Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

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

The forming region and mechanical properties of $CaO-Al_2O_3-SiO_2$ system

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ARTICLE INFO

Keywords:
$CaO-Al_2O_3-SiO_2$
Glass forming regions
Mechanical properties
Bending strength
Compression strength

ABSTRACT

Glass system with compositions of 93.9% (xCaO-$y$$Al_2O_3$-$z$$SiO_2$)–5% MgO-1% B_2O_3–0.1% Fe_2O_3 has been prepared by a conventional melt-quenching technique, and the glass forming region and the mechanical properties of the derived glasses were investigated. The approximate glass forming region was found to be x = 10 ~ 35%, y = 10 ~ 35% and z = 50 ~ 80%, while the rest of the area was crystallization zone or crack zone. As x = 10%, y = 25% and z = 65% (Sample 13), the investigated glass possesses the optimum volume density, bending strength, compression strength and modulus, which are 2.572 g/cm^3, 74.05 MPa, 312.84 MPa and 163.96 GPa, respectively. Compared to sample 13, samples with different compositions have reduced the volume density, lowered the Raman intensity and improved the optical band gap. For the mechanical properties, with decreasing the contents of SiO_2, the bending strength firstly increases, then decreases and finally shows a relatively small increasing trend. The dependence of compression strength and compression modulus on SiO_2 content shows a similar trend to the bending strength. Moreover, the optical band gap and Raman spectrum of the sample 13 indicate that the number of oxygen bonds in the bridge reach the maximum, which could further confirm a significantly improvement on the mechanical properties.

1. Introduction

Glass fibers have attracted great interests due to their high strength, large modulus, extraordinary heat resistance and other excellent properties, which make them suitable for various applications such as aerospace, aviation, weaponry and marine [1–5]. Specially, CaO-Al_2O_3-SiO_2 (CAS) system possess excellent higher tensile strength and monofilament modulus than other systems, which has been widely applied in reinforced material, fan blade and even civil product [6]. Based on the CAS system glass, the Hiper-tex™ and R glass fibers have been produced by American Owens Corning and France Saint-Gobain. The tensile strengths of Hiper-tex™ and R glass fibers are 4600 MPa and 4400 MPa, and the monofilament modulus are 86.9 GPa and 83.8 GPa, respectively [7].

It is well known that the structure and mechanical properties are dependent on the composition of glass fibers. Up to now, intensive efforts have been devoted to investigate the thermal and physical properties of CAS system. For example, Brett studied the liquids temperature of the MgO-CaO-Al_2O_3-SiO_2 system by classic melt-quenching technique, and found that it tends to increase with increasing silica content and decrease at higher alkaline earth-to-alumina ratio. The temperature range of liquid state is around 1331–1500 °C for the CAS system with SiO_2 molar concentration of 64–80% [8]. Glass fibers usually contain a high proportion of alumina [3], and Al plays an important role on the structural properties of glass due to the charge balancing requirement of AlO_4 tetrahedra. Neuville showed that Al was the main residual in tetrahedral position of CAS glasses, and the presence of five-fold coordinated aluminum was the general rule for the ternary CAS system, except for the low silica percalcic region [9]. Moreover, Ulrike et al. investigated the elastic properties and the density of CAS system on the composition. The density and Young's modulus increase with increasing the SiO_2 content from 60.5 to 63 wt% and decrease with increasing the CaO content from 21.4 to 25.4 wt%. Unfortunately, few efforts have been made to investigate the influence of composition on the mechanical properties in the CAS system [10].

In this work, we use magnesium oxide as glass modifier to compensate the negative charge and fill network structure in order to decrease the fragility and the glass softening temperature [11]. Boric oxide works as glass former to improve the glass forming ability and the thermal stability [12]. In addition, iron oxide acts as glass clarify agent to decrease the glass transition temperature [13,14]. We studied the glass forming region on 93.9% (xCaO-$y$$Al_2O_3$-$z$$SiO_2$)–5% MgO-1% B_2O_3–0.1% Fe_2O_3 glasses and presents a systematic investigation of the correlation between glass composition and its mechanical properties.

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http://dx.doi.org/10.1016/j.ceramint.2017.07.101
Received 3 June 2017; Received in revised form 13 July 2017; Accepted 13 July 2017

Table 1
The chemical compositions of the samples in mol%.

Sample	CaO[mol%]	Al_2O_3[mol%]	SiO_2[mol%]	MgO[mol%]	H_3BO_3[mol%]	Fe_2O_3[mol%]
1	5	15	80	5	1	0.1
2	10	10	80	5	1	0.1
3	15	5	80	5	1	0.1
4	5	20	75	5	1	0.1
5	10	15	75	5	1	0.1
6	15	10	75	5	1	0.1
7	20	5	75	5	1	0.1
8	5	25	70	5	1	0.1
9	10	20	70	5	1	0.1
10	15	15	70	5	1	0.1
11	20	10	70	5	1	0.1
12	5	30	65	5	1	0.1
13	10	25	65	5	1	0.1
14	15	20	65	5	1	0.1
15	20	15	65	5	1	0.1
16	25	10	65	5	1	0.1
17	5	35	60	5	1	0.1
18	10	30	60	5	1	0.1
19	15	25	60	5	1	0.1
20	20	20	60	5	1	0.1
21	25	15	60	5	1	0.1
22	30	10	60	5	1	0.1
23	5	40	55	5	1	0.1
24	10	35	55	5	1	0.1
25	15	30	55	5	1	0.1
26	20	25	55	5	1	0.1
27	25	20	55	5	1	0.1
28	30	15	55	5	1	0.1
29	35	10	55	5	1	0.1
30	10	40	50	5	1	0.1
31	15	35	50	5	1	0.1
32	20	30	50	5	1	0.1
33	25	25	50	5	1	0.1
34	30	20	50	5	1	0.1
35	35	15	50	5	1	0.1
36	40	10	50	5	1	0.1

2. Experimental procedure

2.1. Samples preparation

Per-alkaline-earth CAS glasses were synthesized by conventional melt-quenching technique. We prepared 36 samples with the composition of 93.9% (xCaO-$y$$Al_2O_3$-$z$$SiO_2$)–5% MgO-1% B_2O_3–0.1% Fe_2O_3, which was shown in Table 1. In order to improve the reaction activity, the boric acid (H_3BO_3) was used as the source of B_2O_3. The glass batch was made of CaO, Al_2O_3, SiO_2, MgO, H_3BO_3 and Fe_2O_3 powders with purity greater than 99.99% Aladdin chemistry. About 50 g of each component was added into a quartz crucible, melted at 1550 °C for 5 h. And then, the crucible was immediately transferred to a cooling furnace preheated at 850 °C to obtain the samples.

X-ray diffraction (XRD) analysis was used to confirm the amorphous state of the as-prepared glasses. The XRD spectra was recorded within Bragg angle 2θ from 10° to 80° in a diffractometer (D/MAX-IIIA) using Cu Ka radiation with a scanning speed of 0.05° per second.

2.2. Raman spectra and Transmittance spectra

Raman spectra in the range of 100–1600 cm^{-1} were recorded at room temperature on a Labram HR800 micro-spectrometer using the 532 nm line of Renishaw high power diode laser. The measured power was 5 mW and the resolution of the system was less than 1 cm^{-1}.

The transmittance spectrum of each glass was measured using a fiber optics UV–vis spectrometer (Model-AVASPEC 3648) with a dual light source by scanning from 200 nm to 800 nm using air as a reference. According to the Kubelka-Munk law [15], the absorption coefficient, α, can be calculated from the measured transmittance data using the following equation:

$$\alpha = \frac{-\ln T}{t} \tag{1}$$

where T and t are transmittance and thickness of glasses, respectively.

2.3. Density and Mechanical properties

Density of as-prepared glass was determined by conventional Archimedes principle using distilled water. The accuracy of the measurement is better than 0.02 g/cm^3 based on the scale accuracy and a repeatability test (3 replicates).

The mechanical properties were characterized by three-points bending strength, compression strength and compression modulus. All glass samples were polished with SiC papers up to 1200 grits together, then ultrasonically washed with distilled water for ensuring the same parallelism, flatness, and smoothness, and the results of the following tests are obtained from the average of the six samples.

Three-points bending strength tests were carried out via an Electromechanical Universal Testing Machine on 3.00 × 4.00 × 30.00 mm specimens with a loading speed of 0.5 mm/min. The equation of three-points bending strength (B) is expressed as below [16]:

$$B = \frac{3FL}{2at^2} \tag{2}$$

where F is the yield stress, L is the span (20 mm), a is the width of samples, and t is the thickness of samples.

Compression strength carried out via an AG-100KNA test machine on 2.00 × 10.00 ×10.00 mm with a loading speed of 0.5 mm/min. The compression strength (σ) and compression modulus (E_c) of the glass were respectively determined by the following equations [17]: