Materials Characterization 103 (2015) 90–100

Contents lists available at ScienceDirect

Materials Characterization

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

Preparation and characterization of novel foamed porous glass-ceramics

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ARTICLE INFO

Article history:
Received 4 December 2014
Received in revised form 4 March 2015
Accepted 8 March 2015
Available online 18 March 2015

Keywords:
Foamed glass-ceramics
Heating stage microscopy
Sintering
FESEM
XRD

ABSTRACT

Foamed glass-ceramics without using foaming agent have been synthesized in a novel glass system of SrO-CaO-Al_2O_3-TiO_2-B_2O_3-SiO_2-P_2O_5-M_xO_y (where M = Ba, Mg, La, Ce and Ni) by a simple process of powder sintering. The glass and glass-ceramics are characterized by dilatometry, differential scanning calorimetry (DSC), heating stage microscopy (HSM), X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), optical microscopy and Fourier transformed infrared spectroscopy (FTIR). All the glasses formed are amorphous and the glass transition temperature and dilatometric softening temperature of these glasses are found to be in the range 673–678 °C and 706–728 °C respectively. The glasses are highly stable as indicated by the DSC evaluated glass stability parameters of the range 195–240 °C. Quantitative sintering study of glass powder compacts revealed swelling in the samples with NiO and CeO_2 corresponding to a geometry change of 75 and 108% around 900 °C respectively. With reference to this finding the glass powder compacts are heated to 900 °C and the foamed glass-ceramics are obtained. Characteristic crystalline silicate phases have been identified in the XRD studies and their microstructures are recorded by FESEM. Optical microscope study of the foamed samples revealed formation of bigger foamed cavity with residual pores in samples with NiO and CeO_2 in comparison to samples with BaO, MgO and La_2O_3. The mean pore diameters of the samples with NiO and CeO_2 are determined to be 43 and 32 μm, and their respective porosities are 2.34 and 1.82 cm^3/g respectively. Thus NiO and CeO_2 are found to be very effective to obtain foamed glass-ceramics without using foaming agent by the viscous flow sintering of fine glass powder compacts along with the reduction of the respective polyvalent ions.

1. Introduction

Foamed glass is a porous material which is physically a heterophase system consisting of gaseous and solid phases. The solid phase is composed of glass that encloses single cells of several micrometers thick. These cells are filled with the gaseous phase. This material possesses a unique combination of properties as it is lightweight, rigid, freeze-tolerant, nonflammable, thermally and acoustically insulating, chemically inert and nontoxic, rodent- and insect-resistant, and bacteria-resistant [1–3]. It is resistant to water and water vapor and does not burn. All these properties of foamed glass have claimed its utility not only in industries but also in domestic environments as a material for construction [4,5]. Depending on purpose, heat-insulating or soundproof foamed glass can have closed or intercommunicating pores, respectively [6,7]. It has properties superior to glass wool or rock wool as a heat insulating material. So there is a higher demand for heat-insulating foamed glass than for soundproof foamed glass. Besides this foamed glass and glass-ceramics (GCs) have diverse applications such as catalyst support to gas or liquid metal filtration, membranes in combustion technology, and microorganism-immobilized carriers for biological treatment [8,9]. Han et al. [10] have described the applicability of foamed glass depending upon their pore structure and volume porosity.

Generally most foamed glasses are fabricated by sintering of glass powder mixed with foaming agents. These agents release gases in the pyroplastic mass formed by the softened glass matrix [11–14]. Chen et al. [15] have prepared foamed glasses with 50–70% fly ash at 800 °C using it as the main raw material, with calcium carbonate ($CaCO_3$) and sodium borate ($Na_2B_4O_7$) as foaming agent and flux agent, respectively. They have found that foamed glass with a high content of fly ash sintered at 800 °C exhibits low bulk density, high porosity and mechanical strength. Very recently Heydari et al. [16] have reported the effects of temperature and oxidizing agent such as Fe_2O_3 and Co_3O_4 on the physical and mechanical properties of foamed glass made of panel glass from dismantled cathode ray tube using SiC as a foaming agent. A recent study by Hasheminia et al. [17] has concluded that addition of PbO increases the foaming ability as well as the crystallization temperature of diopside based glass-ceramic foams. Binhussain et al. [18] have produced porous glass-ceramics by simple firing of a mixture of selected raw and waste materials wherein the waste materials are capable of producing glass forming oxides, glass modifying oxides and pore forming oxides. In view of the above reported studies it is clear that the source of foaming is either the foaming agent used or any reducing oxide present in the waste.

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http://dx.doi.org/10.1016/j.matchar.2015.03.007
1044-5803/

Although production of foamed glass using a foaming agent is a viable way of waste (glass cullet, blast furnace slag and fly ash) recycling there are certain disadvantages associated with the process. Fernandes et al. [6] have pointed out in their investigation based on influence of type and amount of carbonates as well as of the sintering temperature on the properties of the foamed glass that excess amounts of foaming agents tend to limit the foaming ability of the glass/fly ash based system. The study by Wu et al. [19] reports that foams produced using SiC have to be processed at a higher temperature (1000 °C) which increases production costs despite the relatively short (5 min) sintering time used since SiC effectively acts as a foaming agent at temperatures 950–1150 °C due to oxidation reactions and formation of CO_2 and CO gas bubbles. In addition to this Tulyaganov et al. [20] have reported that parameters like heat treatment schedule, decomposition temperature of foaming agent, content of foaming agent, and particle size should be kept in mind to obtain good quality products in terms of a homogeneous microstructure, uniform pore size distribution, maximum pore volume and impressive mechanical properties. Sometimes finding the proper foaming agent for a type of waste to be recycled is very difficult. Hence the objective of this work is to synthesize foamed glass-ceramics in a novel glass system SrO-CaO-Al_2O_3-TiO_2-B_2O_3-SiO_2-P_2O_5-M_xO_y (where M = Ba, Mg, La, Ce and Ni) by powder sintering method without using a foaming agent and characterizing them using different instrumental techniques.

2. Experimental procedure

2.1. Preparation of precursor glass

Glasses composed of 24SrO-24CaO-2Al_2O_3-2TiO_2-6B_2O_3-39SiO_2-1P_2O_5-2M_xO_y (mol %), where M = Ba, Mg, La, Ce and Ni, were prepared by melt-quench technique. A homogeneous batch mixture, for 100 g glass, of pure raw materials consisting of $CaCO_3$ (98%, Extra pure; Loba Chemie, Mumbai, India), $SrCO_3$ (99%, Extra pure; Loba Chemie, Mumbai, India), Al_2O_3 (Alcoa, CT 1200, SG), TiO_2 (99.5%, Loba Chemie, Mumbai, India), H_3BO_3 (GR, 99.5%; Loba Chemie, Mumbai, India), SiO_2 (99.8%; Sipur A1 Bremtheler Quartzitwerk, Usingen, Germany), $Ca_3(PO_4)_2$ (Extrapure, Loba Chemie, Mumbai, India), $BaCO_3$ (99%, Merck, Mumbai, India), $MgCO_3$ (98%, Loba Chemie, Mumbai, India), La_2O_3 (99.99%, Alfa Aesar, Lancashire, UK), CeO_2 (99.95%, Loba Chemie, Mumbai, India) and NiO (79%, Merck, Mumbai, India) was melted in a 100 ml platinum crucible at 1500 °C for 2 h in air with intermittent stirring. The molten glasses were quenched on a preheated iron plate and subsequently annealed at 630 °C for 2 h. The glass compositions are given in Table 1.

Cylindrical samples of length (L) 25 mm and diameter (φ) 6 mm were prepared from the bulk glasses for dilatometry. The remaining glasses were wet milled in isopropyl alcohol medium in a planetary ball mill (Retsch, Model PM 100) for 2 h at 300 rpm. The glass powder was completely dried and granulated with 2 wt.% polyvinyl alcohol (PVA) solution as binder and the powder compacts (PCs) of cylindrical shape were obtained by uniaxial hydraulic pressing (applying hand pressure). These PCs were placed in a microprocessor controlled resistance heating chamber furnace and sintered at 900 °C for 2 h in open air. The heat treatment schedule comprised of heating to 400 °C at 2 °C/min for binder burn-off, holding there for 2 h followed by heating to 900 °C at 2 °C/min, then holding for 2 h before cooling them to room temperature. The following characterization tools are used in this study.

2.2. Characterization

The glass transition temperature (T_g), dilatometric softening temperature (T_d) and coefficient of thermal expansion (CTE) of cylindrical samples of glasses were determined using a horizontal loading dilatometer (Model DIL 402 PC; NETZSCH-Gerätebau GmbH, Selb, Germany). Differential scanning calorimetry (DSC) of the glass powders (≈30 mg) were carried out in nitrogen atmosphere from room temperature to 1200 °C at a heating rate of 10 °C/min with the help of an instrument (LABSYS evo; Setaram, Caluire, France) to determine the glass transition temperature (T_g) and crystallization peak temperature (T_c). The particle size distribution of the glass powder was determined with the help of an instrument (Malvern; Model Mastersizer 2000, Worcestershire, UK). The sintering behavior of the glasses and glass powder compacts were investigated at a heating rate of 10 °C/min with the help of a heating stage microscope (HSM) (Misura 3HSM; Expert System Solutions, Italy). Samples (dimension: 2 mm × 2 mm × 3.5 mm) were placed on an alumina support contacted underneath with platinum thermocouples. The change in shape of the samples with increasing temperature was photographed at 1 °C intervals using the image analysis system of the instrument synchronized with the programming schedule of the furnace. The cross sectional pieces of all the foamed glass-ceramics were visualized using an optical microscope (Model BX51; Olympus, Tokyo, Japan) under a magnification of 10×. The pore size distribution was determined using a mercury porosimeter (Model Quantachrome PoreMaster33; Florida, USA). The X-ray diffraction (XRD) of the glasses and foamed glass-ceramics were investigated using a XPERT-PRO MPD diffractometer (PANalytical, Almelo, Netherlands). The source of X-ray used was Ni filtered CuK_α (λ = 1.5406 Å) irradiated at 40 kV and 40 mA. The scan range was 5°–90° with a step size of 0.05°. Microstructure studies of the foamed glass-ceramics were done using a field emission scanning electron microscope (FESEM) (Model Gemini Zeiss Supra™ 35 VP, Carl Zeiss Microimaging GmbH, Berlin, Germany). For this experiment the cross section of the foamed samples was taken and coated. The infrared transmittance spectra of foamed glass-ceramics were recorded by KBr pellet method in the wave number range 400–1800 cm^{-1} including 16 consecutive scans with the help of Fourier transformed infrared (FTIR) spectrometer (Model 1615 Series; Perkin-Elmer Corporation, Norwalk, CT, USA) with a resolution of ±2 cm^{-1}.

3. Results and discussion

3.1. Thermal properties of glass

The thermal properties of the glasses determined by dilatometry and differential scanning calorimetry are given in Table 2. The characteristic temperatures obtained from the above studies, viz. T_g, T_d and T_c are more or less the same for the glasses. Among all the glasses G-La and

Table 1
Chemical composition of the investigated glasses.

Glass identity	Composition (mol %)											
	SrO	CaO	Al_2O_3	TiO_2	P_2O_5	B_2O_3	SiO_2	BaO	MgO	La_2O_3	CeO_2	NiO
G-Ba	24	24	2	2	1	6	39	2	0	0	0	0
G-Mg	24	24	2	2	1	6	39	0	2	0	0	0
G-La	24	24	2	2	1	6	39	0	0	2	0	0
G-Ce	24	24	2	2	1	6	39	0	0	0	2	0
G-Ni	24	24	2	2	1	6	39	0	0	0	0	2