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Intense visible photoluminescence of Mn-doped BaTiO₃ nanofibers depended on disordered structure

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Mn-doped BaTiO₃ nanofibers were fabricated by sol-gel combined with electrospinning and subsequent annealing of as-spun nanofibers. The effects of Mn content on the structural and photoluminescence (PL) properties of the BaTiO₃ nanofibers were investigated as a function of annealing temperature from 500 °C to 950 °C. The X-ray diffraction and Raman spectroscopy revealed tetragonal phases in the nanofibers annealed at 950 °C. In case of annealed at 500 °C, undoped BaTiO₃ showed amorphous phase. From the HR-TEM analysis, 1 mol% Mn-doped BaTiO₃ nanofibers was observed partially crystallized BaTiO₃ within the amorphous phase. Intense visible photoluminescence displayed in the undoped BaTiO₃ nanofiber. The observed intense PL was ascribed to a multiphonon process with localized states within the band gap of the highly disordered states.

Key words: BaTiO₃, Mn doping, Electrospinning, Raman, Photoluminescence.

Introduction

Among various lead-free ferroelectric and piezoelectric materials with a perovskite structure, BaTiO₃ ceramics have been extensively investigated for applications such as capacitors, actuators, transducers, thermistors, sensors, and optoelectric devices. Although most studies into BaTiO₃ have mainly been focused on its ferroelectric, thermoelectric, and piezoelectric properties [1-3], there are growing interests in its optical properties recently. It has been reported [4-6] that the visible photoluminescence (PL) was observed in amorphous BaTiO₃ powders and thin films due to their disordered structures. However, they could be inapplicable to practical optoelectric devices because their PL emissions were very weak. The PL properties of amorphous BaTiO₃ are expected to improve further if the materials form nanoscale of particular structures such as nanorods, nanofibers, and nanotubes. These one-dimensional (1D) nanomaterials have attracted great attention because of their unique physical and chemical properties, large specific surface area, high aspect ratio, and potential applications in nanodevices. Especially, nanofibers have been widely studied due to their structure dependent characteristics [7].

A large number of fabrication methods have been developed for generating 1D nanostructures in the form of fibers from various materials. Compared with other methods, electrospinning method provided simplest approach to obtain nanofibers [8]. BaTiO₃ nanofibers have been produced by electrospinning in several studies [9, 10]. These studies were to report the relationship between dielectric property and morphology depended on annealing temperature.

The use of dopants is very effective approach for microstructural control [5], which also affects the PL properties. The PL properties of various oxides were improved by Mn doping [11-13]. Mn as an acceptor dopant can substitute Ti⁴⁺ in Mn-doped BaTiO₃ [13]. Doubly charged oxygen vacancies are generated from the incorporation of Mn^{2+} ion into the lattice. The PL emissions of Mn-doped BaTiO₃ could be attributed to the donor (oxygen vacancies by certain defects)-acceptor (Mn dopant) pair radiative recombination. To the best of our knowledge, the photoluminescence behavior of Mndoped BaTiO₃ nanofibers has not yet been discussed in the literature. In this work, we try to study a correlation between crystal structure and optical properties systematically. The Mn-doped BaTiO₃ nanofibers are characterized by SEM, TEM, XRD, Raman spectroscopy, UV-visible diffuse reflectance and PL. The outcome is very appealing and the optical properties of BaTiO₃ nanofibers are worthy of further interest.

Experimental

Electrospinning was performed using a commercial tool, manufactured by Nano NC Co. Ltd., Korea [14], with two solutions mixed. The first solution contains barium acetate (3.825 g) and desired mol% of manganese acetate (0, 0.1, and 1 mol%) dissolved in a mixture of acetic acid (9 ml) and titanium (IV)-isopropoxide (4.425 ml) through the stirring for 15 hrs.

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The second solution has polyvinylpyrrolidone (PVP, Mw = 1,300,000, 1.2 g dissolved in ethanol (9 ml) through the stirring for 1 hr at room temperature. The second solution was added to the first solution, and the resulting mixture was further stirred for 1 hr to obtain the undoped, 0.1, and 1 mol% Mn-doped BaTiO₃-PVP sol with optimized viscosity and suitable volatility. The prepared solution were loaded into a 10 ml plastic syringe with a metallic needle tip (inner diameter = 0.4 mm) for electrospinning. The solution was electrospun at applied voltage of 12 kV, flow rate of 30 µl/min, and tip-tocollector distance of 15 cm. A grounded aluminum foil served as a counter electrode and collector plate. The asspun nanofibers were annealed at 500 °C, 700 °C, and 950 °C for 1 hr with a heating rate of 2.5 °C/min in order to obtain amorphous and polycrystalline nanofibers.

The morphologies of the annealed nanofibers were observed using a scanning electron microscope (SEM, JSM-6700F, Jeol, Japan). Powder X-ray diffraction (XRD, D/Max-2500V/PC, Rigaku, Japan) was used to identify the crystalline phases of the annealed nanofibers. The crystal structure and surface morphology of the annealed nanofibers were evaluated by the selected area electron diffraction (SAED) and transmission electron microscopy (TEM, ARM1300S, Jeol, Japan). Raman and photoluminescence (PL) spectra were measured at room temperature using the 532 nm line from a solid-state laser (CL532, CrystaLaser, USA). Scattered light from the samples was analyzed through a single grating monochromator with a focal length of 50 cm (SP-2500i, Princeton Instruments, USA) and detected with a liquid nitrogen cooled charge coupled device (CCD) detector (Spec-10, Princeton Instruments, USA). UVvisible diffuse reflectance spectra (DRS) were recorded using a UV-Vis-NIR spectrophotometer (Lambda 950, PerkinElmer, USA) in the wavelength region of 200-1100 nm to study the optical response of the annealed nanofibers.

Results and Discussion

SEM images of undoped and 1 mol% Mn-doped BaTiO₃ nanofibers annealed at 500 °C, 700 °C, and 950 °C for 1 hr are shown in Fig. 1. The diameters of the annealed nanofibers range from 100 nm to 800 nm, which were smaller compared with those of as-spun nanofibers due to the decomposition of the PVP polymer [15-18]. Upper SEM images of Fig. 1(a-c) display pure BaTiO₃ nanofibers depended on annealing temperature. Below SEM images of Fig. 1(d-f) exhibit 1 mol% Mn-doped BaTiO₃ nanofibers depended on annealing temperature. The undoped and 1 mol% Mn-doped BaTiO₃ nanofibers annealed at 500 °C have smooth and uniform surfaces with a random orientation, as shown in Figs. 1(a) and 1(d). With an increasing annealing temperature at 950 °C, the nanofibers showed porous form. This may be due to the evaporation of solvents from the fiber such that the evaporation rate through the fiber surface is lower than the diffusion rate of the fiber, leading to the ballooning of the fiber [15]. Additionally, the organic binder PVP becomes viscous and the fiber is plasticized, preventing the evaporation of solvents and leading to further ballooning at elevated temperatures. With the increase of pressure inside the fiber, an explosion occurs, resulting in the formation of small holes on the fiber surface [16]. The undoped BaTiO₃ nanofibers annealed at 950 °C showed more porous morphologies compared to the 1 mol% Mn-doped BaTiO₃ nanofibers annealed at 950 °C. The difference of morphologies between undoped and 1 mol% Mndoped BaTiO₃ nanofiber is due to the Mn ions acted as a role to have dense morphology.

Fig. 2 shows the XRD patterns of undoped and 1 mol% Mn-doped BaTiO₃ nanofibers annealed at 500 °C, 700 °C, and 950 °C for 1 hr in air. The XRD patterns of the nanofibers annealed at 500 °C showed an amorphous halo at $2\theta = 20-30$ ° along with the secondary phases of BaCO₃ (JCPDS No. 45-1471)



Fig. 1. SEM images of undoped BaTiO₃ nanofibers annealed at (a) 500 °C, (b) 700 °C, and (c) 950 °C; 1 mol% Mn-doped BaTiO₃ nanofibers annealed at (d) 500 °C, (e) 700 °C, and (f) 950 °C.



Fig. 2. X-ray diffraction patterns of (a) undoped $BaTiO_3$ nanofibers and (b) 1 mol% Mn-doped $BaTiO_3$ nanofibers depended on annealing temperature.



Fig. 3. Raman spectrum of undoped and 1 mol% Mn-doped BaTiO₃ nanofibers annealed at 950 $^{\circ}$ C.

[17, 18, 20, 21] and/or BaMnO₃ (JCPDS No. 26-0168) [22] as shown in Figs. 2(a) and 2(b). The BaCO₃ and BaMnO₃ could be induced by unreacted intermediate phase of BaTi₂O₄ at low annealing temperature [19, 21]. In case of 1 mol% Mn-doped BaTiO₃ nanofibers, the peak intensity of BaCO₃ and BaMnO₃ decreased with increasing temperature, whereas that of BaTiO₃ increased with an increase of annealing temperature. A single phase of perovskite structure (JCPDS No. 05-0626) [17] was obtained in the nanofibers annealed at 950°C. In general, the crystalline BaTiO₃ ceramics sintered at high temperature showed the perovskite structure with tetragonal crystal system, which could be confirmed from the peak splitting around $2\theta = 45^{\circ}$ in the XRD patterns. However, no obvious peak splitting around 2θ $=45^{\circ}$ was observed for the nanofibers annealed at 700 °C and 950 °C in this study (Figs. 2(a) and 2(b)). This result could be attributed to the small grain size in the annealed nanofibers [20, 21]. The crystallite size of undoped and 1 mol% Mn-doped BaTiO₃ nanofibers annealed at 950 °C were 34 nm and 23 nm which were calculated using the Debye-Scherer formula [17]. Therefore Mn ions play a role in suppressing grain growth.

To further study the crystal system of the annealed $BaTiO_3$ nanofibers with a single phase of perovskite structure, Raman scattering measurements were carried out. Fig. 3 displays the Raman spectrum of undoped



Fig. 4. TEM images and SAED patterns of undoped $BaTiO_3$ nanofibers annealed at 500 °C (a-b) and 1 mol% Mn-doped $BaTiO_3$ nanofibers annealed at 500 °C (c-d) and 950 °C (e-f).

and 1 mol% Mn-doped BaTiO₃ nanofibers annealed at 950 °C for 1 hr. In general, the cubic BaTiO₃ (space group: Pm3m) has no Raman active modes, whereas tetragonal BaTiO₃ (space group: P4 mm) has eight Raman active modes represented by $4E(TO + LO) + 3A_1$ $(TO + LO) + 1B_1(TO + LO)$ [15, 17, 22]. The characteristic peaks of the annealed nanofibers were clearly observed in the spectrum. Most of these peaks could be assigned to the modes in tetragonal BaTiO₃ as follows: 712 cm⁻¹ (E(4LO) $+ A_1(3LO)), 518 \text{ cm}^{-1}$ (E(4TO) $+ A_1(3TO)), 306 \text{ cm}^{-1}$ $(E(3TO) + E(2LO) + B_1)$, 252 cm⁻¹ (A₁(2TO)), 187 cm⁻¹ $(E(2TO) + E(1LO) + A_1(1TO) + A_1(1LO))$ [22]. However, no significant bands in Raman spectrum could be observed for the nanofibers annealed at 500 °C due to the presence of disorder in the amorphous structure, as reported by Li et al. [7]

Figs. 4(a) and 4(b) show the TEM images and SAED patterns of undoped BaTiO₃ nanofibers annealed at 500 °C. It showed very weak BaCO₃ phase and amorphous halo in the XRD patterns (Fig. 2(a)), these nanofibers have smooth surface with disordered structure and no sign of crystallization. In case of Mn content to 1 °mol%, the surface of the nanofibers annealed at 500 °C becomes much rougher (Fig. 4(c)) and the SAED patterns of these nanofibers showed a ring pattern, which indicates the (101) crystal direction of BaMnO₃ and BaTiO₃ (Fig. 4(d)). This means that BaMnO₃ and partially crystallized



Fig. 5. PL spectra of undoped $BaTiO_3$ nanofibers and 1 mol% of Mn annealed at 500 °C and 950 °C.

BaTiO₃ phase within amorphous phase. For the 1 mol% Mn-doped nanofibers at 950 °C (Fig. 4(e)), the *d* space distance estimated from the lattice fringe is 0.28 nm, which corresponds to the (110) crystal direction, indicating crystallization of the BaTiO₃ nanofibers. Zhuang et al. [19] reported a similar value of space distance (0.285 nm) in the annealed BaTiO₃ nanofibers. As shown in Fig. 4(f), the diffraction rings of (110), (111), (200), and (211) marked in the SAED patterns correspond to tetragonal perovskite BaTiO₃, indicating the polycrystalline structure of BaTiO₃ nanofibers annealed at 950 °C. Therefore, it is concluded from the XRD, Raman, TEM, and SAED results that the BaTiO₃ nanofibers doped with Mn annealed at 950 °C have a single phase of tetragonal perovskite structure.

Fig. 5 shows the PL spectra of BaTiO₃ nanofibers annealed at 500 °C and 950 °C for 1 hr. For the nanofibers annealed at 500 °C (Fig. 5(a)), the undoped BaTiO₃ nanofibers showed an intense broad emission at the wavelength range from 570 nm to 670 nm, which is extremely more intense than those of 1 mol% Mn-doped nanofibers annealed at 500 °C and 950 °C (see enlarged Fig in Fig. 5(b). The highly disordered structure as well as the distribution of the localized electronic states generated within the normal crystalline band gap, is considered to be responsible for the intense photoluminescence of amorphous BaTiO₃ nanofibers covering wide visible region. The intense broad emission is typical of a multiphonon process; i.e., a system in which relaxation occurs by several paths, involving the participation of numerous states within the band gap of the material. This may be coupled with the structural disorder of BaTiO₃ nanofibers which in turn indicates the presence of additional electronic levels in the forbidden band gap



Fig. 6. UV-visible diffuse reflectance spectra (DRS) of (a) undoped and (b) 1 mol% Mn-doped BaTiO₃ nanofibers depended on annealing temperature; inset shows the plots for square root of Kubelka-Munk functions F(R) versus photon energy.

of the BaTiO₃ nanofibers. These results could be attributed to the degree of disorder between amorphous and crystalline materials. Pizani et al. reported similar PL spectra in the amorphous phase of $BaTiO_3$ [4]. The PL emission at room temperature in the visible region is generated from the polaron by the electron-hole recombination, which is attributed to the presence of localized states in the band gap due to the disordered structure of amorphous materials. The undoped BaTiO₃ nanofibers annealed at 500 °C have higher disordered structure due to their amorphous phase. In contrast, from the results of SAED patterns, BaMnO₃ and partially crystallized BaTiO₃ phase within amorphous phase were observed for the 1 mol% Mn-doped nanofibers (Fig. 4(d)). Therefore, it can be concluded that the PL intensity of the 1 mol% Mn-doped nanofibers with slightly ordered structure was lower than those of the undoped BaTiO₃ nanofibers. The PL intensity of the 1 mol% Mn-doped BaTiO₃ nanofibers annealed at 950 °C showed lower PL intensity than the nanofibers annealed at 500 °C due to the increased crystallinity [6].

Fig. 6 shows the UV-visible diffuse reflectance spectra (DRS) of undoped and 1 mol% Mn-doped BaTiO₃ nanofibers annealed at 500 °C, 700 °C and 950 °C for 1 h in air. The optical absorption edge of the undoped and 1 mol% Mn-doped BaTiO₃ nanofibers were shifted to higher wavelength (red-shift) with an increasing annealing temperature. These results could be attributed to the increased structural order of crystalline phases. The DRS are presented in terms F(R), deduced from the recorded reflectance (R) by application of the Kubelka-Munk function $(F(R) = (1-R)^2 / 2R)$ [23]. Since the BaTiO₃ was a direct band gap material, its band gap can be estimated by plotting $(F(R) \times hi)^2$ versus hi (photon energy) as shown in Fig. 6 inset. The optical band gaps of the BaTiO₃ nanofibers were obtained by extrapolating the linear part of the curve to zero, which were about 3.30 eV, 3.35 eV, and 3.68 eV for the undoped nanofibers depended on annealing temperature. The optical band gap of 1 mol% Mn-doped BaTiO₃ nanofibers were 3.37 eV, 3.45 eV, and 3.62 eV. The optical band gap energy of the amorphous BaTiO₃ was reported about 3.74 eV [24]. With increasing annealing temperature, the decrease in the band gap energy nanofibers could be attributed to the increase of crystallinity of BaTiO₃. This result is good agreement of XRD, Raman, TEM, and SAED results.

Conclusions

By using the electrospinning method, the BaTiO₃ nanofibers doped with undoped and 1 mol% Mn were successfully fabricated through the annealing from 500 °C to 950 °C for 1 hr. The nanofibers annealed at 950 °C displayed a single phase of tetragonal perovskite structure. However, the nanofibers annealed at 500 °C exhibited amorphous phase and weak BaCO3 and BaMnO3. For the nanofibers annealed at 500 °C, the strong visible PL emissions of the undoped BaTiO₃. With increasing annealing temperature, the PL intensity of the 1 mol% Mndoped nanofibers decreased due to the decrease of amorphous phase. These results could be explained by the direct band gap values evaluated from the UVvisible DRS. Also, these trends may be used for predictive properties optimization of BaTiO₃ perovskite and other oxide nanofibers.

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