Journal of Non-Crystalline Solids 450 (2016) 12–17

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

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

Investigation of iron redox ratio in zinc borate glass prepared in microwave heating and comparison with conventional glass

Biswajit Mandal [a], Avik Halder [a], Prasanta Kumar Sinha [b], Ranjan Sen [a], Ashis Kumar Mandal [a,*]

[a] Glass Division, CSIR-Central Glass and Ceramic Research Institute, 196, Raja S. C. Mullick Road, Kolkata 700032, India
[b] Materials Characterization and Instrumentation Division, CSIR-Central Glass and Ceramic Research Institute, 196, Raja S. C. Mullick Road, Kolkata 700032, India

ARTICLE INFO

Article history:
Received 19 April 2016
Received in revised form 14 July 2016
Accepted 22 July 2016
Available online xxxx

Keywords:
Iron redox ratio
Zinc borate glass
Microwave heating
Spectrophotometric method
Ferrozine
1, 10 ortho-phenanthroline

ABSTRACT

Glass comprising B_2O_3-Al_2O_3-Na_2O-ZnO with doping iron metal powder has been melted at 1200 °C under microwave heating. The identical batch was melted in resistive heating. UV–Vis-NIR spectroscopy has been employed to determine the ferrous ion intensity in glass within 1000–1200 nm wavelength and recorded spectra for both the glasses indicate higher retention of ferrous oxidation state in borate glass melted in microwave heating. Iron redox ratio (Fe^{2+}/total Fe) in the glass is investigated by spectrophotometric method developing ferrozine colour complex with Fe^{2+} in glass. Ferrozine is chosen as a specific reagent, which forms a deep violet colour complex with Fe^{2+}, which has a broad absorbance peak centered at ~562 nm. The spectrophotometric method using ferrozine reveals iron redox ratio ***0.34 and 0.29*** in the glass obtained from microwave and conventional heating respectively. Another spectrophotometric method using 1, 10 ortho-phenanthroline also demonstrates higher ferrous ion in glass obtained in microwave heating. Thus, microwave heating favours more stabilization of iron in ferrous oxidation state in zinc borate glass, which is unlike in conventional heating.

1. Introduction

Investigation of iron species in glass continues mainly due to its importance as a key colourant in glasses used for optical applications. Although iron may be present in a number of oxidation states, it is usually present in Fe^{3+} (III) with a some of Fe (II) oxidation state [1]. These oxidation states of iron are presents predominantly in 4-fold (tetrahedral) and 6-fold (octahedral) coordination sites. The redox ratio, the coordination polyhedra of iron and the chemistry of the glass matrix are closely interrelated and influence its optical properties significantly [2–7]. The optical absorbance of divalent state is found to be in two broad regions one in the wavelength range 1000–1200 nm for 6-fold coordinated site and other within ~2000–2200 nm for 4-fold coordinated site [8]. Thus, higher retention of Fe^{2+} in glass will produce improved IR absorbing properties.

However, trivalent state [Fe(III)] is more stable in the glass and produce a complicated set of weak absorbance band (within 380–550 nm wavelength) due to the spin forbidden d-d transition [9]. To stabilize divalent state [Fe (II)] in glass, batch is usually melted in a reducing condition incorporating reducing agent in conventional furnace. A complicated arrangement of gas injection system is indeed required to create and maintain reducing atmosphere inside the conventional furnace.

Microwave-assisted material synthesis is a potential alternative method of synthesis mainly due to rapid processing and enormous energy savings [10–12]. Microwave heating has been demonstrated as a potential material processing tool, which can produce material with improved or new properties [13–17]. Improved properties such as microhardness and low OH content in glasses have been identified elsewhere [18,19]. Improved chemical durability and low contamination from the crucible wall have also been observed in borosilicate and phosphate glasses [20,21]. It also yields higher ferrous oxidation state in phosphate glass [22,23]. However, investigation of iron redox-ratio in different other glass system has not yet been explored.

With this background, present work aims to investigate the iron redox-ratio ($Fe^{2+}/\sum Fe$) in zinc borate glass melted in microwave and conventional heating. UV–Vis-NIR spectroscopy is used to understand the intensity of Fe(II) absorbance at 1000–1200 nm. Two spectrophotometric methods developing ferrozine and 1, 10 ortho-phenanthroline colour complexes with the Fe^{2+} have been employed for this study. In order to carry out the study, iron doped zinc borate glass has been melted in microwave heating as well as in conventional heating.

2. Materials and method

Glass of batch composition in mol% (65) B_2O_3, (5) Al_2O_3, (10) Na_2O and (20) ZnO was melted both in microwave and in conventional heating. The source of B_2O_3, primary glass-forming oxide in the batch was H_3BO_3 (Merck, Darmstadt, Germany 99.5% pure). The alkaline oxide Na_2O in the form of carbonate (Na_2CO_3 Merck, Darmstadt,

* Corresponding author.
E-mail addresses: ashis@cgcri.res.in, ashismand@gmail.com (A.K. Mandal).

http://dx.doi.org/10.1016/j.jnoncrysol.2016.07.028
0022-3093/

Germany 99.9% pure), Al_2O_3 (Sigma Aldrich, USA, 99.9% pure) and ZnO (Merck, Darmstadt, Germany, purity ≥99.0) were used. Fe metal powder was added to the batch 0.5 wt.% in excess. Approximately 50 g of each batch with the above composition was mixed thoroughly in an agate mortar and pressed to form a pellet at 4 ton pressure in a hydraulically operated pellet press. The pellet was placed in an alumina/quartz crucible insulated and placed in air atmosphere inside a 2.45 GHz, 3.0 kW multimode microwave furnace. Heating rate was maintained within 12 K/min to 15 K/min up to 1473 K and held for 1 h. Total melting time was 2 h and power consumption was recorded ~5 kWh. Temperature measurement of sample was carried out by in line infrared non-contact pyrometer within 260–1800 °C (with an accuracy ±0.3% of the measured value +1 °C). Manual stirring was adopted to obtain near homogenous glass. The molten glass was cast into a preheated mould and annealed at 823 K for 2 h followed by controlled cooling until room temperature. The annealed glass sample is termed as ZBANFM. Two base glasses were melted using alumina and quartz crucible for residual stress measurement.

2.1. Conventional melting

50 g identical batch with the above composition was mixed and formed pellet as described in earlier section. The pellet was placed in a quartz crucible in air atmosphere in electrical resistance heating furnace at 1473 K with a maximum heating rate 5 K/min. Temperature was monitored in resistive heating furnace using S-type thermocouple (with accuracy from 1.5 to 5 °C). The manual stirring with silica rod was adopted to homogenize the glass melt. At 1473 K, the melt was kept for 1 h (with total melting time 6–7 h) and finally poured into a preheated mould. Then, cast glass was annealed as earlier section. The annealed glass is termed as ZBANFC. Base glass without doping of iron was melted in quartz crucible for measurement of residual stress in the glass.

3. Characterization methods

3.1. Residual stress

Residual stress of glass after cutting and polishing were measured by digital image analysis system (Model: DIAS 1600, M/S Strainoptics, Inc.) across the horizontal length within 10 mm parallel with magnification set up. Digital image including data was analyzed using software DIAS1. The instrument works on the Birefringence phenomenon following Stress-Optic (Brewster's) Law of Eq. (1)

$$(n_{1-}\ n_2) = C_B(\sigma_1 - \sigma_1) = \frac{\delta}{t} \quad (1)$$

Where, n_1, n_2 indices of refraction;

σ_1 σ_2 Principle stresses [Stress (σ) = Retardation(δ)/Thickness(t) × C_B];

C_B is Brewster's constant, t is thickness of material;

Retardation (δ) is directly proportional to the difference between the refractive indices.

3.2. UV–Vis-NIR spectroscopy

The optical transmittance spectra were recorded at room temperature on a UV–Vis-NIR spectrophotometer (Model Perkin Elmer, Lambda 950, USA) in the wavelength range 200–2250 nm.

3.3. Spectrophotometric characterization

3.3.1. Method using ferrozine

Use of spectrophotometric method to determine the different oxidation state of iron developing ferrozine colour complex has been discussed elsewhere [24–26]. Glass samples were ground to a fine powder using an agate mortar and pestle. Glass powder of 50.0 mg was taken in a Teflon beaker. Then, 20 mg of meta-NH_4VO_3, 0.5 ml of concentrated H_2SO_4 and 1.5 ml of concentrated HF were added to it. The liquids were added drop by drop and mixed well with the powder glass sample. The beaker was then heated on a hot plate maintained at 60 °C for 10 min for glass dissolution. After dissolution, 20 ml of a saturated boric acid solution was added and the total volume of the sample was made to 50 ml by adding distilled water. The solution was filtered using Whatman 42 filter paper. Then, 5 ml aliquot and 5 ml ferrozine-buffer solution were mixed and the volume was made to 25 ml by adding distilled water and allowed to develop a stable colour complex for 2 h. The optical absorbance of the solution containing Fe^{2+}-ferrozine colour complex was recorded by UV–Vis spectrophotometer (Model Perkin Elmer, Lambda 45, USA) in the wavelength range 450 to 550 nm. Three measurements have been carried out and average value has been recorded with an estimated error <3%.

For the analysis of total iron, 5 ml of the aliquot was taken in an another volumetric flask and then 5 ml of 5% ascorbic acid (Merck, Darmstadt, Germany, 99% pure) solution was added to reduce all the iron to Fe^{2+} state, followed by the addition of 5 ml ferrozine-buffer solution to develop the colour complex and the volume was made to 25 ml with the addition of distilled water. The intensity of optical absorbance of Fe^{2+}-Ferrozine colour complex (at 562 nm) is the measure of total iron in the solution. The ratio of Fe^{2+}/total Fe was estimated from the absorbance intensity of Fe^{+2}-ferrozine colour complex at 562 nm in the solution without and with the addition of ascorbic acid in the solution. Three measurements have been carried out and average value has been reported with estimated error <1% for total Fe analysis.

3.3.2. Method using 1, 10 ortho-phenanthroline

Phenanthroline is also reported to have been used to investigate the iron redox ratio in solution [27,28]. In order to estimate the ferrous ion concentration using 1, 10 ortho-phenanthroline, 50 mg of the glass powder was taken into a 100 ml Teflon beaker. Then, 0.5 ml of concentrated H_2SO_4 and 1.5 ml of concentrated HF were added to it, followed by heating it at 60 °C for 10 min for sample digestion. An indicating solution was prepared simultaneously using 25 ml of 4% boric acid (Merck, Darmstadt, Germany, 99.5% pure), 7 ml of 10% potassium hydrogen phthalate (Merck, Darmstadt, Germany, 99% pure), 6 ml of 0.25% 1,10 ortho-phenanthroline (Merck, Darmstadt, Germany, 99.5% pure) solution, and 2 ml of concentrated NH_4OH in an another Teflon beaker. After dissolution of glass, the solution was allowed to cool to room temperature and the as prepared indicating solution was added into it. The pH of the mixed solution was adjusted to 3–4 using diluted NH_4OH and/or diluted H_2SO_4. The volume was made up to 100 ml by adding double distilled water.

A reducing agent, hydroquinone (25 mg, Merck, Darmstadt, Germany, 99.5% pure), was added to the solution to reduce all other iron into Fe^{2+} to develop orange-red colour for 2 h. The absorbance intensity of this solution was measured after complete colour development of the orange-red complex which has absorbance peak centered at 510 nm. The intensity of this absorbance peak at 510 nm is a direct measure of total iron content in solution and thereby in glass.

4. Results

Fig. 1 displays photograph of the annealed glasses melted in both conventional resistive heating and microwave heating. The annealed glass melted in microwave heating (ZBANFM) appears to be greenish while light brown colour glass is obtained in resistive heating (ZBANFC). Two glass pieces of dimension 15 × 10 × 1 mm^3 obtained after cutting and polishing from the annealed glasses as shown in inset. Visual inspection shows improved transmission in ZBANFM than ZBANFC.

Fig. 2 exhibits residual stress in base glass A) melted in microwave using alumina crucible, B) melted in microwave using quartz crucible,