Journal of Asian Ceramic Societies 3 (2015) 206–211

HOSTED BY

Contents lists available at ScienceDirect

Journal of Asian Ceramic Societies

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

Physical, thermal, structural and optical absorption studies of vanadyl doped magnesium oxy-chloride bismo-borate glasses

M.S. Dahiya [a,*], S. Khasa [a], A. Agarwal [b]

[a] Physics Department, Deenbandhu Chottu Ram University of Science & Technology, Murthal 131039, India
[b] Applied Physics Department, Guru Jambheswar University of Science & Technology, Hisar 125001, India

ARTICLE INFO

Article history:
Received 4 January 2015
Received in revised form 23 February 2015
Accepted 23 February 2015
Available online 13 March 2015

Keywords:
Melt-quenching
Optical basicity
Glass transition
Glass stability
Optical band gap

ABSTRACT

Oxy-chloride bismuth-borate glasses with composition xMgCl$_2$·(30 − x)MgO·20Bi$_2$O$_3$·50B$_2$O$_3$ containing 2 mol% doping of V_2O_5 (x = 12, 15, 20, 25 and 30) are prepared by melt-quenching technique. The structural, thermal and optical behaviors are explained by analyzing the data obtained from density (D), molar volume (V_m), theoretical optical basicity (Λ_{th}), differential scanning calorimetry (DSC), FTIR and UV–vis results. A decrease in D and increase in V_m (except for sample MBV3 for which D is maximum) on increasing chloride content suggests the formation of non-bridging oxygen atoms. Maximum glass transition temperature (T_g) and crystallization temperature (T_x) have been observed for sample MBV3. The glass stability (S) and stability ratio (S/T_g) have been calculated from the values of T_g and T_x and both are having maximum values for sample MBV3. Study of the FTIR spectra in the mid-IR range reveals the presence of both triangular and tetrahedral coordinated boron. The optical studies through UV–vis spectral analysis show non-sharp edge. The optical band gap (E_g) is also maximum for sample MBV3.

1. Introduction

Borate glasses have some unique properties such as reduced thermal expansion, resistance to thermal shock, enhanced toughness, strength, chemical resistance and durability which makes them suitable for use in fiberglass [1]. It is known that Bi^{3+} ion has small field strength so Bi_2O_3 cannot form glass by itself but in the presence of B_2O_3 glass formation is possible. Heavy metal oxide (HMO) doped glasses have attracted considerable attention due to their high refractive index, high infrared transparency, thermal stability and high density. It is also considered that the addition of Bi_2O_3 results in increased stability and chemicals durability of oxide glasses making these glasses suitable for use in ceramics, reflecting windows, etc. [2]. When we add alkali and alkaline earth metal oxides to the bismuth-borate glass matrix it results in network formation or modification. Subsequently it gives rise to different non-linear optical properties making these glasses suitable for optoelectronic applications [3].

The formation of glass in the system ZrF_4-BaF_2-NaF-Nd_3 (the so-called halide glass) was studied in 1974 by Poulain and Lucas [4]. The first practical application of BeF_2 based halide glass as the glasses having lowest refractive index and highest Abbe number, was reported by Baldwin et al. in 1981 [5]. Besides these properties, the halide glasses are highly toxic and hygroscopic resulting in few studies on these glasses [6]. The oxy-halide glasses are quite important for applications as host materials in high power laser systems [7]. Subsequently, these glasses due to high ionic conductivity of mobile halogen ions can be used in fuel/solar cells [8]. Moreover, the oxy-halide glasses containing phosphates are believed to be less thermally stable [9] but their borate counterparts may be having good thermal stability as observed in our work. Although many reports are available on the electrical [10–17] properties of oxy-halide borate glasses but when it comes to the study of thermal and optical properties relatively lesser attention has been paid [18–20].

As V^{4+}, vanadium is usually coordinated to six ligands forming an octahedral complex and with oxygen as ligand, one V—O bond becomes very distinct which is termed as vanadyl ion (VO^{2+}) [21]. The vanadium is generally used as impurity for understanding the orientation, phase transition and structural properties of the host glass and is studied with interest in the recent past [22–24]. In our earlier work, we have studied the oxy-chloride borate glasses in

* Corresponding author at: INSPIRE Fellow, Department of Physics, DCR University of Science & Technology, Murthal, Sonepat 131039, Haryana, India.
Tel.: +91 99969 87095/130 2484136; fax: +91 130 2484003.
E-mail address: ms.dahiya12@gmail.com (M.S. Dahiya).
Peer review under responsibility of The Ceramic Society of Japan and the Korean Ceramic Society.

http://dx.doi.org/10.1016/j.jascer.2015.02.006

Table 1
Density (D), molar volume (V_m), theoretical optical basicity (Λ_{th}), glass transition temperature (T_g), crystallization temperature (T_x) and glass stability (S) and stability ratio (S/T_g) of xMgCl$_2$·(30 − x)MgO·20Bi$_2$O$_3$·50B$_2$O$_3$ + 2% V$_2$O$_5$ (x = 12, 15, 20, 25 and 30) glasses.

Sample code	x	D (g/cm^3)	V_m (cm^3/mol)	Λ_{th}	T_g (°C)	T_x (°C)	S (°C)	S/T_g
MBV1	12	3.76	32.0	0.465	523	822	299	0.57
MBV2	15	3.51	35.5	0.468	524	791	267	0.51
MBV3	20	3.68	36.0	0.472	550	949	399	0.73
MBV4	25	3.43	41.5	0.476	524	812	288	0.55
MBV5	30	3.40	44.0	0.480	529	810	281	0.53

the systems BaO·BaCl$_2$·B$_2$O$_3$ [25,26] and CaO·CaCl$_2$·B$_2$O$_3$ [27,28] containing vanadyl ions. The oxy-chloride systems are presumed to result in volatilization of chlorine during melting, so the final composition may differ a bit from the actual composition [29]. In the system of oxide glasses containing alkaline earth oxides, the MgO-B$_2$O$_3$ system is of particular interest because MgO is a principal constituent of the linings of steelmaking furnaces and part of furnace slag consists of MgO [30]. However the MgO-B$_2$O$_3$ system is characterized by the narrowest glass forming region among the family of alkali earth borate glasses [31]. The addition of Bi$_2$O$_3$ can result in wider glass forming region and lower melting temperatures, which results in an ease in glass formation. Moreover, the oxy-chloride counterparts in MgO-B$_2$O$_3$-Bi$_2$O$_3$ system may serve as hosts (owing good thermal stability) for high amplification laser systems. Keeping in view the above facts, we have prepared the magnesium oxy-chloride bismo-borate glasses with composition xMgCl$_2$·(30 − x)MgO·20Bi$_2$O$_3$·50B$_2$O$_3$ (x = 12, 15, 20, 25 and 30) and studied their thermal, structural and optical properties. The results along with their interdependence are reported in the present paper.

2. Experimental

2.1. Sample preparation

The preparation was carried out using standard melt-quenching technique. The analar grade chemicals H$_3$BO$_3$, MgO, MgCl$_2$, Bi$_2$O$_3$, and V$_2$O$_5$ required as the starting materials were obtained from Loba Chemie. Each chemical was crushed and weighed in proper amount by using a digital electronic balance (CAS CAUY220). The powders were then mixed with an agate pestle and mortar for half an hour. The mixture so obtained was put into a high alumina crucible for melting at 1100 °C in an electrical muffle furnace for one hour. The melt was then rapidly quenched by sandwiching it between two pre-heated stainless steel plates to obtain samples in the form of discs [32]. Titular representation of the prepared samples is MBV1, MBV2, MBV3, MBV4 and MBV5 for x = 12, 15, 20, 25 and 30 respectively.

2.2. Density and basicity measurements

The density has been measured using Archimedes principal as

$$D = D_x \frac{W_a}{W_a - W_x} \quad (1)$$

where D_x is density of xylene, W_a is weight of sample in air and W_x is weight in xylene. The molar volume (V_m) thus has been calculated as $V_m = M/D$ with M as the molecular mass of the sample. The theoretical optical basicity is calculated [33] by using the following relation:

$$\Lambda_{th} = \sum \frac{Z_i r_i}{Z_o \gamma_i} \quad (2)$$

where Z_i is the oxidation number of the cation i, r_i is the ratio of cation i with respect to total number of oxides and $\gamma_i = 1.36(x_i - 0.26)$ with x_i as Pauling electro-negativity [34] and Z_o as cation oxidation number.

2.3. DSC, FTIR and optical absorption measurements

The DSC measurements of samples in the bulk form were carried out in the temperature range of 200–1000 °C on a thermal analyzer (Perkin Elmer STA 6000). The heating rate and nitrogen flow rate used to carry out analysis were 10 °C/min and 100 ml/min respectively. For FTIR measurements, as-prepared samples were first crushed into fine powder and then mixed in approximately 0.15 g of KBr in the ratio ~1:100. A circular pellet of diameter 13 mm was formed with this mixture using a hydraulic press. The pellet so formed was analyzed for FTIR using universal sample holder and a Perkin Elmer Frontier FTIR spectrophotometer in the mid-IR range. For any sort of noise and background correction Spectrum 10 software provided with the IR system was used [35]. For optical absorption measurements, the samples with thickness ranging 0.5–1.2 mm were polished to optical quality. The absorption and transmission spectra of the polished samples were recorded in the wavelength range of 200–800 nm at ambient temperature using a UV–vis spectrophotometer (Shimadzu UV2450).

3. Results and discussion

3.1. Density, molar volume and basicity

The measured values of density (D) and calculated values of molar volume (V_m) are reported in Table 1. These values are of the same order as reported for alkaline earth oxy-halide glasses [25]. In oxide glasses, study of D and V_m becomes important as both are presumed to provide very good insight about the network forming and modifying units. The variations of V_m and density are shown in Fig. 1. It is quite visible from this figure that V_m is increasing and density is decreasing (except for sample MBV3). The increase

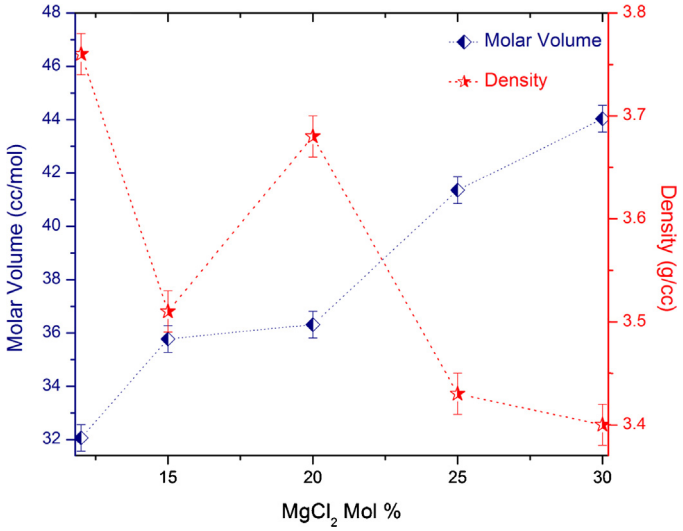

Fig. 1. Composition dependence of density and molar volume of xMgCl$_2$·(30 − x)MgO·20Bi$_2$O$_3$·50B$_2$O$_3$ + 2% V$_2$O$_5$ (x = 12, 15, 20, 25 and 30) glasses.