Short Communication

Influence of batch moisture and atmosphere on the melting behavior of As_2O_3- and Sb_2O_3-containing glasses

Ebba de Kever[1]) and Günther Heinz Frischat

Institut für Nichtmetallische Werkstoffe (Professur für Glas), Technische Universität Clausthal, Clausthal-Zellerfeld (FRG)

Dedicated to Prof. Dr. Adolf Dietzel on the occasion of his 90th birthday

Sand–potash–dolomite glass batches with the addition of 2 wt% As_2O_3 and Sb_2O_3, respectively, were heated in a gradient furnace. Further parameters were the melting atmosphere (normal air, nitrogen, and air loaded with 30 vol.% H_2O, respectively) and the batch moisture content (up to about 10 % H_2O). X-ray diffraction showed the nature and sequence of the different phases obtained. In no case arsenic- or antimony-containing reaction products could be detected, however, the decomposition or formation of other compounds, e.g. dolomite and silicates, was influenced strongly. The batch moisture had a stronger impact than the melting atmosphere.

Einfluß der Gemengefeuchte und der Atmosphäre auf das Schmelzverhalten As_2O_3 bzw. Sb_2O_3 enthaltender Gläser

Glasgemenge, bestehend aus Sand, Pottasche und Dolomit, wurden nach Zugabe eines Massenanteils von 2 % As_2O_3 bzw. Sb_2O_3 in einem Gradientenofen erhitzt. Weitere Parameter waren Schmelzatmosphäre (Luft, Stickstoff bzw. Luft mit einem Voumenanteil von 30 % H_2O) und Gemengefeuchtigkeit (bis zu 10 % H_2O). Mittels Röntgenbeugung konnten die Art und die Abfolge der entstehenden Phasen festgestellt werden. Arsen bzw. Antimon enthaltende Reaktionsprodukte wurden nicht entdeckt, jedoch wurde durch diese Bestandteile die Zersetzung bzw. Bildung anderer Verbindungen, z. B. Dolomit bzw. Silicate, stark beeinflußt. Dabei hatte die Gemengefeuchte einen stärkeren Einfluß als die Schmelzatmosphäre.

1. Introduction

The chemistry of glass melting is complex and many factors may be of influence, e.g. batch composition, chemical form and grain size of the batch materials, heating rate, and cullet content. In recent work [1 to 4] it was shown that especially batch water contents and in some cases also melting atmospheres are very important for the nature and sequence of different reactions. Moreover, if the batch also contains heavy-metal compounds, their reactions, vapor pressures, etc., have also to be taken into account [5 and 6].

Arsenic still is used in some cases for fining, e.g. lead oxide-containing glasses. However, due to its high toxicity efforts are made to avoid it, e.g. by the use of Sb_2O_3. It is the aim of the present paper to investigate the reactions occurring in a simple sand–potash–dolomite system after addition of As_2O_3 and Sb_2O_3, respectively, to the batch.

2. Experimental

The base glass composition (in wt%) was 70 SiO_2, 15 K_2O, and 15 $CaO \cdot MgO$. Additionally, 2 wt% As_2O_3 or Sb_2O_3, were added to the respective batch. All raw materials (sand, potash, dolomite, As_2O_3,

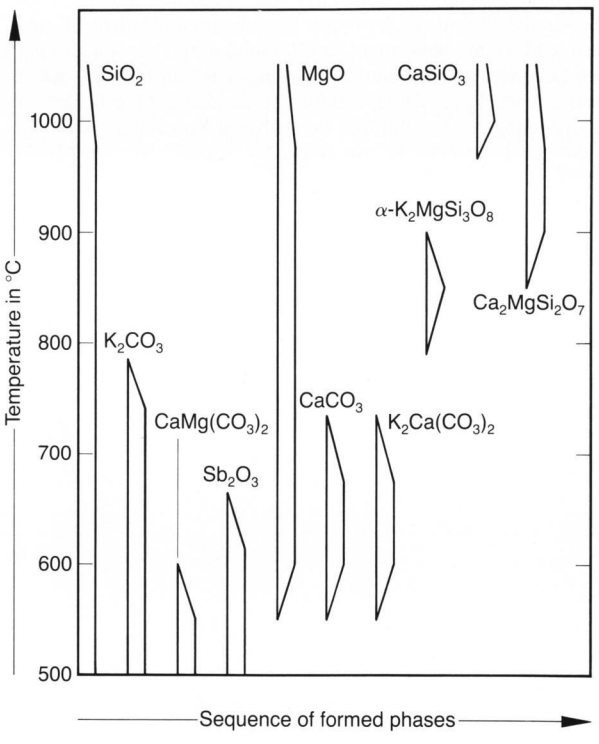

Figure 1. Nature and sequence of phases which form during heating (under normal air atmosphere) of a sand–potash–dolomite glass batch at an addition of 2 wt% Sb_2O_3 and at a batch moisture content of 10.2 vol.% H_2O. The batch was prepared in relation to a base glass composition (in wt%) of 70 SiO_2, 15 K_2O and 15 $CaO \cdot MgO$.

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[1]) Now with: Gesellschaft für Management- und Organisationsberatung mbH, Köln (FRG).

and Sb_2O_3) were of technical grade. After the batch was weighed it was carefully mixed for 24 h. A defined amount of water was added and the batch was again mixed for 24 h. The water contents of the batch mixtures were determined after a sample of the batch was dried for 24 h at 200 °C.

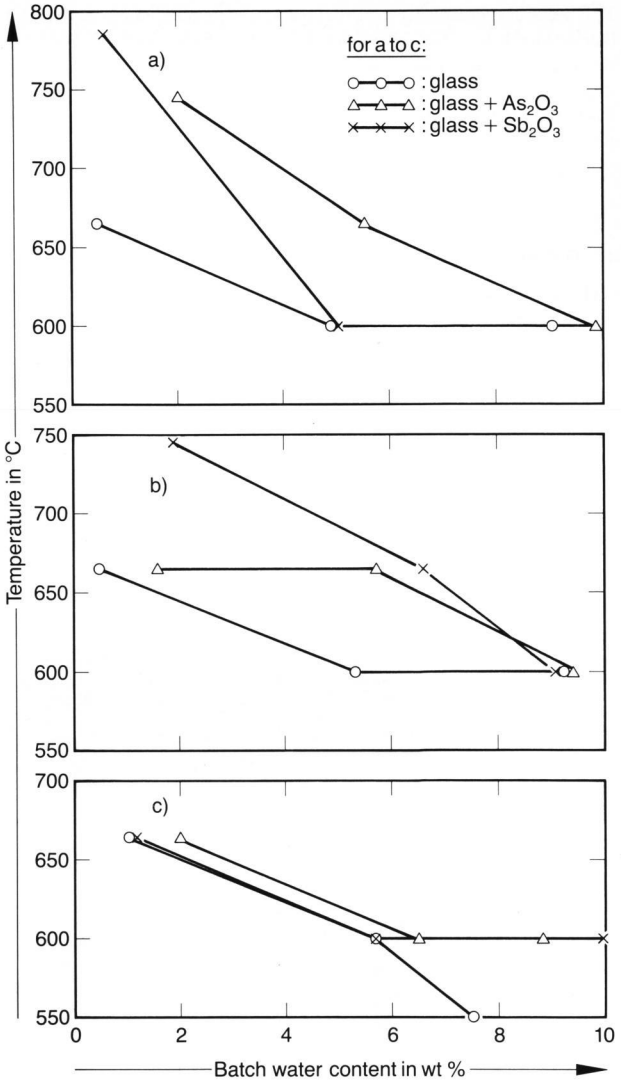
The batch mixture was immersed as 50 g portions into a platinum boat (40 cm long) in a gradient furnace, with temperature differences between the various sample positions of 50 K. Final temperatures between 550 and 1050 °C were reached after heating for 40 min. After the reacted material was cooled, it was removed from the furnace, crushed in an agate mortar and analyzed by X-ray diffraction. This method gives qualitative results only, and the detection limit lies normally between 3 and 5 wt% of a compound present in the material. For heavy metal-containing material it may be as low as 1 wt%. Besides air also N_2 and air, loaded with 30 vol.% H_2O, were used as atmospheres.

3. Results and discussion

The results for a glass batch with Sb_2O_3 are typical and are shown in figure 1. In no case arsenic- or antimony-containing reaction products could be detected. However, although the reaction sequence is similar to what has been found earlier [2], there are also distinct differences. Thus, the compound $Ca_2MgSi_2O_7$ could only be detected for air and N_2 atmospheres and not for the H_2O-loaded air atmosphere. Instead of that in the latter case the compound $CaMgSi_2O_6$ was found. For normal air atmosphere and low batch moisture contents Sb_2O_3 was stable up to about 600 °C. On increasing the batch moisture this temperature was raised to about 665 °C. For N_2 and H_2O-loaded atmospheres Sb_2O_3 was stable up to 600 and 665 °C, respectively, independent of the batch moisture content.

The compound most influenced by the addition of As_2O_3 or Sb_2O_3 was dolomite. Figures 2a to c show the decarbonization temperatures of dolomite for normal air, nitrogen, and H_2O-loaded air atmospheres, respectively, with and without As_2O_3 or Sb_2O_3. In normal air atmosphere the decomposition temperature was drastically increased to nearly 800 °C at low batch water contents, whereas for more batch water the differences vanished (figure 2a). A similar but less strong tendency could be found for nitrogen atmosphere (figure 2b). If one uses an air atmosphere loaded with 30 vol.% H_2O, there is nearly no difference whether As_2O_3 or Sb_2O_3 were added to the batch or not (figure 2c).

Since the systems described here are complex and the number of variables is high, it is difficult to explain why the reactions occur how they occur. However, some tendencies can be formulated. Generally, increase in batch moisture facilitates melt formation, enhances the reaction rates and lowers the respective decomposition temperatures. As experiments [7] show the addition of As_2O_3 and – in a similar but less pronounced way – Sb_2O_3 leads to the formation of silicates at lower temperatures. This is probably due to the formation of As_2O_3- or Sb_2O_3-rich melts. Increased batch moisture enhances this melt formation and accelerates the silicate formation. Reduction of the decarbonization temperatures of dolomite and $CaCO_3$ further enrich the melt with CaO and make the silicate formation even more probable. As shown the melting atmosphere does have some influence on the ongoing reactions, however, the strongest impact comes from the batch moisture.



Figures 2a to c. Decarbonization of dolomite in a sand–potash–dolomite glass batch without and with an addition of 2 wt% As_2O_3 or 2 wt% Sb_2O_3 in dependence on the batch moisture content and the melting atmosphere. As melting atmospheres were used: a) normal air, b) nitrogen, c) air loaded with 30 vol.% H_2O.

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