



Effects of B_2O_3 content variation on the Bi ions in Bi_2O_3 – B_2O_3 – SiO_2 glass structure



Xiaomeng Zhu, Chengle Mai, Mingyu Li*

School of Materials Science and Engineering, Harbin Institute of Technology, Shenzhen Graduate School, China

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ABSTRACT

The Bi-based lead-free frit for silicon solar cell front contact has a shortage of conversion efficiency compared with traditional products that contain Pb. One feasible method to increase conversion efficiency is by improving the current flow at the interface. The current flow establishment is controlled by the reaction of Bi ions to Ag, SiNx, and the Si wafer. However, the microstructure of Bi ions in the glasses remains unclear. In this work, two groups of Bi_2O_3 – B_2O_3 – SiO_2 glasses were studied through differential scanning calorimetry (DSC), X-ray diffraction (XRD), infrared, and Raman and X-ray photoelectron spectroscopies. The results suggest that the Bi^{3+} to Bi^{5+} transformation is induced by the increase in B_2O_3 content in both the 30 mol% and 60 mol% Bi glasses. The coexistence of $[BiO_3]$ and $[BiO_6]$ is confirmed in all ternary samples. The $[BO_4]$ units exhibit in all borosilicate glass. The $[BO_3]$ structure only emerges in a high boron concentration. The glass transition temperature (T_g) is strongly affected by the ratio of Non-Bridging Oxygen. The Oxygen packing density also has influence on T_g but not obvious.

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1. Introduction

The increasing appeal of environmental concerns promotes studies on Bi-based glasses to replace the Pb containing products. Attempts to substitute Pb with Bi for the silicon solar cell front contact have been booming in both the industry and academia [1–8]. In silicon solar cell front contact, the Pb or Bi glasses establish the current flow from the n+ emitter to Ag electrodes by performing three functions: (i) etch SiNx coating; (ii) form ohmic contact between Ag electrodes and (iii) provide mechanical strength of electrodes.

Lower conversion efficiency is the main drawback of the Bi-based frit compared with Pb products, in both screen print and seed layer techniques. To raise the efficiency, the reaction of Bi ions in the front contact formation and the current path at the interface became primary considerations. Previous studies suggested two current transport paths, including direct silver–silicon interconnections and the multi-step tunneling process, in the glass layer because of the silver recrystallites [4,8]. These two mechanisms are greatly influenced by the reactions of the Bi ions to Ag, SiNx, and the Si wafer as revealed by Kim et al. [3]. Therefore, the network structure and the valence state of bismuth ions before sintering are worth addressing an investigation as these ions participate in the reactions of the current flow formation.

At present, the Pb-free glass frits are shown to be based on the Bi_2O_3 – B_2O_3 – SiO_2 ternary system with additives such as ZnO and Al_2O_3 [3,4,6–8]. Studies on Bi_2O_3 – B_2O_3 – SiO_2 ternary glasses are abundant;

however, the atomic scale structure understanding of Bi-based glasses remains controversial. One possible reason for this issue is the sensitivity of the Bi ions in the network with glass composition variation. For instance, Bi^{3+} ions act as the modifier in the network structure in the Bi_2O_3 – B_2O_3 glass when Bi_2O_3 content is over 45 mol% [9], and the emerging $[BiO_6]$ structure for a high Bi_2O_3 content plays the same role in glass [10]. Another possible reason for the confusion is the closeness or overlap of the IR and Raman spectra of the Si–O in the glass network with that of the Bi–O and B–O units.

This study was conducted to verify the Bi ion microstructure with a wide range of B_2O_3 and SiO_2 contents. The content of Bi_2O_3 in the frit at about 30 and 60 mol% was reported [3,7]; thus, samples were prepared in two groups based on the Bi_2O_3 contents. The Bi_2O_3 – B_2O_3 and Bi_2O_3 – SiO_2 binary glasses are introduced to each group for comparison. IR spectra, Raman spectra, and XPS were used to analyze the glass microstructures. The glass transition temperature (T_g) of glass is an important factor for fast sintering both in screen print and seed layering process, so DSC was conducted to characterize the thermal properties [1].

2. Experimental

2.1. Sample preparation

The nomenclature of all the samples in this work is in the form of xBi_yB , where x and y are the mole ratios of Bi_2O_3 and B_2O_3 , respectively, and the rest is SiO_2 . The samples were divided into two groups: Group A with samples of 30Bi_yB ($0 \leq y \leq 70$) and Group B with 60Bi_yB ($0 \leq y \leq 40$) samples. All of the glasses were fabricated through the conventional melt-quenching method. Raw materials were sourced from

* Corresponding author at: Room 406B, D Buld., HIT Campus, Shenzhen University Town (518055), China.

E-mail address: myli@hit.edu.cn (M. Li).

Aladdin® with 99.99% Bi₂O₃, 99.9% B₂O₃, and 99.99% SiO₂ powder. Two stages of mixing (ultrasonic oscillations and manual grinding) were performed. Batches of 5 g powder mixture were loaded in the alumina crucible and heated up to 1300 °C at a heating rate of 5 °C/min in a muffle furnace (CARBOLITE® HTF1700). The temperature was maintained for 20 min then the melts were directly poured into deionized water. The products were manually ground into powders in agate mortar.

2.2. Sample characterization

X-ray diffraction was performed prior to the FT-IR, Raman, and XPS measurements to confirm the non-crystal nature of all samples. X-ray diffraction was performed in Rikagu D/Max 2500 at a scan rate of 4°/min. The samples were compressed into thin pellets using KBr for the infrared measurement. The infrared spectra were recorded using Nexus FT-IR at a range of 400 cm⁻¹ to 4000 cm⁻¹ at room temperature. The IR spectral resolution was set at 4 cm⁻¹. The Raman measurements were conducted using the Renishaw (InVia) spectrometer with a range of 100 cm⁻¹ to 3200 cm⁻¹ at room temperature. All samples were placed on glass slides for the spectral recording. The peaks in the Raman spectra were decomposed using Gaussian distribution. The XPS measurements were performed using a VG Escalab MK spectrometer, which provides an Mg-Kα X-ray at 1253.6 eV. The pressure inside the analyzer chamber was 2 Pa to 10⁻⁸ Pa. A C1s peak at 284.6 eV was used to calibrate the drift of the electron binding energy caused by the surface charge effect. The XPS spectra peaks were deconvoluted through Gaussian distribution with a Shirley deduction of the background. The density measurement was based on the Archimedes law with deionized water and the results were summarized in Table 1. The NETZSCH STA 449F3 was used for the DSC test. The heating rate was set at 5 K/min under the nitrogen atmosphere.

3. Results

3.1. IR spectra

3.1.1. Group A

The Group A IR spectra are shown in Fig. 1a. The 30 Bi ternary samples generally presented similar absorption bands with subtle changes. For the ternary samples, the bands at around 490 cm⁻¹ may be due to the combination of Bi vibration in [BiO₅] and the Si–O bend vibration, as summarized in Table 2. Absorptions within 696–710 cm⁻¹ ranges became significant with the increase of B contents, so they present not only the stretching vibrations of Bi–O bonds in [BiO₃] but also the

bending stretching in [BO₃]. All ternary samples exhibited bands in the range of 680 cm⁻¹ to 750 cm⁻¹, which may respond to the dual effect of Bi–O and [BO₃] bending. Strong absorption from 860 cm⁻¹ to 900 cm⁻¹ represents the Bi–O vibration in the [BiO₃] unit. The band in the 30Bi10B and 30Bi20B samples was 877 cm⁻¹, which was reduced to 870 cm⁻¹ in the 30Bi30B sample and increased to 883 cm⁻¹ in the 30Bi40B sample. Bands around 1000 cm⁻¹ shown in the 30 Bi ternary samples are caused by the superimposed effect of the B–O–B stretch vibration in [BO₄] and the Si–O–Si bending. The band ranges from 1200 cm⁻¹ to 1300 cm⁻¹ are attributed to B–O–B stretch vibration in [BO₃]. No noticeable absorption in this range was observed in the 30Bi10B sample, but in 30Bi30B and 30Bi40B samples the absorption was intense. The band ranging from 1310 cm⁻¹ to 1340 cm⁻¹ emerged in the 30Bi20B sample, and the intensity enhanced with the increase of the B₂O₃ content. This absorption is assigned to the [BO₃] unit vibration.

The 30Bi0B and 30Bi70B binary samples appeared individually in Fig. 1a. The 30Bi0B binary sample showed a band at 490 cm⁻¹ in the low wave number area, which shifted to about 510 cm⁻¹ in the 30Bi70B sample. This agrees with the fact that the bridging oxygen bending in the Si network has lower absorption wave numbers (440–470 cm⁻¹). The band of the 30Bi0B sample at 706 cm⁻¹ is attributed to the Bi–O bending, whereas the band of the 30Bi70B sample at 716 cm⁻¹ belongs to the B–O–B bending in the [BO₃] structure [11]. For the band in 860 cm⁻¹ to 900 cm⁻¹ range the binary samples showed scattered value of 873 cm⁻¹ in the 30Bi0B and 897 cm⁻¹ in the 30Bi70B samples. The variation suggests the effect of boron content to Bi–O vibration in the [BiO₃]. The absorption at 1001 cm⁻¹ and 1180 cm⁻¹ is caused by the S–O–Si bending as shown in the 30Bi0B binary sample [12].

3.1.2. Group B

In the Group B IR spectra, the ternary samples showed consistent trend. Owing to the high Bi content, all curves exhibited absorption at around 710 cm⁻¹ which belongs to Bi–O stretching vibrations. Between 800 cm⁻¹ and 1000 cm⁻¹ the ternary samples showed a shoulder with two bands at about 870 cm⁻¹ and at 970 cm⁻¹. The absorption intensity at about 870 cm⁻¹ was stronger than that at 970 cm⁻¹, but the situation in Group A was reversed. This is due to the higher Bi content in Group B that results in a stronger spectrum of [BiO₃].

In Group B the binary samples exhibited distinguishing features to ternary samples. In the range of 400 cm⁻¹ to 600 cm⁻¹, the 60Bi0B sample showed a band at 475 cm⁻¹ whereas the rest of the group barely presented bands. This band may be caused by the non-bridge oxygen vibration in the Si network. In the 60Bi40B sample, the band

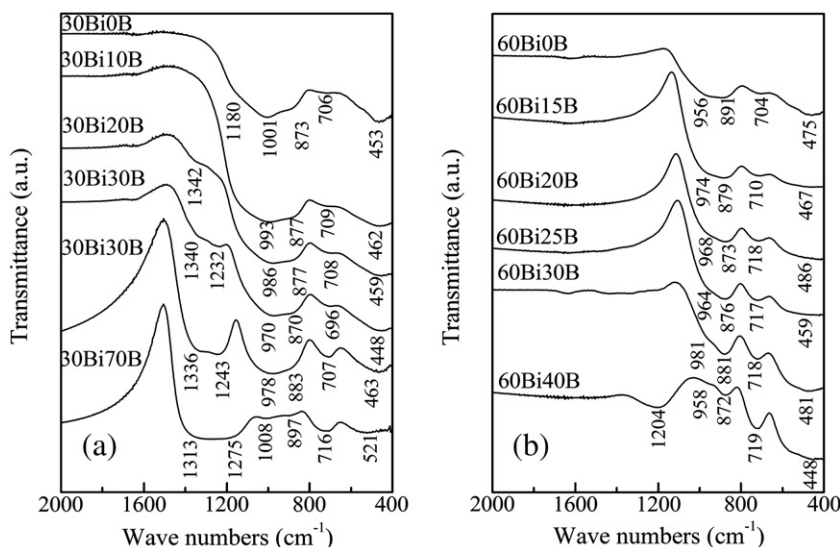


Fig. 1. The infrared spectra of (a) 30Bi and (b) 60Bi group.

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