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# The physicochemical basis of the exothermic effect at DTA and DSC curves below glass transition temperature in chalcogenide and oxide glass forming substances

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Endothermic effect of glass transition, fixed by means of DTA and DSC at glass heating is well-known. In some cases these methods record also exothermic effect that appears both at glass heating and at melt cooling. Now there is no clear understanding of physicochemical essence of this effect. The analysis of structure of various crystal polyforms, glass forming liquid, glass of individual chemical substances (ICS), able to form glass Se, $GeS_2$, $As_2Se_3$, $H_2O$, Ca $(PO_3)_2$, etc., made on base polymeric-polymorphous concept of a glass and glass forming liquids structure shows that the ex-effect below $T_g$ is a result of a transformation of the structural fragments from glass, which have no long-range order (polymorphoids) of high-temperature polymorphous modifications (HTPM) into low-temperature polymorphous modifications (LTPM). The effect in glass is originally connected with similar effect in crystal which is the result of polymorphous transformation HTPM → LTPM.

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## 1. Introduction

The differential thermal analysis (DTA) and differential scanning calorimetry (DSC) of a number of chalcogenide and oxide glasses shown heating curves (and, in some cases – cooling curves) an exothermic effect before the endothermic effect at glass transition temperature, $T_g$. That effect is observed in glass forming $As_2Se_3$ (Ludwig [1] – 1975), $H_2O$ (Johary [2] - 1987), Se (Kasap [3] - 1989), $GeS_2$ (Linchun Cai, Boolchand [4] - 2002), basalt glass, Ca $(PO_3)_2$ (Yue [5]–2005) etc.

In our point of view has not got a clear explanation of the given effect neither within the frames of the old Zachariasen [6] model of the continuous chemically ordered random network [7], nor within the frames of any other models [8]. An explanation of this effect gives the concept of a polymeric-polymorphous structure of glass and glass forming liquid (CPPGLS) of individual chemical substance (ICS) being a special case of the polymeric-nanoheteromorphous concept structure of simple and complicated glass forming substances which have arised on the basis of the analysis by diffractometry, spectroscopy (Raman-spectrum), calorimetry and other researches methods for various polymorphous modifications (PM), glass forming liquids and glasses $SiO_2$, $GeO_2$, $H_2O$, Se, $GeS_2$, $GeSe_2$, SiSe, $SiSe_2$, $BeCl_2$, etc. [8-12].

At the heart of CPPGLS lies the representation about polymorphoids – fragments of structure of various PM of the given substance, having no long-range order. Interconversion of polymorphoids of various PMs of the given substance in glass and glass forming liquid, and change of their concentration ratio (CRP) in non-crystalline ICS under the influence of external factors is the fundamental reason of structure and properties of non-crystalline substance changing. CRP is the major internal parameter of non-equilibrium thermodynamic system of non-crystalline substance.

## 2. Glass transition

Glass transition of ICS consists of two indissolubly united parts: copolymerization-depolymerization: copolymerization of various PMs polymorphoids and depolymerization of a formed copolymer at the expense of disintegration of unstable above $T_g$ low-temperature polymorphous modification (LTPM) polymorphoids, and unstable below $T_g$ high-temperature polymorphous modification (HTPM) polymorphoids, as illustrated in Fig 1.

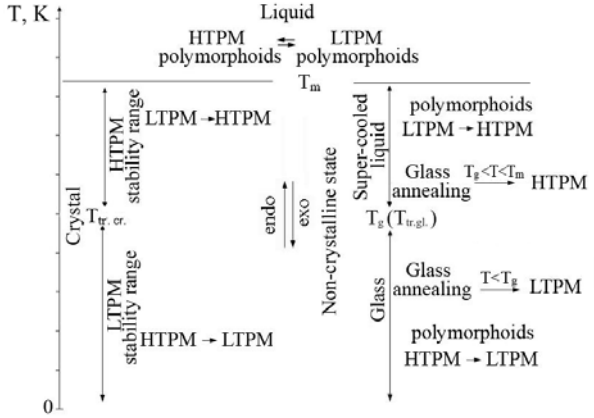

*Fig. 1. The schematical image of condensed glass forming substance relaxation processes, $T_m$ – melting temperature. $T_{tr.cr.}$ – polymorphous transformation temperature in crystal substance. $T_g$ ($T_{tr.gl.}$) – glass transition temperature (temperature of reversible polymorphoids transformation HTPM ↔ LTPM during the glass transition (at cooling) and glass-to-liquid (at heating) processes). LTPM – low-temperature polymorphous modification. HTPM – high-temperature polymorphous modification.*

The essentially important circumstance of the given scheme and processes of a temperature relaxation that is reflected by it, is the affinity of temperatures [12] of polymorphous transformations into crystalline state $T_{tr.cr.}$ and, so-called glass transition temperature $T_g$ which, in our opinion, was correct to be named temperature of changing direction of transformation of HT- and LTPM polymorphoids during the glass transition (at cooling) – and glass-to-liquid (at heating) processes, – $T_{tr.gl.}$

The temperarures $T_{tr.cr.}$ and $T_{tr.gl.}$ correspond to the threeshold of the substance enthalpy $H_{thr}$. The reaching of $H_{thr}$ during heating or cooling changes the direction of polymorphoids transformation HTPM ↔ LTPM.

Presented on basis [8-12] the scheme of relaxation processes in condensed substance that is capable to form the glass (Fig. 1) testifies to a genetic intercommunication of the processes proceeding in crystal, liquid and glass forming substance.

What is physico-chemical essence of the exothermic effect at glass forming substance heated previously to endothermic effect at $T_g$, or is more exact at $T_{tr.gl}$?

In crystal substance process of LTPM→HTPM transformation goes with heat absorption, with endothermic effect [13]. Naturally, as transformation process of polymorphoids LTPM→HTPM in glass goes also with endo-effect that is considered usually to be endothermic effect of glass transition. This process is shown for selenium in Fig. 2 [3].

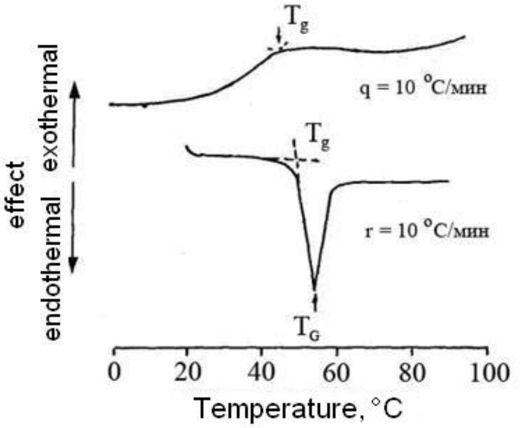

*Fig. 2. Typical DSC heating and cooling scans on a-Se films: r – heating and q – cooling rate [3].*

The process of transformation HTPM→LTPM in crystal substance goes with the exothermic effect [13]. The exothermic effect of polymorphoids HTPM→LTPM of cooled melt transformation process (fig. 2 [3]) proceeds also at temperature $\leq T_{tr.gl.}$.

This effect is shown at heating on curves DTA and DSC of glass forming $As_2Se_3$ [1], $H_2O$ [2], $As_{50}Se_{50}$ [14], $GeSe_2$ [15], $GeS_2$ [4], $Ca(Po)_2$ [5] etc.

In Iohari work [2] thermograms of glass forming $H_2O$ in the conditions described in the caption to Fig. 3 are shown.

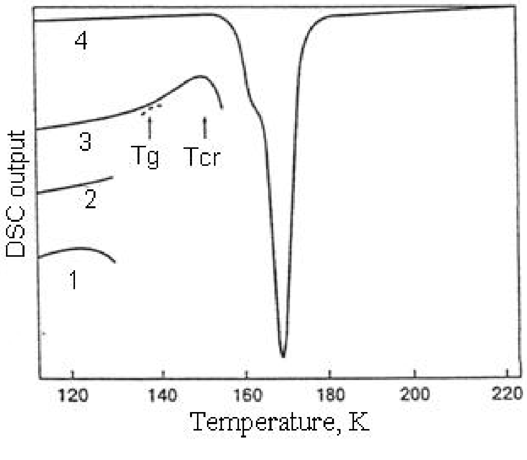

*Fig.3. The DSC scans of the hyperquenched glassy water (prepared by using a 300 μm aperture) taken during heating at 30 K $min^{-1}$. Curve 1 is for 17.7 mg sample heated to 130K. Curve 2 is for the same sample, but after annealing for 95 min at 130K, cooled to 103K and heated to 130K. Curve 3 is for the same sample which was cooled from 130K to 103K and again heated to 283K. Curve 4 is the same as curve 3, but plotted on a reduced scale (1/8th) to show the crystallization peak of glassy water to cubic ice. $T_g$ is the glass transition temperature and $T_c$ is the crystallization temperature, all corresponding to 30K·$min^{-1}$ heating rate [2].*

In experiment Johari [2] the exothermic effect below $T_g$ is a result of transformation unstable below $T_g$ ($T_{tr.gl}$) rich of enthalpy HTPM polymorphoids (ice I), tempered by fast cooling in polymorphoids LTPM (apparently ice II), possessing considerably smaller enthalpy. Accumulation of the LTPM polymorphoids at annealing below $T_g$ during 95 min at 130K allows to fix return transformation LTPM → HTPM with endothermic effect at $T_g$ ($T_{tr.gl}$), not shown without annealing (it is not enough maintenance of LTPM).

In Yue work [5] existence of exo-peak explained by coexistence in glass of structural regions with the lowered and raised energy level (that corresponds to energy levels of LTPM and HTPM polymorpoids and is argument in favour of CPPGLS).

The most information experiment for interpretation of relaxation processes in glass above and below $T_g$, and, in particular, for exoeffect interpretation below $T_g$, is Ludwig's experiment Fig. 4 [1], in our opinion.

In Fig. 4 three curves of glass $As_2Se_3$ heating with the same speed equal to 3 °/min, are presented. The samples of glass are different in the speed of melt cooling– 0.5 °/c, 10 °/c and 20 °/c.

According to the polymeric-polymorphoids glass structures concept, process of polymorphoids HTPM into LTPM transformation proceeds at glass forming melt cooling below $T_g$ ($T_{tr.gl}$). The more slowly cooling, the more in glass ratio of LTPM: HTPM polymorphoids. At increase in speed of cooling (0.5 → 10.0 → 20.0 ºC/s) – the quantity of HTPM polymorphoids considerably increases in glass. Accordingly enthalpy of a melt increases. At glass heating and approach its temperature to $T_g$ process of HTPM→LTPM polymorphoid transformation becomes more active. The more HTPM: LTPM ratio in the glass the more exoeffect of this transformation.

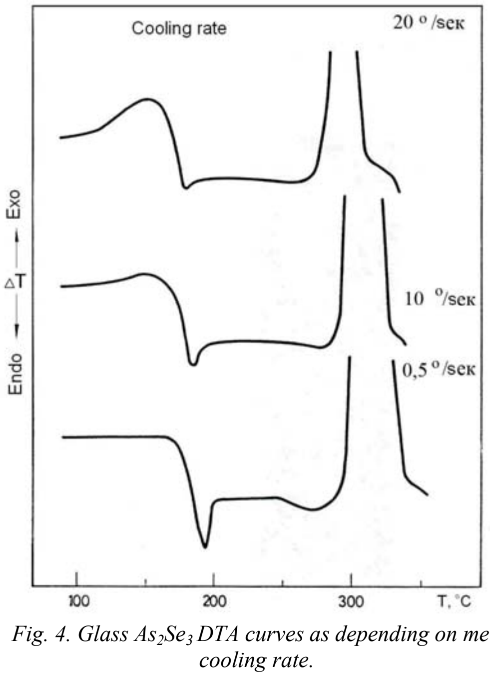

*Fig. 4. Glass $As_2Se_3$ DTA curves as depending on melt cooling rate.*

The shift of effect of glass transformation into the super-cooled liquid aside more high temperatures with reduction of cooling speed from 20 to 0.5 °/s is explained by reduction of concentration HTPM, so both of substance enthalpy reduction and late achievement of the $H_{thr}$ level that is necessary to start transformation LTPM→HTPM by it.

And at last, endothermic effect and its growth with reduction of cooling speed are connected with increase of LTPM polymorphoids quantity in a melt, formed in the course of its cooling below $T_g$, and, accordingly, with big endothermic effect of transformation LTPM→HTPM.

Ludwig's experiment once again shows that glass transition process at melt cooling continues below $T_g$ ($T_{tr.gl}$) at which viscosity of substance is only $10^{12.3}$ Pa·s at the same time viscosity, characteristic for solid glass is $10^{19}$ Pa·s [16, p. 240].

## 3. Conclusion

The analysis of the structure of various polyforms of crystals glass forming liquids, glasses that was carried out on the basis of polimeric-polimorphous concepts of a structure of glass and glass forming liquid shows that exoeffect below $T_g$ is a result of transformation of fragments of the structure which have no long-range order (polymorphoids) of high-temperature polymorphous modifications in polymorphoids of low-temperature polymorphous modifications.

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