THE GLASS TRANSITION OF WATER AND AQUEOUS SYSTEMS

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Abstract

After a brief introduction of the terms supercooling, amorphous solid state, glass transition and devitrification, the known ways of production of amorphous solid water are discussed. DSC experiments with quench cooled aqueous solutions show the phenomenon of glass transition and devitrification.

Keywords: amorphous solid water, aqueous systems, DSC, glass transition, supercooling

Introduction

In the solid state of aggregation most substances of low molar mass are crystalline. Crystallization usually takes place when a molten substance is cooled below the melting point. It usually does not occur spontaneously at the temperature of fusion: there is the well known phenomenon of supercooling due to the limited rate of nuclei formation and growth. Supercooling increases with increasing cooling rate. With high enough cooling rates most substances remain in the amorphous state [1], they form a glass or 'vitrify'. The necessary cooling rates range from 1 to $10^7$ K min$^{-1}$.

In the glassy solid state the mobility of the molecules or atoms is too small for crystallization, thus the substance remains in the amorphous state. On heating, the mobility increases at the so-called glass transition temperature. Above this glass transition temperature, substances of low molecular weight form a more or less viscous liquid, polymers become rubber-elastic. In this state most substances form crystals: 'devitrification' or 'cold crystallization' takes place. According to Ostwald's rule often metastable crystalline phases are formed. On further heating the crystals melt at the temperature of fusion of the respective modification.

Even though water shows marked supercooling (Fig. 1) it is extremely difficult to quench cool the liquid phase in order to obtain the amorphous solid water
Fig. 1 Two DSC cooling curves of distilled water measured at a cooling rate of 10 K min$^{-1}$. The small water sample begins to crystallize at $-16.9^\circ$C. The earlier crystallization is caused by the addition of 15 mg $\alpha$-alumina powder as a crystallization aid. Only the lower part of the peaks are shown to demonstrate the change in heat capacity between liquid and crystalline state. The integral baseline enables a correct determination of the enthalpy change.

(ASW): droplets of approx. 3 $\mu$m diameter thrown at supersonic speed towards a metallic wall cooled by liquid nitrogen (hyper quenching) form a layer of ASW. With this treatment cooling rates of approx. $10^5$ K min$^{-1}$ are reported [2]. Another quite complicated method is by compression of hexagonal ice at 77 K [3]. Condensing water vapor on a surface cooled by liquid nitrogen [4] seems to be the easiest way of preparation of ASW. The expected value of the glass transition temperature is $-137^\circ$C.

Binary systems on the other hand are known to crystallize not readily, e.g. molten eutectic compositions often do not crystallize: impure organic compounds are sticky and tacky due to resin like parts. This effect also is true for aqueous solutions. Some solutions only need cooling rates below 1000 K min$^{-1}$ achievable by quench-cooling in the pre-cooled DSC cell or in liquid nitrogen.

The heat of crystallization depends on the actual supercooling (Fig. 2).

**Experimental and results**

The measurements have been performed in a Mettler-Toledo STAR$^\circ$ system with DSC821 and liquid nitrogen cooling.

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