore structures are reported in literature [3–7,9,10,14]. It is observed that the isovalent substitution in $\text{Ln}_2\text{Zr}_2\text{O}_7$ (Ln = Rare-earth) stabilizes the structure in a wider range of composition and their ionic conductivities are governed by the extent of anion or cation ordering in the lattice [1,2,5,14]. However, only a limited solubility of aliovalent (A^{2+}) cation at the rare-earth site is observed. The studies on $\text{Sm}_{2-x}\text{Ca}_x\text{Zr}_2\text{O}_7$ indicate that single phase pyrochlore structure is formed only within $x = 0.20$ [3]. An increasing trend of oxide ion conductivity with increasing Ca^{2+} content is reported for $\text{Sm}_{2-x}\text{Ca}_x\text{Zr}_2\text{O}_7$. Similar studies on electrical properties of $\text{Y}_{2-x}\text{Ca}_x\text{Ti}_2\text{O}_7$, $\text{Gd}_{2-x}\text{Sr}_x\text{Zr}_2\text{O}_7$, $\text{Nd}_{2-x}\text{Sr}_x\text{Zr}_2\text{O}_7$, $\text{La}_{2-x}\text{Ca}_x\text{Zr}_2\text{O}_7$ etc. indicate an increasing conductivity with the increase in alkaline earth metal ion concentrations [3,4,7]. The enhanced conductivity has been attributed to the increasing anion vacancies in the structure. The segregation of perovskite type phase beyond solubility limit decreases conductivity in such pyrochlores. Studies on single phase pyrochlore type $\text{La}_{2-x}\text{Ca}_x\text{Zr}_2\text{O}_{7-\delta}$ ($0 \leq x \leq 0.07$) compositions show maximum conductivity at $x = 0.05$ [7]. The variations of ionic conductivity with compositions have been explained by the concentration and clustering of vacancies. However, similar studies on the rare-earth ions having multiple valences, in particular with Pr are limited in literature. The rare-earth ions having multiple valences are likely to exhibit electronic as well as ionic conductivities [9,14,15]. Easy percolation of oxide ions in the structure and fluctuation of valence of cations can lead to ionic and electronic conductivities in the zirconates of Pr and Ce. Further, the adaptive crystal chemistry of such zirconates makes them promising materials for efficient catalysts for various redox reactions and oxygen storage capacitors [9,11–13,15–17]. The experimental evidences for mixed ionic and electronic conduction (MIEC) in the rare-earth containing pyrochlore compounds have been reported in literature [15,16]. Such materials can be promising electrodes for effective transfer of the oxygen to the electrolytes [17] and hence can prevent undue degradation of electrode and electrolyte interface fuel cell.

It has been reported in literature that the pyrochlore type cerium zirconates can easily introduce mixed Ce^{3+} and Ce^{4+} which are effective to control the ionic and electronic conduction [6,9–13]. However, the structural stabilities of mixed valent cerium zirconates are appreciably lower compared to praseodymium zirconates. The higher stability of Pr^{3+} compared to the Ce^{3+} is expected to make $\text{Pr}_2\text{Zr}_2\text{O}_7$ a better MIEC. The substitution of Pr^{3+} in zirconia and other oxide ion conductors introduces electronic conductivity in them [11,17].

Despite its prospects for MIEC, the cation substituted $\text{Pr}_2\text{Zr}_2\text{O}_7$ compositions have never been investigated. In order to understand the solubility limit, structural stability and electrical properties we have prepared several Ca^{2+} substituted pyrochlore-type $\text{Pr}_2\text{Zr}_2\text{O}_7$ compositions and characterized by various techniques, like XRD, Raman and ac impedance spectroscopy. The details of the structural and electrical properties the Ca^{2+} substituted pyrochlore-type $\text{Pr}_2\text{Zr}_2\text{O}_7$ compositions are explained in this manuscript.

Experimental procedure

Stoichiometric compositions of $\text{Pr}_{2-x}\text{Ca}_x\text{Zr}_2\text{O}_7$ ($0.0 \leq x \leq 0.20$) samples were prepared by a combined gel combustion and high temperature reaction method. Reagent grade chemicals, such as Pr_6O_{11} , $\text{Ca}(\text{NO}_3)_2$ and zirconium oxynitrate were used as starting materials for preparation. Weighed quantities of appropriate reactants for desired composition were dissolved in 1:1 ratio of $\text{HNO}_3:\text{H}_2\text{O}$ solution. Calculated amount of glycine, for fuel to oxidant ratio of 0.75:1.00, was added to the above solution. The solution was slowly heated until the formation of a viscous gel. On further heating the gel undergoes auto ignition and transforms to floppy powder. The as synthesized powder samples were calcined at 700°C for 12 h in air to remove the residual carbon. The pellets of calcined powder were then heated at 1250°C for 48 h under flowing Argon–Hydrogen ($\text{Ar}_2:\text{H}_2 = 95:5$ volume ratio) atmosphere (flow rate: 200 mL/min). In another set of experiments the pellets of calcined powder of $x = 0.00, 0.075$ and 0.10 compositions were heated at 1500°C for 4 h in flowing argon (flow rate: 200 mL/min).

The obtained final products obtained after 1250°C in argon–hydrogen were characterized by X-ray diffraction (XRD) method by using X'Pert Pro powder X-ray diffractometer (PANalytical, Netherland). $\text{CuK}\alpha$ (wavelength $\text{K}\alpha_1 = 1.5406$ and $\text{K}\alpha_2 = 1.5444$ Å) radiation was used for recording the diffraction patterns. Diffraction data were collected in the two theta range of $10–80^\circ$, with step width and step time of 0.02° and 3 s, respectively. *In situ* high temperature XRD patterns of the samples were recorded in static air on an X'Pert Pro diffractometer equipped with Anton Parr high temperature attachment. The XRD patterns were recorded in the two-theta range of $10–70^\circ$ with step width and step time as 0.02° and 1.5 s, respectively. The Raman spectra of the compositions were recorded in the frequency range of $200–800\text{ cm}^{-1}$ using STR-300 micro-Raman spectrometer (SEKI Technotron, Japan). Samples were excited at 532 nm (power ~ 20 mW at the sample spot) and the scattered light was detected by a thermoelectric cooled charge-coupled device (CCD). Oxidation behaviors of the samples were investigated by recording the thermogravimetric data while heating the samples from ambient to 1000°C (heating rate $10^\circ\text{C}/\text{min}$) in flowing air. Setaram simultaneous TGDTA set up was used for the thermogravimetric studies. The pellets obtained after heating at 1500°C in argon atmosphere were characterized by powder XRD data and scanning electron microscopy. SEM images were recorded by using Scanning electron microscope (Mini-SEM, Model SNE 3000M). Densities of pellets were determined by

Download English Version:

<https://daneshyari.com/en/article/7716089>

Download Persian Version:

<https://daneshyari.com/article/7716089>

[Daneshyari.com](https://daneshyari.com)