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# Optical characteristics of $Bi_{4-x}Eu_xTi_3O_{12}$ ferroelectric thin films on fused silica substrates

**Kaibin Ruan · Guangheng Wu · Hong Zhou · Dinghua Bao**

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**Abstract** $Bi_{4-x}Eu_xTi_3O_{12}$ (BEuT) ferroelectric thin films were prepared on fused silica substrates by using chemical solution deposition technique. The attained samples had a polycrystalline bismuth-layered perovskite structure, and their optical properties were composition dependent. The thin film samples had good optical transmittance above 500 nm wavelength. A blue shift of the optical absorption edge was observed in the BEuT thin films with increasing $Eu^{3+}$ concentration. The optical band gaps of BEuT thin films were estimated to be about 3.57, 3.60, 3.61, 3.63, and 3.69 eV for the samples with $x$=0.25, 0.40, 0.55, 0.70, and 0.85, respectively. Photoluminescence measurements showed that two emission peaks of BEuT thin films originated from two transitions of $^5D_0 \rightarrow {}^7F_1$ (594 nm) and $^5D_0 \rightarrow {}^7F_2$ (617 nm) had maximum intensities when $Eu^{3+}$ concentration was $x$=0.40. The relatively high quenching concentration of $Eu^{3+}$ content was thought to be related to the layered structure of BEuT thin films. These results suggested that multifunctional BEuT thin film materials could have promising applications in optoelectronic devices.

**Keywords** Ferroelectric thin films · Chemical solution deposition · Photoluminescence

## 1 Introduction

Rare earth doped bismuth titanate (BLnT) thin films have attracted much attention for their excellent ferroelectric and dielectric properties, which could be competitive in the applications of nonvolatile random access memories, microsensors and microactuators devices, etc [1–3]. Meanwhile, the series of materials have also been reported to exhibit excellent optical properties such as large optical nonlinearity, high optical transparency in the visible wavelength region, which are attractive for the potential uses in optic and optoelectronic devices [4, 5]. Recently, optical properties of BLnT thin films were further studied; the thin film materials were found to exhibit photoluminescence (PL) property, which may be a new kind of potential luminescent thin film material [6–10]. The PL property is strongly related to the doping rare earth ions in BLnT thin films. The doping rare earth ions not only act as structural modifier which greatly improve the electrical properties of the thin films [11], but also act as the activators of luminescent materials. Our previous studies have demonstrated that highly transparent europium doped bismuth titanate (BEuT) thin films exhibited good electrical properties and obvious photoluminescence, which could be a new multifunctional material for optoelectronic devices [6–10]. But before these thin films can be used in devices for commercial use, their optical properties should be further studied, of which the chosen of proper optical substrates should be an important issue. In this work, fused silica substrate, a widely used optical substrate which exhibits high transparency and extremely high thermal stability, is used as the optical substrate for deposition of BEuT thin films. The effect of $Eu^{3+}$ concentration on optical properties of BEuT thin films on fused silica substrates is investigated.

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K. Ruan
College of Mechanical and Electrical Engineering,
Fujian Agriculture and Forestry University,
Fuzhou 350002, People's Republic of China

G. Wu · H. Zhou · D. Bao (✉)
State Key Laboratory of Optoelectronic Materials and Technologies, School of Physics and Engineering,
Sun Yat-Sen University,
Guangzhou 510275, People's Republic of China
e-mail: stsbdh@mail.sysu.edu.cn

## 2 Experimental procedure

$Bi_{4-x}Eu_xTi_3O_{12}$ ($x$=0.25, 0.40, 0.55, 0.70 and 0.85) thin films were prepared by chemical solution deposition technique. The precursor solutions were synthesized using $Bi(NO_3)_3{\cdot}5H_2O$, $Eu(NO_3)_3{\cdot}5H_2O$ and $Ti(OC_4H_9)_4$ as the Bi, Eu and Ti sources, respectively. 10 % excess of $Bi(NO_3)_3{\cdot}5H_2O$ was added in the solution to compensate for the Bi loss during the thermal annealing. 2-methoxyethanol and acetic acid were used as co-solvents and acetylacetone as stabilizer of the solutions. Meanwhile, a proper amount of $H_2O_2$ was added to prevent $Ti^{4+}\rightarrow Ti^{3+}$ transition [12]. The solutions were then adjusted to 0.06 M. The obtained solutions were spin-coated on fused silica substrates at a high speed rotation, followed by baking on the hot plate to remove organics. The procedure was repeated for several times, and then the dry thin films were put into a furnace and heated at a rate of 1.5°C/min to 700°C. After keeping at this temperature for 1 h, the samples were cooled down with furnace naturally, and BEuT thin films with a thickness of about 300 nm were obtained.

The structure of BEuT thin films was characterized by an X-ray diffractometer (XRD, Rigaku, D/MAX 2200 VPC) with working current and voltage of 20 mA and 40 kV, respectively. Raman analysis was carried out by using Renishaw inVia+Plus LaserMicro-Raman Spectrometer within the wavenumbers of 50 $cm^{-1}$ and 1000 $cm^{-1}$. The optical transmittance spectra measurement in the wavelength of 200–1400 nm was performed by a Shimadzu UV-3150 spectrophotometer, and the photoluminescence spectra were obtained by the use of Shimadzu RF-5301PC Spectrofluorophotometer.

## 3 Results and discussion

The structure characteristics of BEuT thin films are studied via XRD as well as Raman spectra. Figure 1 shows the XRD patterns of BEuT thin films with $x$=0.55 and 0.85. As a comparison, the XRD pattern of $Bi_4Ti_3O_{12}$ (BiT) powder annealed at 700°C for 1 h is also shown in Fig. 1. The XRD peaks can be indexed according to the standard diffraction pattern data of BiT in the JCPDS card. From Fig. 1, BEuT thin films exhibit XRD patterns similar to that observed for BiT powder sample, indicating that europium substitution does not destroy the bismuth layered perovskite structure of BiT. The thin film samples show a random orientation since (117) and (200) peaks are dominant reflections. No other peaks from impurity phase or secondary phase are observed, suggesting that there is no obvious interfacial reaction between BEuT thin films and fused silica substrates.

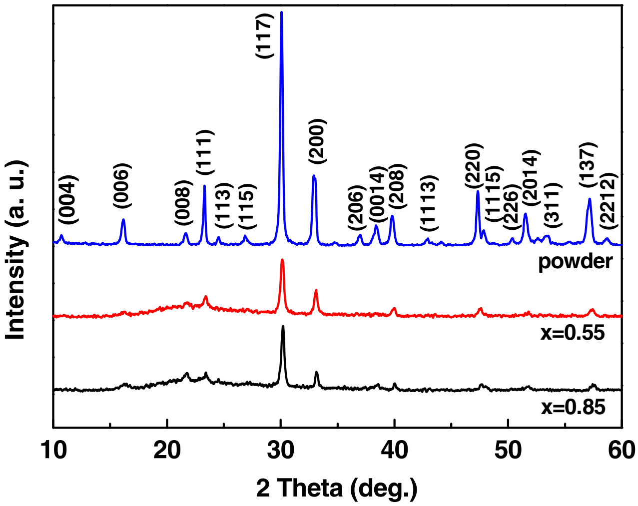

**Fig. 1** XRD patterns of BiT powder and BEuT thin films with $x$=0.55 and 0.85

As is known, pure BiT has a layered intergrowth structure consisting of alternate stacking of perovskite-like $(Bi_2Ti_3O_{10})^{2-}$ and fluorite-like $(Bi_2O_2)^{2+}$ layers along c axis [1, 13]. When doped with rare earth ions, those rare earth ions, for example, $Eu^{3+}$ in this work, would replace $Bi^{3+}$ ions in $(Bi_2Ti_3O_{10})^{2-}$ layer (A site) and form $(Bi_{2-x}Eu_xTi_3O_{10})^{2-}$ instead [14, 15]. This could be confirmed by Raman spectra of samples. Usually there are many Raman modes in the low frequency region (< 200 $cm^{-1}$) for non-doped BiT [16]. But if $Bi^{3+}$ ions in A site are displaced by different sizes of other ions, the positions of some related Raman peaks would move and may overlap due to the possible orthorhombic distortions of the material. Figure 2 shows Raman spectra of $Bi_{3.45}Eu_{0.55}Ti_3O_{12}$ and $Bi_{3.15}Eu_{0.85}Ti_3O_{12}$ thin films. From Fig. 2, both two BEuT thin film samples appear only one obvious peak at ~160 $cm^{-1}$ in the low frequency region. The peak of $Bi_{3.55}Eu_{0.45}Ti_3O_{12}$ thin films is broader than that of $Bi_{3.15}Eu_{0.85}Ti_3O_{12}$ thin films, indicating that the overlapping of Raman bands is not so complete for the sample with lower $Eu^{3+}$ content. This phenomenon of Raman modes suggests that $Eu^{3+}$ ions indeed occupy A site of BEuT samples. In the higher frequency region of wavenumbers more than 200 $cm^{-1}$,

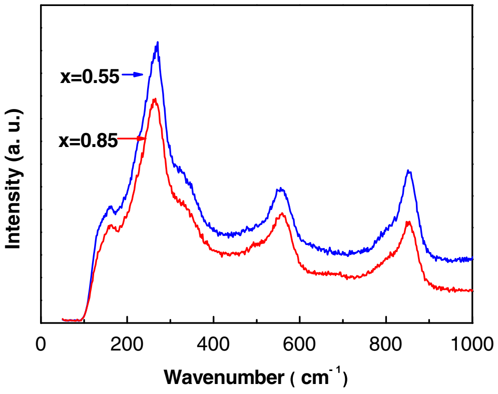

**Fig. 2** Raman spectra of the BEuT thin films with $x$=0.55 and 0.85

there are three main Raman modes located at the positions of ~266 cm$^{-1}$, ~559 cm$^{-1}$ and ~854 cm$^{-1}$, respectively. These modes have been usually observed in BiT or rare-earth doped BiT thin films as well as other bismuth layered-structure ferroelectrics [17, 18]. All of them are the internal modes of $TiO_6$ octahedra, and insensitive to $Eu^{3+}$ substitution. This is because the intergroup bonding energy of $TiO_6$ is much larger than the crystal bonding energy. As a result, the Raman modes frequencies are mainly determined by the Ti-O bonding.

BiT and rare-earth doped BiT thin films are also known as highly transparent materials [19, 20]. In this work, the optical properties of BEuT thin films with various $Eu^{3+}$ concentrations were studied. Figure 3 shows the optical transmittance of $Bi_{4-x}Eu_xTi_3O_{12}$ ($x$=0.25, 0.40, 0.55, 0.70 and 0.85) thin films as well as the fused silica substrate itself as a comparison. The transmittance of the fused silica is more than 90 % above the wavelength of 300 nm and quite stable which is very suitable for the use of transparent substrate. But the transmission spectra of BEuT thin films appear differently compared to that of fused silica substrate. The appearance of fringes in the thin film samples could be mainly due to the interference between substrate and thin film interface as well as thin film and air interface. From Fig. 3 we can see that the thin films show good optical transmittance above wavelength of 500 nm. While the wavelength is below about 400 nm, the optical transmittance exhibits abrupt decrease to nearly opaque for all thin films. In this high absorption region, the relationship of transmittance $T$ and coefficient $\alpha$ could be determined by the following simple equation:

$$T = R\exp(-\alpha d) \tag{1}$$

Here, $R$ is nearly equal to unity at the absorption edge, and $d$ is the thickness of thin films. Assuming that the transition between valence and conduction bands is direct for our BEuT thin films, the absorption coefficient $\alpha$ as a function of photon energy can be expressed by the well-known relation [21]:

$$(\alpha h\nu)^2 = C(h\nu - E_g) \tag{2}$$

Where $h\nu$ is the incident phont energy, $C$ is a constant, and $E_g$ is the band gap energy. The inset of Fig. 3 shows the plot of $(\alpha h\nu)^2$ vs $h\nu$. From the inset we can see that all the plots agree with linear fittings, which implies that the hypothesis of the direct rather than indirect band gap for our BEuT samples is proper. The optical band gaps of thin films could be obtained by extrapolating the linear portion of the plots to $h\nu$ axis. Thereby, the band gaps of thin films were identified to be about 3.57, 3.60, 3.61, 3.63, and 3.69 eV for $x$=0.25, 0.40, 0.55, 0.70 and 0.85, respectively. These values are larger than 2.80 eV of BiT thin films [19, 22], 3.25 eV for BLT thin films [23], and nearly the same to the reported value of 3.61 eV for BNT thin films [24]. Also from the inset we can see that the optical band gaps of BEuT thin films are very obviously composition dependent. So, the band gaps of BEuT thin films could be easily adjusted by modifying Eu concentrations. This blue shift phenomenon of the band gap could be explained as follow: in $ABO_3$-type peroskite compounds, the $BO_6$ ($TiO_6$ here) octahedra determine the basic energy level, while other ions in the structure contribute small effects on the optical energy bands of materials. However, the substitution of $Eu^{3+}$ into the $Bi^{3+}$ could induce the distortion of lattice due to the different sizes between two kinds of ions. The distortion of $TiO_6$ octahedra would further change the crystal field, and result in the shifts of band gap absorption edge at last [25].

The PL properties of BEuT thin films were also investigated in this work. Figure 4 shows the excitation and emission spectra of $Bi_{4-x}Eu_xTi_3O_{12}$ ($x$=0.25, 0.40, 0.55, 0.70 and 0.85) thin films. The excitation spectra were monitored at

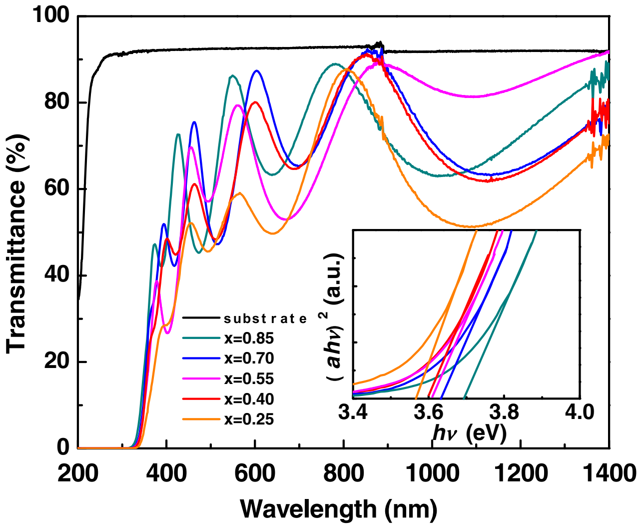

**Fig. 3** Optical transmittance of BEuT thin films with different $Eu^{3+}$ concentrations. The inset is the curve of $(\alpha h\nu)^2$ vs $h\nu$

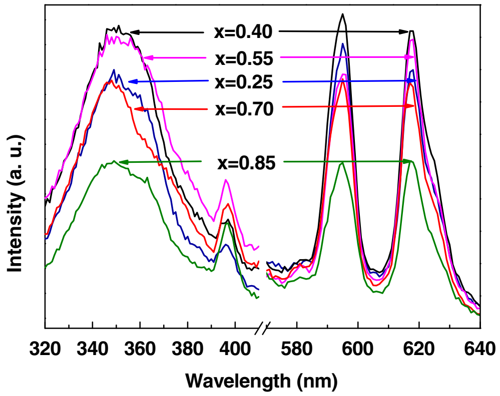

**Fig. 4** Photoluminescence spectra of BEuT thin films with different $Eu^{3+}$ concentrations

617 nm and the emission spectra were observed by excitation at 350 nm. From Fig. 4, there are two excitation bands for $Eu^{3+}$ excitation. The relatively weak peak centered at ~397 nm corresponds to the $^7F_0 \rightarrow ^5L_6$ of $Eu^{3+}$ transition, which is known as the characteristic excitation of $Eu^{3+}$ ions. While the other wide excitation band centered at ~350 nm shows much more effective excitation, which is mainly due to the energy transfer from the host lattices to $Eu^{3+}$ ions [10]. Therefore, when the BEuT thin films were excited at about 350 nm, the host lattices would absorb the incident light firstly, and then transfer the absorbed energy to the activator $Eu^{3+}$ ions. Thus, the $Eu^{3+}$ ions were excited from the ground state of $^7F_0$ to the higher level of $^5L_6$. At last, $Eu^{3+}$ emission consisted of transitions from the excited $^5D_0$ to the $^7F_j$ ($j$=0-4) levels occurred.

From Fig. 4, the emission intensity is obviously $Eu^{3+}$ concentration dependent and all emission spectra include two peaks located at ~594 nm and ~617 nm, respectively. The $Eu^{3+}$ emission peak at ~594 nm is known as a magnetic dipole transition ($^5D_0 \rightarrow ^7F_1$) which is almost independent of the symmetry site of the $Eu^{3+}$ ions, whereas the peak at ~617 nm caused by $^5D_0 \rightarrow ^7F_2$ transition is an electric dipole transition, and it occurs when $Eu^{3+}$ ions occupy the noncentrosymmetric sites. The $^5D_0 \rightarrow ^7F_2$ transition is very sensitive to the environment of $Eu^{3+}$ ions, which could be used to show the environment variation of $Eu^{3+}$ ions [26].

The effect of $Eu^{3+}$ concentration on PL property shows that the activator concentration increases to a certain level, PL intensity begins to decrease, the maximum PL intensity locates in the $Eu^{3+}$ concentration of $x$=0.40. This behavior could be due to quenching effect of $Eu^{3+}$ ions. That is, with increasing $Eu^{3+}$ concentration, the proportion of non-radiative energy transfer between nearby $Eu^{3+}$ ions would increase, when the concentration of $Eu^{3+}$ ions exceeds the critical value, the luminescence begins to quench. This quenching concentration of $Eu^{3+}$ ions in BEuT thin films is relatively high compared with other $Eu^{3+}$ doped thin film materials reported to exhibit quenching effect [27]. This unusual concentration quenching effect of photoluminescence could also be observed in some $Eu^{3+}$-ion-activated layered perovskite luminescent powder materials [28]. The phenomenon in this work could be related to the bismuth layered perovskite structure of BEuT thin film itself. As we pointed out above, $Eu^{3+}$ ions in BEuT thin films are mainly substituting for the $Bi^{3+}$ ions in $(Bi_{2-x}Eu_xTi_3O_{10})^{2-}$ perovskite-like layers rather than in $(Bi_2O_2)^{2+}$ layers, so $Eu^{3+}$ ions would be separated much more completely. Thus, the proportion of nearby $Eu^{3+}$ ions would be reduced, and the high quenching concentration results.

In conclusion, highly transparent $Bi_{4-x}Eu_xTi_3O_{12}$ thin films have been prepared on fused silica substrates by chemical solution deposition technique. The results show that optical band gaps and PL properties are composition dependent for BEuT thin films. With increasing $Eu^{3+}$ concentration, the band gap exhibits blue shift. The maximum PL intensity is observed in the $Bi_{3.6}Eu_{0.4}Ti_3O_{12}$ sample, which is thought to be an unusual concentration quenching photoluminescence. These results suggest that the preparation of multifunctional BEuT thin films on fused silica substrates and the study of their optical properties should be useful to find applications in new optoelectronic devices.

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