Optical Materials 36 (2014) 1463–1470

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Fabrication and enhanced photoluminescence properties of Sm^{3+}-doped $ZnO–Al_2O_3–B_2O_3–SiO_2$ glass derived willemite glass–ceramic nanocomposites

Anal Tarafder [a,*], Atiar Rahaman Molla [a], Sunanda Mukhopadhyay [b], Basudeb Karmakar [a,*]

[a] Glass Science and Technology Section, Glass Division, CSIR-Central Glass and Ceramic Research Institute, 196 Raja S.C. Mullick Road, Kolkata 700 032, India
[b] Department of Chemical Technology, Calcutta University, 92 A.P.C. Road, Kolkata 700 009, India

ARTICLE INFO

Article history:
Received 22 November 2013
Received in revised form 14 March 2014
Accepted 26 March 2014
Available online 6 May 2014

Keywords:
Transparent glass–ceramics
Nanocomposites
Zinc silicate
Samarium
Optical properties

ABSTRACT

The transparent willemite, Zn_2SiO_4 (ZS) glass–ceramic nanocomposites were prepared from melt-quench derived $ZnO–Al_2O_3–B_2O_3–SiO_2$ (ZABS) precursor glass by an isothermal heat-treatment process. The generation of willemite crystal phase, size and morphology with increase in heat-treatment time was examined by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM) techniques. The average calculated crystallite size obtained from XRD is found to be in the range 80–120 nm. The decreased refractive index with increase in heat-treatment time attributed to partial replacement of ZnO_4 units of willemite nanocrystals by AlO4 units and simultaneous generation of vacancies in the Zn-site. Fourier transform infrared (FTIR) reflection spectroscopy exhibits the structural evolution of willemite glass–ceramics. The photoluminescence spectra of Sm^{3+} ions exhibit emission transitions of $^4G_{5/2} \rightarrow {}^6H_J$ ($J = 5/2,\ 7/2,\ 9/2,\ 11/2$) and its excitation spectra shows an intense absorption band at 402 nm. These spectra reveal that the luminescence performance of the glass–ceramic nanocomposites is enhanced up to 14-fold with crystallization into willemite.

1. Introduction

Recently, rare earth oxide doped glass and glass–ceramics are attracting great interest in solid state lasers, laser cooling, optical communications, storage, optical devices for the three dimensional color displays and upconverting optical devices [1–6]. Glasses act as smart hosts for the different rare-earth (RE^{3+}) ions. For this reason planar waveguides and optical fibers can be produced easily with them compared to the crystalline competitors.

The willemite (zinc orthosilicate, Zn_2SiO_4, ZS) is one of the zinc ore minerals and having the phenakite structure. In Zn_2SiO_4, all the atoms occupy general position and composed of tetrahedral framework where in zinc and silicon positioned in three different fourfold crystallographic sites: two slightly different zinc sites Zn1 (⟨Zn–O⟩ 1.950 Å) and Zn2 (⟨Zn–O⟩ 1.961 Å), and Si (⟨Si–O⟩ 1.635 Å), so resulting in rhombohedra symmetry with lattice parameters $a = b \sim 13.948$ Å, and $c \sim 9.315$ Å [7].

This kind of rigid lattice, with only non-centrosymmetric cationic sites, gives the chance to get special optical properties. For this reason, synthetic willemite is very important and widely used as a phosphor in neon discharge lamps, fluorescent lamps, oscilloscopes, black-and-white/color televisions and many other displays and lighting devices (e.g. with Eu^{3+}, Mn^{2+}, Tb^{3+}, Ce^{3+} doping) [8–14]. It is found that this willemite can be used as dielectric ceramics for wireless applications [15]. This kind of crystal containing glass–ceramics is reported by many researchers [16–21] as well. This glass–ceramics material could be used as potential optical host materials for solid state lasers when they are doped with rare earth ions [22–24]. To the best of our knowledge the reports on luminescence of RE oxide doped transparent willemite glass–ceramics are very few [25]. Luminescence is very sensitive to variation in the local structure of luminescent species, surrounding host composition and their interaction. Among various rare earth, Sm^{3+} has emerged as a promising candidate for the optical amplification as it provide strong emission in the visible range (orange–red) in glasses and glass–ceramics with high ZnO content. Moreover, the Sm^{3+} ion has a number of strong absorption bands where effective pumping sources are available.

In the present work, the preparation of Sm^{3+}-doped novel $ZnO–Al_2O_3–B_2O_3–SiO_2$ (ZABS) based glass by melt-quench technique and willemite glass–ceramic nanocomposites by isothermal controlled crystallization of precursor glasses is reported. The

* Corresponding authors. Tel.: +91 33 24733469; fax: +91 33 24730957.
E-mail addresses: anal@cgcri.res.in (A. Tarafder), basudebk@cgcri.res.in (B. Karmakar).

http://dx.doi.org/10.1016/j.optmat.2014.03.035
0925-3467/

crystallization process has been studied by differential thermal calorimetry (DSC), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and Fourier transform infrared (FTIR) reflection spectroscopy. The glass and derived glass–ceramics were characterized by studying their thermal, structural, mechanical and optical properties including visible photoluminescence emissions and excitation. The main advantage of $ZnO–Al_2O_3–B_2O_3–SiO_2$ (ZABS) based glass systems compared to normal zinc–alumino–silicate glass systems is that the melting and processing temperature will decrease substantially. This will reduce the cost of production of this glass–ceramics. In view of above fact, the aim of this paper is the fabrication and photoluminescence property study of Sm^{3+}-doped willemite glass–ceramics in ZABS glass system. Another objective is to study of this ZS glass–ceramic nanocomposites' potentiallity for use in the field of photonics as solid-state laser materials.

2. Experimental

2.1. Precursor glass preparation

The mother glass having molar composition $60ZnO–5Al_2O_3–15B_2O_3–20SiO_2$ doped with Sm_2O_3 (0.5 wt% in excess) prepared by conventional melt-quenching method. In this work Sm^{3+} doped $ZnO–Al_2O_3–B_2O_3–SiO_2$ glass is designated as Sm-ZABS-0 h glass. High purity raw materials such as zinc oxide, ZnO (99.9% Sigma–Aldrich, St. Louis, MO, USA); silica, SiO_2 (99.8%, Sipur A1 Bremtheler Quartzitwerk, Usingen, Germany); boric acid, H_3BO_3 (99.5%, Fluka Chemie Gmbh, Buchs, Germany); aluminium oxide, Al_2O_3 (99%, Aldrich, Milwaukee, WI, USA); and samarium (III) oxide, Sm_2O_3 (99.99%, Indian Rare Earth Limited, Mumbai, India) were used.

About 200 g batch of raw materials was mixed and melted in a 100 ml platinum crucible in an electric furnace at 1400 °C for 1.5 h in air with intermittent stirring. The glass melt was poured into a preheated iron mould. It was annealed at 500 °C for 5 h to remove internal stresses of glass and then slowly cooled down to room temperature. The as-prepared glass blocks were cut into desired dimensions and optically polished for ceramization and subsequent characterization.

The as-prepared glass samples were heat-treated at 660 °C for varying duration of 0, 10, 30 and 50 h after nucleating at 580 °C for 2 h to prepare the ZS glass–ceramics. In the present study, the obtained samples were labeled as a (Sm-ZABS-0h), b (Sm-ZS-10h), c (Sm-ZS-30h) and d (Sm-ZS-50h) respectively for convenience.

2.2. Characterization

The density of precursor glass was measured with the density measurement accessories supplied with a Mettler Toledo balance at room temperature using Archimedes principle and water as buoyancy liquid. Differential thermal calorimetry (DSC) of precursor glass powder was carried out up to 1200 °C from room temperature with a heating rate of 10 k/min using a NETZSCH instrument (Model: STA 449 F3 Jupiter$^{(R)}$, Selb, Germany) to ascertain the glassy nature of the as prepared glass and to find out the glass transition temperature (T_g) and crystallization peak temperature (T_p). The coefficient of thermal expansion (CTE), glass transition temperature (T_g) and dilatometric softening temperature (T_d) of the precursor glass of cylindrical test sample (φ = 6 mm, L = 25 mm) was measured with an accuracy of ±1% using a horizontal-loading dilatometer (Model: DIL 402 PC, NETZSCH-Gerätebau GmbH, Selb, Germany) after calibration with a standard alumina reference. The CTE in the temperature range 50–350 °C is reported here. The refractive indices were measured by a Prism Coupler (Model: 2010/M, Metricon Corporation, Pennington, NJ, USA) at five different wavelengths (λ = 473, 532, 633, 1064 and 1552 nm). XRD patterns were recorded using an X'Pert PRO MPD diffractometer (PANalytical, Almelo, the Netherlands) and the measurements were carried out with Ni-filtered Cu Kα = 1.5406 Å radiation as the X-ray source at 40 kV and 40 mA to identify the developed crystalline phases. The 2θ scan range was 10–90° with a step size of 0.05°. A high resolution FESEM (Gemini Zeiss Supra™ 35 VP model of Carl Zeiss Microimaging GmbH, Berlin, Germany) was used to observe the microstructure of freshly fractured surfaces of the heat-treated glass–ceramics after etching in 2% HF aqueous solution for 10 min, dried and then coated with a thin carbon film. The hardness of the precursor glass and glass–ceramic nanocomposites were measured by taking micro-indentation measurements on the polished surface. The ultrasonic longitudinal and transverse sound velocities of the precursor glass and glass–ceramics were determined by using the pulse-echo overlapping methods at room temperature by making use of ultrasonic flaw detector (Model: EPOCH 1000 Series, Olympus NDT Incorporation, Waltham, MA, USA) and 20 MHz transducers. The transducers were brought into contact with each sample by means of a couplant to avoid any air void between the transducer and the specimen. Micro-indentations were performed using a micro indentation hardness testing systems (Clemex CMT, Longueuil, Canada) equipped with a conical Vickers indenter at an indent load of 300 g. About ten indents were taken for each sample with identical loading condition. The diagonals of the Vickers indents were carefully measured using optical microscope and subsequently, the hardness was calculated using the standard equation for the Vickers geometry.

$$HV = 1.8544\frac{P}{d^2} \tag{1}$$

where HV is the Vickers hardness number (VHN) in kg/mm^2, P is the normal load in kg, and d is the average diagonal length of the indentation in mm. The fracture toughness (K_c) of these glass and glass–ceramics were measured by the following equation which is proposed by Antis et al. [26]:

$$K_c = a\left(\frac{E}{H}\right)^{0.5}\left(\frac{P}{C^{1.5}}\right) \tag{2}$$

where P is the applied load and C is the mean length of the two radian cracks. E and H are the Young's modulus and hardness of the sample, respectively, measured at the same applied load P at which the K_c for the sample is measured. For Vickers indenters, the a value was taken as 0.016. The FTIR reflectance spectra of all Sm^{3+}-doped glass and glass–ceramics were recorded using a FTIR spectrometer (Model: Frontier IRL 1280119, Perkin–Elmer Corporation, Waltham, MA, USA) in the wavenumber range 400–2000 cm^{-1} with a spectral resolution of ±2 cm^{-1} and at 22.5° angle of incidence. The room temperature optical absorption spectra of precursor glass and ZS glass–ceramics were recorded in a UV/Vis/NIR spectrophotometer (Model: Lambda-950, Perkin–Elmer Corporation, Waltham, MA, USA). The photoluminescence emission and excitation spectra were measured on a bench top modular spectrofluorometer (QuantaMaster, Photon Technology International, Birmingham, NJ, USA) attached with a Xe arc lamp as excitation source.

3. Results and discussions

3.1. Density and thermal properties of precursor glass

The precursor glass is visually transparent, appearing light yellow due to Sm^{3+} doping. The measured density of the precursor glass is 3.8642 g cm^{-3} and this high value attributes to the presence of relatively high molecular weight of ZnO used as