

STUDY OF UP-CONVERSION LUMINESCENCE IN BaTiO<sub>3</sub>: Ho<sup>3+</sup>  
NANOCRYSTALS

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Visible up-conversion emissions at 435, 545, 580, 675 and 690 nm and 437, 547, 575 and 675 nm have been obtained from BaTiO<sub>3</sub> doped with 4% Ho<sup>3+</sup> ions in two different forms of the prepared samples, powder and thin film, under 808 nm laser diode excitation emissions. Combined with the energy level structure of Ho<sup>3+</sup> ions and the kinetics of the visible emissions, the up-conversion mechanism has been analyzed and explained. The blue, green and red emissions of both samples have been attributed to the ground state-directed transition from <sup>5</sup>F<sub>1</sub>, <sup>5</sup>S<sub>2</sub> and <sup>5</sup>F<sub>5</sub> states, respectively, which are populated through excited state absorption on 808 nm excitation. Nano-structure pure barium titanate and doped with different concentrations of Ho<sup>3+</sup> ions in the form of powder and thin films have been prepared by sol-gel technique, using barium acetate (Ba(CH<sub>3</sub>CHOO)<sub>2</sub>) and titanium isopropoxide (Ti((CH<sub>3</sub>)<sub>2</sub>CHO)<sub>4</sub>) as precursors. The thin films were prepared by spin-coating sol-gel method. The as-grown thin film and powders were found to be amorphous, which crystallized to the tetragonal phase after synthesization at 750 °C in air for 30 minutes. The crystallite size of thin film and powder samples both doped with 4% Ho<sup>3+</sup> ions, were found to be equal to 11 and 16 nm, respectively.

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## 1. Introduction

Research in nanometer-sized materials has been very active in recent years because of their potential applications in different areas such as optoelectronic devices, catalysts, and magnets [1]. BaTiO<sub>3</sub> has been a well-known material and is a potential thin-film integrated optic host because of its electronic and electro-optic prop-

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erties [2–4]. The up-conversion has been an important approach for the generation of short-wavelength laser actions [5,6]. Recently, the interest in up-conversion emission has been increased because of the search for all-solid compact laser devices operating in the blue-green region and the availability of powerful near-infrared GaAs/(Al,Ga)As laser diodes [7].

Uniform BaTiO<sub>3</sub> ultra-fine powders and thin films have previously been prepared by different methods, such as sputtering and sol-gel technique [8,9]. Er<sup>3+</sup>, Ce<sup>3+</sup> and other rare-earth elements doped BaTiO<sub>3</sub> film and powder materials have been prepared and their emissions have also been studied [10,11]. So far, there has not been many reports on the Ho<sup>3+</sup> doped BaTiO<sub>3</sub> powder prepared by the sol-gel method. In comparison with other techniques, the sol-gel method is more suitable to prepare optical materials as it permits molecular-level mixing and processing for the raw materials and precursors at relatively lower temperature and produces nano-structured powders and thin films [12,13].

The properties of the films show strong decrease of dielectric properties as compared to their powder counterparts. In powder materials, certain transport mechanisms (such as viscous flow in amorphous materials and grain boundary diffusion in crystalline materials) produce densification, while other process (surface diffusion and evaporation/condensation) do not. For films, even the latter process can cause densification, because of the short transport path through the thickness of the film. The films differ from the powder gels in several important aspects:

- 1) The initial structure of the gel is profoundly affected by the rapid sol-to-gel transition.
- 2) The constraint imposed by the substrate leads to the development of very strong stresses during drying and firing.
- 3) The substrate provides a site of heterogeneous nucleation of crystals.
- 4) Degradation of the structure can result from chemical or physical interaction with the substrate.

In the present work, the visible up-conversion emissions in BaTiO<sub>3</sub> doped with 4% Ho<sup>3+</sup> ions, prepared by sol-gel technique in two different forms, powder and thin film were compared. The effect of doping of the prepared samples, from the same precursor materials in the form of powder and thin film with two different concentrations of Ho<sup>3+</sup> ions 1 and 4%, on the structural properties is studied using FT-Raman and X-ray diffraction (XRD). Transmission electron microscope (TEM) and scanning electron microscope (SEM) confirmed the morphology of the two forms of the prepared samples.

## *2. Experimental*

Pure and doped BaTiO<sub>3</sub> with 1 and 4% Ho<sup>3+</sup> ions in powder form were prepared by a modified sol-gel method. Barium acetate (Ba(CH<sub>3</sub>CHOO)<sub>2</sub>, Ba(Ac)<sub>2</sub>) and titanium butoxide (Ti(C<sub>4</sub>H<sub>9</sub>O)<sub>4</sub>), were used as the starting materials; acetyl acetone (C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>, AcAc) and acetic acid (HAc)-H<sub>2</sub>O mixtures were adopted as

solvents of Ti(C<sub>4</sub>H<sub>9</sub>O)<sub>4</sub> and Ba(Ac)<sub>2</sub>, respectively. Ho(NO<sub>3</sub>)<sub>3</sub>-H<sub>2</sub>O solution was added to the precursor with molar ratios of BaTiO<sub>3</sub>: 1 and 4 % Ho<sup>3+</sup>. The solution was kept in air at room temperature, yielding transparent solution. The dry gel obtained by baking the gel at 130 °C, was then annealed in air in a conventional oven at 750 °C for 30 minutes.

For the preparation of BaTiO<sub>3</sub> doped with 1 and 4 % Ho<sup>3+</sup> ions in the thin film form, the same resultant solution used for the preparation of powder was utilized. The solution was spun on silica glass substrate at around 3500 rpm for 30 seconds. Then the film was annealed in air in a conventional oven at 750 °C for 30 minutes.

The X-ray diffraction (XRD) patterns of the prepared samples were recorded with Diano X-ray diffractometer using monochromatised CoKα<sub>1</sub> radiation of wavelength 0.179026 nm at 45 kV and 9 mA. The accurate crystallite sizes at FWHM were determined from the Scherrer's equation ( $G = \lambda/(D \cos \theta)$ ) where  $G$  is the grain size,  $\lambda$  is the wavelength of the X-rays,  $\theta$  is the angle of incidence of X-ray beam and  $D$  is the corrected width (in radians) of the peak at half maximum, which is given by  $\sqrt{D_s - D_q}$ , where  $D_s$  is the FWHM of the investigated samples and  $D_q$  is the FWHM of the quartz sample, where, in order to obtain the values of the instrumental parameters, scan has been carried out for strain-free quartz sample of crystallite size ranging between 5 and 10 μm, under exactly the same conditions as used for the investigated samples.

The coarse and fine microstructures of the powder and thin film materials were depicted by scanning electron microscope (SEM) micrographs (JEOL JYA 840 A) electron probe micro-analyzer. Microstructures were studied with a transmission electron microscope [TEM, EM 10 Zeiss].

The excitation and up-conversion emission spectra of the prepared samples were recorded using a laser diode at 808 nm. Incident beam power was 300 mW. The emission was analyzed by Acton Spectra Pre 500 double monochromator (grating 1200) and detected with a photon counter. The photoluminescence (PL) emission was measured using the lock-in amplifier (SR 510-Stanford) technique and recorded by computer. The measurements were performed at room temperature.

### 3. Results and discussion

The excitation spectra of the powder and prepared thin film samples, both doped with 4 % Ho<sup>3+</sup> ions, are shown in Fig. 1. The absorption in the range from 790 to 810 nm, assigned to <sup>5</sup>I<sub>8</sub> → <sup>5</sup>I<sub>5</sub> transition indicates that the laser diodes operating at 808 nm are efficient pump sources for the visible up-conversion emissions. In order to give highlight on the up-conversion emission spectra in the visible regions of the BaTiO<sub>3</sub>:4 % Ho<sup>3+</sup> in powder form, a plot of wavelength in nm as a function of intensity in arbitrary units is shown in Fig. 2. It has been well addressed that the red emissions at 690 and 675 nm have been attributed to the intra-4f transitions of the Ho<sup>3+</sup> ions and are assigned to the <sup>5</sup>F<sub>5</sub> → <sup>5</sup>I<sub>8</sub> transitions. The green and blue emissions at 545 and 435 nm are attributed to another intra-4f transition of Ho<sup>3+</sup> ions which is assigned to the <sup>5</sup>S<sub>2</sub> → <sup>5</sup>I<sub>8</sub> and <sup>5</sup>F<sub>1</sub> → <sup>5</sup>I<sub>8</sub> transitions, respectively.

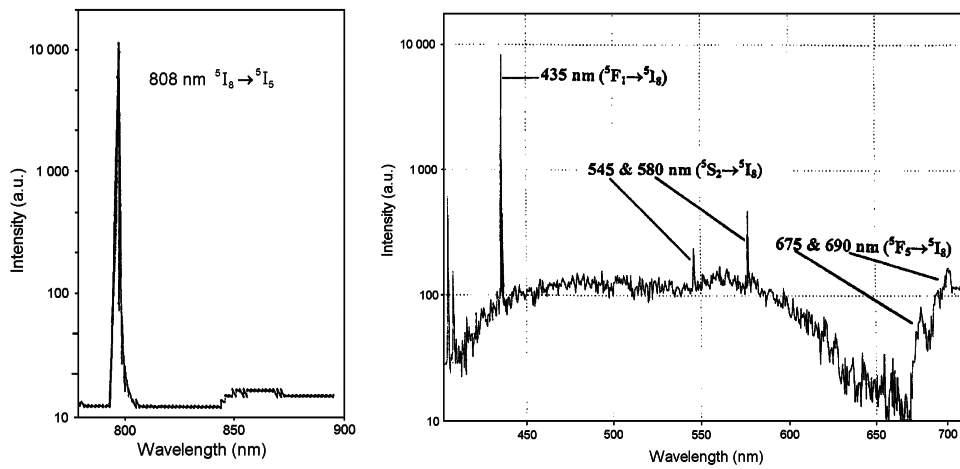


Fig. 1 (left). Excitation spectra of thin film and powder prepared samples, doped with 4%  $\text{Ho}^{3+}$  ions. Fig. 2. Up-conversion emission spectra from  $\text{BaTiO}_3:4\% \text{Ho}^{3+}$  in powder form under 808 nm excitation.

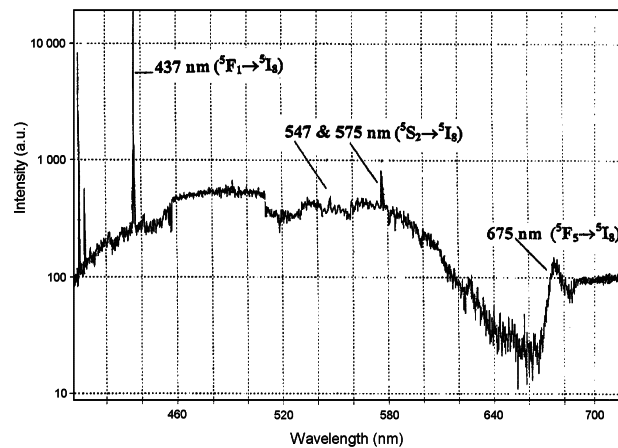


Fig. 3. Up-conversion emission spectra from  $\text{BaTiO}_3:4\% \text{Ho}^{3+}$  in thin film form under 808 nm excitation.

It is well observed from Fig. 3 that the up-conversion emissions spectra of  $\text{BaTiO}_3:4\% \text{Ho}^{3+}$  in thin film form are in the same regions as the powder sample, with a slight shift in the peak positions. The positions of peak up-conversion emission of the two forms of samples doped with 4% of  $\text{Ho}^{3+}$  ions are shown in Table 1. The two peaks between 400 and 408 nm in Figs. 2 and 3 could be attributed to the second harmonic of the laser at 808 nm. The emission from  $\text{Ho}^{3+}$  ions is nearly in the same regions regardless of the difference in the form of the two prepared samples.

TABLE 1. Up-conversion of BaTiO<sub>3</sub>:4% Ho<sup>3+</sup>, synthesized at 750°C in powder and thin film forms.

Up-conversion peak positions		
Powder	Thin film	Intra-4F transition of Ho <sup>3+</sup> ions
675 and 690 nm	675 nm	<sup>5</sup> F <sub>5</sub> → <sup>5</sup> I <sub>8</sub>
545 and 580 nm	547 and 575 nm	<sup>5</sup> S <sub>2</sub> → <sup>5</sup> I <sub>8</sub>
435 nm	437 nm	<sup>5</sup> F <sub>1</sub> → <sup>5</sup> I <sub>8</sub>

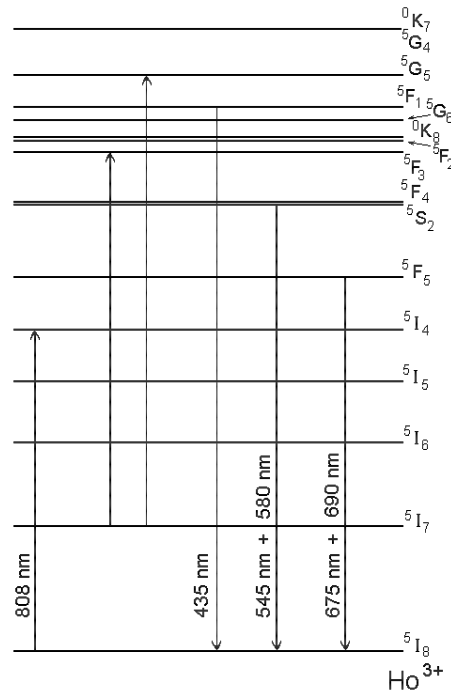
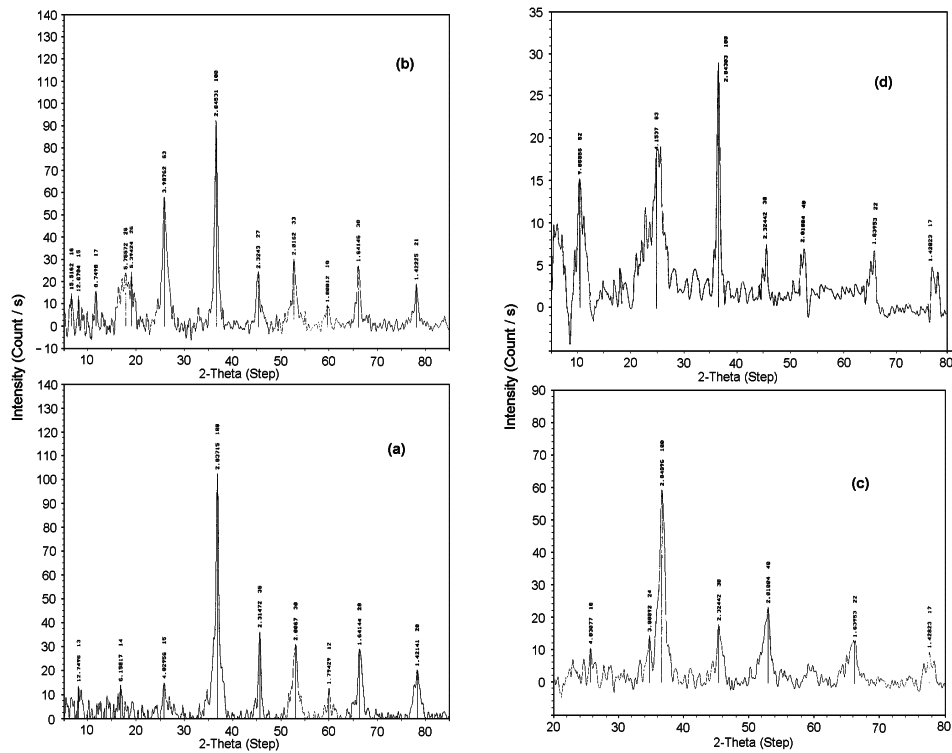

 Fig. 4. ESA process for the up-conversion emissions under 808 nm excitations for powder and thin film BaTiO<sub>3</sub> doped with 4% Ho<sup>3+</sup> ions, and synthesized at 750°C.

Figure 4 schematically shows the excited-state absorption (ESA) processes of the blue emission of Ho<sup>3+</sup> ions upon excitations at 808 nm. In the first stage, the Ho<sup>3+</sup> is pumped to the <sup>5</sup>I<sub>4</sub> excited state by 808 nm photons. From the <sup>5</sup>I<sub>4</sub> state, Ho<sup>3+</sup> decays through a non-radiative process into the <sup>5</sup>I<sub>5</sub> and <sup>5</sup>I<sub>6</sub> metastable levels and subsequently into the <sup>5</sup>I<sub>7</sub> metastable level. In the second stage, the excited-state absorption at 808 nm excites the Ho<sup>3+</sup> ion into the <sup>5</sup>G<sub>5</sub> and <sup>5</sup>F<sub>3</sub> states from which <sup>5</sup>F<sub>1</sub> and <sup>5</sup>S<sub>2</sub> states are populated by the non-radiative relaxation. Also a Ho<sup>3+</sup> ion in the <sup>5</sup>I<sub>4</sub> state relaxes to the ground state non-radiatively and transfers its energy to another neighboring state in the same state <sup>5</sup>I<sub>4</sub>, promoting the latter to the <sup>5</sup>G<sub>5</sub> from which <sup>5</sup>F<sub>1</sub> state is populated through the non-radiative relaxation. The spin-allowed radiative transition from <sup>5</sup>F<sub>1</sub> to the ground state gives rise to the blue up-conversion emission at 435 nm.



by increasing the concentration of  $\text{Ho}^{3+}$  ions, while the thin film has larger FWHM and lower crystallite sizes. The accurate crystallite sizes of the prepared samples are shown in Table 2.

TABLE 2. Crystallite sizes of pure  $\text{BaTiO}_3$  and doped samples, synthesized at  $750^\circ\text{C}$  in powder and thin film forms.

Sample names	$\text{BaTiO}_3$ (Powder)	$\text{BaTiO}_3:1\% \text{Ho}^{3+}$ (Powder)	$\text{BaTiO}_3:4\% \text{Ho}^{3+}$ (Powder)	$\text{BaTiO}_3:4\% \text{Ho}^{3+}$ (Thin film)
$\text{Ho}^{3+}$ ions conc.	0%	1%	4%	4%
Crystallite size nm	3.4	15	16	11

Transmission electron micrographs, TEM, were used to confirm the results obtained by XRD. TEM and diffraction patterns of pure  $\text{BaTiO}_3$  and  $\text{BaTiO}_3:4\% \text{Ho}^{3+}$ , both are in powder form are shown in Figs. 6a, b, c and d. TEM micrographs

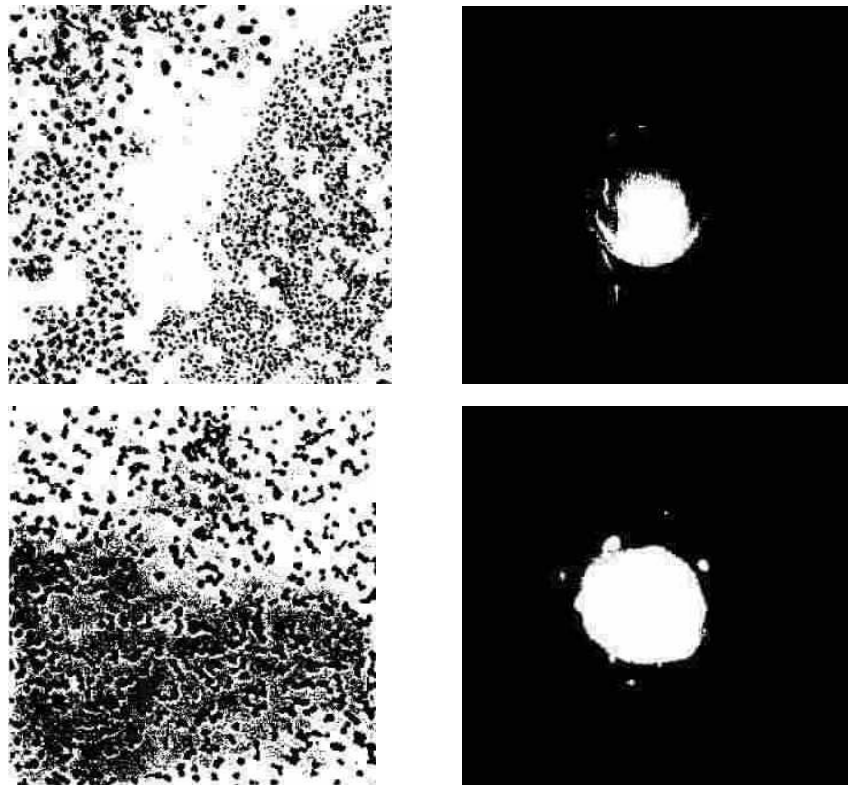


Fig. 6. TEM micrographs (left, upper  $100000\times$ , lower  $60000\times$ ) and diffraction patterns (right) of pure  $\text{BaTiO}_3$  in powder form and synthesized at  $750^\circ\text{C}$  (upper figures) and  $\text{BaTiO}_3:4\% \text{Ho}^{3+}$  ions (lower figures), prepared by sol-gel technique.

of the pure BaTiO<sub>3</sub> which, in contrast with BaTiO<sub>3</sub>: 4% Ho<sup>3+</sup> sample, show particles of a spherical shape, which are present less in the doped sample. These spheres might be due to some aggregates of particles. The obtained diffraction patterns are typical of nano-crystalline BaTiO<sub>3</sub> in which smaller-sized granular structures and radius less than 10 nm were observed in pure and doped with 4% Ho<sup>3+</sup> ions powder samples. These results coincide with the results of the calculated crystallite sizes from XRD shown in Table 2. The faint rings in Figs. 6b and d confirm the presence of the crystalline phase, they display typical diffraction patterns of tetragonal BaTiO<sub>3</sub>.

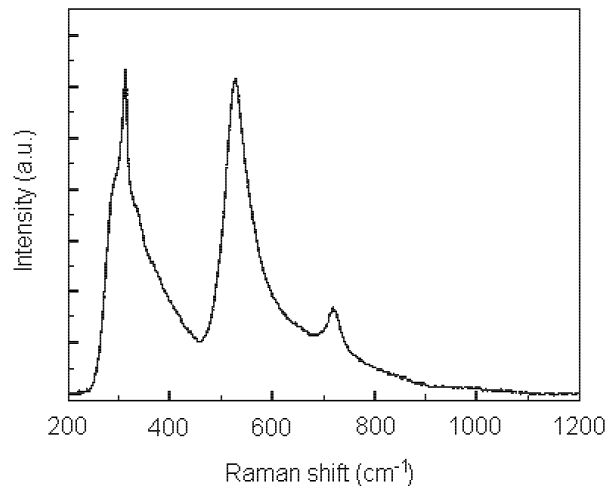


Fig. 7. FT-Raman spectra of pure BaTiO<sub>3</sub> in powder form and synthesized at 750°C, prepared by sol-gel technique.

To further verify the tetragonal symmetry of the pure powder prepared sample, the FT-Raman shift of thermally-treated pure BaTiO<sub>3</sub> in the form of powder was measured and is shown in Fig. 7, where the FT-Raman scattering pattern is given. The spectra of the sample under investigation are composed of peaks corresponding to the well-known vibrational frequencies of this material [2]. The bands observed are a weak peak around 715 cm<sup>-1</sup>, a strong and broad peak around 515 cm<sup>-1</sup> and a strong and sharp at 305 cm<sup>-1</sup>. These result are compatible with those obtained by Zhu et al. [14], who suggested that the same FT-Raman spectra of the BaTiO<sub>3</sub> film bands around 515 cm<sup>-1</sup> are assigned to the TO modes of A<sub>1</sub> symmetry, whereas the sharp peak at 305 cm<sup>-1</sup> has been assigned to the B<sub>1</sub> mode. The weak band around 715 cm<sup>-1</sup> has been associated with the highest frequency longitudinal optical mode (LO) of the A<sub>1</sub> symmetry. The band at 305 cm<sup>-1</sup> is characteristic of BaTiO<sub>3</sub> with the tetragonal symmetry. Then FT-Raman study confirms that the prepared pure samples in powder form produced here are tetragonal BaTiO<sub>3</sub>.

The results of SEM analysis of BaTiO<sub>3</sub>: 4% Ho<sup>3+</sup> in both form powder and thin film are shown in Figs. 8a and b. The as-fired film at 750°C was found to consist of



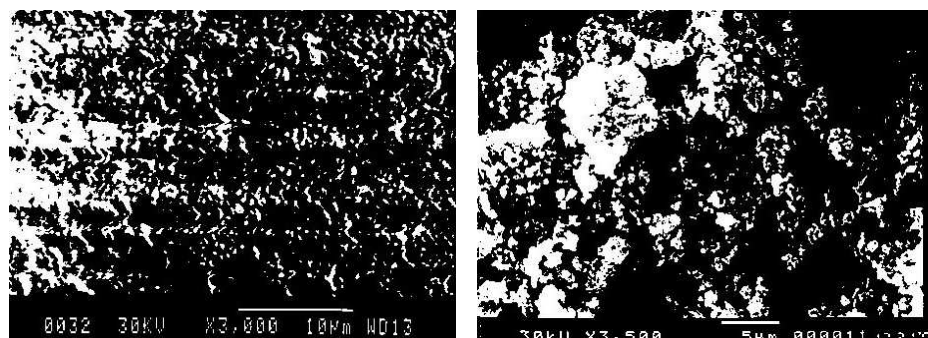


Fig. 8. SEM micrographs, of  $\text{BaTiO}_3:4\% \text{Ho}^{3+}$  ions synthesized at  $750^\circ\text{C}$  (left) in thin film form and (right) in powder form, both prepared by sol-gel technique.

fine particles, which have a granular microstructure with irregularly shaped grains, more or less sponge-like, Fig. 8a. Upon pressing and sintering the powder at the same temperature, the particles coalesce to form larger well-defined crystallites than the thin film, Fig. 8b. Figs. 9a and b reveal the cross-sectional view of  $\text{BaTiO}_3:4\% \text{Ho}^{3+}$ , with  $1300\times$  magnification of a representative film sample synthesized at  $750^\circ\text{C}$ , with a thickness of about 200 nm, Fig. 9 a, while Fig. 9b shows the cross-sectional view at lower magnification of 60 $\times$ . The morphology of the film at this lower magnification exhibits a relatively dense surface. We ascribed this layer to  $\text{BaTiO}_3$ , since if the  $\text{TiO}_x$  remained un-reacted, it should have been converted to anatase. Diffraction and FT-Raman spectroscopy show no evidence of anatase and we believe that all of the starting  $\text{TiO}_x$  has being converted to  $\text{BaTiO}_3$ .

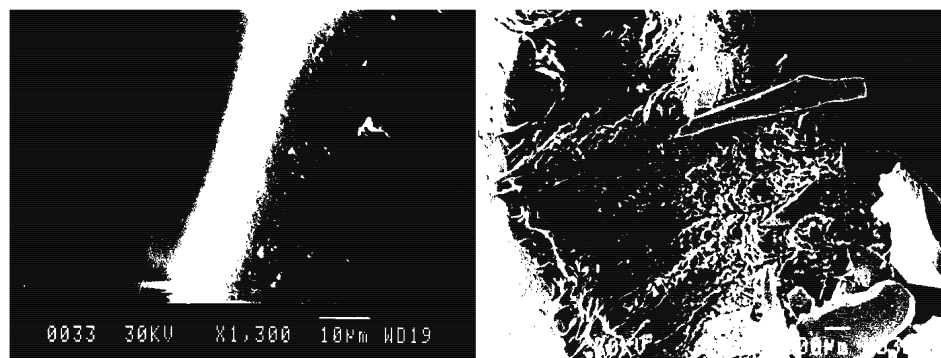


Fig. 9. SEM micrographs of cross-sectional view of  $\text{BaTiO}_3:4\% \text{Ho}^{3+}$  ions synthesized at  $750^\circ\text{C}$  in thin film form, (a) ( $1300\times$ ) and (b) ( $60\times$ ), both prepared by sol-gel technique.

#### 4. Conclusion

The sol-gel technique was successfully applied for preparing nano-structure pure BaTiO<sub>3</sub> and BaTiO<sub>3</sub> doped with 1 and 4 % Ho<sup>3+</sup> ions in two different forms, powder and thin film. The up-conversion properties of the two different forms of prepared samples doped with 4 % of Ho<sup>3+</sup> ions upon excitations with 808 nm laser-diode source was compared. It appears that the emissions from Ho<sup>3+</sup> ions are nearly in the same regions regardless the difference in form between the two prepared samples. Our analysis suggests that, the dominant blue emissions at 435 nm and 437 nm obtained from BaTiO<sub>3</sub> doped with 4 % Ho<sup>3+</sup> ions in powder and thin film forms, respectively, have been produced through an energy-transfer excited-state absorption (ESA) process on 808 nm excitation.

The dried samples upon heating at 750 °C crystallize to tetragonal phase with crystallite sizes 3.5 and 16 nm for pure powder sample and sample doped with 4 % Ho<sup>3+</sup> ions, respectively. While the prepared thin-film sample doped with 4 % Ho<sup>3+</sup> ions shows broader FWHM than the powder sample, indicating a decrease of its crystallite sizes to 11 nm for the sample. The XRD data were confirmed by TEM, where small-sized granular structure of radius lower than 10 nm was observed. The SEM of powder and thin film have been compared. The FT-Raman indicates that pure powder sample is characterized by a significant structural disorder and confirms that it is of tetragonal BaTiO<sub>3</sub> form.

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PROUČAVANJE LUMINESCENCIJE UZBUĐOM NAVIŠE U  
NANOKRISTALIMA  $\text{BaTiO}_3:\text{Ho}^{3+}$ 

Uzbudom laserskom diodom na 808 nm postigli smo emisije u vidljivom području na 435, 545, 580, 675 i 690 nm, te na 437, 547, 575 and 675 nm, u  $\text{BaTiO}_3$  punjenom s 4%  $\text{Ho}^{3+}$  iona u uzorcima dvaju oblika, prahu i tankom sloju. Uzimajući u obzir stanja iona  $\text{Ho}^{3+}$  i kinetiku emisije fotona, analizirali smo i objasnili mehanizam uzbude naviše. Emisije oba uzorka u plavom, zelenom i crvenom području pripisuju se prijelazima u osnovno stanje sa stanja  $^5\text{F}_1$ ,  $^5\text{S}_2$  odn.  $^5\text{F}_5$  koja se pune apsorpcijom fotona 808 nm u višim stanjima  $\text{Ho}^{3+}$  iona. Metodom sol-gel pripremili smo nanostrukturni čist barijum titanat i barijum titanat punjen s dvjema koncentracijama  $\text{Ho}^{3+}$  iona, kao prah i kao tanke slojeve. Rabili smo barijum acetat ( $\text{Ba}(\text{CH}_3\text{CHOO})_2$ ) i titanijev izopropoksid ( $\text{Ti}((\text{CH}_3)_2\text{CHO})_4$ ) za njihovu pripremu. Tanke smo slojeve dobivali centrifugiranjem sol-gela. Svježe pripremljeni tanki slojevi i prah su amorfní, ali se kristaliziraju zagrijavanjem na  $750^\circ\text{C}$  u zraku tijekom 30 minuta. Veličina kristalita u tankom sloju i prahu, svaki punjen s 4%  $\text{Ho}^{3+}$  iona, iznosi 11 odn. 16 nm.