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Polymer-derived yttria stabilized bismuth oxide nanocrystalline ceramics

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Abstract

Boron doped and undoped Bi_2O_3–Y_2O_3 nanofibers were synthesized by the electrospinning method. The nanofibers were then calcined to obtain nanocrystalline ceramics. The synthesized nanofibers and nanocrystalline ceramics were characterized using XRD, FT-IR, SEM and XPS. According to the XRD results the undoped Bi_2O_3–Y_2O_3 nanocrystalline ceramic has a face-centered cubic structure. The XPS results show that nanocrystalline ceramics were pure Bi_2O_3, and there were no peaks related to either bivalent or tetravalent or pentavalent states in Bi_2O_3. The XPS results also show that the crystallinity of the boron doped nanocrystalline ceramic was decreased because of the network former property of the boron. The average fiber diameters for electrospun boron doped and undoped PVA/Bi–Y acetate nanofibers were calculated as 179 nm and 96 nm, respectively. The SEM micrographs of the nanocrystalline ceramics show that the undoped Bi_2O_3–Y_2O_3 ceramic has needle-like crystalline structure. However, the crystallinity of the boron doped Bi_2O_3–Y_2O_3 ceramic decreased because of boron doping.

Keywords: A. Calcination; A. Precursors: organic; B. Nanocomposites; D. Y_2O_3

1. Introduction

Bismuth oxide and its composites have been studied for various applications because of the excellent properties of bismuth oxide. Armelao et al. mentioned that bismuth oxide (Bi_2O_3) has at least four main crystalline forms usually indicated as α, β, γ and δ each showing different chemical and physical properties [1]. The high oxygen-ion conducting δ-phase has a (defect) fluorite structure and transforms to β-phase at about 650 °C and γ-phase at about 640 °C. Both β and γ phase have very low oxygen-ion conducting properties with respect to δ-phase. Defect-fluorite structure δ-phase contains a very large concentration of oxygen vacancies where three quarters of the tetrahedral interstices are randomly occupied by oxide ion. High oxide ion conduction of δ-phase is provided by oxide ion vacancies and interstitial oxide ions. The conductive characteristics of Bi_2O_3 are not retained over long periods of time and also its strength tends to diminish because of a large volume change during phase transformations [2].

The stability is the principal requirement for any realistic device based on Bi_2O_3 solid electrolytes such as solid oxide fuel cell (SOFC) applications [3]. Similar to stabilization of zirconia, yttria or some other oxides (Yb_2O_3, Er_2O_3, Y_2O_3, Dy_2O_3, and Gd_2O_3) have also been used in stabilization of defect-fluorite structure δ-phase Bi_2O_3 [4,5]. After stabilization the final ceramic bismuth yttrium oxides can keep fluorite-type δ-phase structure even at room temperature.

In this study, polymer-derived boron containing Bi_2O_3–Y_2O_3 nanocrystalline ceramics were prepared using electrospinning technique. This technique is cost effective and a functional technique to produce nanofibers, polymer derived nanocrystalline ceramics and nanocomposites [6–8]. Tunc et al. referred to advantages of polymer derived nanocrystalline ceramics prepared by electrospinning in their paper. Tunc et al. said that the main advantages of such polymer-derived ceramics are the applicability of polymer-processing techniques, the homogeneity of the precursors on a molecular level,

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and the low processing temperatures when compared to conventional powder sintering methods [9–12].

Boron oxide (B_2O_3) was used in this study as a dopant because of its properties. Aytimur et al. [13] described the boron oxide and its properties. Aytimur et al. mentioned that B_2O_3 is almost always found as the amorphous form. It is an excellent network former and very effective sintering aid [14–19].

2. Experimental section

In the experiments, poly(vinyl alcohol) (PVA) (average Mw 85,000–124,000; Sigma-Aldrich), bismuth(III) acetate (Sigma-Aldrich), yttrium(III) acetate (Sigma-Aldrich) and boric acid (Merck) were used. Ultrapure deionized water was used as a solvent.

An aqueous PVA solution (8%) was first prepared by dissolving the PVA powder in ultrapure deionized water. In the experiments, two hybrid polymer solutions were prepared. As a typical procedure, proper amounts of the metal acetate salts and boric acid powder were dissolved in ultrapure deionized water (see Table 1). Metal acetate and boric acid solutions were added to the proper amount of the PVA solution to prepare electrospinning solutions.

Obtained electrospinning solutions were poured into syringes, the needle (18 gauge) being connected to the positive terminal of a high-voltage supply (Gamma High Voltage Research) able to generate DC voltages up to 40 kV. Solutions were delivered to the needle by a syringe pump (New Era Pump Systems Inc., USA). The distance between the tip of the needle and the aluminum collector was fixed at 18 cm. The following operative parameters were chosen: flow rate 0.5 ml/h and applied voltage 20 kV. Electrospun nanofibers were dried in vacuum for 12 h at 80 °C. Nanofibers were calcined at 850 °C in the furnace at atmospheric conditions. Major steps of nanocrystalline ceramic material preparation were given in Fig. 1.

The pH and conductivity of the solutions were measured by using Wissenschaftlich-Technische-Werkstätten (WTW) and 315i/SET apparatus. The viscosity of the hybrid polymer solutions was measured with AND SV-10 viscometer. The surface tension of the complex hybrid polymer solutions was measured by using KRUSS model manual measuring system. Fiber morphology, average fiber diameter and distribution were determined by scanning electron microscopy (JEOL JSM 7000F Field Emission) on samples sputtered with gold and observed at an accelerating voltage of 10 kV. Fiber diameter was measured by image processing software, ImageJ (Image Pro-Express, Version 5.0.1.26, Media Cybernetics Inc.). ImageJ is a public domain Java image processing program [20]. The crystal structures of the calcined powders were investigated by means of X-ray diffraction (XRD) (Ultima-IV XRD (Rigaku, Tokyo, Japan) with Cu Kα radiation at 40 kV and 30 mA).

3. Results and discussion

The morphology of the fibers depends on the properties of the electrospinning solution. Therefore, the pH, viscosity, conductivity and surface tension of the PVA/Bi–Y acetate solutions were measured before the electrospinning experiment. Measured values were given in Table 2. The solution viscosity is one of the prime parameter affecting the fiber diameter. A higher viscosity results in a large fiber diameter. Moreover, the viscosity has a meaningful effect on whether the electrospinning jet breaks up into small droplets or whether the resulting electrospun fibers contain beads [21,22]. The conductivity of the polymer solution is important to initiate the electrospinning process. Furthermore, the conductivity of the electrospinning solution is a considerable parameter influencing the diameter of electrospun nanofibers as well as viscosity. An increase in the electrical conductivity of the solution causes a decrease in the diameter of the electrospun nanofibers [21].

Fig. 2 exhibits the FT-IR spectra of the precursor electrospun nanofibers and the calcined nanocrystalline undoped and boron doped ceramics. It is seen that both the undoped and boron doped PVA/Bi–Y acetate nanofibers have approximately the same IR spectrum because of the presence of poly(vinyl alcohol). The broad band around 3200 cm^{-1} and around 1550 cm^{-1} correspond to the stretching vibration and deformation vibration of hydroxyl (–OH) groups, respectively. The existence of these bands indicate the existence of adsorbed water on the surface of the electrospun nanofibers. The band corresponds to the

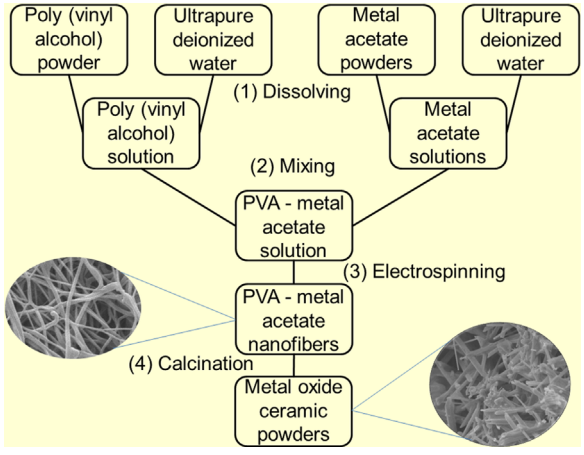

Fig. 1. Major steps of the nanocrystalline ceramic preparation.

Table 1
Amounts of poly(vinyl alcohol), metal acetates and boric acid in the electrospinning solutions.

Solution	Bismuth acetate powder (g)	Yttrium acetate powder (g)	Boric acid powder (g)	PVA solution (g)
PVA/undoped Bi–Y acetate (solution-1)	1.00	0.2297	–	125
PVA/boron doped Bi–Y acetate (solution-2)	1.00	0.2297	0.25	125

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