Materials Research Bulletin 73 (2016) 446–451

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Structure and microstructure dependent ionic conductivity in 10 mol% Dy_2O_3 doped CeO_2 nanoparticles synthesized by mechanical alloying

S. Dutta, A. Nandy, A. Dutta, S.K. Pradhan*

Department of Physics, The University of Burdwan, West Bengal 713104, India

ARTICLE INFO

Article history:
Received 29 May 2015
Received in revised form 7 August 2015
Accepted 28 September 2015
Available online 9 October 2015

Keywords:
A. Ceramics
B. Microstructure
C. X-ray diffraction
D. Impedance spectroscopy
E. Ionic conductivity

ABSTRACT

Nanocrystalline powders of 10 mol% Dy_2O_3 doped ceria (CeO_2) are prepared by mechanical alloying the mixture of CeO_2 and Dy_2O_3 powders within a short duration of 1 h of milling in open air and the powder is further milled for 3 h and 8 h to confirm the phase stability, measure the change in microstructure parameters and find the dependence of ionic conductivity on the microstructure parameters with increasing milling time. Different structural and microstructural parameters such as lattice parameter, particle size, and microstrain in doped CeO_2 nanoparticles are obtained by Rietveld refinement using XRD data employing MAUD software. Ionic conductivities of the compounds for three different milling durations are measured as a function of temperature (350 °C–560 °C). Dy-doping is found to enhance the ionic conductivity of ceria nanoparticles and the 8 h milled sample shows highest conductivity. Increase in ionic conductivity of sample with increase in milling duration is attributed to the change in the structure and microstructure parameters of the compounds.

1. Introduction

Ceria (CeO_2) is a fluorite-structured ceramic material that can be easily doped with various aliovalent (alkaline-earth or rare earth) cations to form solid solutions. When so doped, oxygen vacancies are introduced into the CeO_2 lattice for charge compensation and the materials become good ionic conductors for a variety of electrical applications and promising electrolytes for intermediate temperature (<700 °C) solid oxide fuel cell (SOFC). The ionic conductivity of ceria resulting from oxygen vacancies depends on the nature, radius and the amount of dopants [1]. Doping of trivalent ions such as Gd^{3+} [2],Y^{3+}[3], Sm^{3+}[4], Nd^{3+}[5], Pr^{3+} [6] and Dy^{3+}[7,8] increase the oxygen ion vacancies in the ceria host which further increase the ionic conductivity of doped ceria based electrolytes [9–11]. In this work, we use Dy^{3+} as dopant of ceria due to its lower charge (+3) and ionic radius (1.027 Å)—almost close to that of Ce (0.97 Å). Various reports can be found on Dy-doped ceria and its ionic conductivity [1,7,8]. Those samples were prepared by various methods such as solid state reaction method [1], solution combustion method [7], carbonate co-precipitation method [8], sol–gel method [12] and samples were sintered at high temperatures [1,7]. All these methods required a long sample processing time. So far, there is no report on mechanosynthesis of Dy-doped ceria and its ionic conductivity measurements. Properties of a material are related to the structure, microstructure and method of processing of the material. Here, we have prepared nanocrystalline 10 mol% Dy_2O_3 doped ceria for the first time by mechanical alloying the powdered oxide precursors at room temperature in open air. Mechanical alloying is a single step one pot mechanosynthesis process by which nanocrystalline materials of different kinds can be synthesized with desired size within a very short duration without any contamination either from the precursors or from the milling media and this method is already proved to be successful for doping trivalent ion to ceria [13,14,15]. Nanosized single phase Dy-doped ceria powder is successfully prepared within 1 h of milling. In the previous reports detailed microstructure characterization was not carried out which is necessary to correlate the ionic conductivity properly with structure and microstructure of the compound. The objectives of the present work are to (i) mechanosynthesis of nanocrystalline Dy-doped ceria within a short duration, (ii) structure and microstructure characterizations of milled powders by analyzing the respective powder X-ray diffraction (XRD) patterns employing Rietveld structure and microstructure refinement and (iii) to measure and compare the ionic conductivity of the doped compounds milled for different durations.

* Corresponding author. Fax: +91 3422530452.
E-mail address: skpradhan@phys.buruniv.ac.in (S.K. Pradhan).

http://dx.doi.org/10.1016/j.materresbull.2015.09.029
0025-5408/

2. Experimental

Accurately weighed stiochiometric mixture of 10 mol% Dy_2O_3 powder (Alfa Aesar, purity 99.9%) and CeO_2 powder (Loba Chemie, purity 99.95%) was ball milled in a planetary ball mill (Model P6, Fritsch, Germany) using chrome-steel vial of volume 80 ml with chrome-steel balls. Dry milling of the mixture was carried out at 300 rpm at room temperature in air medium for 1 h, 3 h, and 8 h durations.

X-ray powder diffraction profiles of unmilled and all ball milled powder mixtures were recorded using Ni-filtered CuKα radiation from a highly stabilized X-ray generator operated at 40 KV and 40 mA.The step scan data (step size 0.02°) were recorded for 20°–80° 2θ scattering angle. The ball milled powders were then uniaxially pressed at 70 MPa into cylindrical shaped pellets of 10 mm diameter. The pellets were covered on both sides with conductive graphite paste (MERCK) which was used as electrode and the electrical measurements were performed in a tube furnace by two probe method in air. The electrical data were collected using impedance analyzer (HIOKI Model: 3532-50) in the temperature range 350 °C–560 °C and over the frequency range 42 Hz–5 MHz.

3. Method of analysis

The Rietveld powder structure refinement analysis of X-ray powder diffraction data is one of the best methods for structure and microstructure characterization. The Rietveld software MAUD (version 2.26) [16,17] has been used in our study to refine the microstructural parameters through a least square method. The pseudo-Voigt (pV) function is used to fit experimental profile as it takes care of both the particle size and strain broadening of the experimental data. For fitting the experimental profiles of powder mixtures the simulated XRD pattern is generated including the structural information of both CeO_2 (ICSD code # 167160, cubic, space group: F_{m3m}, $a = 5.4169$ Å) and Dy_2O_3 (ICSD code # 82421, cubic, space group: I_{a3}, $a = 10.6706$ Å) incorporating all instrumental corrections, and some initial values of crystallite size and rms lattice strain. The structural and microstructure parameters in simulated pattern are then refined to fit the experimental XRD patterns. The background of the patterns is fitted by a polynomial function of degree 4. Positions of all peaks are corrected by successive refinements with zero-shift error. To consider the integrated intensity of the peaks as a function of structural and microstructure parameters, the Marquardt least-squares procedures are used for minimization of the difference between the observed (experimental) and simulated powder diffraction patterns. The minimization is monitored using the reliability index parameter, R_{wp} (weighted residual error), and R_{exp} (expected error) and the ratio of these two leads to the value of goodness of fit (GoF) [18,19–23]:

$$\mathrm{GoF} = \frac{R_{wp}}{R_{exp}}$$

The GoF values for all patterns are within 1.04–1.13, signifies that fitting quality of these patterns is quite well [24].

4. Results and discussions

4.1. Structural characterization

Fig. 1 illustrates the XRD patterns of unmilled (0 h) mixture of CeO_2 and 10 mol% Dy_2O_3 and ball milled mixture for 1 h, 3 h, and 8 h durations. From the indexed pattern it is evident that in the 0 h pattern, intensity ratios of both CeO_2 and Dy_2O_3 phases are in accordance with their relative compositions and there is no trace of any impurity phase in the pattern. It may be noted that reflections of both phases are quite sharp and the lattice parameters of both these cubic phases are very closely related to each other ($a_{CeO_2} \approx 1/2a_{Dy_2O_3}$). As a result, all Dy_2O_3 reflections appear adjacent to each CeO_2 reflection in the XRD pattern. It indicates that crystallite sizes of both powders are quite large and lattice mismatch between these two phases is quite small. It is interesting to note that just after 1 h of milling all Dy_2O_3 reflections disappeared completely and Dy-doped ceria powder has been synthesized within 1 h of milling. In addition to that all CeO_2 reflections are broadened significantly within 1 h of milling. With further milling up to 8 h, significant amount of both peak shift and peak broadening are noticed due to cumulative effect of Dy-doping and high energy impact of mechanical alloying.

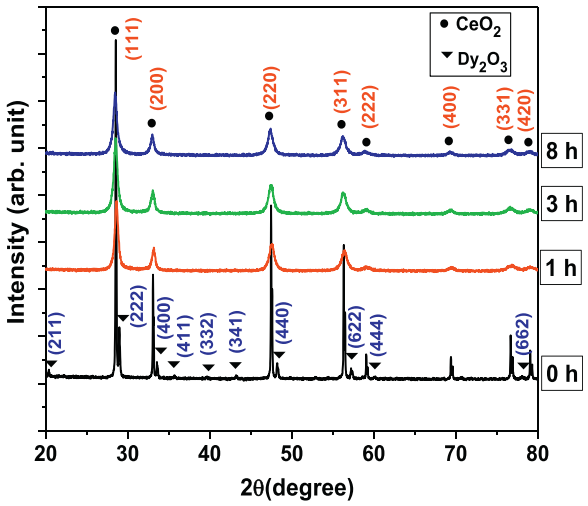

Fig. 1. XRD patterns of the unmilled (0 h) and ball milled powder mixture of 10 mol % Dy_2O_3 and CeO_2 milled for 1 h, 3 h and 8 h durations.

The Rietveld refined outputs of all these XRD patterns are shown in Fig. 2. The residue of fitting (I_o–I_c) of each pattern is plotted under respective XRD pattern. From the fitting output, it is

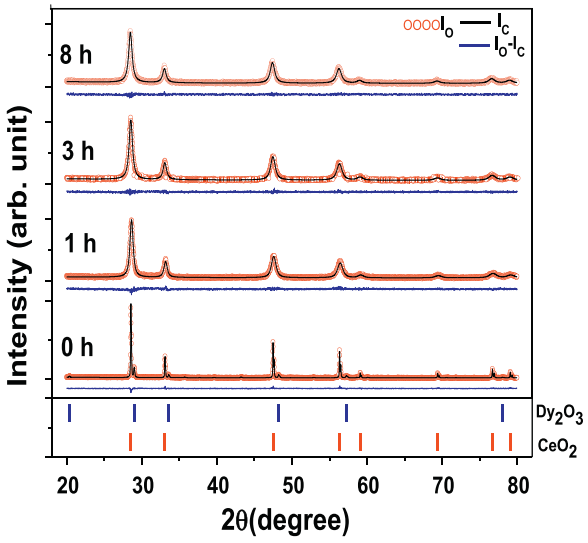

Fig. 2. Observed (o) and refined simulated (–) X-ray powder diffraction patterns of powder mixture of CeO_2 and Dy_2O_3 with milling time 0 h,1 h,3 h and 8 h from Rietveld powder structure refinement analysis. (I_o–I_c) represents the difference between the observed and calculated patterns.