AMORPHOUS SUBSYSTEMS

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The purpose of this work was to examine the possibility of obtaining a subsystem of cations of some binary compounds in the amorphous state. The respective compounds are characterized by the following: 1. Ag^+ or Cu^+ as cation, 2. an anomalously fast ionic conductivity at temperatures well below their melting point (T_m), and 3. transitions between low- (β-) and high-temperature (α-) phase occurring at temperatures ($T_{\beta\alpha}$) of about 400 K. α-phase frequently possesses a conductivity 10^2 or 10^3 times that of β - phase. X-ray analysis indicates that anions maintain a rigid structure while cations are randomly distributed over an excess of lattice sites. This type of distribution, known as "average structure", together with an almost temperature-independent conductivity, suggests that the concentration of mobile species equals the total concentration of appropriate cations. Since the concentration of energetically equivalent sites is fairly greater than the concentration of cations, the sublattice is so disturbed that it may be taken as a liquid[1,2]. Thus the β-α transition corresponds to the fusion of cations.

These facts raise the question under what conditions it is possible to maintain the liquid-like subsystem below the $T_{\beta\alpha}$, i.e. to obtain the subsystem of cations in amorphous state. The idea was that, as in the formation of amorphous solids from a liquid, fast cooling is necessary. In order to obtain only the subsystem in amorphous state, cooling shoud start from $T_{\beta\alpha}$ and not from T_m.

In order to find out how large the cooling rate must be, we applied Uhlmann's[3] kinetic treatment of glass formation to this liquid-like subsystem, using the

parameters of transition[4,5,6a] instead the parameters of fusion. The viscosity (η) of the particular subsystem was found from a slightly modified Eyring's[7] (1) equation:

$$\eta\, \sigma_0 = n^{4/3}\, e^2 \exp(E/kT) \qquad (1)$$

where n is the concentration of cations, k Boltzmann's constant, T temperature in K, e electron charge, σ_0 and E the preexponential factor and the activation energy of ionic conductivity[4,5], respectively. As a result we established the minimum cooling rates required to obtain the amorphous subsystem in several compounds. They are about 10^6 K/s for Cu_2S, Cu_2Se and Ag_2Te, and about 10^8 K/s for Ag_2S, Ag_2Se and AgI. In order to draw comparisons with these rates we applied Uhlmann's treatment also to the pure elements Ag and Cu, using the experimental values of the required parameters[6b]. The cooling rates required to obtain amorphous solids were found to be about 10^8 K/s for both elements.

In conclusion a few words about possible properties of compounds with amorphous subsystems. One may expect that: 1. ionic conductivity can be appreciably higher in compounds having the subsystem in amorphous than in crystalline state, according to the high defect structure of the amorphous state; 2. X-ray patterns obtained from the subsystem in the crystalline and the amorphous state will be different.

References

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