Synthesis and optical characterization of Er-doped bismuth titanate nanoparticles grown by sol–gel hydrothermal method

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ABSTRACT

The Er^{3+}-doped bismuth titanate ($Bi_4Ti_3O_{12}$, BIT) nanoparticles were synthesized by a combined sol–gel and hydrothermal method under a partial oxygen pressure of 30 bar. The composition and morphology were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman scattering. They showed pure and homogeneous spherical BIT nanoparticles with a size below the 30 nm. The incorporation of Er ions showed a strong decrease in the lattice parameters, as well as averaged particle size. The photoluminescence up-conversion (excitation wavelength =1480 nm) showed an enhancement of the infrared emission (980 nm) as Er concentration increased, achieving a maximum for 6% mol, while photoluminescence spectra (excitation wavelength =473 nm) showed a strong green emission (529 and 553 nm) with a maximum at 4% mol.

1. Introduction

Bismuth titanate ($Bi_4Ti_3O_{12}$, BIT) is a member of Aurivillius-type bismuth-layered perovskite oxides, with a general formula (Bi_2O_2) $[A_{m-1}(B)_mO_{3m+1}]$. In this notation A represents a mono-, bi- or trivalent ion, B denotes a tetra-, penta- or hexavalent ion, and m is the number of BO_6 octahedra in each pseudo-perovskite block (m=1, 2, 3, …), where m=3 for BIT compounds. The crystallographic structure consists of a layered arrangement of three perovskite-like cells of $(A_{m-1}(B)_mO_{3m+1})^{2-}$ embedded between two bismuth oxides layers $(Bi_2O_2)^{2+}$ along the c-axis [1,2]. It is widely accepted that the Bi_2O_2 layers have a very important influence on the properties of bismuth layer-structured ferroelectrics (BLSFs), as the Bi_2O_2 layers act as insulating layers and are self-regulated to compensate for space charge due to their net electric charge [3]. This configuration favours outstanding ferroelectric properties, and, as a consequence, it has drawn extensive the attention from the scientific community as one of the most promising candidates to replace the lead-based ceramics.

Due to its low dielectric constant, high Curie temperature and strong anisotropy of the spontaneous polarization, such materials can be used in a broad range of applications, including but not limited to:

piezoelectric, dielectric, pyroelectric, electro-optic, antennas, photocatalytic and biosensing fields, as well as potentially optical-electrical integrated and coupling devices [4–8]. However, its high dielectric loss, small remnant polarization and low fatigue-resistance limit its performance in other applications such as ferroelectric random access memory, FRAM, for example [9].

Recent studies have revealed that the rare-earth ion substitution in the A-site of perovskite structures can effectively overcome such drawbacks [10,11]. Park et al. reported fatigue-free, excellent ferroelectrical properties of BIT films doped with La^{3+} ions [12]. Improved results were obtained by Kim et al. through Nd^{+3} doping in BIT films [13]. The fatigue-free behaviour of these films can be attributed to the enhanced stability of oxygen in the Ti–O octahedron layer, which is caused by the substitution of stable rare-earth ions for volatile Bi ions located near the Ti–O octahedron layer. The enhancement of the ferroelectric properties can be explained by the fact that the substitution of Bi atoms by rare-earth ions, with different ionic radius, produces a structural distortion of the perovskite and, consequently, an enhancement of the remnant polarization [11].

On the other hand, the addition of the rare-earth ions with optical activity in the bismuth layer structure opens the possibility for use as a

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high-performance luminescent material, with a broad field of applications including opto- and microelectronics, as well as photon up-conversion (UC) [14,15]. Near-infrared to visible upconversion (UC) is an important approach for the generation of visible luminescence. The interest in UC emission has increased due to the need for all-solid compact laser devices and three-dimensional displays. Trivalent rare earth doping-ions such as Pr^{3+}, Ho^{3+}, Tm^{3+}, Nd^{3+} and Er^{3+} are used as emission centers in UC materials [16–18].

Among the lanthanide ions, Er^{3+} is found to be the most effective dopant for UC emission, and the metastable levels $^4I_{9/2}$ and $^4I_{11/2}$ of Er^{3+} can be conveniently populated using low cost, low power laser diodes operating at 800 and 980 nm [18]. The search for suitable host materials is gaining importance for realizing high UC efficiency in the visible and the mid-IR region. Various host-material dependent factors such as phase purity, particle size, Er doping content, site substitution, and rare earth ion interactions in the host matrix are found to influence the UC emission [19]. Appropriate host materials offering good thermal stability and sensitivity over a wide temperature range (below and above room temperature) are in demand especially for luminescence thermometry applications.

In recent years, different synthesis methods have been reported in the literature for the fabrication of BIT powders. The choice of synthesis process plays a crucial role in obtaining a BIT with specific microstructure control as well as purity and chemical homogeneity. The control of these parameters has a significant effect on dielectric, ferroelectric and optical properties. Among the most popular processes are solid-state reactions [20] and high-energy ball milling processes [21]. However, these methods present some drawbacks, such as: formation of secondary phases, contamination by impurities, high heat treatment temperatures, long processing times and non-uniform particle size distribution.

An effective way to overcome such drawbacks is through wet chemical or soft-chemistry method. These methods not only ensure a homogeneous phase and well-controlled particle size but also more complex architectures and improvement of the dielectrical, structural, morphological and mechanical properties of BIT oxides [19,22,23]. Among these soft-chemistry routes, the hydrothermal synthesis is one of the most popular one due to it is safe and eco-friendly method, with synthesis processes performed at moderate temperatures, T~200 °C.

In the present work, we studied the structural modifications, surface morphology and Up-conversion luminescence properties of Er^{3+}-doped BIT nanoparticles. The synthesis was carried out by a combined sol–gel hydrothermal method in an oxygen atmosphere. In a previous work, we have shown that the introduction of oxygen atmosphere in the hydrothermal synthesis has a dramatic impact of the particle size and the crystal quality on other titanates [24–26]. However, to the best of our knowledge, similar studies on the BIT synthesis has not been yet reported in the literature. The impact of Er^{3+} concentration was analysed by powder diffraction analysis and Raman studies. The up-conversion emission mechanisms were analysed by exciting at 980 and 1480 nm.

2. Experimental

2.1. Synthesis

$Bi_{4-x}Ti_3O_{12}$:Er_x powders with x=0, 2, 4, 6 and 8 mol%, were synthesized by the sol–gel-hydrothermal process using tetrabutyl titanate (TBT), bismuth (III) chloride ($BiCl_3$, Aldrich) and erbium (III) chloride hexahydrate, 99,9% ($ErCl_3$, Aldrich) as starting materials.

In a procedure, solution A containing 1 mL of TBT (97%) was diluted with 8.5 mL of ethanol for 10 min to form a white solution, which was added dropwise at 60 °C for 3 h with stirring to solution B, which contained 1 mL of HNO_3 in 40 mL of deionised water. An aqueous solution C was prepared by dissolving $BiCl_3 \cdot 6H_2O$ in 1 mL of HCl, and solution D was prepared by dissolving $ErCl_3$ in 2 mL of

deionised water.

To prepare the $Bi_{4-x}Ti_3O_{12}$:Er_x precursor, solutions C and D were added dropwise to solution B. Under stirring and N_2 bubbling, NaOH 10 M was added to the bismuth erbium titanium solution, and a white, homogeneous colloidal bismuth erbium titanium slurry was formed.

The mixed solution was transferred to a 500 mL Teflon-lined stainless steel reactor, sealed and then heated at 180 °C for 48 h under a partial oxygen pressure of 30 bar. At the end of the reaction, the autoclave was cooled down to room temperature. The as-synthesized white powder, attached to the Teflon container, was collected, centrifuged, washed with distilled water and ethanol to remove any remaining ions and dried at 60 °C for 6 h under atmospheric pressure.

2.2. Characterization

Er-doped BIT powders were structurally characterized by X-ray diffraction (XRD). Data were acquired using a Siemens Advanced D-8 diffractometer with CuK_α radiation at 40 kV and 30 mA. Raman spectra were recorded on a WITEC model CRC200, using a 5.5 mW laser with a wavelength of 514.5 nm with a grating of 1200 groove/mm. Surface morphological analysis of BIT nanoparticles was performed by scanning electron microscopy (FEI Quanta 6F Environmental SEM) equipped with an energy-dispersive X-ray spectroscopy (EDX) analyser to measure the sample composition operated at 10 kV. The UC spectra were obtained by exciting with a 980 nm and 1480 nm laser (Alcatel 1933 SMG) with a maximum power of 50 mW. The laser was focused on the samples using a lens with a focal length of 30 mm. The emitted light was collected using a lens with focal length 50 mm and focused on the entrance slit of a CCD spectrograph (Andor Shamrock 303i).

The luminescence decay curves were obtained by exciting with a 10 ns pulsed optical parametric oscillator laser (EKSPLA/NT342/3/UVE) and the emission was focused in the entrance of the spectrograph coupled to a photomultiplier (R928 Hamamatsu in the Vis range or 5509-73 Hamamatsu for the NIR range) and recorded using a digital storage oscilloscope (Tektronix 2430).

3. Results and discussion

3.1. XRD patterns

Fig. 1 shows the XRD patterns of the BIT and Er-doped BIT samples. As shown in Fig. 1 the sharp and well-defined peaks reveal high crystallinity for all of the as-prepared Er-doped BIT powders, which were not submitted to any heat treatment.

The XRD Bragg reflection was assigned by using an orthorhombic perovskite structure (space group *Fmmm*, JCPDS card no 56–0814) of BIT at room temperature. The peak associated with the (117) plane of BIT and Er-doped BIT shows the highest intensity, indicating that all sample compositions conform to the bismuth layered structure with m=3. The results are in agreement with earlier observations reporting that the strongest diffraction corresponds to the (11_{2m+1}) reflection in the Aurivillius phase for bismuth layered structured ferroelectrics compositions [27].

Fig. 2 displays the XRD patterns of BIT and Er-doped BIT in the 28–30° 2Θ range for all of the samples.

The effect of Er-substitution on the BIT structure can be seen in the clear shifting of the (1 1 7) reflection. Fig. 2 shows the X-ray diffraction patterns of BIT and the BIT-doped phases. The shift of the strongest diffraction peak (*hkl*) is closely related to the ionic radii of Er^{3+}, Bi^{3+} and Ti^{4+}. According to Shannon et al. [28], the ionic radii are 1.03 Å for Bi^{3+}; 0.88 Å for Er^{3+} and 0.605 Å for Ti^{4+}. When Er^{3+} replaces Bi^{3+} in the structure, the difference in the ionic radii leads to a decrease in the lattice parameters and the cell volume, this is reflected by the shift of the XRD peak (117) to higher angles as shown in Fig. 2.

To further evaluate the variation of the crystal structure the lattice