Effect of Starting Materials on the Morphological and Optical Properties of Er Doped BaTiO₃ Nanocrystalline Films

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Erbium (5%mol) doped BaTiO₃ films were prepared using different metallic precursors: barium acetate, titanium butoxide and isopropoxide with different molar ratios. Three different experimental methodologies (A, B and C) were proposed in order to obtain optical quality thick films incorporating polyvinylpyrrolidone (PVP) as a rheological agent at the sol stage. In all cases, Er doped BaTiO₃ films were deposited in silica quartz substrates. The morphology was controlled by means of the incorporation of the chelating agent and water molar ratios. Through the three different synthesis routes, Er:BaTiO₃ films presented mainly the cubic phase, as observed by X-ray diffraction. The films presented a homogeneous and crack-free surface of cross-linked particles. Photoluminescent results show that the highest intensity emission of the Er³⁺ (⁴S_{3/2} → ⁴I_{15/2}) was obtained from Er:BaTiO₃ film prepared using C methodology, which could be associated with the film's thicknesses. [doi:10.2320/matertrans.M2012313]

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1. Introduction

The evolution of nanotechnology has increased demands for portable computers, communication equipment and consumer electronic products in recent years. Nanotechnology has emerged as a technological alternative, which allows to fulfill special requirements as improve resolution and quality in devices that will soon become ubiquitous products in our homes, workplaces and elsewhere.^{1,2)} In particular, erbium-doped waveguides films have attracted much attention because of their use as optical amplifiers, which have been used in the detection of infrared radiation by converting the invisible light into the visible range where conventional detectors are effective also in optical storage, printing, display technology and medicine using up-conversion emission at 550 nm.^{3,4)} Furthermore, barium titanate (BaTiO₃) is a very useful host matrix for some applications because it does not absorb energy, allowing it to serve only for support of rare earth ions, which is very useful for these particular applications.⁵⁻⁷⁾ In particular, rare earth (RE) doped NIR-to-visible ceramic oxides represent an alternative and excellent substitute for traditional fluorescent applications. On the other hand, the sol-gel processing is a relatively easy and economical way for making uniform large sized, high quality stoichiometric thin film phosphors, which are especially useful for optical applications.^{8,9)} A new sol-gel process using a high-concentration of alkoxide precursor solutions has proven to have a significant advantage in synthesizing thick-filmed ceramic materials.^{10,11)} By means of this method, transparent, crack-free BaTiO₃ monolithic gels and thin films have been successfully synthesized.^{12,13)} However, the thickness of the films remains below 500 nm,

and it is accepted that it is important to obtain a higher thickness in order to fulfill an optical quality for luminescent devices,¹⁴⁾ so, it is of high technological importance to increase this parameter. A possible alternative to producing high quality and of BaTiO₃:Er³⁺ films is to incorporate PVP (polyvinylpyrrolidone: as rheological agent FW: 360000) during the sol-gel synthesis process.^{15,16)} However, its effect in the morphological and luminescent properties is unclear; therefore, the present work studies, by means of three different experimental procedures, the effect of molar ratio and PVP on morphology and photoluminescent properties of Er-doped BaTiO₃ sol gel thin films.

2. Experimental Procedure

Experimental strategies for the elaboration of Er doped BaTiO₃ precursor solutions were carried out by means of three different procedures. The precursors employed were: barium acetate (Aldrich 99.999% (Ba (CH₃COO)₂)), titanium isopropoxide (Aldrich ≥97%, (Ti[OCH(CH₃)₂]₄)), titanium butoxide (Fluka ≥97% (TiO[O(CH₂)₃CH₃]₄)), as source of barium and titanium respectively. Acetic acid (Aldrich, ≥99% (CH₃COOH)) and acetylacetone (Aldrich, ≥99% (CH₃COCH₂COCH₃)) were used as chelating agents with distilled water in order to promote hydrolysis, and Erbium nitrate (Alfa Aesar, 99.9% (Er(NO₃)₃·5H₂O)) was used as dopant. The molar ratios and special conditions for each type of synthesis (A, B and C) are presented in Table 1. The studied molar relationships correspond to the final results in which a stable sol was formed with varying different synthesis conditions. Synthesis A corresponds to a sol without water, synthesis B has an acetic acid excess, and synthesis C is a modification of the reported procedure¹⁷⁾ without the use of a different solvent (isopropanol) and

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Table 1 Molar ratio and name label used for the elaboration of Er:BaTiO₃ films from different methodologies.

Synthesis Procedure A		Synthesis Procedure B		Synthesis Procedure C	
Precursor	Molar Ratio	Precursor	Molar Ratio	Precursor	Molar Ratio
Ba(OAc) ₂	1 – x	Ba(OAc) ₂	1 – x	Ba(OAc) ₂	1 – x
Er(NO ₃) ₃ *5H ₂ O	x	Er(NO ₃) ₃ *5H ₂ O	x	Er(NO ₃) ₃ *5H ₂ O	x
AcOH	52	AcOH	18	AcOH	7
Ti(Obu) ₄	1	Ti(Obu) ₄	1	TPOT	1
ACAC(H)	4	ACAC(H)	1	ACAC(H)	9.2
Water	—	Water	40	Water	40
PVP	1	PVP	1	PVP	1

Abbreviations: Ba(OAc)₂: Barium acetate; Er(NO₃)₃*5H₂O: Erbium nitrate pentahydrate; AcOH: Acetic acid; Ti(Obu)₄: titanium butoxide; TPOT: titanium isopropoxide; ACAC(H): acetylacetonate; PVP: polyvinylpyrrolidone.

stabilized with the minimum acetic acid content, since an excess of this promotes the formation of cracks and promotes the growth of grain size.¹⁸⁾ In the present work, the concentration of barium in solution was 1 mol L⁻¹ and the doping concentration was fixed at 5 mol%. PVP was incorporated in all solutions at a 1 : 1 molar ratio with respect to barium.

Erbium doped BaTiO₃ films were obtained from the precursor solutions using a dip-coating technique onto fine polished optical silica substrates. In order to obtain optical quality of the films, the substrate were carefully washed using a special protocol.¹⁹⁾ The substrates were dip-coated using a withdrawal speed of 0.25 cm min⁻¹ for all cases. Only a single layer was deposited on the substrate and thermally annealed from room temperature to 700°C at 0.5°C min⁻¹ at 5 min at the final temperature.

2.1 Characterizations

Crystal structure was determined by X-ray diffractometry (D8 Advance, Bruker AXS) using a Cu-K α monochromatized radiation at 35 kV, 25 mA over the 2 θ range 25–90° (0.1°/s), set on powder configuration. Surface morphology was evaluated by field emission scanning electron microscopy (FE-SEM, HITACHI, S5000) and atomic force microscopy with a Nanoscope IV apparatus (Digital Instruments) in tapping mode. Luminescence spectra were obtained by pumping samples with a Spectra Physics Quanta-Ray Nd:YAG-MOPO tunable laser system, and luminescence was collected at a right angle by an optical system and dispersed by an Acton Research SpectraPro 500i spectrometer with Hamamatsu PMT detector, R326 for NIR regions. In order to analyze the optical quality of the prepared films, as well as the thickness, refractive index, density and porosity, m-lines spectroscopy was carried out with a He–Ne laser (543.5 nm) coupled with a LaSF 35 angle 60° prism.

3. Results and Discussion

XRD profiles of Er³⁺ (5 mol%) doped BaTiO₃ monolayer film for each synthesis procedure are shown in Fig. 1. No secondary phases are found within the detection limit of XRD. The results revealed that the dried gel films crystallized after 700°C heat treatment. However, at this temperature Figs. 1(a) and 1(b) shows an amorphous zone in the range of 2 θ = 20–30°, which could be associated with an excess

Fig. 1 X-ray diffraction pattern of Er:BaTiO₃ films obtained from synthesis A (a), B (b) and C (c) methodologies annealing to 700°C.

of acetic acid present during the formation of the sol. Figure 1(c) corresponds with the film obtained from C methodology; in this X-ray pattern, the complete crystallization in the pseudocubic phase is present in accord with the JCPDS 31-0174 card. As observed, the PVP does not affect the normal crystallization of BaTiO₃. The crystallite size shown in the same Fig. 1, ranges from 13 to 20 nm. The different synthesis procedures do not greatly affect the crystal structure of the films, nor the crystallite size; therefore, the differences in the luminescent properties can be attributed to the morphology and thickness of the films.

Figure 2 shows an image of the synthesized films that go along with procedures A, B and C respectively. As can be observed, only the C synthesis produces transparent films, whereas procedures A and B produce opaque films. The surface morphology of the Er³⁺:BaTiO₃ films prepared under A, B and C methodologies using PVP via single-step dip-coating is illustrated in Figs. 3(a)–3(c). The top view of the micrograph for Er³⁺:BaTiO₃ prepared from methodology A (Fig. 3(a)) (without water) showed a heterogeneous surface

due to the decomposition of gaseous species in a violent form during the sol evaporation, which causes the formation of large pores. Furthermore, as observed, several cracks have been formed. The micrograph of the $\text{Er}^{3+}:\text{BaTiO}_3$ film

prepared under B methodology (Fig. 3(b)) present a uniform cross-linked surface, and it is clear that the films present a more homogenous structure as compared with synthesis A. However, for the film prepared under methodology C (Fig. 3(c)), the morphology of the film is considerably different. In this case, the molar ratio of acetic acid/Ba (7 : 1) and water in excess promotes significant differences in the morphological observations, since the surface presents a flowerlike shape composed of an agglomeration of nanocrystallites, and the same aspect of this morphology was observed in a previous work²⁰⁾ in which isopropanol was used as a solvent. Some reports describe this behavior due to the crystal twinning at the onset of growth, their shape and size related with the molar ratio of the starting materials.^{21,22)}

Fig. 2 Images of the synthesized $\text{Er}:\text{BaTiO}_3$ films obtained from synthesis A (a), B (b) and C (c) methodologies annealing to 700°C .

Fig. 3 SEM micrographs at two different magnification: $1200\times$ (left) and $50000\times$ (right) of Er-doped BaTiO_3 films from synthesis A (a), B (b) and C (c) annealing at 700°C .

(a)

(b)

(c)

Fig. 4 Typical AFM micrographs showing the surface of Er-doped BaTiO₃ films from synthesis A (a), B (b) and C (c) annealing at 700°C.

Figures 3(b) and 3(c) exhibit optical qualities on the surface, attributed to strong hydrogen bonding interactions between C=O groups from PVP, acetic acid and the OH groups of the metalloxane Ti–O polymers from BaTiO₃. Such C=O groups can be regarded as the capping agent for the OH groups of the metalloxane polymers; they suppress the condensation reaction and promote structural relaxation.²⁰⁾ Figures 4(a)–4(c) shows the surface images characterized by the AFM analysis. Its mean square roughness (RMS) was estimated at 15, 5 and 13 nm for A, B and C films respectively,

Fig. 5 Emission spectra of Er:BaTiO₃ after $\lambda = 974$ nm excitation.

which demonstrates that the PVP addition doesn't affect the smoothness of the produced films. Agglomeration particles with pores, homogeneous surface and flowerlike particles were observed in accord with MEB observations. Based on these results, it could be concluded that the final optical properties of the films have to be tailored by their microstructure.

m-Lines spectroscopy is a useful method to determine the optogeometric parameters of waveguiding thin films, such as refractive index as well as film thickness. In optical films, light propagation occurs within a transparent material when the film has sufficient thickness to support at least one guided mode: either a transverse electric mode (TE) or a magnetic mode (TM). Therefore, the optical quality of a film can be associated if it can support this propagation. In the present work, only the synthesis C produces a film with the necessary transparency, homogeneity and thickness to be characterized by this technique. The thickness of the film was determined as 720 nm, with a refrax index of 2.1225. The density of the films can be determined by means of the Lorenz-Lorentz equation and the pore content by Drude's equation.²³⁾ The calculated density of the film is 5.17 g cm⁻³ with a pore content of 30.38%. As observed, the obtained density is 85% of the theoretical (6.02 g cm⁻³), which suggests that the material presents a dense structure. On the other hand, as expected, the pore content is relatively high because the presence of the flower-type microstructure observed by SEM and AFM, which is a product of the preferential nucleation of the ceramic.

The excitation spectra monitoring 548 nm emission lines of the Er doped BaTiO₃ films prepared under A, B and C strategies are presented in Fig. 5. In this emission spectra excited at $\lambda = 974$ nm, it clearly shows high luminescence efficiency achieved under IR radiation excitation, and the emission is bright even to the naked eye. When pumped at 974 nm excitation, cooperative energy transfer (CET) also takes place and results in green up-conversion emission. It is known that ⁴I_{11/2} has zero emission probability to the ground state.²⁴⁾ The main shoulder around 550 nm is more intense for the film prepared under C sol preparing conditions than those observed on films prepared for A and B conditions where an excess of acetic acid is present in the sol elaboration step.

In all cases, the whole profile of emission peak seems to remain unchanged, similar to the other erbium doped samples.²⁰⁾ These results are in agreement with the morphological observations, since it is well known that the light yield of films are strongly dependent on transparency and homogeneity; therefore, synthesis C, which is the only one that is crack-free, transparent and dense, presents the highest emission. Finally, although the flower-like microstructure of the film could diminish the emission, this microstructure is the product of the PVP agent and the combination of an adequate molar relationship of acetic acid and acetylacetonate. The PVP is aggregated in order to increment the thickness of the films, since for monolayer films; the typical thickness obtained by sol-gel is 120 nm.²⁵⁾

4. Conclusion

Er:BaTiO₃ films were elaborated from different molar ratios of starting materials synthesized through methodologies A, B and C. X-ray diffraction, scanning electron and atomic force microscopes were utilized to investigate the effect of the starting molar ratios on the microstructure's characteristics. High contents of acetic acid bring on homogeneous and cross-linked particles on the surface films. Using a moderate quantity of acetic acid and an excess of distilled water, the morphology on the surface films changed considerably, forming an agglomeration of particles in flower shapes (methodology C). The Er:BaTiO₃ films prepared under methodology C presented better emission lines in 548 nm when excited at $\lambda = 974$ nm. We may expect that the Erbium ions doped BaTiO₃ films are a possible candidate for optical application.

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