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STABLE AND METASTABLE PHASES IN AgI-CONTAINING SILVER BORATE GLASSES

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This paper studies the thermal stability and the glass formation region the $AgI-Ag_2O-B_2O_3$ system. The miscibility range of the components has been investigated by direct visual observation at 1000°C, i.e. where the system is liquid over the entire compositional range. By combining X-ray and differential thermal analysis (DTA) measurements, the large region of glass formation of the system has been determined. The dependence of the glass transition temperature upon the glass composition is discussed. Series of glasses have been annealed over extended time intervals above the glass transition temperature in order to characterize the "equilibrium" phase diagram for the system. Analysis of the annealed materials shows that several crystalline compounds form upon annealing.

Glasses have long been materials of choice for technological applications, and have recently become the object of fundamental researches in the field of condensed matter. Many efforts are devoted to characterizing the "structure" and thermal stability of glass systems, in the hope of finding the key to the understanding of the "universal" properties of disordered materials [1]. This paper presents an investigation of the system $AgI-Ag_2O-B_2O_3$, which has been undertaken with the aim of providing a well-characterized model system suitable for basic researches. While there is an enormous literature on the subject of glasses made of boron and metal oxides [2], relatively little is known on the ternary systems containing monovalent halides. However, the interest of these compounds is enhanced by their unusual ion transport properties in the solid state [3–7]. Ion conductivity studies allow the selection of technologically promising materials, while providing an aspect of glass dynamics which is not yet fully understood.

Structural studies on borate glasses have a long tradition [2] and several structural "groups" have been identified in the borates. However, this knowledge does not enable us to predict many physical properties of the glasses, even when specific assumptions, such as those introduced by the random network model [2], are made. The reason for the partial failure of the Zachariasen model is that correlations exist between the orientations of adjacent structural units, or that the glass is not "perfectly disordered". The question of the "intermediate range order" has some bearing on the crystallization problem and the glass stability, since crystallization can be depicted as the growth process of the "coherence domains". An analysis such as that presented here should be made before discussing this type of problem. Furthermore, it is hoped that information can be obtained about the "interaction" between the glass matrix and the "doping salt" (in our case AgI), which is responsible for the high ionic conductivities of some of the samples studied.

Experimental methods

Standard glass-making procedures have been used to obtain our silver borate glasses; in particular, the Ag_2O component was obtained by the addition of $AgNO_3$, weighed amounts of the components were brought to ~ 950° and the melt, after evolution of the decomposition products, was quenched in stainless steel molds at room temperature (rt). Standard chemical analysis techniques were used to accurately determine (~ 1%) the composition of the products. The phase equilibria in liquids at 1000° were characterized as follows: AgI was usually sealed in a quartz tube with the desired amount of a $Ag_2O-B_2O_3$ glass (or of the stable $AgI-Ag_2O-B_2O_3$ compound with the lowest AgI content). Direct visual observation of the test-tube at different temperatures was made with an apparatus described elsewhere [8]. X-ray powder diffractometry and differential thermal analysis (DTA) techniques were routinely [4] applied to the samples. The glass-formation region of the $AgI-Ag_2O-B_2O_3$ system was defined as the compositional range where no Bragg peaks were observed in the X-ray patterns. Vitreous samples were usually transparent. The glass transition temperature (T_g) was defined as the point where the DTA recording showed a "sudden" endothermic deviation when the sample was heated at 10 degree/min. Well-defined crystallization peaks were sometimes observed some 50–100° above T_g, mostly in samples with a high AgI content. Annealing of several glass samples for each composition was performed at temperatures ~ 50° above T_g. It should be noted that the choice of the annealing temperature is restricted by the need to avoid the formation of liquid phases, which may occur above the eutectic temperature. The annealing time was determined by periodically examining sample portions with X-ray and DTA techniques. Annealing was stopped when only negligible modifications in the recordings were produced by further annealing over a two-day interval. Typically, the annealing time appropriate for our glasses was found to be 7–10 days.

Results

Some information about the system $AgI-Ag_2O-B_2O_3$ is summarized in the ternary diagram in Fig. 1. As expected, at 1000° AgI and B_2O_3 are completely im-

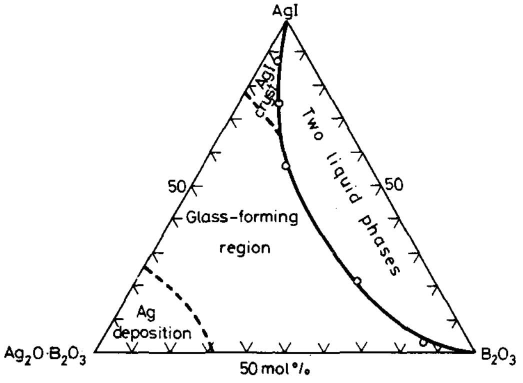

Fig. 1 Ternary phase diagram of the AgI–Ag_2O–B_2O_3 system

miscible. The miscibility of AgI and B_2O_3 increases with increasing Ag_2O content and becomes complete for a mole ratio $[B_2O_3]/[Ag_2O] < 1.5$. The solid curve in Fig. 1 has been drawn along the boundary of immiscibility region at 1000°, while the glass-forming region is bounded by two dashed lines. At high Ag_2O contents, decomposition phenomena and metallic silver deposition take place in the melt. Samples with high AgI contents show X-ray peaks that can be assigned to the β-phase of AgI and are characterized by the sharp transition peak to the α-AgI phase in the DTA diagrams (~ 145°).

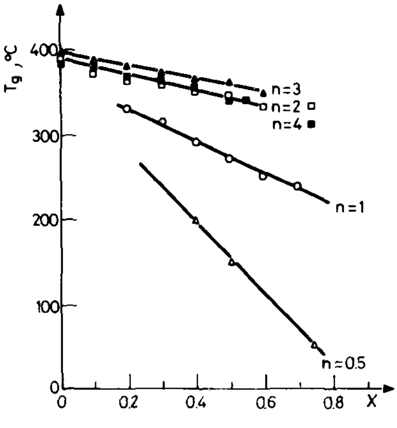

Fig. 2 Compositional behaviour of T_g

Figure 2 shows the behaviour of T_g as a function of the compositional parameter $X = [AgI]/[AgI] + [Ag_2O]$. In this Figure we have put $n = [B_2O_3]/[Ag_2O]$. T_g decreases linearly with increasing X. While this phenomenon is not understood quantitatively, it corresponds to the intuitive fact that the structural strength of a borate glass is due to the boron + oxygen network. This strength is somewhat reduced when the glass matrix houses the metal halide since a less compact network is favoured. However, we have not found spectroscopic evidence for a modification of the borate structural units produced by the addition of metal halides [4]. By direct measurement, or by extrapolation of the experimental data to $X = 0$ for $n < 2$, we have constructed a plot of T_g *vs* n for the "undoped" glasses. T_g reaches a broad maximum in the interval $2 < n < 4$, which roughly corresponds to the compositional range of glasses ideally including the following structural units [2]: pentaborate, tetraborate, triborate and diborate. The fact that a pure boron oxide glass has a substantially lower T_g is certainly related to the fact that such a glass, contains three-coordinated boron, while the coordination and glass stability increase with the content of the metal oxide. However, for $n < 2$, non-bridging oxygens (NBO) are likely to be formed [4]; this fact is believed to be responsible for the substantial drop in T_g.

Figures 3 and 4 report the equilibrium phase diagrams for the systems $AgI-Ag_2O \cdot 2 B_2O_3$ and $AgI-Ag_2O \cdot B_2O_3$, respectively, as determined from the annealing experiments. The existence of stable crystalline compounds is indicated by maxima in the intensity of both the Bragg peaks and the DTA melting transition peaks as a function of the compositional parameter. The figures show the DTA-determined crystallization temperatures of the crystalline compounds. A study of the equilibrium phase diagram of the $Ag_2O-B_2O_3$ system has already been reported in the literature [9]. Our results agree with this early report. We have identified the formation of the following compounds: $AgI \cdot 2 (Ag_2O \cdot 2 B_2O_3)$, $2 AgI \cdot Ag_2O \cdot 2 B_2O_3$ (see Fig. 3) and $AgI \cdot 2 (Ag_2O \cdot B_2O_3)$ (see Fig. 4). In Table 1 the characteristic reflection angles (2ϑ) for these compounds are reported.

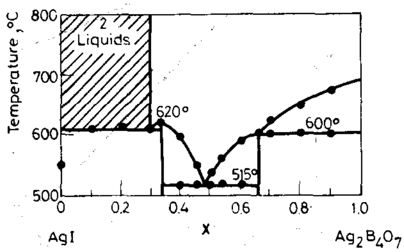

Fig. 3 Equilibrium phase diagram of the $AgI-Ag_2O \cdot 2 B_2O_3$ system

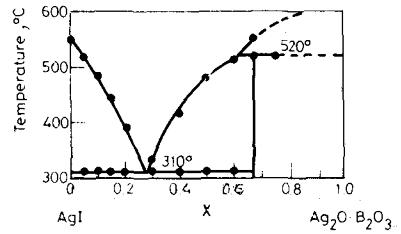

Fig. 4 Equilibrium phase diagram of the AgI–$Ag_2O \cdot B_2O_3$ system

Table 1 Main reflections observed for the indicated compounds

$2\,AgI \cdot Ag_2O \cdot 2\,B_2O_3$		$AgI \cdot 2\,(Ag_2O \cdot 2\,B_2O_3)$		$AgI \cdot 2\,(Ag_2O \cdot B_2O_3)$	
2ϑ	I/I_0	2ϑ	I/I_0	2ϑ	I/I_0
12.20	35	12.85	60	13.15	15
12.75	30	15.00	65	15.05	15
16.15	35	26.50	30	19.20	85
21.05	10	28.15	60	26.35	10
31.75	100	30.85	75	27.10	25
33.30	25	31.30	25	29.00	80
38.15	50	34.45	100	33.20	30
42.65	20	35.85	35	34.70	35
		37.70	30	36.20	75
		40.05	40	38.95	100
				42.65	10

Conclusions

A discussion of our data on the basis of theories of amorphicity, or a comparison of different structural models for borate glasses, is beyond the scope of this work. Here, we wish simply to point out in which sense the type of analysis that we have presented is related to the ionic conductivity studies [5] on the borate glasses. In [5] we measured the rt ionic conductivities for several sets of glass compositions as a function of X (with n = const.); for $[AgI] = 2\,[Ag_2O]$ all glasses attained the same conductivity. This fact strongly indicated the existence of a structural unit comprised of a $Ag^+{-}BO_4^-$ group which coordinates two AgI molecules. The analysis presented in this paper suggests that more than one configuration is favored in the AgI-containing borate glasses. Obviously, the glass-formation capability depends upon the existence of different configurations having small differences on the energy scale. Further, the "intermediate range order" in the metastable phases is believed to depend upon these energy differences, an understanding of which is crucial for a description of glass properties.

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Zusammenfassung — Im System AgI—Ag_2O—B_2O_3 werden die thermischen Bedingungen und die Komponentenverhältnisse, unter denen eine Glasphase existent ist, untersucht. Der Bereich der Mischbarkeit der Komponenten wurde durch direkte visuelle Beobachtung bei einer Temperatur von 1000°C untersucht, bei der das System über den ganzen Bereich der Zusammensetzung hinweg flüssig ist. Der ausgedehnte Bereich der Glasbildung im untersuchten System wurde durch kombinierte röntgendiffraktometrische und differentialthermoanalytische Messungen bestimmt. Der Zusammenhang zwischen Transformationstemperatur und Zusammensetzung des Glases wird diskutiert. Eine Serie von Gläsern wurde über längere Zeit oberhalb der Glastransformationstemperatur getempert, um ein "Gleichgewichts"-Phasendiagramm für das System zu bestimmen. Bei thermischer Behandlung werden in den getemperten Materialien verschiedene kristalline Verbindungen gebildet.

Резюме — Изучена термоустойчивость и область стеклообразования системы AgI—Ag_2O—B_2O_3. Область смешиваемости компонент была исследована прямым визуальным наблюдением при 1000°C, где система является жидкой во всей области состава. Комбинированием рентгенографических и ДТА измерений, определена область стеклообразования в этой системе. Обсуждена зависимость температуры расстекловывания от состава стекла. Для определения формы "равновесной" фазовой диаграммы системы, серия стекол была подвергнута отжигу выше температуры расстекловывания при различных интервалах времени. Анализ отторженных образцов показал, что в процессе термической обработки образуется несколько кристаллических соединений.