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Structural investigation of boron undoped and doped indium stabilized bismuth oxide nanoceramic powders

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Abstract

The synthesis of boron undoped and doped indium stabilized bismuth oxide nanoceramic powders via the polymeric precursor technique were described. The physical properties of the precursor polymer solutions (pH, surface tension, viscosity and conductivity) were measured.

The morphological and structural characteristics of the nanoceramic powders were investigated by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR).

The lattice constant, average particle size, microstrain and dislocation density of the samples were calculated. The results show that the average particle size decreased while both the microstrain and the dislocation density values increased in the boron doped indium stabilized bismuth oxide. The structure proposed from FTIR spectra is mainly based on BiO_6 and BiO_3 units.

Keywords: Bismuth oxide; Indium; Boron doped; Nanoceramic powders

1. Introduction

Nanocrystalline materials have attracted much attention, because of their specific properties in optical, electronic, magnetic and mechanical applications [1].

Bismuth oxide based materials exhibit high oxide ionic conductivity and has been proposed as good electrolyte materials for applications, such as solid oxide fuel cells (SOFC) and oxygen sensors [2–4]. Solid oxide fuel cells are viewed as important to the future of greener and more efficient energy sources.

Bismuth oxide (Bi_2O_3) exists as five crystallographic polymorphs (monoclinic α-phase, tetragonal β-phase, body centered cubic γ-phase (bcc), face centered cubic δ-phase (fcc) and triclinic) [5,6]. The monoclinic α-phase and γ-bcc forms are semiconductors, whereas the β-tetragonal and δ-fcc forms are oxide ion conductors. δ-phase bismuth oxide (δ-Bi_2O_3) has a fluorite type structure and high conductive oxide ion conductor [3,7,8]. However, this phase only stable between 730–825 °C. It is possible to obtain at room temperature by doping with some transition metal and rare earth metal ions and oxides [9,10].

δ-Bi_2O_3 can be stabilized down to room temperature by the additions of indium oxide (In_2O_3). In_2O_3 in the bulk form has been widely used in solar cells and organic light emitting diodes [11,12]. Indium stabilized δ-Bi_2O_3 can be synthesized by various techniques including mechanochemical synthesis, powder milling and mixing and the polymeric precursor technique (PPT). The PPT appears the most attractive for the preparation of cubic δ-Bi_2O_3 based ionic conductors which employs of complexing of metal acetate/nitrate precursor in a polymer solution for example PVA. The main advantage of polymeric precursor technique is the homogeneity of the precursors on a molecular level.

Boron oxide, B_2O_3 formed by the thermal fusion of boric acid (H_3BO_3). It has amorphous form and is an excellent

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network former. Boron oxides have the advantage of low heat expansion and high refractive index. Because of these natures, boron oxides are used widely in glass ceramics composition. According to previous experimental results [9,13–15], the addition of boron oxide to the bismuth oxide is very beneficial and it is very effective as a sintering aid. It reduced the processing temperature because of its low melting point and could help resulting in smaller grain sizes and grain boundary strengthening during the calcination stage.

The purpose of the present study was to investigate of boron doped and undoped indium stabilized bismuth oxide nanoceramic powders in order to establish the structural changes induced by indium and boron to the bismuth oxide. Nanoceramic powders were obtained by the calcination method to remove of the organic phase from precursor polymer solution.

The physical properties of solutions such as pH, surface tension, viscosity, and conductivity were measured. The structures of boron doped and undoped indium stabilized bismuth oxide nanoceramic powders were investigated by X-Ray diffraction (XRD), FTIR spectroscopy and Scanning Electron Microscope (SEM).

2. Experimental section

2.1. Materials and method

In the experiment, bismuth (III) acetate (99 · 99%, Aldrich), indium acetate (99 · 99%, Aldrich) and polyvinyl alcohol (PVA) (Aldrich, molecular weight=85,000–124,000) were used as starting materials and ultrapure deionized water was used as a solvent. Boric acid was obtained from Merck and ultrapure deionized water was used as a solvent. The experimental procedure is schematically shown in Fig. 1.

Aqueous PVA solution (10%) was first prepared by dissolving PVA powder in distilled water and heating at 80 °C with stirring for 2 h, then cooling to room temperature. Then, 1.5 g of bismuth(III) acetate and 0.3781 g of indium acetate were added to the 30 g aqueous PVA at 60 °C separately and the solution was vigorously stirred for 1 h at this temperature. Stirring was continued for 3 h at room temperature. Thus, viscous gels of PVA/Bi-In acetate hybrid polymer solution (solution In1) were obtained. Boron doped solution (solution In2) was prepared using the same procedure of solution In1 and adding 0.25 g of the boric acid. Finally, the boron undoped and doped hybrid polymer solutions were calcined at a rate of 8 °C/min for 2 h at 850 °C at atmospheric conditions. The resulting oxide nanoceramic powders obtained from solutions were ground into powder using a mortar.

2.2. Measurement and characterization

The pH and conductivity of the polymer solutions were measured using pH 315i meter (Wissenschaftlich-Technische Werkstätten (WTW) GmbH & Co. KG) and conductivity meter (Wissenschaftlich-Technische Werkstätten (WTW) GmbH & Co. KG), respectively. The viscosity of the solutions was determined using a SV-10 viscometer. Surface tension measurements were performed using a KRUSS manual measuring system.

X-ray powder diffraction patterns of nanoceramic powders were collected using a PANalytical Empyrean X-Ray diffractometer using Cu Kα radiation ($\lambda = 1.54$ Å).

The surface morphology of nanoceramic powders was examined by using Field Emission Scanning Electron Microscopy (FESEM-Carl Zeiss, Supra 40 VP) with an accelerating voltage of 10 kV. The samples were sputter-coated with platinum (Qourum Q 150 R ES DC Sputter). ImageJ-Image-Pro

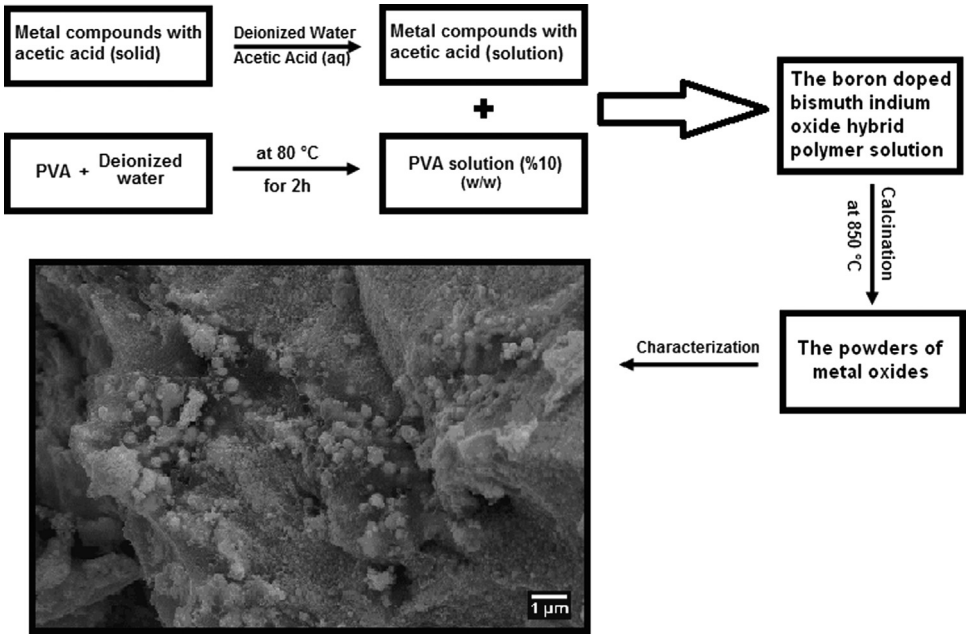

Fig. 1. Schematic of experimental procedure for synthesizing nanoceramic powders.