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Enhanced photoluminescence and electrical properties of 0-3 type ZnO/$Bi_{3.6}Eu_{0.4}Ti_3O_{12}$ nanocomposite thin films

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ABSTRACT

0-3 type ZnO/$Bi_{3.6}Eu_{0.4}Ti_3O_{12}$ (BEuT) nanocomposite films with ZnO nanopowders in BEuT host were prepared by chemical solution deposition. The effects of ZnO content on the structure, photoluminescence, and electrical properties of the films were investigated. The ZnO/BEuT molar ratio strongly affected the grain size and growth orientation of BEuT, dielectric and ferroelectric properties, as well as emission intensity. The nanocomposite films showed strong red emission peaks due to $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+} ions. Good electrical properties with high dielectric constant of 480 (at 1 kHz) and large remanent polarization ($2P_r$) of 32 $\mu C/cm^2$ were obtained for the nanocomposite films having a ZnO/BEuT molar ratio of 1:2. The mechanisms for enhanced photoluminescence and electric properties were discussed. The results suggest that the nanocomposite thin films are promising candidate materials for multifunctional optoelectronic devices.

1. Introduction

$Bi_4Ti_3O_{12}$ (BiT)-based ferroelectric materials are one of the most promising lead-free and environment-friendly candidate materials for various ferroelectric devices, including capacitors, nonvolatile memories as well as sensors [1,2]. It has been widely reported that rare-earth substitution for partial Bi^{3+} ions in BiT thin films can effectively improve the electrical properties of BiT thin films [3–5]. For example, Hu et al. reported that $Bi_{3.15}Pr_{0.85}Ti_3O_{12}$ films had a remanent polarization ($2P_r$) of 56 $\mu C/cm^2$ and a coercive field E_c of 50 kV/cm, respectively, which were comparable to those for well-studied Pb-based ferroelectric films. Recently, photo-induced luminescence in rare-earth doped BiT materials has been reported [6–8]. For example, Eu-doped BiT films showed the red emission peaks centered at 594 nm and 617 nm, respectively. The emission was believed to result from $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+} ions [9]. Highest emission intensity was observed in $(Bi_{3.6}Eu_{0.4})Ti_3O_{12}$ (BEuT). Furthermore, good electrical properties and enhanced photoluminescence (PL) were obtained in Eu/Gd-codoped BiT thin films [10]. These suggested multifunctional properties of the rare-earth doped BiT thin films.

More recently, our work demonstrated that incorporating BEuT with ZnO to form ZnO/BEuT nanocomposite films can improve the luminescence and electrical properties of the BEuT films. For example, the 1-3 type ZnO/BEuT nanocomposite thin films with *c*-axis-oriented ZnO nanorods in BEuT host showed PL intensity as 10 times as that for pure BEuT films [11]. In 2-2 type ZnO/BEuT nanocomposite multilayer films, the PL intensity was enhanced by 2–3 times [12]. An effective energy transfer between ZnO and BEuT was suggested to be responsible for the PL enhancement [13]. Besides, enhanced ferroelectric properties with $2P_r$ of 25 $\mu C/cm^2$ were also observed in 2-2 type ZnO/BEuT nanocomposite films. However, the study on 0-3 type ZnO/BEuT nanocomposite thin films with ZnO nano-powders in BEuT host is still lacking.

Lin et al. investigated the PL properties of Eu^{3+} doped SiO_2 films incorporating with In_2O_3 nanocrystals. Their results suggested that the PL intensity could be enhanced by two orders of magnitude, and the PL enhancement can be ascribed to the effective absorption of incident photons by In_2O_3 nanocrystals [14]. Ningthoujam et al. studied the PL properties of SnO_2:Eu^{3+} nanopowders uniformly dispersed in TiO_2 matrix. Significant improvement in the exciton mediated energy transfer between SnO_2 and Eu^{3+} ions was observed [15]. Thus, it is reasonable to expect that 0-3 type ZnO/BEuT nanocomposite thin films may have good luminescence and electrical properties.

In this study, we prepared the 0-3 type ZnO/BEuT thin films with ZnO nanopowders in BEuT host and systematically investigated the effects of ZnO concentrations on the structure, photoluminescence, and electrical properties of the nanocomposite thin films. Our study revealed that the 0-3 type ZnO/BEuT nanocomposite films exhibited strong red photoluminescence,

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high dielectric constant, and well-defined ferroelectric hysteresis loops.

2. Experimental procedure

The 0-3 type ZnO/BEuT nanocomposite thin films were prepared by using a chemical solution deposition method. The synthesis of BEuT solutions was similar to that described elsewhere [9]. ZnO nanopowders were commercially obtained. Their average diameter was about 20 nm which has been confirmed by transmission electron microscope. The solutions for 0-3 type ZnO/BEuT nanocomposite films were synthesized by adding the ZnO nanopowders to the BEuT solutions. The process for synthesizing the precursor solutions is shown in Fig. 1. The precursor solutions were spin-coated onto fused silica, ITO-coated glass, and $Pt/TiO_2/SiO_2/Si$ substrates at 3000 rpm for 30 s. Then, the wet films were baked at 300 °C for 5 min in air. After each coating and baking, the films were annealed at 650 °C for 5 min. This procedure was repeated several times until desired thickness was obtained. The total thickness of the nanocomposite films was about 600 nm.

The crystallization and structural properties of the nanocomposite films were analyzed by using X-ray diffraction (XRD, D/MAX 2200 VPC, Rigaku) using Cu Kα radiation, and the working voltage and current were 40 kV and 20 mA, respectively. The phase structures were also studied by Raman measurement (Renishaw inVia Laser Micro-Raman Spectrometer). The morphologies of the nanocomposite thin films were observed using field-emission scanning electron microscopy (SEM, JSM-6330F JEOL) and the images were taken at 15 kV. The element distribution of the nanocomposite films was also examined by energy dispersive spectrometer (EDS, attached to SEM). The morphology and grain size of the ZnO nanopowders were observed using transmission electron microscope (TEM, FEI Tecnai G2 Spirit). The excitation and emission spectra of the nanocomposite films were measured by a spectrofluorophotometer (Shimadzu RF5301). The ferroelectric properties were characterized using a Radiant precision workstation ferroelectric analyzer, and the dielectric properties were measured using Agilent 4284a with the applied ac signal amplitude of 100 mV. Prior to electrical measurements, Pt top electrodes with a diameter of 300 μm were deposited on the surface of the thin films through a shadow mask.

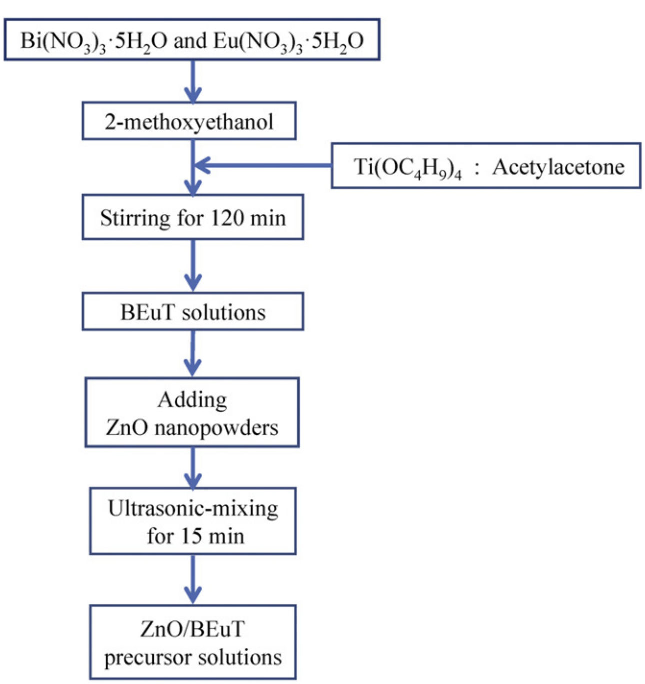

Fig. 1. Synthesizing process of ZnO/BEuT precursor solutions.

3. Results and discussion

Fig. 2 shows the XRD patterns of 0-3 type ZnO/BEuT nanocomposite films with different ZnO contents. The main diffraction peaks were indexed according to the standard diffraction pattern data of $Bi_4Ti_3O_{12}$ in the JCPDS card. Only the diffraction peaks from $Bi_4Ti_3O_{12}$ phase with Bi-layered perovskite structure and from ZnO were observed. No other peaks from impurity phase were detectable. The average grain size of BEuT was calculated by Scherrer equation using the data of (1 1 7) peaks. As the ZnO/BEuT molar ratio α increased from 1:50 to 1:2, the full width at half maximum (FWHM) of the (1 1 7) diffraction peaks of BEuT decreased from 0.31 to 0.22. This suggested that adding ZnO nanopowders in BEuT host may increase grain size from 30 nm to 50 nm and lead to better crystallization of BEuT. However, when α was over 1:2, the FWHM of the (1 1 7) diffraction peaks of BEuT increased to 0.25 with increasing α, indicating that higher concentration of ZnO nanopowders may decrease the grain size

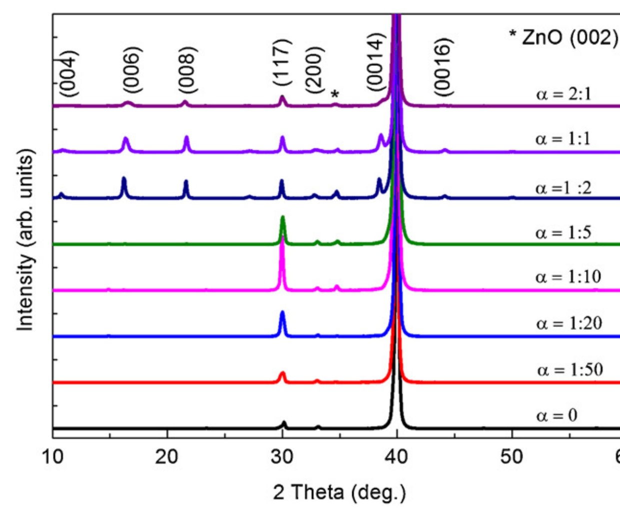

Fig. 2. XRD patterns of 0-3 type ZnO/BEuT nanocomposite films with different ZnO/BEuT molar ratios.

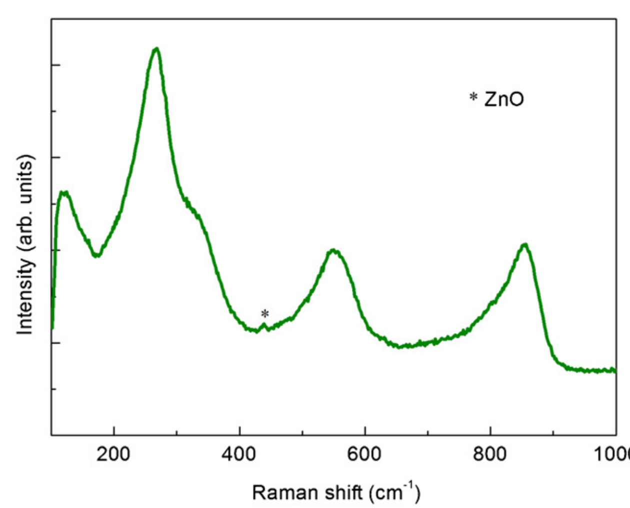

Fig. 3. Typical Raman spectrum of 0-3 type ZnO/BEuT nanocomposite film with a ZnO/BEuT molar ratio α of 2:1.