Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Network structure analysis of modifier CdO doped sodium borate glass using FTIR and Raman spectroscopy

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ARTICLE INFO

Keywords:
Borate glass
FTIR
Raman spectroscopy

ABSTRACT

Ternary oxide glass system of chemical composition of $80B_2O_3$–(20-x)Na_2O–xCdO (where x = 0, 2, 4, 6, 8, 10, 12, 14 mol%) have been prepared by conventional melting and quenching method. The micro structural and morphological investigation of synthesized glass samples were carried out by using XRD, FE-SEM. The supporting physical and composition dependent properties such as experimental and theoretical density, molar volume, oxygen packing density, ionic concentration, interionic distance and polaron radius were determined. Density of glass samples increases, while molar volume decreases with the increasing cadmium oxide concentration from 0 to 14 mol%. X-ray diffraction profiles and FE-SEM images confirmed amorphous nature of investigated glass samples. Elemental analysis and information about the chemical composition of glass matrices have been ascertained by using EDS spectra. The interpretation of functional groups [BO_3] and [BO_4] units present in the oxide glass was simulated by using deconvoluted Raman spectra and FTIR spectroscopy. B—O stretching, metal cation active vibrational modes and bending vibrations of B—O—B linkage in borate glass network are cross verified by using FTIR and Raman spectroscopy.

1. Introduction

Borate glasses are having wide variety of applications, it offers varying physical and chemical properties by changing the chemical composition. Boron possesses the ability to change its coordination with oxygen between three or four. Hence it forms variable structural units in the glass network and such behavior is quite different than that of silicon, phosphorous which forms only tetrahedral coordinated units with oxygen. Borate glasses have been extensively studied as a glass forming system [1,2]. Mainly the borate glasses are having so many potential applications like thin amorphous films for battery application, bioactive glasses for tissue engineering, nuclear waste disposal, photonic applications, development of tunable or short pulse lasers, optical fibre amplifiers and fibre lasers etc. [3–7].

Among oxide glasses, borate glass structure having disordered geometry with the formation of tetrahedral coordination of BO_4 units. According to, Zacharrisen glass formation theory the oxides of metal cation (e.g. Cd^{2+}) with valence one or two plays the important role as glass modifier. Some of the bridging oxygen of tetrahedral (BO_4) units combines with glass modifier coordinated by six, eight or even more oxygen atom to form glass network with non-bridging oxygen [8].

Recently, oxide glasses containing ZnO and CdO get much importance. Since, their use in various technological fields. Heavy metal oxides (PbO and CdO) glasses have also attracted the attention as a result of their high optical nonlinearity and their infrared transmittance [9,10]. CdO can be chosen as network former and network modifier when it is added to network forming oxide glasses, depending upon its concentration. CdO acts in some borosilicate glasses as both network former and network modifier when its content exceeds 50 mol % [9,11].

The addition of alkali oxides to borate glass can improve its physical properties as well as modify the preparation conditions. So that, transition metal oxide (like CdO, ZnO etc.) doped alkali borate glasses are important for photonic and potential battery applications. Also it opens an interesting category of glasses to study the effect of the alkali ion on the glass forming network, particularly the transition metals and rare-earth ions [12–15]. CdO is also found to be a promising candidate for optoelectronics, solar cells, photo-diodes and gas sensors etc.

Sodium oxide (Na_2O), boron trioxide (B_2O_3) is the major components of many industrial important glasses [16]. The main application of these glasses ranges from cookware to laboratory glassware to optical glass [17]. Because of this reason, many glass researchers have been conducted structural, physical studies to understand how the density, molar mass of each oxide affects the glass network structure.

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http://dx.doi.org/10.1016/j.jnoncrysol.2017.08.028
Received 4 July 2017; Received in revised form 29 July 2017; Accepted 19 August 2017

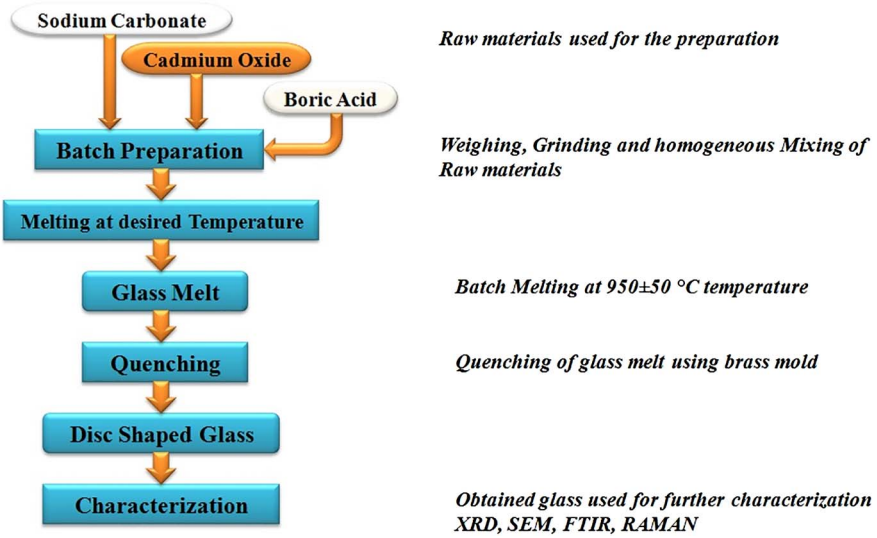

Fig. 1. Flow chart of melting and quenching preparation method of glass.

Subsequent studies include identification of the structural building blocks by using several spectroscopic techniques such as Raman [18], Infrared spectroscopy [19].

This article is focused on the physical, structural study and network analysis of sodium borate glasses and on how the structure of glassy networks is modified by cadmium oxide as dopants belonging to transition metals. The chemical composition-dependent study of present oxide glasses is also summarized in the present article. In the present study analysis of Raman spectra of oxide glass samples was done with the help of Gaussian deconvolution method. This article is very useful for understanding the formation of glassy networks and their modification due to varying CdO concentration.

2. Experimental

2.1. Synthesis method

The oxide glasses with nominal composition of $80B_2O_3$–(20-x) Na_2O–xCdO with x = 0, 2, 4, 6, 8, 10, 12, 14 mol% were prepared by conventional melting and quenching techniques. Synthesis method flowchart has been shown in Fig. 1 and the chemical composition and respective codes of oxide glass samples are summarized in Table 1. Raw materials of analar grade (H_3BO_3, Na_2CO_3 and CdO with 99.9% purity) are toughly ground for 1 h in an agate mortar and pestle to get homogeneous mixture. The porcelain crucible containing batch was transferred in an electrically heated furnace at a temperature of 450 °C, which helps to remove the moisture, carbonates, decomposition of borate and react with other batch constituents before melting. Then the temperature increased up to 950 ± 50 °C for 2 h with heating rate of 10 °C/min. During melting process, the glass melt was stirred in order to get homogeneous and bubble free melt. The glass melt was poured and quenched between two well-polished preheated brass plates. The obtained circular disc shaped glass samples were cut and polished carefully with various grit sized micro polish papers for further characterizations.

Table 1
Chemical composition of $80B_2O_3$–(20-x)Na_2O–xCdO (where x = 0, 2, 4, 6, 8, 10, 12, 14 mol%).

Glass code	Chemical composition (mol%)		
	B_2O_3	Na_2O	CdO
BNC-0	80	20	00
BNC-1	80	18	02
BNC-2	80	16	04
BNC-3	80	14	06
BNC-4	80	12	08
BNC-5	80	10	10
BNC-6	80	08	12
BNC-7	80	06	14

2.2. Density (ρ), molar volume (V_m) and oxygen packing density (OPD)

The density of prepared glass samples at room temperature was measured by using Archimedes principle with Xylene as inert immersion liquid (density of Xylene 0.865 g/cm^3). Systematic density measurement of three bubble free glass samples were carried out and averaged density is reported in Table 2. The density was calculated with the help of following formula[20,21].

$$\rho = \frac{W_a}{(W_a - W_b)} \cdot \rho_x \quad (1)$$

where W_a is the weight of sample in air, W_b is the weight of sample in xylene and ρ_x is the density of xylene at room temperature. All the weight measurements were carried using a sensitive analytical balance (ViBRA HT) with desired accuracy. Also, the chemical composition dependent theoretical density of the oxide glass samples were calculated for cross checking with the experimental density summarized in the Table 2.

The molar volume (V_m) of the glass samples was calculated as the mean molecular mass of the glass composition divided by its density (ρ) [22,23].

$$V_m = \frac{\sum x_i \cdot M_i}{\rho} \quad (2)$$

where x_i is the molar fraction of oxide and M_i is the molecular mass of the oxides present in the glass composition. The sum of these expressed as average molecular mass of the glass sample.

In order to measure the tightness of the borate glass network oxygen packing density (OPD) was calculated the using the formula [24]

$$OPD = \frac{\rho}{M} \times n \quad (3)$$

where M is the molecular mass of the glass sample and n is the number of oxygen atoms per formula units.

X-ray diffraction pattern was recorded in the range 20–80° with the scanning rate of 5°/min, by using Cu (40 kV, 40 mA) as X-ray source. Powdered glass sample were used to take X-ray diffraction (XRD), scanning electron microscope (FE-SEM), energy dispersive X-ray