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Eu^{3+}-doped $Ba_2TiSi_2O_8$ glass-ceramic powder incorporated in sintered porous glass: Structural and optical characterization

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ABSTRACT

A porous silica glass was used as host for Eu^{3+}-doped $Ba_2TiSi_2O_8$ (BTS) glass-ceramic powder, which was embedded in the porous structure. Fluorescence upon UV excitation changes drastically from pink color in the untreated porous glass to blue color in the sintered glass, in which the characteristic Eu^{3+} emission in red-orange spectral range is inhibited. The native and the sintered porous glass present an intrinsic fluorescence in the blue spectral region upon UV excitation, which is related with defects in the silica network. The microstructure and elemental distribution in the sintered glass was investigated by TEM and EDX and related with the luminescence properties.

1. Introduction

The doping of glasses and glass-ceramics with rare-earth (RE) ions aiming at their application as luminescent materials is very well known [1,2].

Crystalline fresnoite ($Ba_2TiSi_2O_8$, BTS) exhibits luminescence, pyro-, piezo- and ferroelectric properties [3], and possesses non-linear optical properties [4]. Ti^{4+} ions hosted in a square-pyramidal TiO_5 structure are responsible for blue luminescence when irradiated in the UV range, which is more than one order of magnitude more intense in crystalline fresnoite than in the fresnoite glass [5,6]. This explains the increasing interest in BTS-glass-ceramics, which combine the excellent properties of crystalline BTS with the advantages of glass production. The preparation of BTS glass-ceramics by heat treatment of the parent glasses is well known [7–13]. Moreover, by selecting the appropriate RE ions to dope BTS glass, it is possible to obtain a broad range of optical emissions near the intrinsic blue emission of BTS [14,15]. Among lanthanides, Eu^{3+} is widely used as fluorescent probe and presents characteristic orange and red emission upon UV excitation.

Silica-based glasses offer important advantages like high optical transmittance and good workability. Therefore, silica glasses play a key role in technological applications when doped with RE ions [16].

In an attempt to employ pure silica glasses as matrix for RE ions, Anpo et al. [17] introduced in 1980 the use of a porous glass with approx. 96% SiO_2 (Vycor glass) as an adsorber for RE ions in solution. Later on, Blasse [18] and Reisfeld et al. [19,20] made great progresses by employing not only porous silica glass but also pressed silica-gel, which forms a porous network after sufficient pressing. When the porous glass is immersed in an aqueous RE solution (in form of nitrate, for example), the ions are adsorbed into the glass pores. Its luminescence properties were proofed to be similar to those in RE doped bulk glasses. More recently, Chen et al. [21] reported the adsorption of a Eu^{3+} solution in a Vycor glass and its further sintering at 1100° for 2 h under a reducing atmosphere. The pores favor the reduction of Eu^{3+} to Eu^{2+}, giving rise to much higher visible emission intensity under UV excitation. Nano-porous glasses were also used as matrices for Yb^{3+}/Tb^{3+} ions [22] and for combination of several RE in order to obtain white light emission [23], among others.

The main advantage of the use of porous glass against bulk RE doped glasses is the possibility of produce RE-doped silica glasses, which cannot be produced easily due to high melting temperatures.

In our previous publication, we reported on the milling procedure of the Eu^{3+}-doped BTS glass-ceramic [24]. In Eu^{3+}-doped BTS the Eu^{3+} ions incorporate in Ba^{2+} sites and Ba^{2+} vacancies are generated to maintain the electrical neutrality [15]. Different milling routes led to BTS powders with different morphologies, particle sizes and particle size distributions [24]. It was also shown, that the intensity of the blue emission decreases with decreasing particle size.

Other porous matrices used as hosts of active particles can be found among others in zeolites [25,26].

In the present work, we report on the preparation of porous silica glasses containing Eu^{3+}-doped BTS glass-ceramic powders. In this way,

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a further step to the use of porous glasses as hosts of luminescence ions is put forward.

The works found in literature are focused on the optical properties of the porous glasses hosting RE ions and to the best of our knowledge, the structural characterization of the porous glass containing the optically active ions is rarely reported. Thus, this work highlights the relevance of the microstructure investigation in these materials and how the particular location of optically active centers, here Eu^{3+} ions, changes the expected optical properties.

2. Experimental

A fresnoitic glass of the composition $40BaO$-$20TiO_2$-$40SiO_2$ (mol%) doped with 0.2 mol% Eu_2O_3 was prepared by conventional melt-quenching technique. The glass was melted in a middle frequency furnace at 1500 °C for 1 h under stirring with a rotation frequency of 40 min^{-1}. Then it was kept for another 30 min at the same temperature without stirring. The melt was cast on a brass block, which leads to a partial crystallization. The glass was heated at 740 °C just a little bit above T_g, to eliminate the residual stresses. Finally, the glass was thermally treated at 900 °C for 24 h to obtain a crystallized fresnoite $Ba_2TiSi_2O_8$ glass-ceramic.

2.1. Milling procedure

The BTS:Eu^{3+} bulk glass-ceramic was manually pre-milled in an agate mortar to achieve pieces < 1 mm diameter. The obtained powder was then milled with a planetary mill *Pulverisette 7 premium line* (Fritsch GmbH), using a zirconia container and zirconia grinding balls of 3 and 0.5 mm diameter, following the procedure in Ref. [24]. The resulted milled powder solution was used to immerse the porous glasses in the next step.

2.2. Immersion of porous glasses in BTS:Eu-solution and sintering

The porous glass is a Vycor-type glass. Different pore diameters were investigated (Table 1), ranging between 400 and 10 nm. Pore diameter was measured by the manufacturer by mercury porosimetry and the error is ± 2 nm. The employed granulate was produced from milling of porous glasses of different pore sizes. Although the majority of the pore size is around 100 nm, the pore size distribution is broader than in the bulk porous glasses, between 10 and 200 nm. Bulk pieces of the porous glass with 400 and 150 nm pore size were cut and immersed in the BTS:Eu^{3+}powder solution for 72 h at room temperature. The BTS:Eu^{3+} powder solution with the immersed glass pieces was placed in a vacuum chamber and exposed to low-pressure of 140 mbar for 15 min, in order to support the air leaving the pores. When the vacuum is switched off the solution with the BTS:Eu^{3+} powder tends to go inside the pores. Then, the glass pieces were dried at room temperature and sintered in an electric furnace under air atmosphere at different temperatures for 2 h: at 1050 °C and at 1100 °C. The heating rate was 25 K/min.

Table 1
Sample nomenclature referring to pore diameter, sample size and heat treatment.

Sample	Average pore diameter (nm)	Sample size	Heat treatment
PG-400-BTS:Eu-RT	400	Bulk	Room temperature
PG-400-BTS:Eu-1050	400	Bulk	1050 °C-2 h
PG-400-Eu-1050-H	400	Bulk	1050 °C-2 h H_2/Ar
PG-150-BTS:Eu-1100	150	Bulk	1100 °C-2 h
PG-G-RT	10–200	Granulate, < 75 µm	Room temperature
PG-G-1100	10–200	Granulate, < 75 µm	1100 °C-2 h

A porous-glass granulate possessing a particle size below 75 µm and with pore diameter between 10 and 200 nm was annealed at 1100 °C for 2 h. This sample was not subjected to infiltration of any optically active solution.

Another porous glass sample was immersed for 72 h in a 0.1 M Eu $(NO_3)_3 \cdot 6H_2O$ solution following the same procedure of vacuum infiltration. This impregnated porous glass was sintered at 1050 °C for 2 h in an electric furnace under reducing atmosphere of H_2/Ar in a ratio of 4:1 (sample PG-400-Eu-1050-H). For clarity, Table 1 summarizes the samples prepared.

2.3. Microstructural characterization by Scanning Electron Microscopy (SEM) and (Scanning) Transmission Electron Microscopy ((S)TEM) and energy dispersive X-ray spectroscopy (EDXS)

One drop of the milled BTS:Eu^{3+} glass-ceramic powder solution in which the PGs were immersed was deposited with a pipette on a glass slide. After drying in air, the resulting dried powder was placed in a C-pad for investigation by scanning electron microscopy SEM (Carl Zeiss Supra 55VP microscope).

One of the pieces of the annealed porous glass sample PG-400-BTS:Eu-1050 was prepared for TEM inspection. Samples were prepared by wedge-polishing by the grinding and polishing tool Multiprep, Allied company. The samples were then subjected to double-sided, ion-beam milling using low-energy (2.5 keV) Ar^+ ions under a small angle of incidence (6°) until the central part of the samples became electron transparent (precision ion-polishing system, PIPS, Gatan Company). Selected areas of the sample were coated with carbon using a special coating mask [27] prior to TEM investigation in order to reduce charging effects resulting from interaction with the electron beam. Bright field images in TEM mode and STEM (camera length 70 mm) images were recorded with an FEI Tecnai G2 F20 microscope operating at 80 and at 200 kV. EDXS area analyses of Si (K-line), Ti (K-line), Ba (L-line), Na (Na-K) and Eu (L-line) were recorded in STEM mode at 200 kV in the same microscope.

Additionally, the sample PG-400-BTS:Eu-1050 was investigated in a FEI $Titan^3$ 80–300 electron microscope (FEI Company) at 300 kV. EDXS analysis was performed by means of a Super X-EDXS detector (FEI Company) that consists of four silicon drift detectors pointed to the sample, thus offering a maximum collection angle of 0.9 sr. Elemental mappings of the above mentioned elements were obtained, in order to gain information about the elemental distribution with high spatial resolution. The analytical accuracy in EDXS is around 2%.

2.4. Optical characterization

In order to have a visual inspection of the sample, the porous glasses were exposed to an UV lamp Camag at 254 nm excitation wavelength (1.2 mW/cm^2 of excitation density) after immersion in the BTS:Eu^{3+} solution and after heat treatments and pictures were taken.

The luminescence spectra of the milled samples were recorded. Powders of the undoped BTS- and BTS:Eu^{3+}-glass-ceramics were also measured. The spectrum of a 0.1 M $Eu(NO_3)_3 \cdot 6H_2O$ solution was acquired as reference for the Eu^{3+} emissions. Spectra of the native untreated PG and sintered at 1100 °C for 2 h were recorded in powder form as reference of the glassy matrix. Samples were measured as aqueous solution or as powder, by evaporating the water. The spectra were recorded in a Shimadzu RF-5301PC spectrometer under 250 nm and 395 nm excitation. Emission spectra were recorded from 300 to 800 nm.

2.5. X-ray spectroscopy (XAS)

XAS experiments were carried out in the bulk porous glass