

CHARACTERIZATION OF ELECTROSPUN BaTiO₃/POLYVINYLPIRROLIDONE (PVP) NANOFIBERS

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Introduction

Barium titanate (BaTiO₃, BTO) ferroelectrics are polar material that exhibits net spontaneous polarization without external applied field [1,2]. The polarization can be reoriented by applying the electric field. BTO with perovskite structure is widely used due to their ferroelectric, pyroelectric and piezoelectric properties in various electronic applications such as multi-layer ceramic capacitors (MLCCs), transducers, sensors and actuators, solid oxide fuel cell, and ferroelectric random access memories (FRAMs) [1,2].

BTO nanofibers were fabricated by drying electrospun BTO/polyvinylpyrrolidone(PVP) nanofibers for 1 h at 80°C in vacuum and subsequent annealing for 1 h at 750°C in air. During the annealing, PVP was removed and the crystallization was completed. The properties of electrospun BTO nanofibers were evaluated by using a TG/DSC, an XRD, a scanning SEM, a TEM, a Cannon-Fenske viscometer, a pycnometer, a dynamic tensiometer, and a FT-IR.

Experimental

Barium acetate (Aldrich, Ba(CH₃COO)₂), 1.275 g was dissolved in acetic acid, 3 ml, for 30 min at 60°C. Then, 1.475 ml of titanium isopropoxide (Junsei, [(CH₃)₂CHO]₄Ti) was added dropwise into the solution under magnetic stirring for 2 h. PVP (Aldrich, Mw=1,300,000) dissolved in ethanol was then added to the BTO precursor solution for rheological properties. The surface tension of the precursor solution was measured by using a dynamic tensiometer (Nima, DST9005, USA). The kinematic viscosity was measured with a 200 gage Cannon-Fenske viscometer, while the density was measured by a pycnometer. The dynamic viscosity was calculated from kinematic viscosity and density data.

The electrospinning apparatus consisted of a syringe pump (KDS-200, Stoelting Co., USA), a 22 gage B-D metal needle, a grounded collector and a high voltage supply (ES30P-5W, Gamma High Voltage Research Inc., USA) equipped with current and voltage digital meters [6-10,13]. The solution was placed in a 5 mL B-D luer-lok syringe attached to the syringe pump and was fed into the metal needle at a flow rate of 0.4 mL/h. A piece of flat aluminum foil was placed 7 cm below tip of the needle to collect the nanofibers at a DC voltage of 15 kV. The as-spun nanofibers were dried for 1 h at 80°C in vacuum. The dried mat was calcined for 1 h at temperatures from 650 to 750°C in air.

The fibers were evaluated with an aid of TG/DSC (Netzsch STA 409C/31F, Germany) and XRD (Mac Science, KFX-987228-SE, Japan). The TG/DSC analysis was performed in the temperature range from room temperature to 1000°C at a heating rate of 10°C/min. The XRD analysis was carried out with a scan speed of 5° 2θ/min in the 2θ range of 10° to 80°.

The diameter and the morphology of the fibers were evaluated using SEM (Hitachi S-3000H, Japan) and TEM (JEM-2000EX, Jeol, Japan). For SEM observation, the fibers were collected by placing silicon wafers on the aluminum foil during electrospinning. The properties of the fibers were further evaluated by using FTIR (Simazu Prestage 21, Japan) to obtain absorbance spectra.

Results and Discussion

Rheological properties of various oxide/polymer solutions are investigated. The lower values of surface tension than that of water (72 mN/m at 25°C) may lead to formation of fibers instead of polymer droplets [3]. The density, kinematic viscosity, dynamic viscosity, and surface tension of the BTO/PVP precursor solution are determined to be 1.0354 g/cm³, 31.1 mm²/s, 32.2 cP, and 23.5 mN/m, respectively. It is noted that the change in surface tension is negligible with the change in concentration. The viscosity was attributed to the morphology of electrospun fibers [3].

The thermal decomposition behavior of BTO/PVP fiber is shown in Fig. 1. The weight loss occurred until ~750°C. Endothermic peaks at 105°C and 300°C in the DSC curve was observed probably due to the evaporation of water and trapped solvent [1,2]. Exothermic peaks at 360°C, 470°C and 625°C were observed. Weight losses occurred at 360°C and 470°C probably due to the decomposition of barium acetate [1,2]. Another exothermic peak at 625°C may correspond to the decomposition of main chain of PVP and the formation of metal oxide phase of perovskite BTO [1]. The TG/DSC results revealed that most of the organic groups were vanished approximately at 750°C.

XRD results of the BTO/PVP fibers calcined at various temperatures are studied. The as-spun nanofibers were amorphous. Intermediate phases of orthorhombic barium carbonate (BaCO₃, JCPDS-45-1471) at 24°, 27°, 34°, 42°, 45°, 47°, and 55° of 2θ were observed when the fibers were calcined at 650°C [2]. After calcination at 700°C, onset of BTO perovskite crystallization was evident although non-perovskite peaks at 24°, 27° and 42° of 2θ still remained [2]. Disappearance of non-perovskite peaks is indicative of intermediate phase

decomposition. At 750°C, the perovskite peaks located at 31°, 45°, 56°, and 65° became stronger due to its thermal decomposition and complete reaction in the formation of BaTiO₃. The raw data and curve fits for the (110) and (200) peaks are deconvoluted and then identified as the mixtures of the (101) and (110) peaks and the (002) and (200) peaks, respectively, implying that it is tetragonal perovskite structure (JCPDS-05-0626) [1,2].

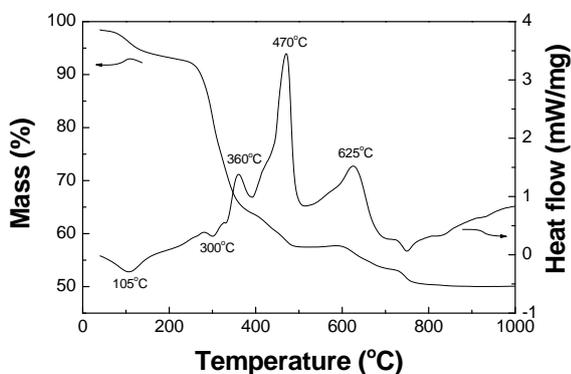


Fig. 1. TG/DSC curves of electrospun BaTiO₃/PVP composite fiber.

The formation of BTO was further evaluated by FT-IR measurement, as shown in Fig. 2. The FT-IR studies of BTO/PVP fibers showed main bands at around 3430, 2935, 1425, and 570 cm⁻¹ corresponding to O-H, C-H, O-H, and Ti-O stretching vibrations, respectively. The intensities of the O-H stretching vibration bands (at 3430 and 1425 cm⁻¹) became weaker with increasing the calcination temperature, implying the lower content of organics in the BTO/PVP composite fibers. A broad band at 570 cm⁻¹, Ti-O vibration, became sharper and narrower after calcination at 750°C due to the formation of metal oxide bonds as demonstrated in the XRD results.

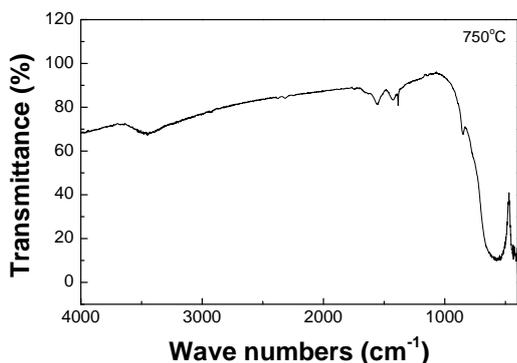


Fig. 2. FT-IR spectra of electrospun BaTiO₃/PVP nanofibers calcined for 1 h at various temperatures.

TEM image of BTO/PVP nanofibers calcined at 750°C is displayed in Fig. 3. The diameter of nanofibers calcined at 750°C was 160 nm. The morphology of the fibers changed from smooth and uniform to a linked-particle tubular form due to the decomposition of the inner PVP matrix. The surface roughness rose with

increasing calcination temperature but fiber continuity was maintained. The surface roughness is likely to be increased due to the formation of a polycrystalline microstructure. The selected area electron diffraction patterns of these fibers calcined at temperatures above 700°C show spotty rings that can be indexed to highly crystalline tetragonal perovskite structure. This result is particularly important because the calcination temperature is attributed to the fiber morphology and crystal structure.

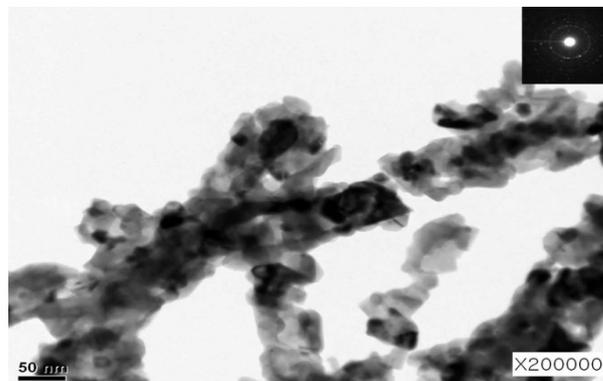


Fig. 3. TEM images with corresponding selected-area electron diffraction (inset) of electrospun BaTiO₃/PVP nanofibers calcined at 750°C.

Conclusion

BaTiO₃ nanofibers with diameters of 160~300 nm were prepared by using electrospun BaTiO₃/PVP composite fibers by drying them for 1 h at 80°C in vacuum with subsequent calcination for 1 h at 750°C in air. The BTO/PVP nanofibers with diameters of about 160 nm and tetragonal perovskite structure were observed for the electrospun fibers after calcination for 1 h at 750°C, confirmed by XRD, FT-IR measurements. Experimental results revealed that the calcinations temperature had the influence on the BaTiO₃ fiber's morphology and crystal structure.

Acknowledgements

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References

1. Yuh, J., Nino, J.C., and Sigmund, W.M., Synthesis of barium titanate (BaTiO₃) nanofibers via electrospinning. *Mater. Lett.*, **59**(2005) 3645.
2. Yuh, J., Perez, L., Sigmund, W.M., and Nino, J.C. Electrospinning of complex oxide nanofibers. *Physica E*, **37**(2007) 254.
3. Lee, D.Y., Cho, J., Cho, N., Lee, M., Lee, S., and Kim, B. Characterization of electrospun aluminum doped zinc oxide nanofibers. *Thin Solid Films*, **517**(2008) 1256.