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A sol–gel route for the development of rare-earth aluminum borate nanopowders and transparent thin films

Lauro J.Q. Maia[a,b,*], Valmor R. Mastelaro[a], Sebastien Pairis[b], Antonio C. Hernandes[a], Alain Ibanez[b]

[a]*Grupo Crescimento de Cristais e Materiais Cerâmicos, Instituto de Física de São Carlos-Universidade de São Paulo, Caixa Postal 369, 13560-970 São Carlos/SP, Brazil*

[b]*Laboratoire de Cristallographie, CNRS, UPR 5031, associé à l'Université Joseph Fourier-Grenoble et à l'INPG, 25 Avenue des Martyrs, BP 166, 38042 Grenoble, France*

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Abstract

A new sol–gel route was applied to obtain $Y_{0.9}Er_{0.1}Al_3(BO_3)_4$ crystalline powders and amorphous thin films by using $Al(acac)_3$, $B(OPr^i)_3$, $Y(NO_3)_3 \cdot 6H_2O$, and $Er(NO_3)_3 \cdot 5H_2O$ as starting materials dissolved in propionic acid and ethyl alcohol mixtures. Our study shows that propionic acid acts as good chelant agent for yttrium and erbium ions while ethyl alcohol allows to dissolve $Al(acac)_3$. This process makes the resulting sols very stable to obtain homogeneous gels and transparent amorphous thin films. In addition, the propionic acid prevents the sol precipitation, making easy porous- and crack-free thin film depositions. Chemical reactions involved in the complexation were discussed. As-prepared powders and films are amorphous and present a good thermal stability due to their high glass transition (746 °C) and crystallization temperatures (830 °C). This new sol–gel route showed to be adequate to obtain dense and crack-free thin films free of organic and hydroxyl groups that can be considered as promising materials to be used in integrated optical systems.

Keywords: Sol–gel; Propionic acid; $Y_{0.9}Er_{0.1}Al_3(BO_3)_4$; Nanopowders; Thin films; Thermal analyses; XRD; SEM; FEG

1. Introduction

Growing demand of optical systems and due to their future potentialities, there is stimulating research for devices composing a network system with excellent flexibility and larger information capacities at much faster rates. Among several devices in telecommunication systems, the invention of optical amplifiers [1] can be compared to that of the transistors in electronics in terms of its technological impact. The technology to directly amplify the light signal without the conversion of light/electricity/light has been achieved with rare-earth-doped fibers which realize ideal amplification with high gain and low noise [2]. Optical properties of rare-earth ions incorporated in glass hosts are of great interest in opto-electronic technology [3]. Rare earth trivalent ions in some solid compounds emit light at characteristic wavelengths due to intra-4*f* or internal 4*f*–5*d* transitions. In the case of Er^{3+}, the emission at 1.54 μm corresponds to a dipole forbidden intra 4*f* transition $^4I_{13/2}$ to $^4I_{15/2}$, coinciding with the low-loss window of standard optical telecommunication silica fiber.

Recently, remarkable progress has been achieved in the development of single-mode Er-doped optical fiber amplifiers and lasers [4–6]. Development of Er-doped planar waveguide amplifiers has also been investigated [7,8] to be applied in integrated optical systems, but integrated optical amplifiers should be as small as possible (a few centimeters), so that much higher rare-earth concentrations are required than in Er-doped fiber amplifiers (EDFAs). However, due to the onset of concentration quenching at low doping levels in silica hosts, the relatively low gains/unit length which can be achieved has made such development difficult. Consequently, SiO_2 is an unsuitable host in small, compact amplifiers due to the low erbium solubility.

*Corresponding author. Fax: +55 16 3373 9824.
E-mail address: lauro@if.sc.usp.br (L.J.Q. Maia).

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Thus, there is a great interest to find other host matrices with high solubility for rare-earth elements, especially erbium, for integrated systems. One potential host candidate is the yttrium aluminum borate ($YAl_3(BO_3)_4$, YAB), where yttrium can be substituted by erbium due to their similar ionic radii (0.096 nm for Er^{3+} and 0.093 nm for Y^{3+}) [9,10]. The YAB composition exhibits good properties for solid-state lasers, high physical and chemical stability, high thermal conductivity, good mechanical strength [11], and a rather high non-linear optical coefficient [12]. Moreover, Er:YAB can be used as a waveguide core ($n = 1.6$–1.7) on SiO_2 substrates ($n = 1.45$). This high refractive index contrast allows a large signal admittance angle and high signal confinement within the core, increasing the pumping and the amplification efficiency [13,14].

In addition, there is a great interest for homogeneous glassy thin films to be used as waveguides because there are no grain boundaries that can cause a high optical loss as in polycrystalline films. The glassy borate system around the YAB composition is very suitable for this purpose because it presents a high glass transition temperature ($T_g \sim 700\,^{\circ}C$). Furthermore, there is interest to obtain a transparent YAB ceramic composition which can be used as laser medium. Recent results presented in the literature confirm that ceramic laser materials became an attractive alternative to single crystal due to their easy manufacture and low cost [15]. In this way, Er-doped YAB matrices are interesting materials for integrated amplifiers and laser medium.

The sol–gel process allows the preparation of bulk materials, thin films as well as powders that can be used to prepare ceramics. The major advantages of this low-temperature chemical route are the large variety of materials that can be doped to modify their properties, the excellent control of the chemical purity, low cost of fabrication and possibility to obtain nanometer powders with a controlled size particle for transparent ceramics manufacture. Since thin sol–gel films can be easily made through dip-coating or spin-coating techniques, this method is considered ideal for the fabrication of active integrated optical devices like optical waveguide lasers and amplifiers [16–19].

In this paper, we present an investigation on the development of a new sol–gel route to obtain homogeneous Er-doped YAB nanometer-sized powders and transparent vitreous thin films free of cracks and porosity with relatively thick monolayers. We describe the chemical reactions of our sol–gel process and the thermal, structural and micro-structural characterizations of the corresponding samples. The results should contribute to establish a new sol–gel route that could be used to prepare other complex materials.

2. Experimental section

2.1. Sol preparation

In this study we have involved aluminum acetylacetonate ($Al(acac)_3$, Aldrich 99%), aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$, Prolabo 98%), or aluminum *s*-butoxide ($Al(OBu^s)_3$, Strem 98%) as precursor for aluminum; triethylborate ($B(OEt)_3$, Strem > 98%), tri-*i*-propylborate ($B(OPr^i)_3$, Strem 98%), or tri-*n*-butilborate ($B(OBu^n)_3$, Strem 99%) for boron; yttrium acetate dihydrate ($Y(O_2CCH_3)_3 \cdot 2H_2O$, Aldrich 99.9%), yttrium nitrate hexahydrate ($Y(NO_3)_3 \cdot 6H_2O$, Aldrich 99.9%), or yttrium chloride hexahydrate ($YCl_3 \cdot 6H_2O$, Aldrich 99.9%) for yttrium, and erbium acetate dehydrate ($Er(O_2CCH_3)_3 \cdot 2H_2O$, Aldrich 99.9%), erbium nitrate pentahydrate ($Er(NO_3)_3 \cdot 5H_2O$, Aldrich 99.9%), or erbium chloride ($ErCl_3$, Aldrich 99.9%) for erbium, as source for precursors elements to obtain the $Y_{0.9}Er_{0.1}Al_3(BO_3)_4$.

The precursor's dissolution was first carried out in acetic acid (AcOH, Fischer 99.7%) in airtight silica cells (silica glass flasks) to avoid any solution evaporation. Ethyl alcohol (EtOH, Riedel-de Haen 99.8%), Malic acid (Aldrich 99%), citric acid monohydrate (Aldrich 99.5%), acetylacetone (AcacH, Aldrich 99%) or propionic acid (PropAc, Merck 99%) were also involved to obtain homogeneous initial solutions (sols).

The same procedure was always followed to prepare the sols in a dry glove box (N_2-rich atmosphere). Firstly, the powdered precursors was mixed, secondly the solvent and liquid precursors were added and finally, after complete powder dissolution at 80 °C (2–6 h), pure water was added for the hydrolysis (80 °C—1 h). In all our experiments the relative molar amounts of cation precursors (corresponding to the YAB composition), and water were fixed at: 0.9 Y: 0.1 Er: 3 Al: 4 B: $5H_2O$.

2.2. Powder and thin film preparation and characterization

2.2.1. Homogeneous gels and powders

In order to obtain homogeneous powders, it was necessary to prepare homogeneous gels by controlling the solvent evaporation without any precipitation. Thus, gels and homogeneous powders were prepared by slow solvent evaporation at 80 °C during 14 days, placing the solutions inside silica glass flasks with two holes of 0.7 mm in diameter on the covering. Then, the resulting gels were heated at different temperatures to eliminate the organic compounds and crystallize the YAB composition under O_2-rich atmosphere.

X-ray diffraction (XRD) analyses were performed in transmission geometry in a Siemens D5000 equipped with a nickel filter, Cu $K\alpha 1$ ($\lambda = 1.5406$ Å) radiation and a graphite-diffracted beam monochromator. The weight losses of dried gel powders over a temperature range of 50–980 °C was monitored by Thermogravimetric Analysis (Netzsch, TASC414/3 controller and TG209 cell) under an oxygen atmosphere and heating rate of 2 °C/min. DSC technique (Netzsch, 404 S) was used to evaluate the decomposition reactions of gels and the crystallization of powders (pre-calcined at 400 °C/24 h and 700 °C/24 h) under O_2 atmosphere and heating rate of 2 or 5 °C/min over a temperature range of 50–1000 °C. Powder