Journal of the Korean Ceramic Society
Vol. 44, No. 8, pp. 419~423, 2007.

Behavior of Oxygen Equilibrium Pressure in CRT Glass Melts doped with Sb and Ce ions from the Viewpoint of Fining

Ki-Dong Kim,† Hyo-Kwang Kim, and Jun-Hong Kim

Department of Materials Science and Engineering, Kunsan National University, Kunsan 573-701, Korea
(Received August 6, 2007; Accepted August 24, 2007)

ABSTRACT

The behavior of oxygen gas participating in fining was observed in CRT (Cathode Ray Tube) glass melts doped with Sb_2O_5 or CeO_2 by means of a yttria-stabilized zirconia (YSZ) electrode. The temperature dependence of the oxygen equilibrium pressure (P_{O2}) or the activity in both melts showed typical behavior corresponding to a theoretical redox reaction. In other words, the P_{O2} value of melts with CeO_2 was lower than that of melts with Sb_2O_5 above 1250°C. The result implies that Sb_2O_5 is more efficient as a fining agent compared to CeO_2. On the other hand, melts from a batch containing Sb_2O_5 and KNO_3 showed much higher P_{O2} values compared to melts without KNO_3 above 1350°C. It is suggested that the addition of KNO_3 to a CRT glass batch contributes partly to the first fining of the melts.

Key words **: *Fining, Oxygen Equilibrium pressure, Redox reaction***

1. Introduction

Raw materials used in the glass industry are mostly in the form of oxides, carbonates and nitrates. During the melting of these materials gases are released and generate a large amount of bubbles in the glass melts. These bubbles are nuisances in the optical and mechanical quality control of the final products.[1] Therefore, they have to be eliminated by what is known as a physicochemical fining process consisting of two stages.[2] The first stage of the fining involves the growth of bubbles, characterized by their buoyant rise and collapse at a high temperature, in the melter. The second stage, known as refining involves the shrinkage of bubbles and their dissolution into the melt in the refiner or the conditioner. In order to enhance the fining process chemical agents are commonly used.

The chemical fining is most important in the manufacture of CRT glasses consisting of mixed alkali-mixed alkaline earth-silica as the glasses as the component of a display device permit very few or no bubbles. Chemical fining by oxygen generation in the manufacture of CRT glass is completed by the redox reaction of polyvalent ion-including oxides, antimony oxides and cerium oxides. Among these oxides, antimony oxide is used as a traditional fining material and the main role of cerium oxide is to prevent solarization of the glass. Therefore cerium oxide serves as a fining agent to some extent in the glass melt as well as a preventive oxide against solarization in glass products. The following redox reactions theoretically occur during the fining process of melts by the generation or dissolution of oxygen.[3-5]

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

Here, M is a polyvalent ion such as Sb, or Ce and n is the number of electrons transferred from one valence state of M to another. Electrons are provided or occupied by oxygen during the reaction.

The redox behavior of antimony ions and cerium ions in melts has been studied qualitatively using square wave voltammetry[6] as well as quantitatively via the in-situ measurement of the oxygen equilibrium pressure[3,9-12] or with aid of a chemical analysis of polyvalent ion pairs in quenched glasses.[7,8] By square wave voltammetry it was found that the redox reaction of antimony in CRT glass melts consist of two steps: Sb^{5+}/Sb^{3+} and Sb^{3+}/Sb^0 depending on the temperature.[6] Krol et al.[8] investigated the equilibrium state of the Sb^{3+}/Sb_{total} in black & white CRT glass melts using a quenching method. Wondergem-de Best[3] showed that in black & white CRT glass melts the reduced state of cerium is favored at higher cerium contents. Kraemer[11] measured the oxygen partial pressure for color CRT glass melts containing polyvalent ions such as Sb or Ce. However, finding related to the Ce^{4+} concentration based on the oxygen partial pressure during the cooling of melts were controversial as data related to the temperature dependence was inconsistent with that of general fining theory. There have been few works in which the oxygen equilibrium pressure of both fining agents in color CRT glass melts is approached systematically from the viewpoint of melt fining. In particular, the glass batch in the CRT glass industry contains KNO_3 as an oxygen supplier to burn out organic materials included

†Corresponding author : Ki-Dong Kim
E-mail : kdkim@kunsan.ac.kr
Tel : +82-63-469-4737 Fax : +82-63-469-4731

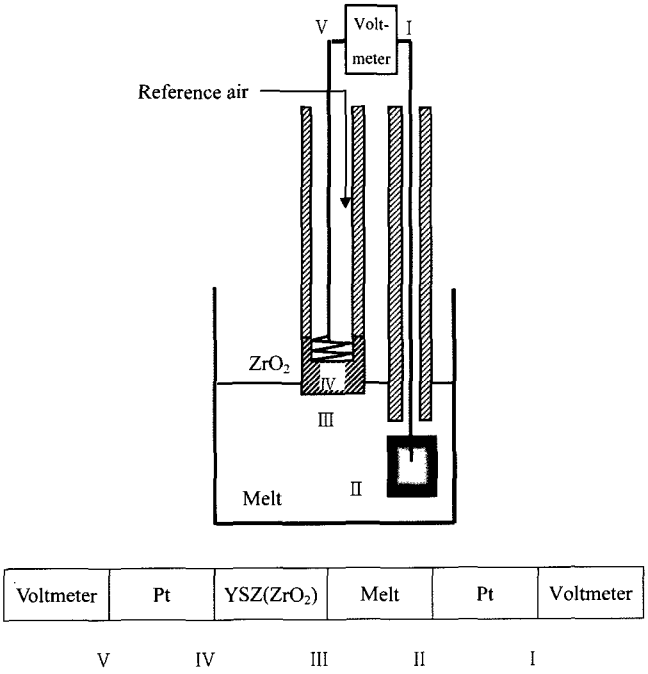

Fig. 1. Electrochemical cell for an oxygen equilibrium measurement and the connection state of electrodes.

in the batch. This oxidizing component can eventually influence the redox reaction of polyvalent ions; thus, related study is necessary in this area.

In the present work, electrochemical measurements were performed in a melt state using a zirconia solid electrode. The oxygen equilibrium pressure in the glass melts containing antimony oxide without KNO_3 and with KNO_3 or containing cerium oxide was determined at temperatures ranging from 1400 to 1000°C by the potential difference and its temperature dependence is discussed in terms of the redox reaction of each fining agent.

2. Experimental Procedure

2.1. Preparation of glass melts

The glass compositions in mol% were $73.7SiO_2$, $1.4Al_2O_3$, $9Na_2O$, $5K_2O$, 6SrO, 4BaO and $0.9ZrO_2$ in which SiO_2 was replaced by $0.07Sb_2O_5$ or $0.11CeO_2$. For the batches with KNO_3, corresponding amounts at 4 wt% and 2 wt% of the total glass batches containing Sb_2O_5 were added, here 0.81 mol% and 1.62 mol% of K_2O was supplied by KNO_3. High purity raw materials were used to exclude the effect of other polyvalent impurities such as Fe. Glass batches of approximately 300 g were melted at 1400°C in a Pt/Rh crucible for 60 min in an electric furnace and the melts were stirred using a Pt/Rh rod for 60 min so that they were homogenized. The Crucible with bubble-free homogeneous glass melts was transferred to another electric furnace to the conduct oxygen equilibrium pressure measurements.

2.2. Determination of oxygen equilibrium pressure

Fig. 1 shows a schematic presentation of an electrochemical cell whose essential parts include two electrodes that enable the measurement of the oxygen activity according to the potential difference. One Pt electrode termed a counter electrode was dipped into the glass melts and the other Pt electrode, here termed the reference electrode was connected to the O^{2-} conducting Y_2O_3-stabilized ZrO_2 (YSZ) material[13,14] which was in contact with the melts and was flushed by reference air with a known oxygen partial pressure (P_{rO2}) during the measurement procedure. If the oxygen equilibrium pressure (P_{O2}) in the glass melts differed from the oxygen partial pressure (P_{rO2}) of the reference air, a potential difference (ΔE_m) between both electrodes arises and then becomes the driving force of the redox reaction (1). ΔE_m is expressed as the following Nernst equation.

$$\Delta E_m = \frac{R_g \bullet T}{4F} In \frac{P_{O2}}{P_{rO2}} \quad (2)$$

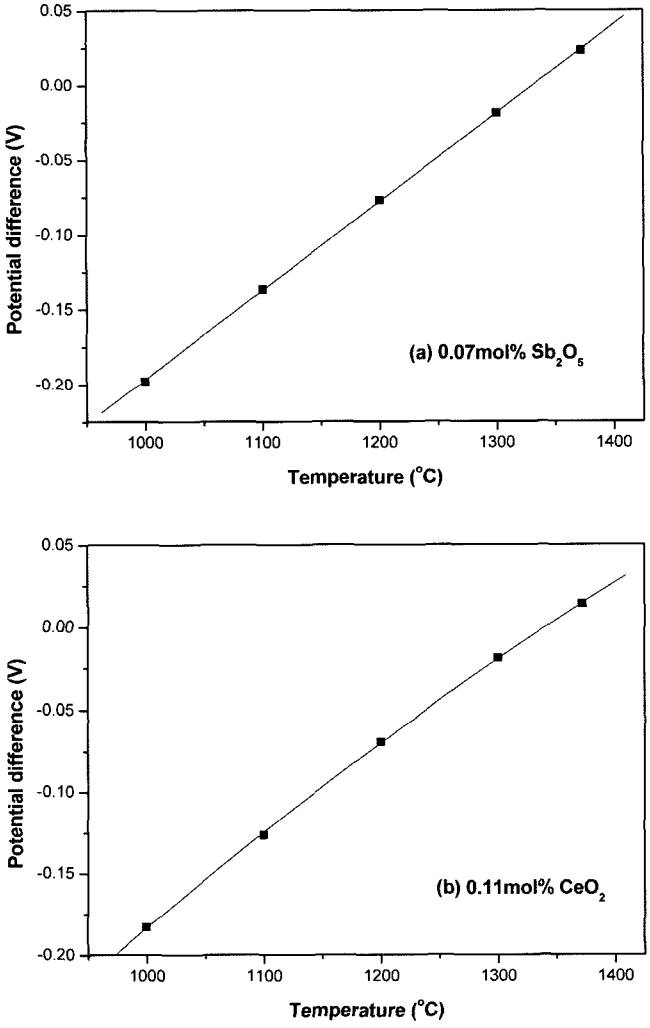

Fig. 2. Measured potential difference between the counter electrode and the reference electrode in CRT glass melts containing (a) 0.07 mol% Sb_2O_5 and (b) 0.11 mol% CeO_2.

Here, R_g is the gas constant and F is the faraday constant. A rearrangement of Eq. (2) result in Eq. (3), given below, and the oxygen equilibrium pressure (P_{O2}) in the glass melts at T is determined

$$P_{O2} = P_{rO2} \bullet exp\left[\frac{4 \cdot F \cdot \Delta E_m}{R_g \cdot T}\right] \quad (3)$$

Therefore, the oxygen equilibrium pressure in the melt can be calculated for a constant oxygen partial pressure (P_{O2}: 0.21 bar) of reference air if the potential difference is measured at T.

While the prepared glass melts were maintained at 1400°C in the furnace, the electrodes were dipped into the glass melts. The potential difference between both electrodes was measured continuously by a voltmeter (34401A, Agilent, USA) and then it was converted to the oxygen equilibrium pressure by using equation Eq. (3). In order to exclude the influence of the atmosphere on the oxygen equilibrium pressure in the melt,[11] an alumina lid was used as a crucible cap and N_2 gas was flushed into crucible during measurement.

3. Results and Discussion

Fig. 2 shows the dependence of the measured potential difference on the temperature for glass melts containing $0.07Sb_2O_5$ and $0.11CeO_2$. The curves follow a straight line. The calculated oxygen equilibrium pressure P_{O2} is presented as a function of the temperature in Fig. 3. P_{O2} in the measuring temperature range is lower than the atmosphere pressure, 1.013 bar. As in the present work the glass batch was melted at 1400°C and the resulting glass melt was even homogenized chemically via a stirring process, the first fining stage by the bubble growth, rise and collapse must finish according to the following redox reaction (4) and (5) during the melting process of the batch.

$$Sb^{5+} + O^{2-} \Leftrightarrow Sb^{3+} + 1/2O_2 \quad (4)$$

$$Ce^{4+} + 1/2O^{2-} \Leftrightarrow Ce^{3+} + 1/4O_2 \quad (5)$$

At the first fining stage, fining oxygen gases are generated by reduction from $Sb^{5+}(Ce^{4+})$ to $Sb^{3+}(Ce^{3+})$ and become a source of the oxygen partial pressure increment. The concentration gradient due to the oxygen partial pressure difference that exist in the bubbles and the melt causes newly evolved oxygen gases diffuse into the existing bubbles, which become larger and escape out of the glass melt. This explain why P_{O2} remains less than 1 bar up to 1400°C as shown in Fig. 3. However, although the concentration of CeO_2 is higher than that of Sb_2O_5, the P_{O2} value of the glass melts at 1400°C, 0.45 bar is much lower than the 0.65 bar value of the glass melts containing Sb_2O_5. This result reflects to some extent the amount of generated oxygen per mol of the fining agent when the above redox reaction (4) and (5) proceeds on the right hand side.[14] Hence, Sb_2O_5 would be more efficient as a fining compared to CeO_2.

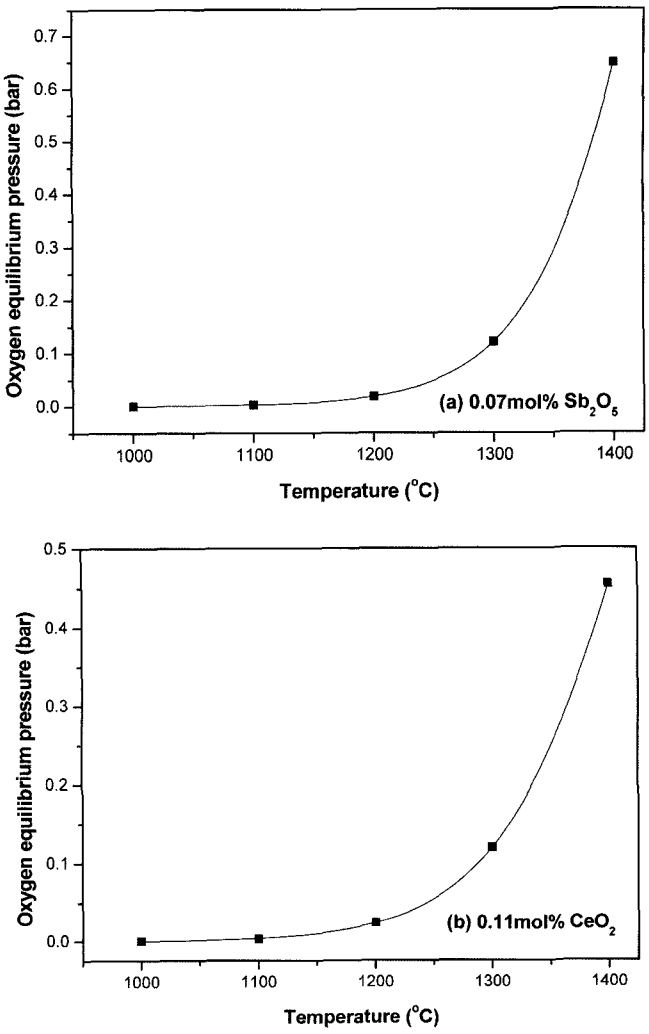

Fig. 3. The oxygen equilibrium pressure in CRT glass melts containing (a) 0.07 mol% Sb_2O_5 and (b) 0.11 mol% CeO_2.

As temperature decrease, as shown in Fig. 3 P_{O2} decreases and then approaches nearly zero at 1150-1200°C corresponding to the refiner temperature of the CRT glass melting tank furnace. Such P_{O2} behavior with the temperature decrease indicates that during the cooling of the glass melts the redox reaction proceeds preferably on the left hand side, that is to say, oxidation from $Sb^{3+}(Ce^{3+})$ to $Sb^{5+}(Ce^{4+})$ while the oxygen solubility into the melts increases. As this behavior is not likely to enlarge the existing bubbles, the second fining stage due to bubble shrinkage and dissolution is dominant in the course of cooling. In the second stage the physically dissolved oxygen gases are primarily converted to chemically dissolved free oxide ions ($O_2 \rightarrow O^{2-}$), resulting in complete dissolution into the melt followed by a then decrease in P_{O2}.

In Fig. 4 (a) and (b), P_{O2} values for glass melts whose batches contained both Sb_2O_5 and KNO_3 is presented as a function of the temperature. Compared with the oxygen

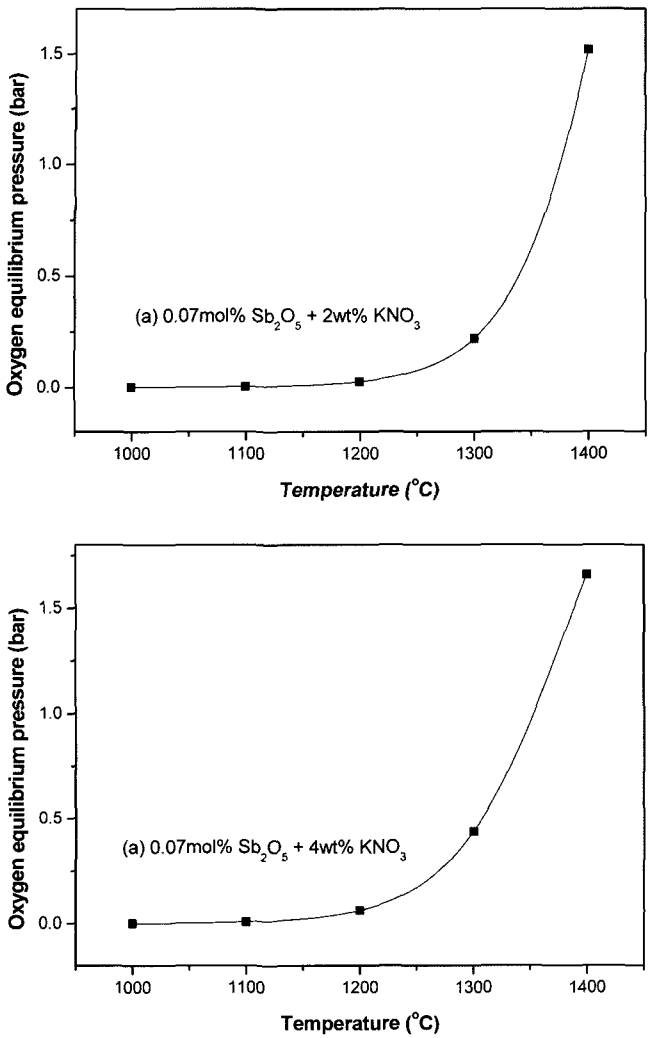

Fig. 4. Oxygen equilibrium pressure in CRT glass melts with (a) 2 wt% KNO_3 and (b) 4 wt% KNO_3 of glass batches containing 0.07 mol% Sb_2O_5.

equilibrium pressure of the glass melts with only Sb_2O_5 shown in Fig. 3 (a), the P_{O2} values of both glass melts in Fig. 4 is actually higher in the measured temperature range, especially at 1400 and 1300°C. Although the first fining of the melt was completed, P_{O2} is nearly 1.65 bar for 4 wt% KNO_3 and 1.5 bar for 2 wt% KNO_3 at 1400°C. However, these values would approach the atmosphere pressure under long-time maintenance at 1400°C, which is essentially the equilibrium condition. During the cooling of the melts P_{O2} decreases due to the oxidation of Sb^{3+} and due to the release of excessive oxygen that is over its solubility. Finally, P_{O2} approaches to the atmosphere pressure at approximately 1350°C and shows nearly similar behavior to the melts with only Sb_2O_5 at temperatures lower than 1200 °C.

In glass industry, nitrates such as like KNO_3 must be added to the batch in order to oxidize the antimony during the heating of the batch if antimony is introduced in a trivalent form (Sb_2O_3) into the glass batch [16]. Such a KNO_3 effect on Sb_2O_3 has been reported experimentally by measurement of the oxygen equilibrium pressure.[17] Antimony is oxidized from Sb^{+3} to Sb^{+5} at 600-700°C by oxygen generated from dissociation of KNO_3 (or $NaNO_3$). At temperatures higher than 1100°C, Sb^{+5} is reduced again to Sb^{+3} and this reduction generates oxygen by which the bubbles in melts are enlarged and removed as explained above. However, it was reported that in alkali lime silicate glass melts a fining via a single use of Sb_2O_5 was as efficient as the Sb_2O_3+nitrate combination.[18] In CRT glass industry antimony is introduced to glass batches in a pentavalent form (Sb^{5+}: Sb_2O_5). As an industrial batch is generally polluted with various types of carbonaceous materials such as plastics, papers or wood-chips, Sb^{+5} may be reduced by oxidation of those contaminants during the heating of the batch, which results in a decrease of the fining efficiency. Therefore, it is necessary to add a small amount of nitrate *(approximately 2 wt% of the total batch) to the batch in* order to oxidize these carbonaceous materials. In other words, for the Sb_2O_5+KNO_3 combination, KNO_3 plays the role of an oxygen supplier to oxidize carbonaceous contaminants as described in the following reactions (6) and (7) as antimony is originally introduced into the batch as a state of Sb^{+5}.

$$KNO_3 \rightarrow 1/2\ K_2O + 1/2N_2 + 5/4O_2\text{: reduction} \quad (6)$$

$$\text{Carbonaceous materials} + O_2 \rightarrow CO_2\text{: oxidation/combustion} \quad (7)$$

In the case of the present batch, the calculated oxygen volume generated by 2 wt% KNO_3(1.6 mol $KNO_3 \rightarrow$ 2 mol O_2) is approximately 28 times higher than of the 0.07 mol Sb_2O_5 (0.07 mol O_2). Given that the present glass batches are free from carbonaceous contaminants and because KNO_3 is dissociated at a low temperature, no combustion by oxidation occurs, and the total out-gassing of oxygen generated from KNO_3 can be expected during the melting of the batch. However, a comparison of the oxygen equilibrium pressure between Fig. 3(a) and Fig. 4 implies that some of the oxygen generated by the dissociation of KNO_3 at 600-700°C is dissolved in the melts without full emission during the melting of the glass batch. Therefore, it can be suggested that oxygen generated from KNO_3 can also take part in the first fining. However, its contribution to the fining may depend on the degree of contamination in the glass batches. Considering the NO_x emission it is important to determine the optimal percent of KNO_3 for the glass batch.

4. Conclusions

Oxygen equilibrium pressure (P_{O2}) measurements were conducted in four CRT glass melts doped with 1) 0.07Sb_2O_5, 2) 0.11CeO_2, 3) 0.07Sb_2O_5+2 wt% KNO_3, and 4) 0.07Sb_2O_5 +4 wt% KNO_3. In terms of the redox reaction during the fining process, the temperature dependence of P_{O2} in each melt is discussed. Based on the P_{O2} values in the melts, it can be concluded that in terms of the fining efficiency Sb_2O_5 is

superior to CeO_2. The P_{O2} values of the melts whose batch contained Sb_2O_5 and KNO_3 were much higher than that of the melts with only Sb_2O_5 and increased as the KNO_3 content increased. Therefore, it is expected that the addition of KNO_3 to a CRT glass batch with Sb_2O_5 will contribute significantly to the first fining of melts.

Acknowledgements

This work was supported by a Korea Science and Engineering Foundation (KOSEF) grant funded by the Korean government (MOST) (No. R01-2006-000-10252-0)

REFERENCES

1. H. Jebsen-Marwedel and R. Brueckner, "Glastechnische Fabrikationsfehler," pp.193-261, 3rd ed. Berlin, *Heidelberg*, New York, Springer, 1980.
2. F. E. Woolley, "Melting/Fining, Engineered Materials Handbook Vol. 4 Ceramics and Glasses," *The Materials Information Society*, ASM International, 386-93 (1992).
3. A. W. M. Wondergem-de Best, "Redox Behavior and Fining of Molten Glass," pp.184-224, Ph.D Thesis at Technical University Eindhoven, Netherlands, 1994.
4. A, Paul, "Chemistry of Glasses," *Chapman and Hall*, 219-239 (1990).
5. K. D. Kim, "Fining of TV screen glass melts containing ZnO," *Glasteknisk Tidskrift*, **55** [1] 1-7 (2000).
6. H. S. Jung, K. D. Kim, H. K. Kim, and Y. H. Kim, "Redox Equilibrium of Antimony by Square Wave Voltammetry Method in CRT Display Glass Melts," *J. Kor. Ceramic. Soc.*, **44** [1] 1-5 (2007).
7. A. Paul and R. W. Douglas, "Cerous-ceric Equilibrium in Binary Alkali Borate and Alkali Silicate Glasses," *Phys. & Chem. of Glass.*, **6** [6] 212-15 (1965).
8. D. M. Krol and P. J. Rommers, "Oxidation-Reduction Behavior of Antimony in Silicate Glasses Prepared from Raw Materials and Cullet," *Glass Tech.*, **25** [2] 115-18 (1984).
9. O. Lafroukhi, J. Hertz, J. P. Hilger and G. Cornier, "Electrochemical Measurement of Oxygen Activity in Lead Glass by Means of a Stabilized ZrO_2 Sensor," *Glastech. Ber.*, **64** [11] 281-90 (1991).
10. T. Hayashi and W. G. Dorfeld, "Electrochemical Study of As^{3+}/As^{5+} Equilibrium in a Barium Borosilicate Glass Melts," *J. Noncry. Solid.*, **177** 331-39 (1994).
11. F. W. Kraemer, "Sauerstoffpartialdruecke, Sauerstoffgehalte und Redox-verhaeltnisse von Antimon, Cer und Eisen in Einem Technischen Alkali-Erdalkali-Silikatglas," Proceeding of 69th Glastechnische Tagung, Deutsche Glastechnische Geselschaft, Wuerzburg, 22-4, May (1995).
12. M. Yamashita and H. Yamanaka, "Oxygen Activity Change in Soda-lime-silica Glass Melts with or without Refining Agent," *Glastech. Ber. Glass Sci. Technol.*, **70** [12] 371-74 (1997).
13. T. Tran and M. D. Brungs, "Application of Oxygen Electrodes in Glass Melts. Part I. Oxygen Reference Electrode," *Phys. Chem. Glass.*, **21** [4] 133-40 (1980).
14. T. Tran and M. D. Brungs, "Application of Oxygen Electrodes in Glass Melts. Part II.Oxygen Probes for the Measurement of Oxygen Potential in Sodium Disilicate Glass," *Phys. Chem. Glass.*, **21** [5] 178-83 (1980).
15. H. Jiang and W. LaCourse, "Foaming in the Soda-lime-silica Glass Melts with Antimony and Cerium Oxide Fining Agents," Proceedings of XVIII ICG, San Francisco, 1998.
16. J. Hlavac, "Glass Science and Technology Vol. 4, The Technology of Glass and Ceramics, An Introduction," Elsevier Scientific Publishing Co, 111-19, 1983.
17. M. Yamamoto, H. Kushitani, A. Takada, and C. Tanaka, "Effects of Batch Compositions on the Redox States of Antimony in TV Glass Melts," Proceedings of XVIII ICG San Francisco, 1998.
18. B. Jonson, "Non Nitrate Antimony Aided Refining," Glasteknik Tidskrift," **53** [3] 69-73 (1998).