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IONICALLY CONDUCTIVE GLASSES IN THE SYSTEM Li_2Cl_2—Li_2O—B_2O_3

Part I. Changes in the composition of glasses on melting

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Considerable vaporization of Li_2Cl_2 and B_2O_3 takes place in the course of melting of glasses in the system Li_2Cl_2—Li_2O—B_2O_3 at 950 °C. The vaporization of Li_2O is negligible compared to that of Li_2Cl_2 and B_2O_3, and the relative representation of Li_2O in the glasses prepared is therefore relatively increased.

INTRODUCTION

Glasses in the system Li_2Cl_2—Li_2O—B_2O_3 exhibit excellent ionically conductive properties and can therefore be ranked among glassy electrolytes. Their ionic conductivity depends for the most part on their content of Li_2Cl_2 and Li_2O [1]. However, vaporization in the course of melting brings about changes in the relative representation of the individual components in the glasses. The problem has been dealt with by several authors, but the results published show considerable differences. The most significant differences arise in assessing the loss of lithium chloride. Two extremes are represented by the study by Button et al. [2] and by Soppe et al. [3]. Using chemical analyses, Button found a satisfactory agreement between the chemical composition of the glasses prepared and their nominal initial chemical composition. On the other hand, Soppe mentions a loss of chloride of up to 80 % due to vaporization, while the contents of Li_2O and B_2O_3 did not differ from the nominal intial composition.

EXPERIMENTAL

The initial chemical composition of the raw material mixtures can be exprressed as follows:
X Li_2Cl_2—Y Li_2O—7 B_2O_3 (mol) — abbreviated record X—Y—7. The glasses of the following compositions were studied:

X—3—7 $\quad X = \langle 0; 3.0 \rangle$
2—Y—7; 2.5—Y—7; 3—Y—7 $\quad Y = \langle 3.0; 4.5 \rangle$

The glasses were prepared from standard commercial reagents of A. R. purity (Lachema). The boric oxide was prepared by melting boric acid H_3BO_3, lithium oxide was introduced into the raw material mixture in the form of lithium carbonate Li_2CO_3, lithium chloride Li_2Cl_2 was treated by drying at 110 °C.

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The raw material mixtures 20 g in weight were homogenized, and the glasses melted in a covered platinum crucible at 950 °C with isothermal holding for 15 minutes. The melting was effected in air atmosphere. The melted glass was cooled by immersing the crucible in a water bath. The samples obtained were further tempered at 300—320 °C for 15 hours to eliminate undesirable stresses. After cooling, the samples were kept in a desiccator to rule out effects of atmospherical humidity. The glasses prepared were clear, colourless in the system Li_2O—B_2O_3, and those containing chloride showed orange to pink colour.

The chemical composition of the glasses allowed them to be decomposed in water at elevated temperature and pressure, so that the chemical analyses were simplified to those of solutions. The samples were decomposed in an autoclave for 6—12 hours at 120 °C. Samples of about 2 g in weight were analyzed. The content of boric oxide was determined by alkalimetric titration of manitoboric acid. Lithium was determined by flame photometry (Varian Techtron). The content of chlorides was determined by two volumetric methods: (i) argentometric and (ii) mercurometric. The content of lithium oxide was established from the known total content of lithium in the samples and from the calculated content of lithium chloride.

EXPERIMENTAL RESULTS AND DISCUSSION

The losses of Li_2Cl_2 established varied over the interval of 20—30 mol. %, which represents a decrease of relative chloride content in the glasses by 2.5 to 6 mol. %. The B_2O content also decreases considerably. The loss of 14 to 26 mol. % represents a relative decrease of B_2O_3 content in glasses by 10 to 14 mol. %. Determination of Li_2O content showed the relative content of Li_2O in glasses increased by 12 to 20 mol. % with respect to the decreased contents of Li_2Cl_2 and B_2O_3.

The vapour pressure of components present in the melt at the melting temperature is one of the parameters determining the changes in chemical composition. Lithium chloride exhibits the highest vapour pressure among all the other components. At 950 °C it is about 2 000 Pa [5]. The vapour pressures of the other components are negligible at the melting temperature. Vaporization of B_2O_3 is significantly affected by the presence of moisture. The vaporization is the more intensive, the higher the concentration of water vapour. At lower concentrations of water vapour, B_2O_3 vaporizes in the form of metaboric acid HBO_2, while as at lower temperatures and higher water vapour pressures the B_2O_3 vaporizes in the form of boric acid H_3BO_3 [6]. It is also necessary to consider chemical reactions between the individual components in melt and the associated formation of chemical compounds, where each exhibits its own pressure of saturated vapours (borates are formed by reaction of Li_2O with B_2O_3).

Lithium chloride does not probably react with the other components present in the melt, and its loss can be associated with the high vapour pressure at the melting temperature. The loss of boric oxide is strongly affected by moisture (melting was carried out in the presence of atmospherical humidity). At the melting temperature, Li_2O combines with B_2O_3 forming borates, whose vapour pressures are somewhat higher than those of the pure components. Li_2O therefore vaporizes from the melt in the form of borates; however, its loss is negligible compared to that of Li_2Cl_2 and B_2O_3.

CONCLUSION

The results of this study indicate considerable differences between the chemical composition of the initial raw material mixtures and the final glasses. In the course of melting, Li_2Cl_2 is lost owing to its high vapour pressure at the melting temperature, and the decrease of the content of B_2O_3 results from the presence of atmospherical humidity. Compared to the losses of Li_2Cl_2 and B_2O_3, that of Li_2O is negligible, so that its relative content in glass increases. A comparison of the results obtained with the data by other authors indicates that the changes in chemical composition of glasses due to melting depend strongly on the actual experimental conditions.

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IÓNOVÉ SKLÁ V SÚSTAVE Li_2Cl_2—Li_2O—B_2O_3. ČASŤ I: ZMENY ZLOŽENIA SKIEL PRI TAVENÍ

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Iónová vodivosť skiel zloženia Li_2Cl_2—Li_2O—B_2O_3 je rozhodujúcou mierou ovplyvňovaná obsahom Li_2Cl_2 a Li_2O. Pomerné zastúpenie týchto zložiek sa však počas tavenia skiel pri teplote 950 °C vplyvom vyparovania jednotlivých zložiek mení. Analytické stanovenia ukázali značné zníženie obsahov Li_2Cl_2 a B_2O_3. Vyparovanie Li_2O je v porovnaní s vyparovaním Li_2Cl_2 a B_2O_3 zanedbateľné, v dôsledku čoho sa pomerné zastúpenie Li_2O v pripravených sklách zvyšuje.

ИОННЫЕ СТЕКЛА В СИСТЕМЕ Li_2Cl_2—Li_2O—B_2O_3 I. ИЗМЕНЕНИЕ СОСТАВА СТЕКОЛ ПРИ ВАРКЕ

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Ионная проводимость стекол составом Li_2Cl_2—Li_2O—B_2O_3 является существенно под влиянием содержания Li_2Cl_2 и Li_2O. Однако количественный состав приводимых компонентов во время варки стекла при температуре 950 °C под влиянием испарения отдельных компонентов изменяется. Аналитическое определение показывает значительное понижение содержания Li_2Cl_2 и B_2O_3. Испарением Li_2O по сравнению с испарением Li_2Cl_2 и B_2O_3 можно пренебрегать, в результате чего относительный количественный состав Li_2O в полученных стеклах повышается.