Journal of Non-Crystalline Solids 388 (2014) 68–74

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Synthesis and characterization of strontium and barium bismuth borate glass-ceramics

S.R. Rejisha [a], P.S. Anjana [a], N. Gopakumar [b], N. Santha [c,*]

[a] Department of Physics, All Saints' College, Thiruvananthapuram, Kerala, India
[b] Post-Graduate Department of Physics, M. G. College, Thiruvananthapuram, Kerala, India
[c] Department of Physics, University of Kerala, Thiruvananthapuram 695581, Kerala, India

ARTICLE INFO

Article history:
Received 1 October 2013
Received in revised form 20 January 2014
Available online 11 February 2014

Keywords:
Glass ceramics;
Boron sillenite;
FT-Raman & FT-IR spectroscopy;
Dielectric properties

ABSTRACT

Glass ceramics in the $20MO.55Bi_2O_3.25B_2O_3$ (M = Sr, Ba) system were prepared by conventional melt quenching method, followed by heat treatment. XRD patterns show that the crystalline phase boron sillenite ($Bi_{24}B_2O_{39}$) was formed on thermal treatment. The variation in the microstructure of the sample as a function of crystallization temperature was studied using scanning electron microscopy. The structural changes due to heat-treatment of the glasses have been explained on the basis of the changes in FT-IR and FT-Raman spectra. The glass ceramics in the present study have relatively high dielectric constant and low dielectric loss.

1. Introduction

Restriction on the use of materials containing lead or cadmium has stimulated investigations on the development of eco-friendly glasses, glass-ceramics and ceramics, with attractive properties. Alkaline earth bismuth borate ternary system is a potential candidate for replacing lead containing materials, as borate glasses containing alkaline earth oxides along with ZnO, PbO, Bi_2O_3 and/or TeO_2 have wide applications in the field of optical communications and optoelectronic devices [1]. Egorysheva et al. have made extensive investigations on the crystalline compounds and the phase formation in the M_xO_y–Bi_2O_3–B_2O_3 [M = Li, K, Na, Ca, Sr, Ba and Al] systems [2–8]. Among these systems, BaO–Bi_2O_3–B_2O_3 system is of special interest as it includes, among other compounds, the two potential non-linear optic materials, β-BaB_2O_4 and BiB_3O_6, that are widely used for frequency conversion in the visible and UV spectral range. In this system, a variety of other stable phases are also known to exist: $Bi_{24}B_2O_{39}$, $Bi_4B_2O_9$, $Bi_3B_5O_{12}$, $BiBO_3$, α-, β-, γ-, δ-BiB_3O_6 and α-$Bi_2B_8O_{15}$, β-$Bi_2B_8O_{15}$ [9]. Glass ceramics based on heavy metal oxides are promising materials for laser technology as they combine the advantage of crystalline hosts with relative ease of manufacturing and lower production cost [10]. Bajaj et al. [11] have prepared $Bi_3B_5O_{12}$ and $Bi_4B_2O_9$ phases of the Bi_2O_3–B_2O_3 system by devitrification of bismuth borate glass and characterized them by X-ray diffraction, FT-IR and MAS-NMR experiments. Bismuth borate ($BiBO_3$) phase was synthesized by Iordanova [12] by crystallization of binary and ternary glass compositions in the Bi_2O_3–MoO_3–B_2O_3 system. In the glass system Bi_2O_3–ZnO–B_2O_3, the crystallization tendency increases with a decrease of B_2O_3 content resulting in the precipitation of boron sillenite ($Bi_{24}B_2O_{39}$) [13]. However, the crystallization of $Bi_{24}B_2O_{39}$ has not been reported earlier in the MO–Bi_2O_3–B_2O_3 (M = Sr, Ba) glasses.

We have earlier reported [14] the synthesis and characterization of $20MO.xBi_2O_3$. $(80 - x)B_2O_3$ (M = Ca, Sr and Ba; x = 15 and 55) glass. In the present study, we have crystallized $Bi_{24}B_2O_{39}$ by devitrification of $20MO.55Bi_2O_3.25B_2O_3$ (M = Sr, Ba) glasses for the first time. As both sillenites and MO–Bi_2O_3–B_2O_3 (M = Sr, Ba) system are of considerable interest in view of their unusual optical and electro-optical properties, it is important to study the structure of these glass-ceramics. The crystallization behavior and microstructure were characterized respectively by X-ray diffraction and scanning electron microscope. FT-Raman and FT-IR spectroscopic techniques were used to understand the structural changes due to heat treatment. Room temperature a.c. dielectric properties of the samples crystallized at different temperatures were also measured.

2. Experimental

Glass samples of composition $20SrO.55Bi_2O_3.25B_2O_3$ (SBB) and $20BaO.55Bi_2O_3.25B_2O_3$ (BBB) were prepared by normal melt-quench technique, from reagent grade chemicals of B_2O_3, $BaCO_3$, $SrCO_3$ and Bi_2O_3. Appropriate amounts of these chemicals were mixed in an agate mortar and then melted in a platinum crucible at 1100 °C for 1 h using an electric furnace under atmospheric conditions. During melting, the mixture was shaken frequently to ensure homogeneity. The melts were poured in brass mold and pressed with brass sheet to get button shaped samples. The prepared glass samples were annealed at 300 °C for 3 h to remove thermal strains. The samples thus obtained were

* Corresponding author. Tel.: +91 471 2440817.
E-mail address: drnsantha@gmail.com (N. Santha).

0022-3093/$ – see front matter © 2014 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jnoncrysol.2014.01.037

found to be transparent and yellowish in color. The amorphous nature of all the samples was confirmed by the absence Bragg's peak in the diffraction pattern. As a typical example, the diffraction pattern of $20SrO.55Bi_2O_3.25B_2O_3$ is given in our earlier paper [14]. Hence, the XRD patterns of the as-quenched glass samples are not included in this paper. The glass transition temperature, onset crystallization temperature, peak crystallization temperature and melting temperature of the glass samples determined by differential thermal analysis (DTA) were also reported in our earlier paper [14]. The DTA thermograms [14] show sharp exothermic crystallization peaks (T_p) ~443 and 482 °C for BBB and SBB glasses respectively, suggesting the formation of a crystallized phase. The samples were hence heat treated at temperatures ranging from 450 to 650 °C. The nucleation temperature was fixed to 350 °C in all cases. The samples were holded for 1 h at the nucleation temperature and 2 h at the crystallization temperatures. The heating and cooling rates were fixed to 1 °C/min. The temperature at which the samples were crystallized is given along with the glass code. For example, SBB glass crystallized at 500 °C is named as SBB500. X-ray diffraction patterns of the powdered samples were collected with Philips X'Pert Pro diffractometer using Cu K_α radiations (1.54060 Å) at a scan rate of 0.05° 2θ s^{-1}. The Fourier transform infrared (FT-IR) transmission spectra of the samples were recorded in the region 400–4000 cm^{-1}, before and after heat treatment, by a Shimadzu FT-IR spectrometer, employing the KBr pellet technique. Room temperature FT-Raman spectra of the glasses and glass-ceramics were recorded in the region 50–4000 cm^{-1} using 1064 nm line of a Nd:YAG laser and Bruker FT-Raman Spectrometer (RFS 100/s, Germany) at a resolution of 4 cm^{-1}. The pulverized glass frits were mixed with a 3 wt.% solution of polyvinyl alcohol (PVA) as binder, ground well, dried and uniaxially pressed to a disk shape and heat treated at temperatures 450–650 °C, under the same conditions of preparation of glass ceramics. The microstructures of as sintered glass pellets were examined using a scanning electron microscope (JEOL Model JSM-6390LV). For dielectric measurements, silver paste was applied on both the surfaces of the pellets and electrodes were made. The dielectric properties of the heat treated pellets were measured at room temperature, in the frequency range 1 kHz to 1 MHz with an LCR meter (Hioki-3530-50, Japan).

3. Results

3.1. X-ray diffraction

The XRD patterns of the as-quenched BBB and SBB glasses [14] do not show any peak, but only broad hump characteristic of amorphous structure. Crystalline peaks start to appear in the XRD pattern of BBB450 (no peaks for SBB450), but are of very weak intensity. Hence, only the XRD patterns of samples heat treated in the temperature region 500–650 °C are shown in Figs. 1 & 2. In general, the intensities of the peaks increase as the crystallization temperature is increased.

3.2. SEM

The scanning electron micrographs of the glass ceramic samples obtained by thermal treatment of the glasses at different temperatures are presented in Figs. 3 & 4. It can be observed that the surface microstructures of BBB500 and SBB500 (Figs. 3a & 4a) contain crystalline aggregates comprising numerous randomly oriented fine crystallites. The similarity of the morphology confirms the XRD results that the crystallites of the same compound ($Bi_{24}B_2O_{39}$) are formed in both cases.

3.3. FT-IR spectra

Raman and FT-IR spectroscopic techniques are effectively used to study the structure of local arrangements in glasses and glass-ceramics. We have earlier reported the FT-IR and Raman spectra of the BBB and SBB glasses [14]. To determine the structural changes due to heat

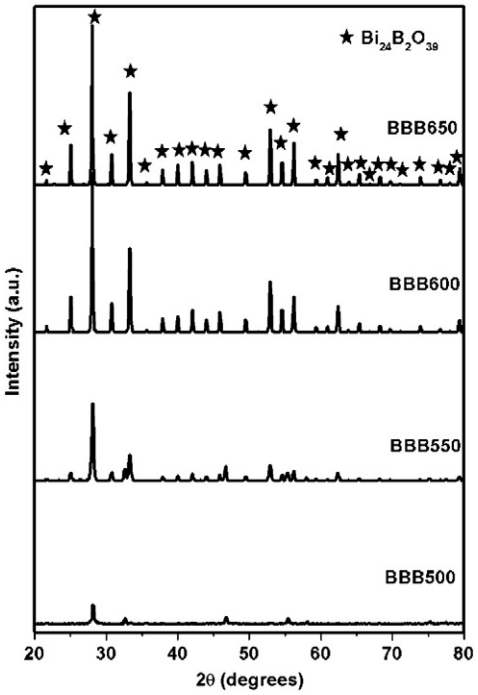

Fig. 1. XRD patterns of $20BaO.55Bi_2O_3.25B_2O_3$ (BBB) glass heat-treated at temperatures 500 °C, 550 °C, 600 °C and 650 °C.

treatment, the FT-IR spectra of untreated BBB and SBB glasses [14] are compared with those recorded for the samples BBB600 and SBB600 (Figs. 5 & 6). The assignments of the IR bands of BBB and SBB samples heat-treated at different temperatures are summarized in Table 1.

3.4. FT-Raman spectra

Raman spectra of BBB and SBB glasses and glass ceramics contain a large number of bands due to the vibrations of $[BO_3]^{3-}$ and $[BO_4]^{5-}$

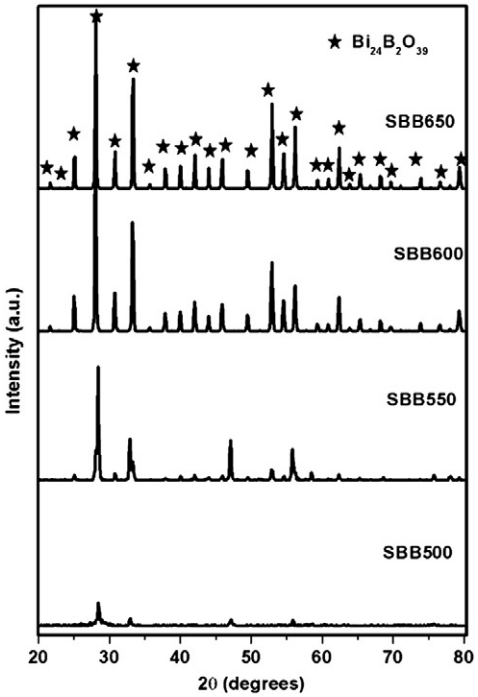

Fig. 2. XRD patterns of $20SrO.55Bi_2O_3.25B_2O_3$ (SBB) glass heat-treated at temperatures 500 °C, 550 °C, 600 °C and 650 °C.