Radiation Physics and Chemistry 139 (2017) 152–156

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

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

Effect of γ-irradiation on structure and properties of Nd^{3+} doped Perovskite

P. Mahadik[a], Pranesh Sengupta[a,*], B. Vishwanadh[a], S.K. Mishra[b], V. Sudarsan[c], G.K. Dey[a]

[a] Materials Science Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
[b] Solid State Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India
[c] Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

ARTICLE INFO

Keywords:
Perovskites
Nuclear waste
Gamma radiations
Structure-property correlations

ABSTRACT

Perovskite is one of the potential host matrices for immobilization of high level nuclear waste. In the present investigation Nd^{3+} doped $BaZrO_3$ materials were synthesized by conventional solid state route and their phase structure was evaluated by X-ray diffraction technique. Phase pure Nd^{3+} doped $BaZrO_3$ materials were exposed to gamma radiation and their defects in structure as well as strain produced was measured. Structural defects and morphology before and after gamma irradiation were investigated using photoluminescence (PL) spectroscopy, Raman spectroscopy and Transmission electron microscopic (TEM) analysis. Both undoped and Nd^{3+} doped $BaZrO_3$ compositions showed excellent resistant to gamma irradiation with no change in structure, morphology and optical properties.

1. Introduction

Alloy melting route has been proposed as a potential way to immobilize radioactive zircaloy and stainless steel based hulls (Das et al., 2012; Bairi et al., 2010; International Atomic Energy Agency, 1985). The idea is to take appropriate mixtures of irradiated zirconium (Zr) and iron (Fe) based hulls/or other similar contaminated materials, close to eutectic bulk compositions, and melt the same so as to stabilize phases which can incorporate fission products and actinides within their lattices. However, since some amount of spent nuclear fuels, oxide coatings etc are always associated with such contaminated metals or alloys (Sengupta et al., 2004; Poulard et al., 2002; Biddle and Rees, 1987), the melting process is expected to develop radioactive slag on the molten mass. Immobilization of such radioactive slag is a major concern and so far no attention has been given in this direction. In the present investigation an attempt has been made to address this issue through developing perovskite materials.

In the absence of any data on such slag materials it is very difficult to understand the composition of the same. Preliminary experimental studies at the laboratory with Zr-based hull materials showed that the slag material is expected to contain significant amount of ZrO_2, along with FeO, Cr_2O_3, NiO, SnO_2, Nb_2O_5 and other fuel materials (UO_2, ThO_2 etc.) and fission products (Cs, Sr, REEs etc.). As perovskite type structure can host many of these components within its lattice structure (Lee et al., 2006; Ojovan and Lee, 2005, 2007; Ringwood et al., 1979; Donald, 2010; Jafar et al., 2014a, 2014b), ZrO_2 based perovskite has been attempted here. Synthesis of barium zirconate i.e. $BaZrO_3$ was performed in the present study over other ZrO_2 based perovskites because of an earlier success history of immobilization of sulphate containing waste within barium borosilicate glass matrix which showed that introduction of Ba^{2+} can modify the network structure suitably so as to host wide range of radionuclides (Kaushik et al., 2006; Sengupta et al., 2015; Mishra et al., 2007, 2008). This also opens up the possibility of adding/mixing barium borosilicate glass melt with barium zirconate perovskite for better immobilization of radioactive slag materials. Further, $BaZrO_3$ is a well studied material (often referred as BZO also) for its numerous applications in / as ferroelectrics, humidity sensors, high temperatures superconductors, proton conducting electrolyte materials for solid oxide fuel cells and thermal/diffusion barrier coatings (Auciello et al., 1998; Viviani et al., 2001; Erb et al., 1995; Kamitani et al., 2004; Vassen et al., 2000; Ma et al., 2008; Kreuer, 2003; Chang et al., 2013; Yamanaka et al., 2003).

$BaZrO_3$ is exists in ideal cubic perovskite form with space group *Pm3m* and a lattice constant of 4.182 Å at room temperature and can be doped easily by divalent or trivalent rare earth ions. Ionic radii of Nd^{3+} (r = 0.983 Å) in its 6-fold coordination are comparable with ionic radii of Am^{3+} (r = 0.975 Å), Cm^{3+} (r = 0.97 Å) and also with the Pu^{3+} (r = 1.00 Å) and therefore can be treated as a surrogate for wide range of radionuclides. Therefore for the present study Nd^{3+} doped $BaZrO_3$ was synthesized and its response to gamma irradiation was examined. It has been observed previously that gamma irradiation of perovskite materials such as $CaTiO_3$ lead to an increase in their lattice parameters and formation of stable defects which altered their dielectric properties (Kabirov et al., 2000). Additionally, high doses of

* Corresponding author.
E-mail address: sengupta@barc.gov.in (P. Sengupta).

http://dx.doi.org/10.1016/j.radphyschem.2017.05.003
Received 26 September 2016; Accepted 2 May 2017
Available online 03 May 2017
0969-806X/

gamma radiations may affect on the migration of defects which changes the mobility of domain walls and Curie temperature and suppress the polarization properties of ceramics (Peshikov, 1986).

2. Experimental

2.1. Synthesis of materials

$BaZr_{1-x}Nd_xO_{3-\delta}$ (x = 0, 0.1, 0.2 and 0.3) compositions were prepared by conventional solid state route. They are labelled as BZO, BZNd1O, BZNd2O and BZNd3O for x = 0, 0.1, 0.2 and 0.3 respectively. As Nd^{3+} ions may exceeds its solubility limit within $BaZrO_3$ lattice leading to the phase separation, so up to 30 mol% of Nd^{3+} was added in $BaZrO_3$ for the present studies. $BaCO_3$ (Sigma Aldrich, purity > 99.0%), ZrO_2 (Loba Chemie, purity > 99.5%), and Nd_2O_3 (US Research Nanomaterials, Inc. 99.95%) were used as the starting materials. All the reactants were pre-heated overnight at 600 °C. Stoichiometric quantities of reactants were mixed and ground in an agate mortar. Well homogenised powders were heated at 1000 °C for 24 h and 1200 °C for 24 h in air with intermittent grinding after each heating. Powders were then pressed into pellets by a hydraulic press under a pressure of 2 MPa and finally sintered at 1450 °C for 24 h.

2.2. Irradiation of Nd^{3+} doped $BaZrO_3$ samples

Bulk gamma irradiation of the Nd^{3+} doped $BaZrO_3$ samples was carried out using a ^{60}Co irradiator at 175 KGy dose and the average dose rate was 2.6 KGy/h. Samples were kept in a gamma chamber in powder form.

2.3. Characterization techniques

2.3.1. Powder X-ray Diffraction

Powder X-ray diffraction (XRD) studies were carried out using a Cu anode-based powder diffractometer operating in the Bragg–Brentano focusing geometry, and a curved crystal monochromator in the diffraction beam. For powder XRD, 1450 °C heated pellets were crushed using mortar-pestle and ground to a fine powder. Structural refinements were performed using the Rietveld refinement program FULLPROF. XRD measurements were also carried out after the irradiation.

2.3.2. Micro-Raman spectroscopy

The spontaneous micro-Raman spectra of the samples were recorded at room temperature using a STR-300 micro-Raman spectrometer (SEKI Technotron, Japan). Powder sample mounted on the glass slide was excited at 532 nm (power ~20 mW at sample position, continuous wave (CW) YAG laser) using a 100X objective lens (Olympus). The scattered light was collected through fiber-coupled 300 mm spectrograph (Action series SP 2300i, 1200 gr/mm) and detected by a thermoelectric cooled (−75 °C) charge-coupled device (CCD). The spectrograph was calibrated using the 520.5 cm^{-1} line from silicon wafer and was verified by measuring the Raman spectrum of naphthalene. Acquisition time for each spectrum was kept as 20 s (20 s × 3) and spectra of all samples were acquired at the same experimental conditions.

2.3.3. Photoluminescence

Photoluminescence (PL) measurements are known as a material characterization tool and are commonly used to evaluate the structural properties with respect to defects in the structure of material. All steady state luminescence and lifetime measurements were carried out on pure $BaZrO_3$ (BZO) and Nd^{3+} doped $BaZrO_3$ (i.e. BZO-Nd) samples before and after irradiation at room temperature by using an Edinburgh Instruments FLSP 920 system, having 450 W Xe lamp, nanosecond and micro second flash lamps as excitation sources. Emission spectra were corrected for the detector response as well as using the optical filter to remove the secondary lights from measurements. Emission measurements were carried out with a resolution of 5 nm. For steady state measurements, samples were exposed to light from 450 W Xe lamp for total time duration of 1 min. The trigger delay used for recording the decay curves is ~2 ns. Spectrum calibration was done using Rhodamine 6 G dye.

2.3.4. Transmission electron microscopy

Samples for Transmission electron microscopic (TEM) were prepared from the 10 mol% Nd^{3+} doped $BaZrO_3$ as-sintered and gamma irradiated powder samples. For TEM, the particles were dispersed in a methanol and mixed in a sonicator for approximately 30 min prior to sampling. A drop of this solution was then added onto a carbon coated copper grid and was dried properly prior to loading in TEM machine. TEM images (bright field low magnification) and selected area electron diffraction (SAED) pattern were recorded using 160 keV electrons in a FEITecnai T20 Transmission Electron Microscope (TEM).

3. Results and discussion

3.1. Structure and morphology

XRD pattern of 1450 °C heated $BaZr_{1-x}Nd_xO_{3-\delta}$ samples are shown in Fig. 1. It has been observed that systematic shift of peaks to the higher d-value with increasing concentration of Nd^{3+}. This illustrates the lattice expansion of $BaZrO_3$ due to the ionic radius of Nd^{3+}(0.98 Å) which is greater than ionic radius of Zr^{4+}(0.72 Å) in coordination number 6 (Shannon and Prewitt, 1969, 1970). All compositions are found to be phase pure and highly crystalline in nature. Analysis of XRD patterns were carried out by Rietveld refinement method with unit cell parameters and space group using a suitable profile function. This method helps to generate accurate unit cell parameters by accounting overlapping reflections of the contributing phases.

XRD pattern of $BaZr_{1-x}Nd_xO_{3-\delta}$ compositions are refined on the basis of cubic geometry with space group *Pm3m* and corresponding cell parameters are listed in Table 1. Rietveld refined XRD patterns of the

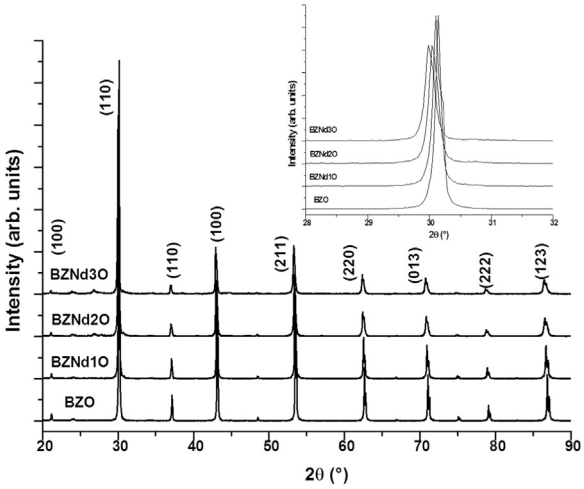

Fig. 1. Powder XRD pattern of $BaZr_{1-x}Nd_xO_{3-\delta}$ compositions in the 2θ region of (20–90°) and inset (2θ = 28° − 32°) given shows the systematic peak shift to the lower 2θ or higher d-value with increasing Nd content.

Table 1
Calculated cell parameters of $BaZr_{1-x}Nd_xO_{3-\delta}$ compositions from XRD pattern.

Composition	Lattice parameter [Å], a	Cell volume [Å^3]	Crystallite size [nm]
$BaZrO_3$	4.19745	73.95	193.6
$BaZr_{0.9}Nd_{0.1}O_{3-\delta}$	4.19879	74.02	166.0
$BaZr_{0.8}Nd_{0.2}O_{3-\delta}$	4.20368	74.28	67.1
$BaZr_{0.7}Nd_{0.3}O_{3-\delta}$	4.20481	74.34	67.8