JOURNALOF

Ceramic Processing Research

Fabrication and characterization of boron doped BaZrO₃ nanofibers via an electrospinning technique

T. Tunç^{a,*}, İ. Uslu^b and S. Keskin^c

^aScience Department, Faculty of Education, Aksaray University, Aksaray, 68100, Turkey ^bChemistry Department, Faculty of Education, Gazi University, Ankara, 06900, Turkey ^cCentral Laboratory, Middle East Technical University, Eskisehir Yolu, Ankara, 06531, Turkey

In this study, boron doped and undoped poly(vinyl) alcohol/zirconium-barium acetate (PVA/Zr-Ba) nanofibers were prepared using an electrospinning technique then calcinated at three different temperatures; 250 °C, 500 °C, 800 °C for 2 h. The originality of this study is the addition of boron to metal acetates. The fibers were characterized by FT-IR, DSC, XRD and SEM. The addition of boron did not only increase the thermal stability of the fibers, but also increased their diameters, which gave stronger fibers. The FT-IR spectra of the fibers were in good accordance with literature data. The DSC results indicate that the glass transition (Tg) and melting temperatures (Tm) showed a change with the addition of boron. Also, boron doped fibers were observed to degrade at higher temperatures. XRD analyses showed that after further heat treatment at 800 °C, zirconia exists in two phases of tetragonal and monoclinic modifications. The systematic evolution of morphological features in the spun and the processed fibers were studied by scanning electron microscopy. The SEM appearance of the fibers showed that the addition of boron resulted in the formation of cross linked bright surfaced fibers.

Key words: Electrospinning, Boric acid, Nanofibers, Zirconium- barium acetate, PVA.

Introduction

Nanoscale hybrid or composite materials in the form of nanofibers, nanowires, nanorods and nanowhiskers have gained much interest in diverse fields, such as filtration, medicine, fabrication of electronic devices such as diodes, transistors, photo detectors, sensors, solar cells because of their unexpected and unprecedented properties which are unattainable in normal materials [1-3]. Recently, there has been much interest in the synthesis of organic-inorganic hybrid nanoparticles with different combinations of several components, due to their important physical properties for high-performance engineering materials. These hybrid particles combine the advantageous properties of inorganic particles (e.g., metals) with organic counterparts (e.g., polymers) and exhibit many new characters that singlephase materials do not have [4]. Physical mixing and sol-gel technique methods are the easiest and commercialized chemical incorporation routes for producing hybrid nanoparticles.

Zirconia is a very important ceramic material because it has an excellent combination of electrical, thermal, and mechanical properties. Pure zirconia exists in three polymorphs at low pressure (monoclinic, tetragonal and cubic) and in an orthorhombic form at high pressure. Among them the tetragonal and cubic phases are metastable forms but monoclinic is the stable form at room temperature. Stabilization of cubic and tetragonal forms are gaining importance because of their excellent thermal stability, chemical resistance, mechanical properties and oxygen conductivity [5].

The perovskite structure is adopted by many oxides that have the chemical formula ABO₃. Many alkaline earth perovskites exhibit high proton conductivities at moderately elevated temperatures (400-700 °C). These materials have attracted attention for their potential applications as electrolytes in fuel cells and chemical sensors [6]. Doped perovskites, such as barium cerate (BaCeO₃), strontium cerate (SrCeO₃), and barium zirconate (BaZrO₃), have been widely studied in recent years as proton conducting electrolytes for a variety of electrochemical devices including fuel cells [7].

A simple method to synthesize barium zirconate (BaZrO₃) can be the traditional solid state reaction route in which appropriate amounts of zirconia and barium carbonate are mixed together, ball milled so that a uniform and small powder size is obtained. It is also necessary to make several cycles of grinding/firing during a rather long heating time in order to complete the reaction and obtain fine powder. Powders produced by such a process may still have a high degree of aggregation and sometimes inhomogeneities [8]. Alternatively, the sol-gel route may be used [9].

Recent years, to overcome the drawbacks of conventional

^{*}Corresponding author: Tel : +90-5065057102 Fax: +90-3822801180

E-mail: tctunc@gmail.com

solid state synthesis and to obtain homogenous very fine powder, solution processing for example the sol-gel route has gained much interest and has proved to give better results [10]. Use of a fine powder of BaZrO₃ results in a large dielectric constant of a capacitor itself at a normal temperature. The fine powder is very suitable as an electrostrictive, piezoelectric or transparent ceramic material.

Recently, many research groups have studied the influence of boric acid (H_3BO_3) on the properties of some ceramics [11-13]. Kushnirenko *et al.* [11] investigated the effect of an addition of H_3BO_3 on the sintering of ZnO, and found that the addition of boric acid resulted in a rise of the grain size, an increase of the grain conductivity, a quenching of defect-related luminescence, and the enhancement of exciton emission.

Misirli *et al.* [14] investigated the effect of an addition of boric oxide (B_2O_3) to the sintering of Al_2O_3 , and found that the porosity of the materials, which were made using a spray-drying technique, could be controlled by the level of addition of B_2O_3 . This porous structure gave the material a good strength, making it a potential candidate for use in ceramic filters and for ceramic-metal composite preforms [12]. This paper reports on the effect of the addition of B_2O_3 on the properties of sintered $BaZrO_3$ nanofibers. B_2O_3 has been chosen as an effective sintering aid because of its low melting point (460 °C), which could help during the sintering process by forming a liquid phase [15].

Electrospinning is a unique fiber spinning process because electrospun fibers have a very high specific surface area and small pore size so they can be used in a number of applications including membranes, tissue scaffolding and other biomedical applications and nano sized composite polymer preparation. A schematic representation of the electrospinning process is shown in Fig. 1.

Many polymers have been successfully electrospun into ultrafine fibers through solvent solution or melts. Poly (vinyl alcohol) (PVA) has been largely used in fiber and film products for many years. At the same time, boric acid has been occasionally used as a cross-linking agent in PVA and enhances its stability [16].

In this study, PVA/zirconium-barium acetate (PVA/Zr-Ba)



Fig. 1. Schematic representation of the electrospinning process.

composite nanofibers were prepared using a sol-gel process and an electrospinning technique. After calcination of the thin fibers, ultra-fine powders of BaZrO₃ were prepared. The effect of heat treatment temperature on morphology and crystal structure was investigated at 250, 500 and 800 °C. The study also establishes the effect of boron doping on the morphology of BaZrO₃ nanopowders at various calcination temperatures.

Experimental Procedure

Materials

The PVA with a molecular weight of 72000 g/mol and boric acid (H_3BO_4 , 99.9% purity) were supplied by Merck. Zirconium acetate, a solution in dilute acetic acid (Zr, 15-16%) and barium acetate was obtained from Sigma Aldrich. Ultra pure deionized water was used as a solvent.

Sol preparation

An aqueous PVA solution (10%) was first prepared by dissolving PVA powder in distilled water and heating at 80 °C with stirring for 3 h, then cooling to room temperature and stirring for 24 h. 2 g of the zirconium acetate solution in adequate dilute acetic acid, 0.2 g of barium acetate solution and 0.2 g of boric acid solution were added to the 50.0 g aqueous PVA at 60 °C separately and dropwise and the solution was vigorously stirred for 1 h at this temperature. Stirring was continued for 2 h at room temperature. Thus, PVA/Zr-Ba acetate hybrid polymer solutions doped and undoped with boron were obtained. These mixtures were aged at room temperature for about 12 h.

Preparation of nanofibers

The hybrid polymer solutions was poured into a syringe, 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. The suspension was 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 (diameter 10 cm) was fixed at 11-13 cm. The following operative parameters were chosen: flow rate 0.8 ml/h, applied voltage 18 kV. The fibers thus formed were dried in vacuum for 12 h at 80 °C. Free nanofiber mats were obtained by peeling off from the aluminum foil. Nanofiber mats were heat treated at 250 °C, 500 °C and 800 °C.

Measurement and characterization

pH values of polymer solutions were determined with a pH meter (WTW 315 I Set Sentix 41 electrode, Wissenschaftlich-Technische Werkstätten GmbH & Co., Weilheim, Germany). Solution viscosity and conductivity measurements were performed with a SV-10 viscometer (A&D Company, Ltd., Tokyo, Japan). The surface tension of the complex hybrid polymer solution was measured using a K-100 model (KRÜSS, GmbH, Hamburg, Germany) manual measuring system. Fourier transform infrared (FTIR) spectra were obtained on a Bruker Vertex 70 (Bruker Optics Inc., Ettlingen, Germany) spectrometer equipped with a diamond protected Attenuated Total Reflectance (ATR) crystal unit. FTIR spectra were acquired in the range of 4000 cm⁻¹ to 500 cm⁻¹, and fifty scans were obtained and averaged to a resolution of 4 cm⁻¹.

Differential Scanning Calorimetry (DSC) measurements were carried out on Shimadzu DSC-60 (Shimadzu, Kyoto, Japan) equipment using nitrogen as the carrying gas. The temperature was raised from room temperature to 200 °C then cooled to room temperature and heated again to 500 °C with a heating rate of 10°K·minute⁻¹. The crystal structures of the BaZrO₃ powders calcined at 250 °C, 500 °C and 800 °C were investigated by means of X-ray diffraction (XRD) (Philips X'Pert-PRO System, Cu Kα radiation).

Fiber morphology, average fiber diameter and distribution were determined by scanning electron microscopy (QUANTA 400, FEI Company, Eindhoven, Netherlands) on samples sputtered with gold and observed at an accelerating voltage of 10 kV. Fiber diameter was measured by image processing software (Image Pro-Express, Version 5.0.1.26, Media Cybernetics Inc.), calibrated using an image of known diameter. Fiber diameters were quantitatively measured using ImageJ software. ImageJ is a Java-based public domain program that contains basic digital image processing tools, and includes numerous tools that facilitate quantitative measurements which was originally developed at the National Institute of Health [17].

Results and Discussion

Physical properties of the polymer solutions

The pH, viscosity, conductivity and the surface tension of the polymer solutions before the electrospinning experiment were measured and are given in Table 1. Boron is used as a cross-linking agent in this study. The addition of boric acid as a boron source increased the conductivity, viscosity and the surface tension of the hybrid polymer solution as expected. Boric acid (H₃BO₃) is a white odorless, crystalline solid with a specific gravity of 1.51 and a melting point of 170.9 °C. It is not combustible and has a water solubility at 20 °C of 4.7%. When heated it loses water, first forming metaboric acid (HBO₂) and on further heating converts to boric oxide (B₂O₃).

FT-IR spectra

Fig. 2 shows the FT-IR spectra for the boron doped and

Table 1. Physical properties of the polymer solutions

Polymer solution	Conductivity mS	Viscosity Pas	pН	Surface tension mN/m
PVA/Zr-Ba acetate	3.63	1.46	4.90	44
B doped PVA/Zr-Ba acetate	3.73	1.70	4.77	47



Fig. 2. FT-IR spectra of PVA/Zr-Ba acetate nanofiber samples, boron (a) doped and (b) undoped.

undoped PVA/Zr-Ba acetate nanofiber samples. As can be observed, both boron doped and undoped samples have approximately the same spectrum indicating that the effect of PVA is dominant over all the spectra. The large bands observed between 3500 and 3200 cm⁻¹ are linked to the stretching O-H. The vibrational band observed between 2800 and 3000 cm⁻¹ refers to the stretching C-H from alkyl groups and the peak at 1710 cm⁻¹ is due to the stretching C = O vibration. Peaks at about 1555, 1410, 1090 cm⁻¹, correspond to vC = C, vC-H₂, vC-O-C, respectively. The peaks at about 2932, 1555, 1410, 1324, 1092, 920, 840 cm⁻¹ are in good accordance with the literature [18].

Differential scanning calorimetry (DSC)

DSC thermograms of electrospun boron doped and undoped PVA/Zr-Ba acetate nanofibers are shown in Fig. 3. The endothermic melting peak (Tm) of PVA generally appears around 257 °C [19]. In this study, it can be seen from the thermograms of undoped and doped PVA/Zr-Ba acetate nanofibers that the melting endothermic peak appears around 277 °C and 280 °C, respectively. The intensity of



Fig. 3. DSC thermograms of electrospun boron (a) doped and (b) undoped PVA/Zr-Ba acetate nanofibers.

the peak decreased as the PVA is fully cross-linked with boron by forming an amorphous structure. By crosslinking PVA fibers with boron using boric acid, the endothermic peak of boron doped PVA fibers became less prominent and almost disappeared. This indicated that the ordered association of the PVA molecules was decreased by the presence of boric acid in PVA, saying that the PVA molecules were highly constrained by the chemical crosslinking of PVA with boron. This shows that crosslinking decreases the degree of crystallinity which is in good accordance with the literature [20].

PVA composite fibers undoped with boron have two degration peaks at 386 and 459 °C, but boron doped fibers do not have such a clear degradation peak. This can be explained because the imperfect crystals were conformed by the addition of boric acid. The regularity of PVA crystals decreased and the peak related to the degradation of boron doped PVA/Zr-Ba acetate nanofibers broadened due to the intercrosslinking by boric acid.

XRD Analysis

XRD curves for boron undoped and doped samples after calcination at 500 °C and 800 °C are shown in Fig. 4(a-d). XRD peaks of boron undoped and doped barium stabilized zirconia particles following heat treatment at 500 °C are given in Fig. 4(a) and Fig. 4(b) and the curves following heat treatment at 800 °C are given in Fig. 4(c) and Fig. 4(d).

XRD peaks given in Fig. 4(c)-(d) corresponds to a typical XRD spectrum of zirconia in the tetragonal phase appearing at $2\theta = 30.05$ (111), 34.8 (200), 50.0 (220), 59.5 (311). Increasing the heat treatment temperature from 500 °C to 800 °C enhanced and increased the peak sizes, well-defined peaks appeared and the crystallite size for all samples is increased as expected.

It is seen from Fig. (4) that barium as a stabilizer is a

proper choice to obtain the desired tetragonal form of zirconia and this phase is predominant for all samples produced at a wide range of temperatures and no phase conversion is observed. The phase transformation from the metastable tetragonal form to the stable monoclinic phase results in about a four percent volume increase within the crystal lattice of the zirconia material. To avoid the cracking problem due to the volume increase during the phase change it is desirable that barium zirconate stays in the tetragonal phase over a relatively wide range of temperature [21].

The values of 2θ , 22.319, 28.967. 41.385, 47.596, 55.404 and 58.195 according to JCP2 024-0129 card number is in good agreement with Fig. 4(d) that the addition of boron improved densification of zirconia and barium zirconium borate crystal structures are also formed. Smith also used boron as a sintering aid for calcia stabilized zirconia and in his studies densification of zirconia with borates showed that B_2O_3 is an effective sintering aid to form low-melting borate phases [22]. If boron was used as a sintering aid and fully stabilized barium zirconium was heated at temperatures higher than 800 °C, according to the reaction given below H₃BO₃ used as a boron source in PVA/Zr-Ba acetate electrospun nanofibers can produce very severe destabilization:

$$2H_3BO_3 \rightarrow B_2O_3 + 3H_2O \tag{1}$$

This is the reason why we have chosen the highest heat treatment temperature at 800 °C.

SEM analysis

SEM micrographs of the electrospun boron doped and undoped PVA/Zr-Ba mat are given in Fig. 5. The average fiber diameter for electropsun boron doped PVA/Zr-Ba



Fig. 4 XRD patterns of barium stabilized Zirconia after calcination (a) undoped (at 500 °C), (b) doped (at 500 °C) (c) undoped (at 800 °C) (d) doped (at 800 °C).



Fig. 5 SEM micrographs of PVA/Zr-Ba acetate nanofibers, boron (a) undoped, (b) doped.



Fig. 6 SEM micrographs of PVA/Zr-Ba acetate nanofibers heat treated at 250 $^{\circ}$ C, boron (a) undoped, (b) doped.

acetate nanofibers was 797 nm and boron undoped nanofibers was 466 nm. The images show that the nanofibers have smooth and uniform surfaces with random orientation with no beadings. In Fig. 6, micrographs of heat treated boron doped and undoped samples at 250 °C are presented. Some bundles and junctions were also evidenced after the heat treatment of the electospun mats.

In order to make nano powders of BaZrO₃, the assynthesized electrospun materials were subjected to calcination at 500 °C and 800 °C in air. During these calcinations, zirconium oxide stabilized with barium oxide was formed from the PVA/Zr-Ba acetate. Fig. 7(a) and Fig. 7(b) shows boron doped and undoped PVA/Zr-Ba acetate nanofibers after calcination at 500 °C, respectively. Fig. 7(a) shows that the nanofiber morphology was changed and crystal line grains were formed. This crystallization is clearly related to the formation of a particulate morphology, but is not complete even after calcination at this temperature. Fig. 7(b) reveals that due to crosslinking of boron with PVA, the fiber morphology was not changed and still kept an average diameter of the fibers which shrank to 157 nm.

In Fig. 8, SEM micrographs of boron undoped and doped calcined samples at 800 °C are presented. In Fig. 8(a), thin crystals approximately 10 µm long can be clearly seen. SEM micrographs from the study of the morphology of the heat treated (800 °C) boron doped barium stabilized zirconia nanocrystalline composite powders are shown in Fig. 8(b). The average dried nanofiber diameter of boron doped PVA/Zr-Ba acetate nanofibers heat treated at 250 °C (Fig. 6(b)) were 789 nm while that of the heat treated boron doped barium stabilized zirconia was 197 nm. A significant decrease in fiber diameters were observed in SEM micrographs which reveals that this decomposition



Fig. 7 SEM micrographs of PVA/Zr-Ba acetate nanofibers heat treated at 500 $^{\circ}$ C, boron (a) undoped, (b) doped.



Fig. 8 SEM micrographs of PVA/Zr-Ba acetate nanofibers heat treated at 800 °C, boron (a) undoped and (b) doped.

of the inner PVA matrix was complete.

Conclusions

In conclusion, boron doped PVA/Zr-Ba composite fibers were prepared using a sol-gel process and an electrospinning technique. After the calcination of the nanofibers, stable barium zirconium-borate and barium stabilized zirconium oxide ultra-fine fibers could also be prepared.

X-ray diffraction experiments show that the addition of boron to barium stabilized zirconia promotes the crystal structure and diffraction data were in agreement with the literature. An increase of the calcination temperature from 500 °C to 800 °C also improved the crystal structure. Crystal structures of boron doped and undoped barium stabilized zirconium oxide samples prepared after calcination at 800 °C can be easily seen from SEM micrographs. These results indicate that PVA polymerized synthesis method for BSZ oxide composite materials was an effective route for the preparation of nanocrystalline materials.

Acknowledgement

This study has been supported and funded by the Selçuk University Commission for the Scientific Research Projects (BAP).

References

- D. Bjorge, N. Daels, S. De Vrieze, P. Dejans, T. Van Camp, W. Audenaert, J. Hogie, P. Westbroek, K. De Clerck and Stijn W.H. Van Hulle, Desalination 249 (2009) 942-948.
- 2. Z.M. Huang, Y.Z. Zhang, M. Kotaki and S. Ramakrishna,

- İ. Dökme, Ş. Altındal, T. Tunc and İ. Uslu, Microelectron. Reliab. 50 (2010) 39-44.
- 4. M.R. Karim, H.W. Lee, I.W. Cheong, S.M. Park, W. Oh, and J.H. Yeum, Polym. Composite. 3[1] (2010) 83-88.
- J.C. Ray, R.K. Pati and P. Pramanik, J. Euro. Ceram. Soc. 20 (2000) 1289-1295.
- P. Babilo and M.H. Sossina, J. Am. Ceram. Soc. 88[9] (2005) 2362-2368.
- 7. P. Babilo, T. Uda and S.M. Haile, J. Mat. Res. 22 (2007) 1322-1330.
- F. Boschini, B. Robertz, A. Rulmont and R. Cloots, J. Euro. Ceram. Soc. 23 (2003) 3035-3042.
- 9. M. Veith, S. Mathur, N. Lecerf, V. Huch and T. Decker, J. Sol-gel and Technol. 15 (2000) 145-158.
- B. Robertz, F. Boschini, R. Cloots and A. Rulmont, Int. J. Inorg. Mater. 3 (2001) 1185-1187.
- V.I. Kushnirenko, I.V. Markevich and A.V. Rusavsky, Radiat. Meas. 45 (2010) 468-471.

- İ. Uslu, M.K. Öztürk, M.L. Aksu and F. Gökmeşe, Synth. React. Inorg. Me. 39 (2009) 199-203.
- A. Dulda, D.S. Jo, W.J. Park, T.Masaki and D.H. Yoon, J. Ceram. Process. Res. 10 (2009) 811-816.
- Z. Misirli, H. Erkalfa and O.T. Özkan, Ceram. Int. 22 (1996) 33-37.
- 15. Y.J. Chen and Y.D. Huang, Opt. Mater. 25 (2004) 271-278.
- 16. J.Y. Woo, E.J. Shin and Y.H. Lee, Polym. Bull. 65 (2010)
- 169-180. 17. http://rsbweb.nih.gov/ij/docs/intro.html.
- M. Helen, B. Viswanathan, S.S. Murthy, J. Membrane Sci. 292 (2007) 98-105.
- C.A. Finch, "Polyvinyl alcohol; properties and applications" (Wiley, London, 1973).
- E.J. Shin, W.S. Lyoo, Y.H. Lee, J. Appl. Polym. Sci. 109[2] (2008) 1143-1149.
- J.P. Chang, Y.S. Lin and K. Chu, J. Vac. Sci. Technol. B 19 (2001) 1782-1787.
- 22. R.A. Smith, Am. Ceram. Soc. Bull. 81[8] (2002) 61-64.