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DTA OF WATER-SALT GLASSES

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DTA investigations of glasses in the system $Al_2(SO_4)_3$–H_2O/55–65 mass% $Al_2(SO_4)_3$ revealed effects at the glass transformation (T_g), crystallization and melting temperature. During storage at ambient temperature, T_g increased, probably due to an annealing process; the increase was the least at the stability maximum for the glasses, at 61–63% $Al_2(SO_4)_3$.

Water-salt glasses are distinguished by their low glass-formation temperatures (T_g) (from $-130°$ to -60°), which is due to the presence of hydrogen-bonds in the structure of the glasses. Water is always present in the compositoon of water-salt glasses, and therefore T_g depends on the water content of the glass (the higher the water concentration, the lower T_g). Since water-salt glasses contain salt and water, they may be regarded as aqueous solutions, and glasses with salt contents in excess of the solubility of the salt in water ($T_g > 0$) as highly concentrated aqueous solutions. Therefore, study of the glasses of this class is of interest not only as concerns the understanding of the nature of the glassy state, but also to establish the structures and properties of concentrated aqueous solutions, since the region of homogeneous solutions limited by salt solubility and accessible to traditional investigations can thereby be extended.

Glasses in the $Al_2(SO_4)_3$–H_2O system were chosen as the object of the present study. The region of glass formation in this system extends from 55 to 65 mass% $Al_2(SO_4)_3$. The glasses are transparent and relatively unhygroscopic; their stability to crystallization depends on the concentration, and exhibits a maximum at 61–63 mass% $Al_2(SO_4)_3$.

The experimental part of this study was carried out with a TA–AN–500 thermoanalyzer operating in the temperature range from $-150°$ to $+500°$. The TA–AN–500 is provided with a programming unit intended for setting of the temperature–time program. The temperature sensor consists of a small steel pipe with a platinum temperature detector ensuring the high accuracy of the results. The weighed samples did not exceed 20 mg. Heating and cooling rates were 5 deg min^{-1}.

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Three effects were revealed in the DTA curves for all compositions of the glasses: (1) an endothermic effect corresponding to T_g, (2) an exothemic effect of transition from glass to crystal, and (3) an endothermic effect of melting. In the course of the investigation, it was discovered that the T_g values of some samples change with time. Changes in T_g were observed for 7 months and recorded for each composition approximately every 3 weeks. It is interesting to note that for the compositions most resistant to crystallization (61–63 mass% $Al_2(SO_4)_3$) T_d^g was constant throughout the whole period of observations, at 35–38°. Since T_g for glasses in this system is low, keeping the samples at ambient temperature can be regarded as an annealing procedure. Thus, a change in T_g may be a result of stabilization of a glassy state in the course of annealing.

The effect of thermal treatment on the glass properties is revealed by systematic checks of the glass properties over a long period of time. If a glass is held at constant temperature, its properties change with time at a rate depending on the temperature. Such properties as refractive index, viscosity, electrical resistance and others may either decrease or increase with time. Earlier, it was considered that differences in properties of annealed and quenched glasses are caused by mechanical stresses, which always arise when the cooling rate is not low enough. Recently, however, it was postulated that such an explanation was not comprehensive and that the differences in properties of annealed and quenched glasses are related to chemical-structural changes proceeding during thermal treatment. However, to verify this assumption, the thermal properties must be examined, in combination with structural studies.

The constant values of T_g for compositions containing 61–63 mass% $Al_2(SO_4)_3$ seem to show the minimum chemical-structural changes taking place in glasses with these compositions in comparison with other glasses, and thereby distinguish these compositions with respect to their structure. X-ray studies being conducted at presont on glasses in the $Al_2(SO_4)_3$–H_2O system will presumably make it possible to establish which structural changes are responsible for the changes in T_g. It is now quite obvious that the use of DTA to study water-salt glasses permits one to find compositions with special structures having an enhanced stability with respect to crystallization.

Zusammenfassung — Gläser des Systems $Al_2(SO_4)_3$–H_2O mit 55–65 Masse-% $Al_2(SO_4)_3$ zeigen bei der DTA Effekte bei den Temperaturen von Glasumwandlung (T_g), Kristallisation und Schmelzen. Aufbewahren bei Raumtemperatur führt zum Ansteigen von T_g, wahrscheinlich in Folge eines Temperprozesses; dieser Anstieg ist am geringsten bei der Zusammensetzung mit 61–63% $Al_2(SO_4)_3$, d. h. am Stabilitätsmaximum der Gläser.

Резюме — ДТА исследования стекол в системе сульфат алюминия–вода с 55–65 вес.% сульфата алюминия, показали эффекты стеклообразования T_g, кристаллизации и плавления. Выдерживание системы при обычной температуре приводило к увеличению T_g, которое было неибольшим для максимально устойчивого состава стекол (61–63 вес.% сульфата алюминия).