Solid State Ionics 323 (2018) 112–122

Contents lists available at ScienceDirect

Solid State Ionics

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

Structural, optical and impedance spectroscopic characterizations of $RE_2Zr_2O_7$ (RE = La, Y) ceramics

Rejith R.S., Jijimon K. Thomas, Sam Solomon*

Department of Physics, Mar Ivanios College, Thiruvananthapuram 695015, India

ARTICLE INFO

Keywords:
Pyrochlore
Band gap energy
Impedance spectroscopy
Oxygen vacancies

ABSTRACT

Nanocrystalline $RE_2Zr_2O_7$ (RE = La, Y) ceramics with cubic pyrochlore and defect fluorite structure are prepared through the modified combustion technique. The structure and symmetry of the nanoparticles are investigated using X-ray diffraction and vibrational analysis. The particulate properties investigated through TEM analysis are in good agreement with XRD results. The optical properties are studied using the UV–visible and photoluminescent spectroscopy. The prepared samples are sintered by adding 1.6 wt% of ZnO or Ce_2O_3. The impedance spectroscopic studies show that oxygen vacancies play an important role in ionic conduction of these structures. Number of mobile oxide ions and conductivity are increased by ZnO addition whereas decreased by Ce_2O_3 addition. The high ionic conductivity values suggest that these materials are useful for electrolytes in intermediate temperature solid oxide fuel cells (IT-SOFC).

1. Introduction

$RE_2Zr_2O_7$ system having cubic pyrochlore or defect fluorite structure has many industrial applications due to its multi-functional properties. It has been widely used in thermal barrier coating (TBC) [1], host for fluorescent centers [2], photo catalytic reaction [3,4], ferroelectric devices [5], transparent ceramics [6], high permittivity dielectric material for complementary metal oxide semiconductors (CMOS) gates [7] and in solid oxide fuel cells (SOFC) [8,9]. Currently, the goal of SOFCs development is to decrease the operating temperature to an intermediate temperature level, so that the material degradation in the cell at high temperature can be reduced and durability can be increased. $La_2Zr_2O_7$ was formed as a new phase between the Strontium-substituted lanthanum manganite based perovskite cathode and yttria-stabilized zirconia solid electrolyte in SOFCs. The formation of this interphase layer was undesirable since the conductivity of $La_2Zr_2O_7$ was very much less than the conventional YSZ electrolyte [9]. Also, much attention has been paid on $Y_2Zr_2O_7$ in order to replace the conventional yttrium stabilized zirconia electrolyte since the degree of disorder in this structure can enhance the ionic conduction [8]. Hence a study on the structural as well as ionic conduction properties of these compounds derived from nano ceramics is important in the present aspect.

A binary oxide with stoichiometry $A_2B_2O_7$ can form a defect fluorite, pyrochlore or layered perovskite type of structure depending on their cationic radius ratio. If the cationic radius ratio (r_A^{3+}/r_B^{4+}) is less than 1.46, the compound will form a defective fluorite structure, if it is between 1.46 and 1.78, the compound will adopt a pyrochlore structure and if the ratio is greater than 1.78 it will be a layered perovskite structured compound [10]. $Ln_2Zr_2O_7$ and $Ln_2Hf_2O_7$ (Ln = lanthanides) usually favour a pyrochlore or a fluorite structure, whereas the $Ln_2Ti_2O_7$ favours a pyrochlore or layered perovskite structure since the ionic radius of Zr and Hf are comparatively larger than Ti ion. This indicates that the degree of disorder in the structure increases with the decrease in radius ratio, which can be achieved by replacing or doping by a smaller A site or a larger B site cation. Yamamura et al. studied the ionic conduction in lanthanide zirconates by replacing the A site cation with rare earth elements and found that the maximum value of the oxide-ion conduction in $Ln_2Zr_2O_7$ lies in the vicinity of fluorite and pyrochlore phase boundary [11]. Recently, Solomon et al. have studied the oxide-ion conduction in nanoscale $Ln_2Zr_2O_7$ (Ln = Ce, Pr, Nd, Sm, Gd, Dy, Er, and Yb). In that study the impedance measuring temperature was limited to 750 °C. The highest ionic conductivity observed at this temperature was 1.3×10^{-3} S/cm for $Er_2Zr_2O_7$ [12]. In the present study two new rare earth based zirconate ceramics such as $La_2Zr_2O_7$ and $Y_2Zr_2O_7$ are prepared and their ionic transport properties are analysed in the temperature range 500–850 °C. An attempt is done to correlate the ionic conductivity with the oxygen ions ordering effect in the fluorite type $Y_2Zr_2O_7$ by adding ZnO and Ce_2O_3 to it. Apart from the previous studies, variation of oxygen vacancies in the pyrochlore and fluorite structure is also analysed in this paper through the UV–Visible and photoluminescence spectroscopy.

In rare earth zirconates, $La_2Zr_2O_7$ and $Y_2Zr_2O_7$ have a special

---

* Corresponding author.
E-mail address: samdmrl@yahoo.com (S. Solomon).

https://doi.org/10.1016/j.ssi.2018.05.025
Received 7 October 2017; Received in revised form 30 April 2018; Accepted 23 May 2018

interest since these are the two end members of the pyrochlore-fluorite family. The electrical conductivity of pyrochlore structured $La_2Zr_2O_7$ proposed different conduction mechanisms depending on the temperature and surrounding atmosphere. A hole conduction mechanism with a conductivity of 4.2×10^{-4} S/cm at 800 °C was reported in the previous studies by changing the surrounding conditions of the material [11]. Also, oxide ion conductivity of 3×10^{-5} S/cm in dry air and protonic conductivity of 4.2×10^{-5} S/cm in moisture atmosphere at 900 °C was reported by Labrincha et al. [13]. An oxygen ion conductivity 0.016 S/cm was reported in nanofibers of lanthanum zirconate by exploiting the high conduction property of suitable mixed phases of fluorite and pyrochlore structure [14]. Substitution of a lower valence Ca^{2+} cation in the La^{3+} site of $La_2Zr_2O_7$ increases the oxygen vacancy, which in turn increases the ionic conductivity in the pyrochlore structure [15]. The conductivity of $Y_2Zr_2O_7$ was studied by Kumar et al. by adding Mn and Bi oxides [8,16].

The temperature dependent 1 MHz conductivity measurement in rare earth zirconates also depends on the heat treatment temperature at which ceramic samples are prepared [17]. As the heat treatment temperature for the bulk ceramics depend on the size and homogeneity of the initial powder, the preparation methods of the powder then shows an indirect dependency on the dielectric properties and ionic conduction mechanism. There are various methods reported on the preparation of $RE_2Zr_2O_7$, (RE = La, Y) such as co-precipitation calcination [18], sol-gel [19,20], high temperature solid state reaction [21], stearic acid combustion [3], reactive spark plasma sintering [22], hydrothermal [2,23] and glycine nitrate synthesis [24]. All the preparation techniques discussed above have their own advantages and disadvantages like high temperature treatment and prolonged annealing leading to increase in size and agglomeration of the particle, whereas the wet chemistry based routes are time saving but usually need expensive and environment sensitive chemicals. In this paper we report the preparation of $La_2Zr_2O_7$ and $Y_2Zr_2O_7$ nano ceramics through an auto ignited combustion technique.

2. Experimental

(A) Preparation technique and characterization methods used for nano particles

In the auto ignited combustion technique to prepare the $La_2Zr_2O_7$ and $Y_2Zr_2O_7$ nanoceramic, first of all Y, La and Zr ions are prepared by dissolving Y_2O_3, La_2O_3 in dilute HNO_3 and $ZrOCl_2.8H_2O$ in double distilled water. To get the precursor complex, the stoichiometric amount of metal ions containing solution is mixed with citric acid solution, keeping the citric acid to cation ratio unity. Concentrated HNO_3 and liquor ammonia are added to the solution as an oxidant and fuel respectively, keeping the ratio to unity. The product is stirred well for uniform mixing until a clear solution with no precipitation or sedimentation is obtained. The solution containing the precursor mixture at a pH of~ 7 is heated by using a hot plate at~ 250 °C in a ventilated fume hood. The solution boils and undergoes dehydration followed by decomposition leading to a smooth deflation producing foam. On persistent heating the foam gets auto-ignited, giving a voluminous fluffy powder due to self-propagating combustion. The obtained powder is heated in the oxygen atmosphere at 900 °C for 30 min to remove the organic impurities.

In order to structure and phase formation of the nanomaterials, prepared samples are characterized by using X-ray diffractometer (D8 advance, Bruker, Germany) with CuKα radiation in the range of 20–70 in steps of 0.02. Additional information regarding the phase purity of the powder materils are examined by using FTIR and confocal Raman studies. The infrared spectrum of the samples are recorded in the range 400–1000 cm^{-1} on a Fourier Transform Infrared (FTIR) Spectrometer (Spectrum2, Perkin-Elmer, Singapore) using the ATR method. Raman spectrum of the powder samples between 200 and 1000 cm^{-1} are recorded by using a confocal Raman spectrograph (alpha300RA, WITec GmbH, Ulm, Germany) with a 532 nm DPSS laser. Particulate properties of the prepared nanoparticles are imaged using high resolution transmission electron microscopy (Joel/JEM 2100, USA) operating at 200 KV. The diffuse reflectance spectra in the range of 200 to 700 nm of the powder samples are recorded by using a UV–Vis spectrometer (Lamda 35, PerkinElmer, Singapore) with an integrated sphere accessory (RSA-PE-20, Labsphere, USA). In this method Spectralon is used as the standard reference material for the samples. The photo luminescent emissions of the prepared nanopowder are recorded by using a spectrofluorometer (FP-846, Jasco, Japan).

(B) Preparation technique and characterization methods used for bulk ceramic pellets

The phase pure nanopowder is grinded in an agate mortar with polyvinyl acetate as the binding medium. It is then uni-axially compacted into pellets of 12 mm diameter at 20 MPa by using a hydraulic press. Two other materials are also prepared by adding 1.6 wt% of ZnO and Ce_2O_3 to the $Y_2Zr_2O_7$ nano powder for improving the density of the pellets. A high temperature resistive heating furnace with molybdenum heating elements (TE-4050, Therelek, India) is used for the sintering of disc shaped pellets. The relative density of the sintered pellets are calculated using Archimedes method. The structure and phase formation of the bulk ceramics are investigated by using X-ray diffractometer (D8 advance, Bruker, Germany) with CuKα radiation in the range of 10–70 in steps of 0.02. Oxidation state of cerium ions in the Ce_2O_3 added sample is analysed by X-ray photoelectron spectroscopy (PHI 5000 Verssa Probe II, PHI, USA). The sintered pellets are then thermally etched and its surface morphology is examined by Scanning Electron Microscope (6390LV, JEOL, Japan). The chemical composition of the sintered pellets are then analysed by energy-dispersive X-ray spectroscopy (EDAX Octane series, AMETEK, USA). Impedance analysis is carried in an LCR meter (LCR HiTester 3532-50, Hioki, Japan) in the frequency range 100 Hz – 5 MHz at different temperatures from 500 to 850 °C. For this measurement, a disc shaped capacitor is made by applying silver paste on both sides of the pellets and fired up to 800 °C before measurements.

3. Results and discussion

(A) Characterization of nano particles

As the lighter rare earth metal zirconates crystallize in the pyrochlore form and heavier rare-earth metal zirconates crystallize in the fluorite form, $La_2Zr_2O_7$ (LZO) probably adopts a pyrochlore structure containing the distorted LaO_8, ZrO_6 polyhedra and $Y_2Zr_2O_7$ (YZO) adopts a defect fluorite with YO_8 and ZrO_8 polyhedra. A change of phase from fluorite to pyrochlore is reported in the X-ray diffraction pattern of LZO at an annealing temperature 1200 °C [25]. The X-ray diffraction patterns of the prepared LZO and YZO nanoparticles are shown in Fig. 1. All the reflections observed for LZO are indexed by using JCPDS file no: 73–0444 whereas the file corresponding to the YZO is still absent in the reference data. However the crystal structure of YZO is previously reported as defect fluorite structure and the XRD pattern in the present study is similar to the previous reports [8,16,20]. LZO shows the characteristic reflections of a cubic pyrochlore structure with space group Fd-3 m and YZO shows the defect fluorite structure with space group Fm3m. The reflections from (222), (400), (440), (622) and (444) are common to both pyrochlore and fluorite structure except that the fluorite structure reflections are coming from the half indexed planes. The two additional low intensity peaks (331) and (511) formed in the LZO are due to the ordering of oxygen ions in the pyrochlore structure. The cationic radius ratio ($r_A{}^{3+}/r_B{}^{4+}$) of LZO is comparatively larger than YZO. As the radius ratio increases the degree of ordering increases in the fluorite structure. The two low intensity peaks