

## Microstructure and photoluminescence properties of Nd-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanocrystalline

Dan Liu, Yongping Pu\* and Xuan Shi

School of Materials Science and Engineering, Shaanxi University of Science and Technology, Shaanxi Xi'an 710021, China

$\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$  ( $x = 0.25, 0.5, 0.75, 1.00$ ) nanocrystalline was prepared by modified sol-gel method. The powders crystallized well after annealing at 830 °C for 30 min in air. Phase composition and optical properties of  $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$  nanocrystalline were investigated by X-ray diffraction (XRD), scanning electron microscope (SEM), photoluminescence (PL) spectra and ultraviolet-visible (UV-Vis) absorption spectra. In PL spectra, the major up-converted band observed at 534 nm (green) originated from the  $^4\text{G}_{7/2}$   $^4\text{I}_{9/2}$  excited state absorption (ESA) when exciting at 800 nm. It was also found that with increasing of  $x$  value the luminous intensity decreased because of different location of  $\text{Nd}^{3+}$  substitution. The optical energy band gap of the  $\text{Bi}_{3.5}\text{Nd}_{0.5}\text{Ti}_3\text{O}_{12}$  nanocrystalline was found to be 3.17 eV by Tauc equation. The up-conversion mechanisms in the doped system will be discussed by analyzing the energy level structures of  $\text{Nd}^{3+}$ .

**Key words:**  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ , Sol-gel method, Photoluminescence, Up-conversion.

### Introduction

During the past few decades there have been considerable interests in the up-conversion of phosphors, much of the early work aimed at producing up-conversion lamp and all solid-state lasers [1-3]. In recent years, there has been a renewed interest in the rare-earth (RE) ions-doped up-conversion materials due to their potential applications such as IR laser detecting, biomedicine diagnosis, solid-state display and fiber optic amplifiers. RE ions doped inorganic materials have been paid much attention to many potential applications [4]. Among various complex oxides,  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BIT) is a ferroelectric material with a layered perovskite structure built up by the regular intergrowth of  $[\text{Bi}_2\text{O}_2]^{2+}$  layer and perovskite type layers  $[\text{Bi}_2\text{Ti}_3\text{O}_{10}]^{2-}$ , which not only has relatively low phonon energy and good transmission property, but also contributes to energy-transfer in RE ions [5, 6].

Frequency up-conversion in Nd-doped glasses and single crystals were described previously [7-10]. In contrast, much fewer works have appeared on the up-conversion of Nd-doped nanocrystalline BIT, which provide emission of radiation at higher energy than the excitation wavelength. The objective of the present work is to develop nanocrystalline BIT doped with  $\text{Nd}^{3+}$ , in the form of powder materials by using sol-gel technique and annealing at different temperatures for 30 min in air. We will report and discuss the optical band gap, the relationship between doping concentrations

and luminescence intensity, and the up-conversion luminescence mechanism.

### Experimental procedure

The  $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$  precursor solutions were synthesized using  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Nd}(\text{NO}_3)_3$ , and  $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$  as raw materials, ethylene glycol as a solvent and acetic acid as a complexing agent. All of the chemical reagents used in this investigation were of analytical grade.  $\text{Nd}(\text{NO}_3)_3$  and  $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  were first dissolved in ethylene glycol at 60 °C with magnetic stirring.  $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$  mixed with ethylene glycol and acetic acid was added dropwise to the above solution at room temperature under constant stirring. The acetic acid (HOAc) was used to control the chemical reaction during this process. The dry gel obtained by baking the gel at about 70 °C, and then annealed at 400 °C, 500 °C, 600 °C, 700 °C and 830 °C for 30 min to form  $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$  nanocrystalline, respectively.

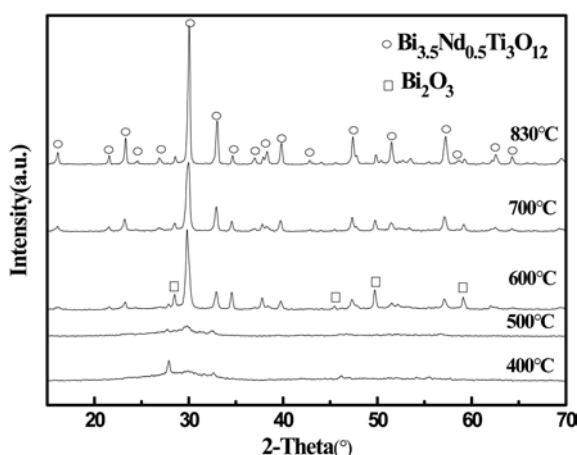
The XRD patterns of BNT powder was recorded on a high resolution X-ray diffractometer (XRD, D/MAX 2200 pc, Japan). Their diffraction patterns were obtained by using Cu K $\alpha$  radiation of wavelength  $\lambda = 0.15418$  nm. The microstructure of the sintered samples was studied on polished and then thermally etched surfaces using a scanning electron microscope (SEM, Hitachi S-4800, Japan). The excitation and up-conversion emissions spectra of the prepared samples were recorded using fluorescence spectrophotometer (Hitachi F-4600, Japan). The absorbance spectrum was determined by Lambda 950 UV/vis spectrometer (PE, USA). All measurements were performed at room temperature.

\*Corresponding author:  
Tel : +86-029-86168803  
Fax: +86-029-86168803  
E-mail: liudan062@yahoo.com.cn

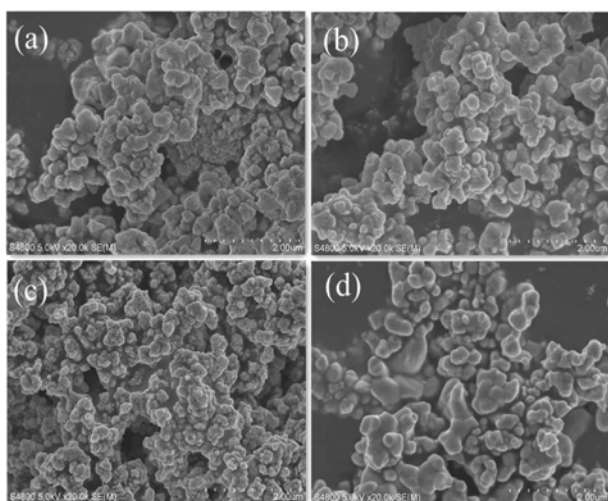
## Results and discussion

The X-ray diffraction (XRD) patterns of  $\text{Bi}_{3.5}\text{Nd}_{0.5}\text{Ti}_3\text{O}_{12}$  annealed at different temperatures for 30 min are shown in Fig. 1. It is seen that the increase of annealing temperature from 400 to 700 °C promoted a reduction of secondary phases ( $\text{Bi}_2\text{O}_3$ ) into the lattice and increased the diffraction peak intensities ascribed to the BIT phase. Possibly, this behavior is caused by the diffusion from  $\text{Bi}_2\text{O}_3$  into the BIT structure. It is verified only the presence of the pure BIT phase with orthorhombic structure until annealing at 830 °C.

Fig. 2 shows the scanning electron microscopy micrographs of  $\text{Bi}_{3.5}\text{Nd}_{0.5}\text{Ti}_3\text{O}_{12}$  annealed at different temperatures. After calcining at 400 °C, the precursor exhibits plate-like grains whose size distribution is wide (from 100 nm to 1  $\mu\text{m}$ ) as shown in Fig. 2(a). They retain a typical expanded structure and the surface morphology is smooth and round. With increasing of calcining temperature, the grains grow up and the coalescence of adjacent grains takes place, which



**Fig. 1.** XRD patterns of  $\text{Bi}_{3.5}\text{Nd}_{0.5}\text{Ti}_3\text{O}_{12}$  annealed at different temperatures.



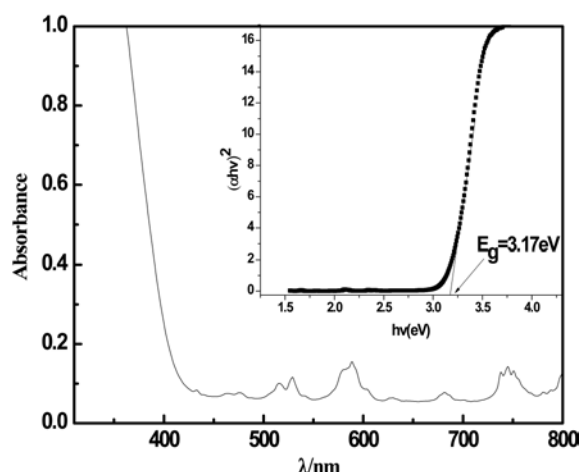
**Fig. 2.** SEM micrographs of  $\text{Bi}_{3.5}\text{Nd}_{0.5}\text{Ti}_3\text{O}_{12}$  annealed at different temperatures: (a) 400 °C, (b) 500 °C, (c) 700 °C, and (d) 830 °C.

indicates a rapid surface diffusion along the primary ones. After calcining at 830 °C,  $\text{Bi}_{3.5}\text{Nd}_{0.5}\text{Ti}_3\text{O}_{12}$  grains grow and the sizes become approximately 100 nm.

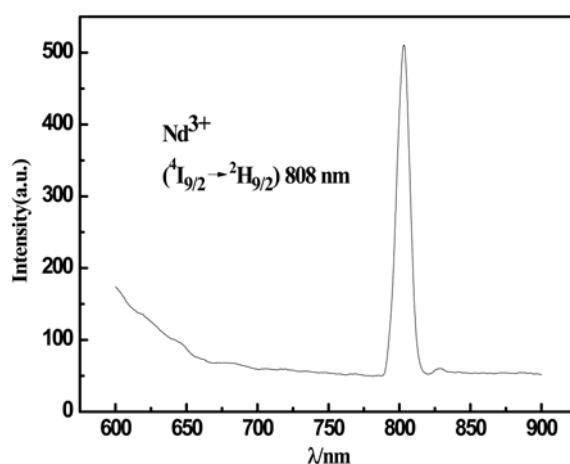
Fig. 3 shows the optical transmittance curves as a function of wavelength for  $\text{Bi}_{3.5}\text{Nd}_{0.5}\text{Ti}_3\text{O}_{12}$  annealed at 830 °C, the insert figure shows the plot of  $\alpha^2$  divided by  $h\nu$ . The band gap ( $E_g$ ) of the BNT, which is very crucial to the optoelectronic applications, we further apply Tauc equation for the determination of band gaps for crystalline, the relation between the optical absorption and  $E_g$  for a direct transition can be expressed by equation (1):

$$\alpha h\nu = B(h\nu - E_g)^n \quad (1)$$

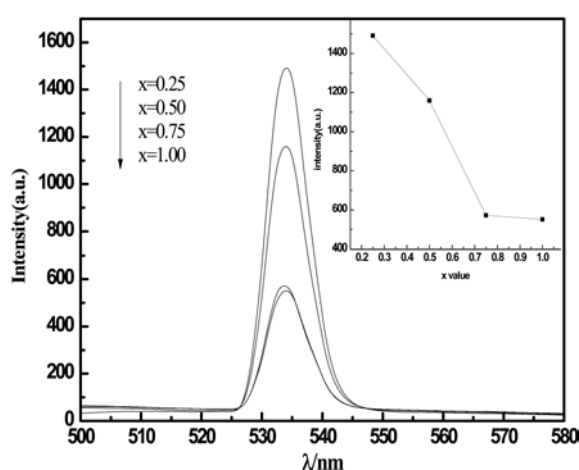
where  $E_g$  is the optical band gap;  $B$  is constant;  $h$  is Planck's constant;  $\nu$  is wave frequency of the incident light;  $n$  is an index characterizing the type of optical transition. For BNT nanocrystalline,  $n$  is 1/2 for a direct allowed transition, the absorption coefficient ( $\alpha$ ) is equivalent to the absorbance. The optical band gaps can be obtained from the extrapolation of the best



**Fig. 3.** Absorbance spectra of  $\text{Bi}_{3.5}\text{Nd}_{0.5}\text{Ti}_3\text{O}_{12}$  annealed at 830 °C and the plot of  $\alpha^2$  divided by  $h\nu$ .



**Fig. 4.** The excited state absorption corresponding to the visible emission of  $\text{Bi}_{3.5}\text{Nd}_{0.5}\text{Ti}_3\text{O}_{12}$  nanocrystalline.

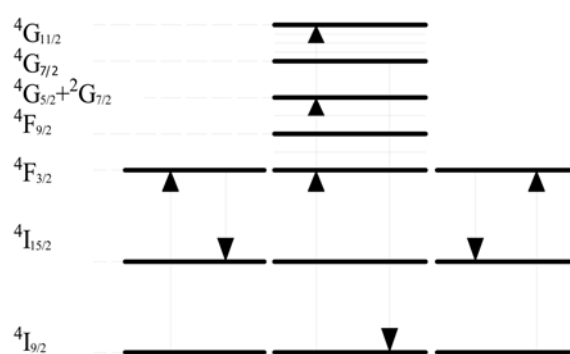


**Fig. 5.** The up-conversion emission spectra of  $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$  with different  $x$  value excited at 800 nm.

linear parts of the curves at  $\alpha = 0$  near the band edge region. The optical band gap of BNT nanocrystalline was found to be 3.17 eV, it was closed to the results reported by other authors [11, 12].

The excited state absorption (ESA) corresponding to the visible emissions of  $\text{Nd}^{3+}$  embedded in BIT nanocrystalline upon excitation at 533 nm is shown in Fig. 4. The absorption in the range from 790 to 810 nm assigned to ( $^4\text{I}_{9/2} \rightarrow ^4\text{H}_{9/2}$ ) indicates that the laser diodes operating at 800 nm are the efficient pump sources for the green and NIR up-conversion emission.

Fig. 5 shows the up-conversion emission spectra of  $\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$  with different  $x$  value under excitation at 800 nm. The major up-converted band observed at 534 nm (green) originated from the  $^4\text{G}_{7/2} \rightarrow ^4\text{I}_{9/2}$  transitions. With the increase of  $x$  value the luminescence intensity decreases, and closes to a fixed value. This may be caused by the concentration quenching. The observed route of the up-conversion emissions is shown in Fig. 6. The up-conversion process has three principal mechanisms by which it accomplished; these are multi-photon absorption, cooperative energy-transfer up-conversion, and the photon avalanche. In this case, cooperative energy-transfer up-conversion plays an important role in process; the absorption of the first pump photon (800 nm) by  $\text{Nd}^{3+}$  in the ground state absorption (GSA) initially excites it to the  $^4\text{F}_{3/2}$  energy level of the same ions. Thus, population ultimately grows in the  $^4\text{F}_{3/2}$  level, two excited  $\text{Nd}^{3+}$  at  $^4\text{F}_{3/2}$  level transferred energy to the third ion at the same level, which increases the possibility of the third one exciting to the  $^4\text{G}_{11/2}$  level (ESA). Also it relaxes non-radiatively (NR) to the lower  $^4\text{G}_{7/2}$  level in the order:  $^4\text{I}_{9/2} \rightarrow ^4\text{F}_{3/2}(\text{GSA}) \rightarrow ^4\text{G}_{11/2}(\text{ESA}) \rightarrow ^4\text{G}_{7/2}(\text{NR})$ . Such excitation of ET resulted in higher population of  $^4\text{G}_{7/2}$  energy emitting levels. Therefore, when  $x = 0.75$  and 1.00, the intensity of photoluminescence decreases sharply due to the different location of  $\text{Nd}^{3+}$  substitution.



**Fig. 6.** Energy levels diagram of the up-converted transitions of  $\text{Nd}^{3+}$  incorporated into BIT nanocrystalline.

## Conclusions

$\text{Bi}_{4-x}\text{Nd}_x\text{Ti}_3\text{O}_{12}$  ( $x = 0, 0.25, 0.5, 0.75, 1.00$ ) nanocrystalline have been prepared by modified sol-gel method successfully. Annealing of the prepared samples at different temperatures for 30 min resulted in nanocrystalline, as confirmed by the XRD analysis. Structural study revealed that the well crystallite temperature was 830 °C. The optical band gap of BNT nanocrystalline was found to be 3.17 eV. Efficient infrared-to-visible conversion in the prepared samples observed, using 800 nm laser diode as excitation source, and its origin investigated. The major up-conversion band was observed to be center at 534 nm (green) originated from the  $^4\text{G}_{7/2} \rightarrow ^4\text{I}_{9/2}$  transitions. In addition, with the increase of  $x$  value the intensity decreases and closes to a fixed value.

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