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Redox Behavior of Sn and S in Alkaline Earth Borosilicate Glass Melts with 1 mol% Na_2O

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ABSTRACT

Redox investigation of Sn and S ion was attempted in alkaline earth borosilicate glass melts with only 1 mol% Na_2O by means of Square Wave Voltammetry (SWV). According to voltammograms, there was only one peak due to Sn^{4+}/Sn^{2+} in melt doped with SnO_2. The calculated standard enthalpy and entropy of the reduction of Sn^{4+} to Sn^{2+} were 116kJ/mole and 62 J/mol K, respectively. The determined redox ratio, $[Sn^{2+}]/[Sn^{4+}]$ in the temperature range of 1300~1600°C was in 0.4~2.1. On the contrary, in the voltammogram of melt doped with $BaSO_4$ there was no peak due to S^{4+}/S^{o} but shoulder that might be attributed to the adsorption of sulfur at the electrode. The absence of the peak related with S^{4+}/S^{o} was discussed from the view-point of the thermal decomposition behavior of $BaSO_4$ in the glass batch.

Key words : Multivalent ion, Redox equilibrium, Alkaline earth borosilicate glass melts, Square wave voltammetry

1. Introduction

Chemical fining in glass melts is operated by oxygen gas released or reabsorbed following the redox reaction (1) of such polyvalent elements M. Here, n is the number of electrons transferred from one valence state of M to another.

$$M^{(x+n)+} + \frac{n}{2}O^{2-} = M^{x+} + \frac{n}{4}O_2 \quad (1)$$

In the last two decades, there have been many studies [1-10] in relation to the electrochemical approach for redox behavior of polyvalent ions in glass melts, and it seems to be the dominant opinion that the Square Wave Voltammetry (SWV) is theis a most optimal technique to trace polyvalent ions in glass melts. In the SWV measurement, if the applied potential is enough to allow electron donation or acceptance between redox species as described in reaction (1), the resulting current-potential curve or voltammogram reveals a characteristic peak at one potential (E_p). The equilibrium constant K(T) at temperature T described using concentration of redox pair ($[M^{x+}]$ and $[M^{(x+n)+}]$) and oxygen equilibrium pressure (P_{O2}) can be expressed in terms of peak potential, E_p, as shown in Equation (2).

$$K(T) = \frac{[M^{x+}] \bullet P_{O2}^{\,n/4}}{[M^{(x+n)+}]} = exp\left[\frac{n \cdot F \cdot E_p}{R_g \cdot T}\right] \quad (2)$$

Here, n is the number of electrons transferred, F is faraday constant and R_g is gas constant. K(T) is also correlated with the standard free enthalpy (ΔG^0), the standard enthalpy (ΔH^0) and the standard entropy (ΔS^0) by the following relationship.

$$-R_g T \ln K(T) = \Delta G^0(T) = \Delta H^0 - T\Delta S^0 = -nFE_p \quad (3)$$

Arsenic oxide (As_2O_5) is the most frequently used chemical fining agent in the borosilicate glass industry. Recently, tin oxide (SnO_2) has been focused as the new fining agent that can replace toxic As_2O_5.[11] It is well known that S contributes to the fining of alkali silicate melts and is normally introduced to glass batches as a sulfate form.[12,13] Many studies concerning redox behaviors of Sn and S in various silicate melts have been performed in situ in the molten state by Square-Wave Voltammetry (SWV) and they offered a lot of thermodynamic, related to the reaction (1). Nevertheless, for the melts with alkali free alkaline earth borosilicate glass compositions consisting of multi-components, there have been only one voltammetric study on polyvalent ions.[21] Alkali free alkaline earth borosilicate systems are of great importance for the production of substrate glasses as a part of the TFT-LCD device. In the present work voltammetric measurements for Sn and S multivalent ion were performed in alkaline earth borosilicate glass melts with 1 mol% Na_2O.

2. Experimental Procedure

The original glass composition was alkali free and in mol% $67.2SiO_2 \cdot 10.5Al_2O_3 \cdot 7.3B_2O_3 \cdot 5.4MgO \cdot 4.6CaO \cdot 5SrO$. But, the blank melts were prepared by modifying the composition, namely by replacing 1 mol% SiO_2 by Na_2O because the melts must have enough electrical conduction in order to perform

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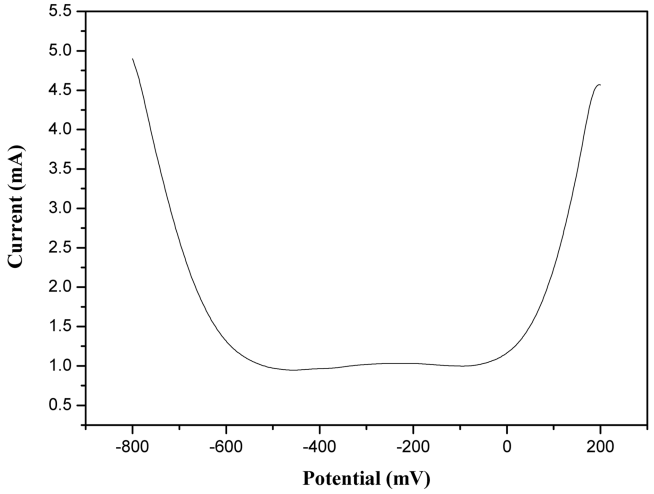

Fig. 1. Voltammogram recorded in alkaline earth borosilicate glass melts without multivalent ions at 1400°C.

voltammetry measurement. Melt doped with Sn or S was also prepared from high purity chemicals. Sn and S were supplied from SnO_2 and $BaSO_4$, respectively. The glass batches of about 300 g were melted at 1700°C in an electric furnace and the homogenized bubble free melts were prepared by stirring the Pt/Rh rod. The electrochemical cell for SWV measurement consisted of three electrodes immersed into a melt of Pt/Rh crucible while the potentiostat (Model 273A, EG&G, USA) connected to the computer. The detailed description of the cell construction is shown in other study.[22]

During the SWV measurement at a given temperature the furnace was switched off to avoid disturbance of the measured signal by the current of the heating elements. SWV measurements in the present work were performed under the applied potential range of +200~−800 mV at 50 Hz. The final voltammogram of each melt at a temperature ranging from 1600 to 1300°C was obtained by subtracting that of the blank melt without multivalent elements from the original recorded voltammogram with a multivalent element. The final voltammogram was analyzed with the aid of a commercial software.

3. Results and discussion

Fig. 1 shows voltammograms recorded at 1400°C in blank melt without multivalent elements. The potential range that can be scanned using SWV has an anodic and cathodic limit for the following reasons[3]: 1) at positive potentials the current increases due to the oxidation of the silicate network and hence it results in the formation of O_2, and 2) at potentials less than −800 mV, the current increases due to the reduction of the silicon ions resulting in the formation of a silicon element.

Fig. 2 shows voltammograms at three different temperatures, (1300, 1400 and 1500°C) recorded in melts doped with (a) $0.4SnO_2$ (b) $0.4SO_3$. In Fig. 2(a), one peak is shown clearly at high temperature and its corresponding peak

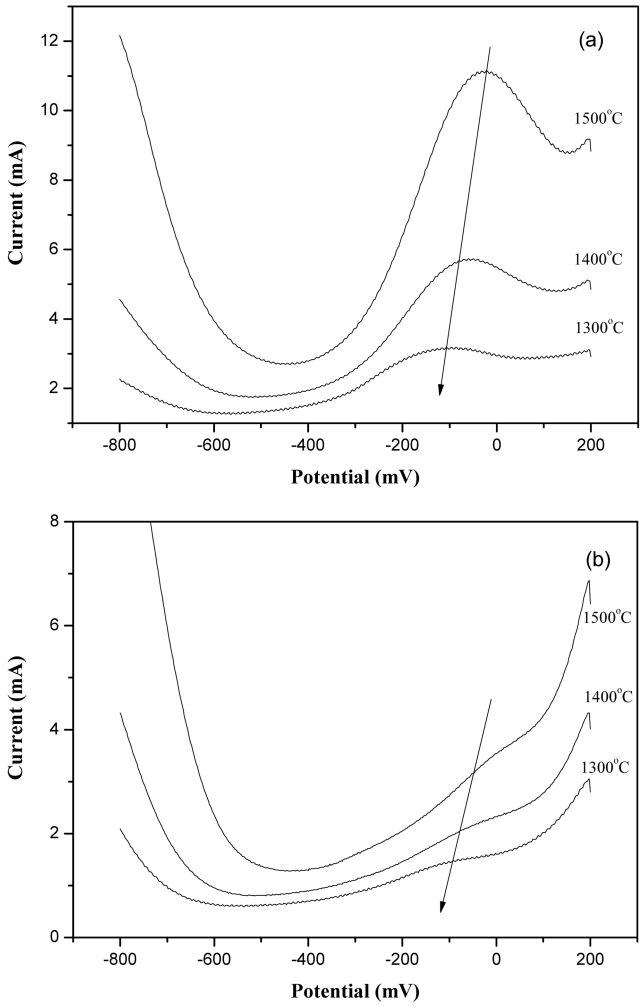

Fig. 2. Voltammograms recorded in alkaline earth borosilicate glass melts doped with (a) Sn and (b) S.

potential (E_p), for example −6 mV at 1500°C moves toward a negative direction when the temperature decreased as marked by an arrow. This indicates that the equilibrium state of reaction (1) shifts to the left, namely to the oxidation state. This peak is attributed to the reduction of Sn^{4+} to Sn^{2+} (expressed as Sn^{4+}/Sn^{2+}).[16] The peak occurrence and its behavior for Sn^{4+}/Sn^{2+} in the present melt are similar to those of other silicates melts.[14-16,21] However, unlike previous studies[14,15,21] the peak due to Sn^{2+}/Sn^0 is not observed. Thus, there is no possibility for the occurrence of metallic tin in the present melt. In the case of SO_3 in Fig. 2(b), only one shoulder instead of normal peak is observed in the potential range of −100~−50 mV.

In general it has been known that two peaks take place in voltammogram of sulfate melts. Some works[17,18] reported that one peak at negative potential (called peak B) was due to S^{4+}/S^o and the other peak at more negative potential (called peak A) was due to S^0/S^{2-}. However, recent several voltammetric studies[9,19,20] elucidated that the peak A is due to S^{4+}/S^o and the peak B comes from the adsorption of sulfur at the working electrode.[9] The shoulder position shown in Fig. 2(b)

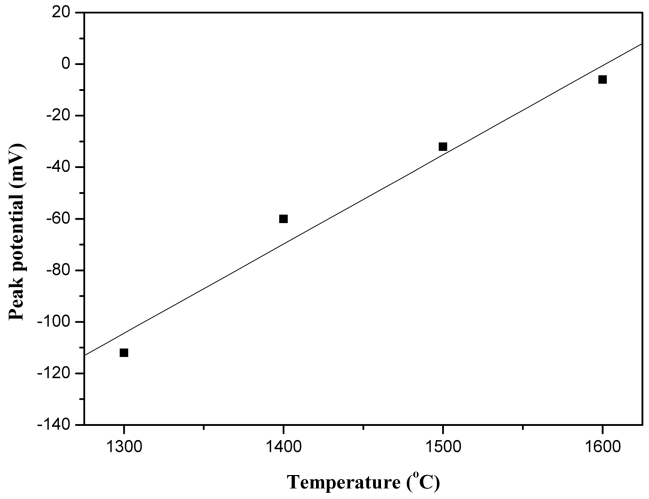

Fig. 3. Experimental plots of peak potential (Ep) for Sn4+/ Sn2+ as a function of temperature.

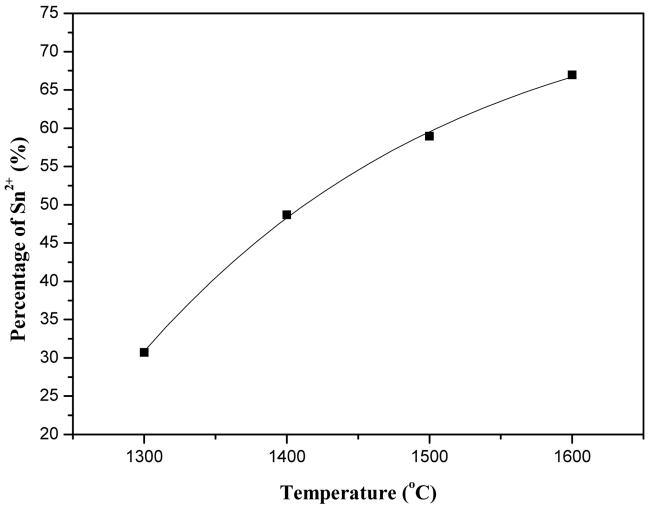

Fig. 4. Percentage of Sn2+ as a function of temperature in alkaline earth borosilicate glass melt.

is located in the similar potential range to that of the peak B. Therefore, the shoulder must be a trace of sulfur adsorption. On the contrary, the absence of the peak A related with S^{4+}/S^{o} in the present melt can be explained by the decomposition behavior of $BaSO_4$ in glass batch. During heating the sulfate ion of $BaSO_4$ undergoes theoretically the following reduction of S^{6+} to S^{4+} by the generation of SO_2 and O_2.

$$SO_4^{2-}(melt, S^{6+}) \rightarrow SO_2(gas, S^{4+}) + \frac{1}{2}O_2(gas) + O^{2-}(melt)$$

The decomposition of $BaSO_4$ alone takes place in about 1400~1500°C. However, when $BaSO_4$ is heated with another component in a glass batch, the rapid evolution of SO_2 can occur and be completed around 1000°C[23] where the melts resulting from chemical reaction of the present alkali free batches consist of liquid and various crystalline phase. This shows they are not viscous enough to permit the dissolution of SO_2. Therefore most of SO_2 gas would disappear in the atmosphere before it takes part in the first fining. This results in a low SO_3^{-2} (S^{4+}) concentration in the melt and an absence of the peak A corresponding to S^{4+}/S^{0}. From these results, it is concluded that $BaSO_4$ is not a proper fining agent for alkaline earth borosilicate glass melts.

Based on the results of Fig. 2(a), E_p is plotted as a function of temperature. In Fig. 3 the temperature dependence of E_p shows a good linearity. The determined standard enthalpy (ΔH^0) and entropy (ΔS^0) for the reaction, $Sn^{4+}+O^{2-} \rightarrow Sn^{2+}+1/2O_2$ were 116 kJ/mole and 62J/mol K, respectively. The redox ratio of tin, $[Sn^{2+}]/[Sn^{4+}]$ in glass melts was calculated using the Equation (2) under the assumption that the melt is equilibrated with air (P_{O2}=0.21 bar). Fig. 4 shows the percentage distribution of Sn^{2+} for the present melt in the temperature range of 1300~1600°C. The percentage of tin in the Sn^{2+} state varies from 30% at 1300°C to 68% at 1600°C. The converted value to redox ratio, $[Sn^{2+}]/[Sn^{4+}]$ lies in 0.4 ~ 2.1 and is similar to those of other silicate melts.[16,21]

4. Summary

Redox behavior of Sn and S ion in alkaline earth borosilicate glass melts with composition of $67.2SiO_2 \cdot 10.5Al_2O_3 \cdot 7.3B_2O_3 \cdot 5.4MgO \cdot 4.6CaO \cdot 5SrO \cdot 1Na_2O$ in mol% was studied with the aid of square wave voltammetry. In voltammograms with a temperature range of 1300 to 1600°C at 50 Hz, there was only one reduction peak due to Sn^{4+}/Sn^{2+} whose potential depends on temperature. Based on the temperature dependence of peak potential the thermodynamic properties for Sn^{4+}/Sn^{2+} were calculated and $[Sn^{2+}]/[Sn^{4+}]$ in glass melts was determined. However, in the case of sulfate doped melts there was no peak but shoulder in voltammogram. The absence of a peak for S^{4+}/S^{o} was explained by the low decomposition temperature of $BaSO_4$ in glass batch and it was concluded that the sulfate generated from $BaSO_4$ did not contribute to the fining of alkaline earth borosilicate glass melt.

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