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The effect of tin on sulfur K-edge X-ray absorption near edge structure spectra of soda–lime–silicate glass: An experimental and comparative study

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ABSTRACT

Considering the strong sensitivity of X-ray absorption near edge structure (XANES) spectra to the oxidation state and local environment, the sulfur K-edge XANES spectra of series of samples, including a typical float glass product, starting soda–lime–silicate glass samples and the SnO_2-bearing glass samples heat-treated at different temperature and durations under the reduced atmosphere of N_2/H_2 (90/10 volume ratio), were systematically investigated in this paper. The gradual evolution of lower energy shoulder of series of samples in the region from 2468.8 eV to 2473.1 eV makes us assure that this shoulder should be related to the Sn—S local coordination of S^{2-} species. In addition, this Sn—S local coordination of S^{2-} species is stable at the temperature lower than 750 °C and it will gradually vanish with the enhancement of temperature. This understanding should be very helpful to the adjustment of parameters of float glass process.

1. Introduction

In the float process, the molten glass is poured onto the tin bath at about 1050 °C, on which it thins to the equilibrium thickness and is further stretched to the required thickness. Subsequently, the flat glass is drawn to the lehr at about 600 °C. It was observed that the surface composition over a few tens of micrometers on both air and tin sides of float glass are different compared with the bulk glass [1,2]. In addition, the oxidation state for Sn, Fe and S was also found varying in the surface layer [3–8]. Among them, the effect of sulfur in the glass melt has pros and cons. On one hand, sulfate is often added to the soda–lime float glass batch as fining agent to accelerate the bubbles leaving from the melt. On the other hand, when the melt enters the tin bath with reducing atmosphere, the sulfate is reduced. Some of which may combine with stannum, causing tin loss and glass defects, such as top speck [3–8]. Therefore, a clear understanding of sulfur species in the float process is very important to the glass defect reduction.

It is well known that sulfur K-edge XANES (X-ray absorption near edge structure) spectra are strongly sensitive to the oxidation state and coordination chemistry of sulfur, and often used as a powerful tool for sulfur species identification [8,9]. With sulfur K-edge XANES, the behavior of sulfur in melts and minerals is found complicated due to its wide range in oxidation sate and chemical affinity, with speciation changing primarily as a function of composition and fugacity of oxygen and sulfur [10]. Sulfur behaves as sulfide (S^{2-}), bonding with metal cation when in equilibrium with reduced systems, whereas it dissolves in glass melts as sulfate (S^{6+}) when in equilibrium with oxidized systems. However, sulfite (S^{4+}) was not found in the silicate glass [9], yet.

Despite the knowledge above, it is not clear about the characteristic of sulfur in the non-equilibrium condition, especially in the float process — the effect of tin to sulfur. Tin sulfide is found in the tin dross and some tin defects; however, no proof directly demonstrates the reaction of Sn and S in glass. Therefore, it is interesting to determine whether or not there is Sn—S bonding in glass, and to investigate the role of the Sn—S bonding. Although the interpretation of XANES spectra of glass is limited by the absence of suitable reference sample [12], the major difference of the air side and tin side of glass is the contact medium, so it is possible to compare the difference of XANES spectra on both sides of glass to study the influence of between the molten tin and the reduced atmosphere to sulfur.

In the present work, we try to reveal the effect of tin on sulfur K-edge XANES spectra of soda–lime–silicate glass. Under the condition of reduced atmosphere, the starting soda–lime–silicate glass together with the ones with various SnO_2 content was heat-treated at different temperatures for various durations. Based on the sulfur K-edge XANES spectra of various samples, we try to verify whether the tin is coordinated with the S^{2-} in glass.

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Table 1
The composition of starting soda–lime–silicate glass from XRF analyses (wt.%).

Composition	SiO_2	Fe_2O_3[a]	Al_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	Cl	Ignition loss
	71.46	0.15	0.88	8.64	3.87	0.27	13.85	0.19	0.041	0.46

[a] All iron reported as Fe_2O_3. The measured glass is powder (less than 200 mesh). Uncertainties are within ±4% of the values reported.

2. Experimental

2.1. Glass samples preparation

2.1.1. Starting soda–lime–silicate glass

The industrial glass batch from Luoyang Glass Company was mixed and melted at 1480 °C in air for 2 h in an electric furnace. Then the homogeneous glass melt was poured on a pre-heated iron plate and immediately annealed at 550 °C for 2 h in air. The obtained glass is named as starting glass. The composition of starting glass is shown in Table 1.

2.1.2. SnO_2-bearing glass

In order to evaluate the effect of tin on sulfur speciation, three samples with various SnO_2 content (0.05 wt.%, 0.2 wt.% and 1.0 wt.%) were prepared by remelting the starting glass (with a particle diameter less than 200 μm) with SnO_2.

2.1.3. Heat treatment process under the reduced atmosphere

The starting glass and SnO_2-bearing glass samples were cut and polished into a size of diameter with 10 mm and thickness with 10 mm. Then, as shown in Fig. 1, the sample was put into a graphite crucible (inside diameter is 11 mm) with 25 g Tin (99.9%) in a quartz tube, and heat-treated at different temperatures for various durations under the reduced atmosphere of N_2/H_2 (90/10 volume ratio). After that, the samples were quenched by moving out the tube from the furnace. The gas-flow was on for the whole process.

2.2. Analytical technique

The samples for XANES spectra were cut to 15 mm × 10 mm × 1 mm by using a diamond saw and a polishing machine. The XANES spectra were collected in fluorescence mode using Si (111) double-crystal monochromators at Beijing Synchrotron Radiation Facility (BSRF). The maximum sampling depths are estimated to be 1000–2000 Å [10,13,14]. The storage ring of BSRF operates at 2.5 GeV with an average stored current of 80 mA. Each spectrum was collected from 2450 eV to 2500 eV with a 0.5 eV step width. The XANES spectra were baseline corrected and normalized using the Athena program of the IFEFFIT package.

3. Results

The sulfur K-edge XANES spectra on both sides of a typical float glass (Luoyang Glass Company, Luoyang, China) are shown in Fig. 2.

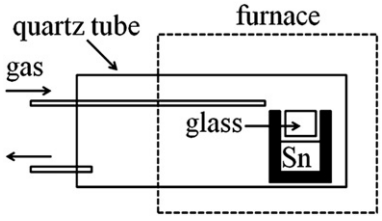

Fig. 1. Schematic diagram of the experimental set-up for heat-treatment under the reduced condition.

In terms of its contour, the sulfur is considered mainly in the form of S^{6+} (2482.4 eV). In addition, two weak peaks associated with sulfide were observed at the lower energy position for both curves [11]: a broader peak at about 2476.3 eV together with a sharper one with an accurate position at 2473.7 eV corresponding to preferential excitation of sulfide in glass (denoted as the S^{2-} for convenience). It is worthy to notice that a weak shoulder peak between 2468.8 eV and 2473.1 eV appears accompanying with the existence of S^{2-} on the tin side while a weak pre-edge occurs at 2466.8 eV on the air side. Even though the assignment of them is still pending, it is certain that the pre-edge is not related to tin [11].

In order to understand the accurate origin of the weak shoulder peak, the XANES spectra on the tin side of glass samples heat-treated at different temperatures (750 °C, 850 °C, 950 °C, 1050 °C) for 30 min in the experimental set-up (Fig. 1) are shown in Fig. 3. With the enhancement of temperature, the peaks corresponding to S^{2-} become sharper and the intensity of the shoulder located at the lower energy decreases until it almost disappears at 1050 °C.

To further understand the evolution of XANES spectra, we chose 750 °C (the temperature at which the intensity of shoulder peak is the highest) and 1050 °C (the temperature at which glass melt starts to enter tin bath) to further characterize the effect of duration on XANES spectra. As shown in Fig. 4, the intensity of the shoulder of the tin side increases with the elongation of duration at 750 °C. However, when it comes to 1050 °C, the shoulder only appears for 20 min in the tin side and disappears with the further increase of duration. It is suggested that the shoulder located at lower energy could be related with the tin and disappear at high temperature for long-duration.

Finally, we further prepared a series of SnO_2-bearing glass samples, which were also heat-treated at 750 °C and 1050 °C for 30 min under the reduced atmosphere of N_2/H_2. As is expected, the shoulder at lower energy shown in Fig. 5 comes out on both sides for the SnO_2-bearing glass when heat treated at 750 °C. In addition, when it comes to 1050 °C, with the prolonged duration, the intensity of the shoulder on both sides becomes weak, clearly giving us the relationship of this shoulder at lower energy with the Sn content in glass and the heat treatment temperature.

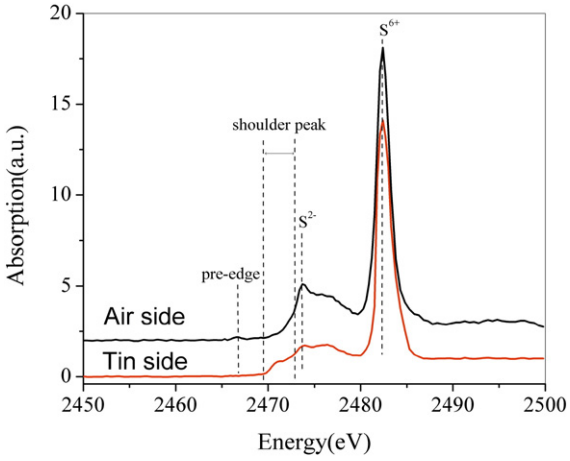

Fig. 2. Sulfur K-edge XANES spectra on the air side and the tin side of a typical float glass prepared by Luoyang Glass Company.