Microstructure and photoluminescence properties of Nd-doped (Ba,Sr)TiO$_3$ thin films

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Abstract. Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ (BST) thin films with different Nd-doped concentrations have been fabricated on silicon substrates by modified Sol-gel process. All the samples were annealed at 700°C for 60 min. The structural and morphological properties of the films were examined by X-ray diffraction (XRD) and Atomic Force Microscopy (AFM). The XRD studies indicated that both pure and doped BST thin films show crystallized perovskite structures, the particle size is about 20 nm. The AFM images displayed that the films have high quality and fine-grained polycrystalline structure. The photoluminescence spectra (PL) were carried out using the 808 nm Ar$^+$ laser line as the excitation source at room temperature. The Nd-doped BST thin films show three NIR luminescence peaks corresponding to $^4$F$_{3/2}$–$^4$I$_{9/2}$ transition at 880 nm; $^4$F$_{3/2}$–$^4$I$_{11/2}$ transition at 1066 nm and $^4$F$_{3/2}$–$^4$I$_{13/2}$ transition at 1345 nm, respectively. The influence of Nd$^{3+}$ concentration on the microstructure and the luminescence properties were discussed. All the results showed that the Nd-doped BST films have great potential uses for novel integrated optic devices.

1. Introduction
In recent years, the attention of researchers has been focused on the fabrication of rare-earth-doped materials for novel optoelectronics devices and next generation flat panel displays[1-4]. Rare-earth ions exhibit a characteristic intra-4f shell luminescence which is both nearly host and temperature independent. According to the previous investigation, many Nd-doped materials have been extensively studied because the laser actions have been realized in a variety of glasses and fluoride crystals[5-7]. Comparing with the previously mentioned materials, Ba$_{1-x}$Sr$_x$TiO$_3$ (BST) have drawn a good deal of attention due to their excellent dielectric and electro-optic properties as well as high dielectric constant, low dielectric loss, large electric-optic coefficient and low absorption coefficient. Therefore, it is a good candidate for a rare-earth doped host material.

In this work, Nd-doped Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ thin films were fabricated on Si substrate by Sol-gel process. The influence of Nd doping on the microstructure and photoluminescence properties were investigated.

2. Experimental
The precursor solutions for both pure and Nd-doped Ba$_{0.8}$Sr$_{0.2}$TiO$_3$ were prepared by the sol-gel process using barium acetate (Ba(CH$_3$COO)$_2$), strontium acetate (Sr(CH$_3$COO)$_2$), neodymium acetate, and others...
(Nd(CH₃COO)₃), titanium (IV) isopropoxide (Ti(C₄H₉O)₄) as starting materials. The solid-state barium acetate, strontium acetate, and neodymium acetate (as a dopant precursor with concentrations ranging from 0 to 5mol%) were initially dissolved in acetic acid and then mixed to obtain a Nd-doped (Ba, Sr) stock solution. Titanium (IV) isopropoxide was dissolved in methoxyethanol. Finally, both starting solutions were mixed to prepare the stoichiometric, transparent, and stable precursor for making Nd-doped BST films.

Both the undoped and doped BST thin films were deposited on silicon substrate by a multilayer spin-coating technique at 4000 rpm for 30 s. After the spin-coating procedure, the samples were kept at 450°C for 30 min in air to remove the organic radicals. Thicker films can be obtained by repeating the spin-coating process. Then, the films were annealed at 700°C for 1 h in oxygen atmosphere for crystallization.

The crystal structure of BST films was examined using X-ray diffraction (XRD, Rigaku D/Max-III C) with Cu-Kα radiation. The surface morphology of BST films was analyzed by an atomic force microscope (AFM, Digital Instrument Nanoscope IIIa) with a tapping mode. The photoluminescence spectra (PL) were carried out using Edinburgh Analytical Instruments F900 type UV-vis spectrophotometer, the 808 nm Ar⁺ laser line was used as the excitation source at room temperature.

3. Results and discussion

The XRD patterns of the pure and Nd-doped BST thin films on Si substrate was shown in Figure 1. The results indicated that both undoped and Nd-doped BST thin films show crystallized perovskite polycrystalline structures and without any crystalline orientation. No additional peaks indicating the presence of rare earth oxides are observed. It indicated that the rare earth ions can completely solid dissolve in the BST lattice. In order to investigate the influence of Nd-doped on the microstructure of the BST thin films, the (200) peaks of the samples were chosen for further discussion. It can be seen from Figure 2 that when the Nd concentration increased from 0% to 3 mol%, the (200) peak of the sample shifted toward higher diffraction angle, but when the Nd concentration increased from 3 mol% to 5 mol%, the peak shifted toward low diffraction angle slightly. It shows that the lattice parameter of the BST thin films decreased as Nd concentration increased from 0% to 3 mol%, but slightly increased when Nd-doping ratio increased from 3 mol% up to 5 mol%. It can be explained by the Nd ions may substitute A site and/or B site ions in ABO₃ perovskite structure. The ionic radius of Nd, Ba, Sr and Ti are 0.995 Å, 1.35 Å, 1.12 Å and 0.605 Å, respectively. When the Nd content below 3 mol%, Nd ions mainly substitute A site (Ba, Sr) ions in the lattice. It result in decrease of the lattice parameter. But when the Nd concentration increased from 3 mol% up to 5 mol%, Nd ions can substitute both A site (Ba, Sr) ions and B site (Ti) ions in the BST structure. The total effect is the slightly increase of the lattice parameter compared to the sample doped with 3 mol% Nd. In our former study, the similar phenomenon was seen in the Ho-doped BST thin films[8]. This result is also corresponding to the report by S.Munrakami et al. [9],they assumed that Eu³⁺ ions substitute La and (Zr, Ti) sites in PLZT.

Figure 1. X-ray diffraction patterns of undoped and and Nd-doped BST thin films.
Figure 2. The (200) peaks of undoped and Nd-doped BST thin films.

The average grain size and the surface roughness of the undoped and doped BST thin films were analyzed with AFM in tapping mode with amplitude modulation. The AFM images were obtained using an area of 2μm×2μm. The surface AFM micrographs for the undoped and Nd doped BST thin films are shown in Figure 3. All the AFM images show smooth surface morphology and the absence of both cracks and pinholes. A trend of decreasing grain size with increasing Nd content is observed and the average grain size of the samples was about 20–30 nm. Figure 4 shows that the root mean square roughness (RMS) of the films decreases as the Nd concentration increases from 0 mol% to 3 mol%, but it increases when the Nd doping concentration exceed 3 mol%.

Figure 3. Two-dimensional AFM images of the surface of the BST:Nd thin films(a. Undope, b. 1 mol% Nd-doped, c. 3 mol% Nd-doped, d. 5 mol% Nd-doped).

Figure 4. The roughness of BST thin films as a function of Nd content.

The mechanism of emission of Nd-contained materials has been well established in the literatures [10-13] and the energy diagram is schematically shown in Figure 5. The PL spectra of undoped and
Nd-doped BST thin films are shown in Figure 6. It can be explained that the peak in the dashed area was caused by one and half time double-frequency of the 808 nm pump laser. In this case, the host material has tetragonal rather than cubic structure and the Nd-related emission can be observed. The near infrared (NIR) luminescence peaks at 880, 1066 and 1345 nm are attributed to the Nd\(^{3+}\) inner shell \(^4F_{3/2}\) to the \(^4I_{9/2}, ^4I_{11/2}\) and \(^4I_{13/2}\) levels, respectively. It can be seen that the 1066 nm emission is more stronger than the others. The characteristic emission peaks in these films were due to the Stark splitting of the degenerate 4f levels under the crystalline field and homogeneous and inhomogeneous broadening caused by the films texture structures and multi-domain structures [14]. As shown in Fig. 6, we found the luminescence intensities reached maximum at 1 mol\% Nd ions dopant concentration, meanwhile, the PL intensity decreased as Nd doping concentration exceed 1 mol\%. The reason for this phenomenon may be due to the cross-relaxation process between the two closely placed Nd ions. From charge compensation mechanism, the Nd\(^{3+}\)-Nd\(^{3+}\) distance is too small in BST lattice and cross relaxation is greatly enhanced, resulting in decrease in luminescence intensity. Very efficient cross relaxation can occur when two or more rare earth ions sit to one another to form a cluster that result in almost immediate interaction between the ions.

![Figure 5. Relevant energy levels in the PL of BST:Nd.](image)

![Figure 6. PL spectra from BST:Nd thin films. excitation wavelength 808 nm.](image)
4. Conclusion
The BST:Nd thin films were prepared by sol-gel process and sintered at 700°C, and studied by XRD, AFM and PL. We found that the Nd doped BST thin films belong to polycrystalline perovskite structure. The surface morphologies of the films is smooth and crack-free. The 3 mol% Nd-doped BST thin film had the minimum root-mean-square roughness. The Nd-doped BST thin films show three NIR luminescence peaks, the 1066 nm emission was the most distinct luminescence. The emission intensities reached maximum at 1 mol% Nd ions dopant concentration and decreased when the Nd doping concentration exceed 1 mol%. The emission efficiency of BST:Nd was proposed to be influenced by the doping concentration of Nd³⁺ and mean distance between Nd³⁺ ions as well. Good performance on both microstructure and luminescence properties of BST:Nd materials may show potential applications in 1066 nm laser and novel photonic devices.

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