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

Study on the structure, thermal and optical properties in Cr_2O_3-incorporated $MgO-Al_2O_3-SiO_2-B_2O_3$ glass

Changwei Lin, Jianlei Liu, Lei Han, Hua Gui, Jun Song, Cui Li, Taoyong Liu*, Anxian Lu*

School of Materials science and Engineering, Central South University, Changsha 410083, China.

ARTICLE INFO

Keywords:
Magnesium aluminosilicate glass
Optical absorption
Electron paramagnetic resonance
Photoluminescence

ABSTRACT

Study of $20MgO-20Al_2O_3-57SiO_2$ (MAS) glasses occupies a crucial position for optimizing glass performances for industrial applications. Here, we employed Cr_2O_3 dopant, and successfully prepared series of $20MgO-(20-x)Al_2O_3-57SiO_2-3B_2O_3-xCr_2O_3$ (MASBC) glasses with a doping level, denoted by x, ranging from 0 to 1 mol%, by conventional melt-quenching method. The investigation was systematically conducted using DSC, XRD, IR, optical absorption, electron paramagnetic resonance (EPR) and luminescence techniques. Structural analysis shows that all glass samples are amorphous in nature, and the glass network was mainly identified as the functional groups of $[SiO_4]$ and $[AlO_4]$. From the optical absorption data, various optical parameters such as optical band gap, Urbach energy, crystal field and Racah parameters can be obtained. Besides, the luminescence and excitated spectra were recorded to confirm the presence of Cr^{3+} in a weak crystal field, and the luminescence lifetime was found to decrease with increased Cr_2O_3 due to the dipole interaction between the Cr^{3+} pairs (Cr^{3+}-Cr^{3+}). The EPR spectra of Cr_2O_3-doped MASBC glass exhibit two resonance signals at g = 5.33 and 1.96, indicating the characteristic of Cr^{3+} ions. Subsequently, according to the calculated bonding parameters, we confirm a strong ionic character of glass samples.

1. Introduction

Glasses, as we know, are characterized by high permeability in visible region. They are also important optical materials, that can be applied in many domains like tunable solid-state lasers and luminescence materials [1, 2]. Intrinsically, their amorphous (isotropous) character can effectively avoid the anisotropy as in crystalline material [3]. To date, the $MgO-Al_2O_3-SiO_2-B_2O_3$ (MASB) glass system has attracted considerable attention and has been widely investigated for fundamental and technological purpose, due to its beneficial properties including high thermal stability, chemical resistance, suitable thermal expansion coefficient and low defects concentrations, etc. [4–6].

In the direction of improving the MASB glass properties, designing multi-component glass systems that can integrate the merits from each component is a feasible path [7, 8]. However, few data concentrating on its optical properties can be detected. Notably, the additives of transition metal (TM) ions seem desirable to enhance the optical, electrical and magnetic properties of glasses thanks to their intrinsically multi-electron (valence) states [9–11]. On the other hand, these TM ions feature with broad radial distribution of outer d-orbital electron functions and strong sensitive response to surrounding cations [12], thus are expected to probe the glass structure. Among all TM ions, Cr^{3+} ions has been found to possess broad and strong absorption signals in the visible and luminescence emission excited in near infrared region, which is of great importance for flash lamp pumped laser materials [13–16], thus driving more and more investigations upon it. Moreover, Cr^{3+} ions are high-efficiency activator that discussed frequently in optical materials. When dissolved in glass matrices, it could also act as a paramagnetic ion, applying strong effects on the optical transmission and insulating strength of the glass materials, in spite of in a very low content [17]. This phenomenon is due to the co-existence of various chromic oxides (oxidation states), wherein Cr^{3+} serves as a modifier, and Cr^{6+} in the form of $CrO_4{}^{2-}$ structural units would act as the glass network [18, 19]. In fact, the influence of Cr^{3+} ions on the optical properties of glasses varies with the matrix structure, since the different bonding environment around each Cr^{3+} ion would lead to great differences of site-to-site in the energy level structure, and thus the radiative and non-radiative transition probabilities of the Cr^{3+} ions throughout glasses. From above, it is easy to understand that besides the introduction of Cr^{3+} ion, the composition of glass matrix is of equal importance for the improvement of optical and luminescence properties. Therefore, exploring a novel Cr^{3+}-doped MASB glass system and achieving comprehensive performances of high thermal stability and excellent optical properties are necessary.

* Corresponding authors.
E-mail addresses: liutaoyong141@csu.edu.cn (T. Liu), axlu@mail.csu.edu.cn (A. Lu).

https://doi.org/10.1016/j.jnoncrysol.2018.08.004
Received 21 June 2018; Received in revised form 3 August 2018; Accepted 3 August 2018

Table 1
Chemical compositions of MASBC glasses, wherein the glasses are numbered as C0-C4 based on Cr_2O_3 content.

Sample	Glass composition (mol %)				
	MgO	SiO_2	B_2O_3	Al_2O_3	Cr_2O_3
C0	20	57	3	20	0
C1	20	57	3	19.9	0.1
C2	20	57	3	19.75	0.25
C3	20	57	3	19.5	0.5
C4	20	57	3	19	1.0

Here, we employ the Cr_2O_3 as Cr^{3+} source, and synthesize series of Cr_2O_3 doped 20MgO-(20-x)Al_2O_3-57SiO_2-3B_2O_3-$x$$Cr_2O_3$ (MASBC) glasses ($x = 0$ to 1 mol%) through conventional melt-quenching method. The aim of this work is to study the effects of Cr^{3+} incorporation and Cr^{3+} content on the structure, thermal and optical properties of MASBC glass system in detail, trying to replenish the basic researches of glasses, at the same time, providing beneficial guidance for developing silicon solar cells and tunable solid laser for industrial applications.

2. Experimental procedure

2.1. Glass preparation

20MgO-(20-x)Al_2O_3-57SiO_2-3B_2O_3-$x$$Cr_2O_3$ (x = 0, 0.1, 0.25, 0.5, 1 mol%) glasses, were prepared by conventional melt-quenching method, using platinum crucibles, at 1650 °C for 2 h at a heating rate of 5 °C/min, in atmospheric air. Specifically, the MgO, SiO_2, H_3BO_3, Al_2O_3, Cr_2O_3, used as starting materials, corresponding to the stoichiometric compositions of MASBC glasses (Table 1) were added. The homogeneous melt was poured onto a preheated stainless-steel plate, and subsequently transferred into a pre-heated muffle furnace (680 °C for 2 h) for annealing operation to remove residual internal stress. After that, the synthesized glass was cut into the desired dimension, and then was optically polished to obtain flat sample surface for test requirement.

2.2. Analytical methods

To determine the glass transition temperature (T_g) and crystallization temperature (T_c) of the parent glasses, the obtained powdered samples were subject to the differential scanning calorimetry (DSC, Netzsch 404PC, Germany) measurement (in air), with a scanning range of 30–1200 °C and a heating rate of 10 K/min. After that, their bulk density (*BD*) was calculated based on the Archimedean method using distilled water as medium, here, at least six tests for each sample were done for obtaining relatively reliable *BD* value. For the characterization of phase structure, X-ray diffraction experiments (XRD, D/max 2500, Japan) with a copper (Cu) *Kα* radiation ($\lambda = 1.5406$ Å) was conducted at room temperature. The infrared spectra in the range of 400–2000 cm^{-1} for powder samples were recorded using Fourier transform infrared spectrophotometer (FTIR, Nicolet 6700, USA). The transmittance spectra of the parent glass were measured by UV spectrophotometer (HITACHI U-4100, Japan) within a wavelength range of 200–800 nm. Before measurement, all glass samples (20 × 20 × 1 mm) were polished (using sandpaper in 2000 mesh), followed by cleaned in an ultrasonic bath, using ethanol solution for 2 min. The electron paramagnetic resonance (EPR) spectra were recorded for powdered glass samples (200 mesh sieve) using EPR spectrometer (BRUKER, A300, Germany) operating at X-band (9.7866 GHz) with a modulation frequency of 100 kHz at room temperature. Fluorescence excitation and emission spectra, luminescence lifetime were recorded on a high-resolution spectrofluorometer (FLS 1000, Edingburgh Instruments, UK), which is equipped with a NIR-region photomultiplier (800–1700 nm, R5509–72), a pulsed xenon flash lamp with an average power of 450 W was used as excitation source.

3. Result and discussion

3.1. DSC curves and physical properties

Here, we have synthesized four MASBC glass samples with various Cr_2O_3 content (C0-C4). As shown in Fig. 1a, the phase structure of as-synthesized various MASBC glasses doped with Cr_2O_3 can be identified. It is found that all patterns reveals broad humps without any crystalline peaks, which indicates the glasses are X-ray amorphous in nature. Therefore, we have succeeded in preparing amorphous MASBC glasses. Fig. 1b presents the DSC curves for all glass samples, in which, the upward peak corresponds to an endothermic process while downward peak is associated with an exothermic process. From which, series of thermal parameters like glass transition temperature (T_g), onset crystallization temperature (T_{onset}) and crystallization temperature (T_c) can be obtained (Table 2). Clearly, all curves display two peaks belonging to endothermic and exothermic peak, respectively, and give a slight

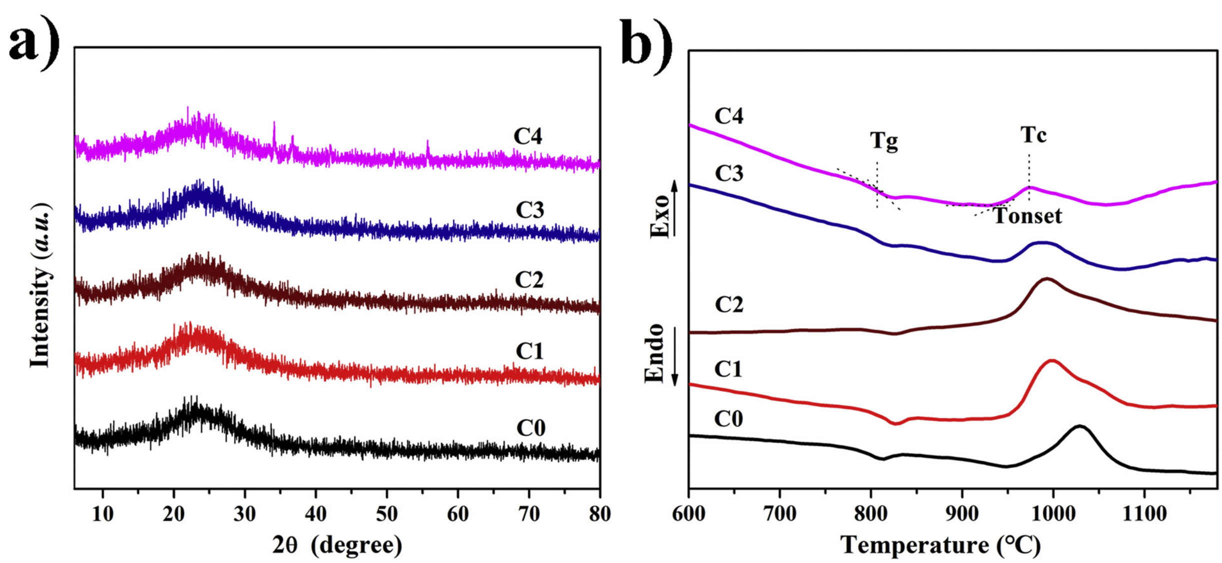

Fig. 1. (a) XRD patterns of MASBC glasses with various Cr_2O_3; (b) DSC curves for MASBC glass samples treated at a continuous heating rate of 10 K/min.