Structural and Optical Characteristics of BaTiO₃:Yb³⁺ Powders

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Yb³⁺ doped Barium Titanate powders were prepared by the sol-gel method in order to study their structural and luminescent properties. These powders have potential to be used to prepare films for luminescent screens. The synthesized powders were obtained at 2, 4 and 8% mol Yb³⁺ doped BaTiO₃. In order to determine organic compound decomposition, weight loss, and establish the crystallization process, we performed TGA and DTA analyses. The powders were also thermally treated at temperatures ranging from 700 to 1200°C in order to study the structure evolution. Pure doped BaTiO₃ powders were carefully studied by X-ray diffraction (XRD). Observations of the powders using scanning electron microscopy (SEM) were done in order to correlate the grain size with the luminescent properties. A comparative study of the spectroscopy properties constituted by emission, absorption spectra, and fluorescence decay measurements using NIR excitation were done. The Yb³⁺ ions pairs emission was measured in the green region at about 500 nm when pumping at 940 nm.

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1. Introduction

There has been a great interest in perovskite-type Barium Titanate material due principally to its ferroelectric properties and its high dielectric constant. This material has been used in the electronic industry for dielectric capacitors, resistors, transducers and ferroelectric memories, as well as in missile guidance, submarine sonar, acoustic mines, filters, and ultrasonic devices.^{1,2)} Additionally, BaTiO₃ perovskite matrix structure is a candidate for use as a rare earth ion host matrix.³⁾ Recently, some reports had confirmed efficient luminescent properties of this matrix when doped with erbium and/or ytterbium.^{4,5)} These properties allow the feasible production of high resolution luminescent thin film panels.⁶⁾ BaTiO₃ has been synthesized by different methods; traditionally, BaTiO₃ has been prepared by a solid state reaction employing high sintering temperatures above 1000°C. The products obtained by this method are not completely homogenous; besides, the presence of some impurities due to abrasion or incomplete reactions is observed by some authors.^{7,8)} One better option seems to be the sol-gel method, because of several advantages: the mixture of precursors at the molecular level with diffusion at nano-size range, and lower temperatures than conventional methods are required. Even more, the homogenous distribution of doped ions is easily reached by the solution routes, avoiding segregation.⁹⁾ The sol-gel method can obtain high purity powders with a control of structure and morphology. The aim of the present work is to synthesize Yb doped BaTiO₃ powders to establish the influence of different ytterbium concentrations on luminescent properties as a thermal treatment. The structural studies and morphological

features of the particles were studied by means of XRD technique and SEM. All samples were studied for luminescent properties and pumped at 940 nm wavelength.

2. Experimental Procedure

Barium 2, 4 pentanedionate (Ba(C₅H₇O₂)₂, Alfa Aesar), ytterbium chloride hydrate (YbCl₃·6H₂O, 99.9%, Alfa Aesar) and titanium isopropoxide (Ti(OPri)₄, 97%, Aldrich) were used as starting materials. The chelating chemical stabilizing agents were: glacial acetic acid (C₂H₄O₂, 99.8%, Fermont) and acetylacetone (2,4-pentanedione, C₅H₈O₂, ≥99%, Aldrich). Ytterbium chloride hydrate was mixed separately with isopropyl alcohol. The barium 2,4-pentanedionate was dissolved with ytterbium chloride hydrate solution in molar ratios of 0.89 : 0.02, 0.89 : 0.04 and 0.89 : 0.08 for 2, 4 and 8% mol respectively; thereafter, the precursor solution was stabilized by adding acetylacetone and acetic acid. (Acac)H and H-(OAc) were added in complexation molar ratios Ti : (acac)H = 1 : 10 and Ti : OAc = 1 : 8. The mixture was vigorously stirred at 70°C for 15 min. The procedure resulted in the preparation of a transparent yellow-orange sol with a 1.25 mol L⁻¹ concentration. The barium titanate xerogels were prepared by drying the doped solutions at 80°C for 24 h. The xerogels were heat-treated at 700°C and 1200°C in order to densify and crystallize the sol-gel powders. The dried gels were investigated by Thermogravimetric (TG) and Differential Thermal (DTA) analyses, and the thermograms were recorded from 25 to 1200°C using a Setaram Setsys 2000 apparatus at a scan rate of 5°C min⁻¹ in air flux. The crystalline phase of the samples was performed at room temperature on a powder diffractometer (Bruker D8Advance) using CuKα radiation (0.15418 nm). Scanning electron microscopy (SEM) obser-

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Fig. 1 DTA and TGA curves for Yb³⁺ doped BaTiO₃ powder.

variations were performed in order to inspect the microstructure of the samples using a scanning electron microscope (HITACHI S-4200). Furthermore, luminescence spectra were obtained by pumping Yb doped BaTiO₃ powders with a Spectra Physics Quanta-Ray Nd:YAG-MOPO tunable laser system and the luminescence was collected at a right angle by an optical system and dispersed by an Acton Research SpectraPro 500i spectrometer with two Hamamatsu PMT-R326 detectors for the NIR region.

3. Results and Discussion

3.1 DTA and TGA analyses of BTO powders

TG and DTA curves of the ytterbium doped BaTiO₃ powders dried at 120°C for 24 h are presented in Fig. 1. The total weight loss (about 30 mass% during the decomposition reaction) is observed in the TG curve. The first weight loss of 7 mass% occurs up to 300°C, results of the evaporation of alcohol and removal of water which is related with an endothermic peak situated at 106°C. Two endothermic peaks situated between 320 and 450°C represent the removal of a carboxylic group of metals present in the gel associated with a mass reduction of ~2 mass% and pyrolysis of organics (9 mass%) occurring during the process of thermal treatments. Additionally, one exothermic peak observed at 376°C is correlated with the decomposition of alkoxy-groups (7 mass% of weight loss). The transformation of amorphous decomposition products in barium titanate takes place when the last portion of organic residues is burning out, and it is marked by the presence of an exothermic peak around 700°C. According to Madarász,¹⁰ it is assumed that there is no significant loss of titanium during the decomposition process; for the TiO(acac)_{0.89} hydroxo complexes for samples with acetylacetone content higher than 0.49, the acetylacetonate anion deficiency is compensated with hydroxide ions considered products of hydrolysis (acac-Ti.. + H₂O-Ti.. + acacH). The samples are releasing freed acetylacetone (acac)H, confirmed by the presence of an endothermic peak at 260°C arising from a one-proton (H⁺) migration to acetylacetonate anions from a neighboring anion (the latter of which becomes double negatively charged), or from OH or H₂O group still present in the micropores of the samples taking place the formation of CO₂ and H₂O. Meanwhile acetic acid and CO might be the degradation products of

organic double charged anions remaining in the condensed phase. After 800°C, an exothermic peak could be associated with the decomposition of the barium carbonate phase formed by a reaction with acetyl groups disappearing with increasing temperature up to 814°C and accompanied by a continuous weight loss (3 mass%). Some reports had shown that some carbonates would be formed during the thermal decomposition process of the Ba-Ti-precursor gel.¹¹ In the present work, the carbonate components are present in a very small concentration; no peaks corresponding to carbonates can be identified in the XRD patterns of the powders annealed at 700–850°C (Fig. 2). A further increase in the temperature beyond 820°C should promote crystallization of BaTiO₃, but no longer relating to any chemical reaction.

3.2 XRD studies and morphology

The samples were heat treated at these temperatures in order to study the structural evolution of the powders. Two effects were studied: the effect of the heat treatment on BaTiO₃:Yb³⁺ powders heat treated at 700°C, 850°C, 1000°C and 1200°C (presented in Fig. 2), and the effect of the Yb³⁺ on the BaTiO₃ structure doped at 2%, 4% and 8% mol powders annealed at 700°C (shown in Fig. 4). Considering first the effect of the heat treatment on BaTiO₃:Yb³⁺ 2% mol, it is observed that the barium titanate gels heat treated at these temperatures show a structure depending on thermal treatments: the BaTiO₃:Yb³⁺ powders thermally treated at 700°C exhibited cubic structure due to the fact that there is no splitting evident in the (2 0 0) diffraction peak; for powders sintered at 850°C, it is possible to observe a shift on the (2 0 0). Nevertheless, as for the samples heat treated at 700°C, the absence of any shoulder peak at 2θ~52° confirms the presence of a cubic phase. For the BaTiO₃:Yb³⁺ powders sintered at 1000°C, the gradual splitting of (2 0 0) plane of the cubic into tetragonal (2 0 0) and (0 0 2) reflections was observed, in agreement with Amami *et al.*¹² After 1200°C thermal treatment, BaTiO₃:Yb³⁺ 2% mol powders show well-defined splitting of (0 0 2) and (2 0 0) peaks at around 2θ~45°. The crystal size of BaTiO₃:Yb³⁺ was estimated from the broadening of the corresponding XRD peaks using the Scherrer equation: $L = K\lambda/(\beta \cos \theta)$; where L is the crystal size, λ is the wavelength of the X-ray radiation (λ .15406 nm) for Cu K α , K is usually taken as 0.89; and β is the line width at half-maximum height after correcting for equipment broadening.¹³ The Rietveld refinement method was used to refine the structure of the all the phases present in the samples. This is a proven method for the quantitative determination of amorphous and crystalline phases so as to determine their structural parameters (c/a). The MAUD program, which applies the RITA/RISTA method,^{14,15} was used for the refinement analysis.

The crystal sizes and tetragonality values of BaTiO₃:Yb³⁺ are presented in Table 1. As can be observed, both the tetragonality and crystal size were gradually increased as the temperature increased. The maximum value obtainable was observed at 1200°C, corresponding to 1.0049 for powders exhibiting a crystal size of ~50 nm, and the minimum tetragonality of 1.0001 was observed for samples sintered at 700°C having a crystal size of ~32 nm. Recently, Yb³⁺ doped BaTiO₃ powders synthesized by sol-gel process,¹⁶

Fig. 2 XRD patterns and the SEM images of BaTiO₃:Yb³⁺ 2% mol powders heat treated at 700°C, 850°C, 1000°C and 1200°C.

Table 1 Crystallite size and tetragonality for Yb³⁺ doped BaTiO₃ as a function of temperature and Yb³⁺ concentration.

Temperature, <i>T</i> /°C	Crystallite size <i>D</i> /nm % mol Yb,			Tetragonality <i>c/a</i>
	2	4	8	
700	32	34	36	1.0001
850	33	—	—	1.0006
1000	44	—	—	1.0045
1200	50	—	—	1.0049

suggested an enhanced stability for the cubic and tetragonal phase structures when the grain size is below 33 nm and above 45 nm respectively. Thus, the stabilization of BaTiO₃:Yb³⁺ cubic phase was observed for 700 and 850°C, due to the presence of particles constituted of nanocrystals with mean diameter sizes of 32 and 33 nm. Based on these observations, the BaTiO₃ ferroelectric tetragonal structure was stabilized by heating powders at a higher temperature.

The XRD patterns for powders synthesized with the different Yb³⁺ doping concentrations are presented in Fig. 4. In this figure, it is possible to observe that barium titanate crystallizes in a cubic phase for Yb³⁺ 2, 4 and 8% mol. The mean crystallite diameters (MCD) were estimated to be in the range 32 to 36 nm. The MCD calculated values for BaTiO₃:Yb³⁺ indicate that the ytterbium doping ion in BaTiO₃ does not affect the crystallite size and the crystal structure, as presented in Fig. 3. It was stated that there are two stages of substitution of rare earth elements in BaTiO₃.¹⁷ In the first stage, Ti⁴⁺ ions located on the Ba site are replaced by the rare earth elements. In the second stage, Ba²⁺ ions on the A site are also mainly replaced by rare earth elements. Yb³⁺ ions (0.098 nm) most probably replaced Ba²⁺ (0.156 nm) cations rather than Ti⁴⁺ (0.065 nm), whose radius

Fig. 3 Relationship between tetragonality temperature of heat-treatment and average crystallite size of the Yb³⁺ doped BaTiO₃ powders.

seems too small. When Yb³⁺ was introduced to BaTiO₃, three Ba²⁺ sites were substituted by two Yb³⁺ neighbors to maintain electrical neutrality, and so one vacancy was created, consequently the composition expected is Ba_(1-0.06)Yb_{0.06}TiO₃. This behavior is similar for barium titanate powders doped with Eu³⁺.¹⁸

Scanning electron micrographs obtained on Yb³⁺ doped BaTiO₃ powders as a function of temperature and Yb³⁺ concentration are presented in Figs. 2 and 4 respectively. Figure 2 shows particles characterized by agglomerates with sizes varying from 0.21 μm at 700°C to 0.52 μm at 1000°C. Spherical forms are associated with smaller particles that form irregular clusters or faceted sheets. After 1200°C thermal treatment, the morphology was characterized by agglomerates and nearly spherical particles of about 0.56 μm. A small fraction of bigger crystals of about 3 μm was also detected. Figure 4 shows the Yb³⁺ content dependence on the powders' microstructure. The morphology associated with 2% mol Yb³⁺ doping concentration changed dramati-

Fig. 4 XRD patterns and the SEM images of BaTiO₃ powders doped at different Yb³⁺ concentrations heat treated at 700°C.

Fig. 5 Absorption spectra of BaTiO₃ powders doped at different Yb³⁺ concentrations heat treated between 700 to 1200°C.

Fig. 6 Emission spectra of 2, 4 and 8% mol Yb³⁺ doped BaTiO₃ powders heat treated at 1200°C and 4% mol heat treated at 700°C.

cally from regular and rounded particles to irregular clusters with faceted sheets when barium titanate powder was doped at 4% mol Yb³⁺. At a higher doping concentration, a morphology and texture modification occurred, showing aggregates of 500 nm in size, which could be associated with the formation of secondary phases as the pyrochlore Yb₂Ti₂O₇, as was reported for Yb³⁺ doped BaTiO₃ powders with a concentration equal to or more than 5% at.¹⁹⁾

3.3 Absorption and emission spectra

The absorption spectra of BaTiO₃ doped 2, 4 and 8% mol Yb³⁺ powders annealed at 1200°C is shown in Fig. 5; that of BaTiO₃:Yb³⁺ 4% mol heat-treated at 700°C is also shown for comparison. The broad absorption band between 900 and 950 nm (splitting of the multiplet ²F_{5/2}) on the BaTiO₃ crystallized in cubic phase (700°C) changed to a single band situated around 900 nm in the powder heat-treated at 1200°C.

This absorption of Yb³⁺ is similar to that observed in many other Yb³⁺ doped crystals and is related to the electronic transitions ²F_{5/2} → ²F_{7/2} within 4f electronic shell of Yb³⁺ ions.²⁰⁾ Notice that in Fig. 5 the absorption intensity increases with the doping concentration.

The fluorescence spectra of BaTiO₃:Yb³⁺ (2, 4, and 8% mol) powders heat-treated at 1200°C excited at 940 nm are presented in Fig. 6. This figure also shows the emission spectrum of the BaTiO₃:Yb³⁺ (4% mol) annealed at 700°C. The emission spectrum of the cubic barium titanate gel powder (700°C) shows an emission peak at 980 nm; nevertheless, when the structure is heat-treated at 1200°C (presence of the tetragonal phase), the emission spectra consists of a broad band from 970 to 1010 nm, with a maximum at 980 nm corresponding respectively to the ²F_{5/2} → ²F_{7/2} transitions (5→1). Changes in emission spectra due to the Yb³⁺ ions concentration are shown in

Fig. 7 Fluorescence decay curves of 2, 4 and 8% mol Yb^{3+} doped BaTiO_3 powders calcined at 1200°C and 4% mol calcined at 700°C .

Fig. 6. The most intense emission bands correspond to the $\text{BaTiO}_3:\text{Yb}^{3+}$ 8% doped sample, while the lowest intensity band corresponds to the $\text{BaTiO}_3:\text{Yb}^{3+}$ 2% doped sample.

3.4 Luminescence decay curves

Luminescence decay curves were measured for three samples with concentrations at 2, 4 and 8% mol upon 940 nm excitation (Fig. 7). The lifetime curve of the $\text{BaTiO}_3:\text{Yb}^{3+}$ 4% mol heat-treated at 700°C is also shown in Fig. 7. As can be seen in this figure, the decay curves are slightly non-exponential. For the three samples heat-treated at 1200°C in tetragonal phase, the non-exponentiality can be associated with the Yb^{3+} non-equivalent centers and energy transfers between different sites; also, this non-exponentiality became more intense in samples treated at 700°C that presented a cubic phase.⁹⁾ When the samples were pumped at 940 nm, we also measured the fluorescence in the 500 nm region. To explain the ytterbium cooperative emission, one might consider that two neighboring ions are close enough to form pairs and thus these two ions emit not in the $1.0\ \mu\text{m}$ region but in the 500 nm.¹⁶⁾ When samples were synthesized, the Ba/Ti ratio was less to unity, so ytterbium ions were most probably replacing the divalent barium ions.

4. Conclusions

In this work, we have reported the elaboration and characterization of $\text{BaTiO}_3:\text{Yb}^{3+}$ powders heat treated at 700°C and 1200°C . $\text{BaTiO}_3:\text{Yb}^{3+}$ powders exhibit a tetragonal structure, and as the temperature increases the c/a ratio is higher. The obtained results show that the particle size has an effect on the c/a ratio structural phase, and also the heat treatment time has a great influence on the luminescence

properties. Decay curves change from non-exponential to an almost exponential stage. Crystal size of the powders considerably decreases as the temperature increases from 700 to 1200°C . The doping concentration did not show an influence on the structure of the powders. Thin films and their luminescence properties will be produced based on this work.

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