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High temperature structural and thermal expansion behavior of pyrochlore-type praseodymium zirconate

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ARTICLE INFO

Article history:

Received 30 May 2015

Received in revised form

12 September 2015

Accepted 16 September 2015

Available online 9 October 2015

Keywords:

Pyrochlore

Crystal structure

X-ray diffraction

Neutron diffraction

Thermal expansion

ABSTRACT

In this communication we report the high temperature structural details of pyrochlore-type $\text{Pr}_2\text{Zr}_2\text{O}_7$, a potential mixed electronic and ionic conducting material, as observed from the *in situ* variable temperature powder neutron diffraction in vacuum. The evolution of structural parameters with temperature revealed a smooth expansion of the lattice while a feeble decreasing trend in the oxygen parameters of pyrochlore structure. The analyses of the structural parameters further indicate a larger expansion of the Pr–O bonds ($\alpha = 11.32 \times 10^{-6} \text{ K}^{-1}$) compared to that of Zr–O bonds ($\alpha = 8.83 \times 10^{-6} \text{ K}^{-1}$). The temperature dependent unit cell parameters measured under vacuum deviates from those measured in air and the coefficient of axial thermal expansion (α_a) of $\text{Pr}_2\text{Zr}_2\text{O}_7$ lattice is $10.18 \times 10^{-6} \text{ K}^{-1}$ (in vacuum). The analyses of structural parameters indicated a larger distortion in PrO_8 polyhedra compared to ZrO_6 octahedra of the $\text{Pr}_2\text{Zr}_2\text{O}_7$. The differences in high temperature behaviour in air and vacuum have been explained by the contributions of oxidation of Pr^{3+} to Pr^{4+} .

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Introduction

The pyrochlore or defect fluorite-type $\text{A}_2\text{B}_2\text{O}_7$ compositions have been of interest due to their interesting crystal chemistry as well as diversified technologically relevant physical or chemical properties. The pyrochlore-type structure is formed with cubically coordinated AO_8 and six coordinated BO_6

polyhedral units. Thus the formations of the desired polyhedra and charge neutralities strictly require only cations of appropriate ionic radii and oxidation states in pyrochlore [1]. With Zr^{4+} as B site cation, the trivalent rare-earth cations (Ln^{3+}) form either pyrochlore or anion deficient fluorite-type structures depending on the ionic radii of Ln^{3+} . Such rare-earth zirconates ($\text{Ln}_2\text{Zr}_2\text{O}_7$, Ln = trivalent rare-earth ions) find diversified applications ranging from fuel cell, sensor,

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<http://dx.doi.org/10.1016/j.ijhydene.2015.09.059>

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catalysis, thermal barrier coating to host matrices for immobilizing radioactive nuclear waste [2–7]. In addition the $A_2B_2O_7$ type pyrochlore with cations having unpaired d and/or f electrons show interesting magnetic properties like spin glass or frustrated magnetism as well as catalytic properties for various redox reactions in either synthetic chemistry or mitigation of CO emission and mixed electronic and ionic conduction properties [7–13]. The fluctuation of oxidation states of rare-earth ions in $Ln_2Zr_2O_7$, $Ln = Ce$ and Zr incorporates additional anions in the lattice without any significant alteration in the crystal structure and thus facilitate the variation of anion stoichiometry and following redox catalytic reactions [11–15]. The potential of the zirconates of Ce and Pr for the redox reactions involved in three way catalyst have been reported in literature [11–15]. A detailed structural analysis of a pyrochlore-type composition of cerium zirconate with varying oxygen concentration revealed that the incorporation of excess anion in the lattice transforms the structure from $Fd3m$ → $F-43m$ → $P2_1a$ [16]. The unpaired electron in Ce or Pr substituted zirconia introduces electronic conduction along with oxide ion conduction [15,17–23]. It is known that the pyrochlore-type cerium zirconates, $Ce_2Zr_2O_7$, can easily introduce mixed Ce^{3+} and Ce^{4+} which significantly affect the ionic and electronic conduction in it [11,12,16,18,24,25]. However the analyses of the structure of analogous compositions, like $Pr_2Zr_2O_7$ [19] and $Pr_2Ti_2O_7$ [26] did not reveal any such change in structure with oxidation as observed in $Ce_2Zr_2O_7$ [16,27]. The preparation of $Pr_2Zr_2O_7$ samples at different temperatures indicates that the sample prepared at higher temperature preferentially stabilize Pr^{3+} ion compared to Pr^{4+} even in air [19,28]. Further it is also observed that the oxidation of Pr^{3+} to Pr^{4+} is not complete in air even at higher temperature. It has also been reported that the oxidation state of Pr^{3+} in $Pr_{1-x}Zr_xO_{2-x}$ composition is sensitive to the values of x [28,29]. The coexistence of Pr^{3+} and Pr^{4+} in the intermediate temperature range in air treated samples favour for mixed ionic conduction in Pr containing materials and thus such materials are promising candidates for MIEC applications [11,15,17–19,25–31]. The high temperature XRD studies in air revealed a smooth expansion in the lattice with increasing temperature, which is a cumulative effect of the oxidation of Pr^{3+} to Pr^{4+} , incorporation excess anion in the lattice due to oxidation of Pr^{3+} and temperature induced bond expansion [19]. Studies of Fu-kang et al. [32] on pyrochlore-type $Pr_2Zr_2O_7$ indicate similar behaviour but the coefficient of thermal expansion is higher compared that observed in intermediate temperature [19]. In order to delineate the bond contribution to the high temperature behaviour, and accurate structural parameters of $Pr_2Zr_2O_7$ lattice, *in situ* high temperature neutron diffraction in vacuum are carried out and they are compared with those measured in static air environment.

Experimental

Polycrystalline sample of $Pr_2Zr_2O_7$ was prepared in a similar manner as reported in literature [19]. In brief, for the preparation of sample required amounts of reagent grade Pr_6O_{11} and zirconium oxy-nitrate were dissolved in minimum

volume of dilute nitric acid. To this solution calculated amount of glycine on the basis fuel to oxidant ratio of 0.75:1.00, was added and slowly heated on a hot plate. On heating further, the solution transforms to a viscous gel and then undergoes an auto process leading to floppy brown powder. The recovered was calcined at 700 °C for 12 h in air. The calcined powder was pressed to pellets of about 10 mm diameter and 2 mm thickness. The pellets were heated at 1250 °C for 48 h under flowing Argon–Hydrogen (95:5 v/v) atmosphere and cooled room temperature under same atmosphere.

The pellets were crushed to powder product and characterized by powder XRD data recorded on a rotating anode based X-ray diffractometer using Cu-K α radiation. The neutron diffraction data were collected with a linear 5-PSD based Debye-Scherrer type powder diffractometer (PD-2) at 100 MW Dhruva Research Reactor, BARC, Mumbai. About 4 gm of well ground powder sample was filled in a quartz tube and placed inside a vanadium tube under high vacuum. The sample tube was placed inside a furnace with a dynamic vacuum of about 10^{-6} atm. About 4 gm of sample was filled in a quartz tube and placed inside a sealed vanadium container under high vacuum. This vanadium container was placed inside ILL type High-temperature furnace for neutron diffraction with a dynamic vacuum better than 10^{-6} mbar. The furnace is equipped with cylindrical vanadium foil as heating element and eight heat shields to maintain uniformity of the temperature across the sample. Two of the heat shields are used as windows for incident and outgoing monochromatic ($\lambda = 1.2443$ Å) neutron beam. The temperature was raised to a desired temperature and allowed to equilibrate for 60 min before collection of scattered data. The diffraction data were collected in the two-theta range of 15–100° over a period of 6 h at each temperature. The obtained scattered signals were corrected for the scattering contributions from quartz sample holder as well as empty furnace background. The analyses of the powder XRD and neutron diffraction patterns were carried out by using Fullprof-2K software package [33].

Results and discussion

The powder XRD pattern of the prepared $Pr_2Zr_2O_7$ sample is shown in Fig. 1. All the observed reflections could be assigned to the earlier reported cubic pyrochlore-type lattice [16,19]. Further structural studies were carried out by Rietveld refinement method using the observed powder neutron diffraction (PND) data at ambient condition. The background of the diffraction pattern was modeled by linear interpolation of selected points to create a smoothly varying background profile. The Bragg peaks were modeled using pseudo-Voigt profile function. Initially the unit cell parameter and scale factor were refined and subsequently the half-width (U , V , W and η) parameters of peak profile function and asymmetry parameter were included in the refinement process. The ambient temperature (298 K) neutron diffraction data was refined by using reported structural model for $Ce_2Zr_2O_7$ with three sites for anions, namely O1 (4f), O2 (8b) and O3 (8a) sites of the space group $Fd3m$ [16]. In this structural model Pr and Zr atoms were placed in 16c and 16d sites, respectively. The

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