The quantitative approach to structure identification of chalcogenide, oxide and halide glass forming substances

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On the basis of results by the researches of difractometry , spectroscopy (Raman-spectroscopy), calorimetry and other methods of crystal polymorphic modifications (PM), of glass forming liquids and glasses SiO_2, H_2O, Se, GeS_2, $GeSe_2$, $BeCl_2$, etc. is achieved the quantitative approach to structure identification of chalcogenide, oxide and halogenide glasses and glass forming liquids. Within the frame of the concept of polymeric-polymorphous structure of glass and glass forming liquid, the quantitative characteristics of their structure, specific ratio of structural fragments (polymorphoids) of various polymorphic modifications that have no long-range order but have short-range order and intermediate-range order appears.

1. Introduction

The existing theories, models and concepts of glass formation can be divided into three groups: structural, kinetic, thermodynamic (Uhlman, 1977) [1]. The satisfactory theory of glass forming can be created only under condition of the non contradictory agreement (correlation) of all three approaches. Such coordination was not possible till now in the absence of quantitatively defined characteristic (parametres) of structure of glass and glass forming liquids. The structure is defined by the concept of polymeric-nanoheteromorphous structures of glass forming substance and its special case – concept of polymeric–polymorphous structure of glass and glass forming liquid of individual chemical substance – ICS (an element or a chemical compound).

The basical theses of this concept are given in [2-5]. The main conclusions are the following:

• The individual chemical substance in glass forming state represents a copolymer of structural fragments of various crystal polymorphous modifications (polymorphoids), having no translation symmetry (long-range order), but being carriers of the intermediate (average) order that is inherent to PMs, taking part in glass formation [4].

• Interconversion of polymorphoids of various PM and change of the concentration ratio of polymers (CRP) in glass forming ICS under the influence of external factors is the fundamental reason of change of structure and properties of glasses.

• The temperature of glass transition, T_g, of glass forming substances is interpreted by polimeric-polymorphoid concept as a temperature of reversible transformation is non-crystalline state, $T_{tr.n-cr}$, of low - and high-temperature polymorphoids of polymorphous modifications (LTPM↔HTPM); Tg in glass is an analogue of temperature of polymorphic transformation in crystal $T_{tr.cr}$.

2. Polymorphism and glass structure

In this work we will discuss mainly the unicomponent glasses (ICS).

Brückner [6,7] was the first who announced the idea (based on a wide spectrum of experimental researches) that in glass appears fragments which are in «preordered states» in which tetrahedra of $SiO_{4/2}$ form cristobalite- and quartz-like structures.

The presence of quartz - and cristobalite like fragments in glass was revealed by Porai-Koshits (1940, 1992) [8,9], he has received a sodium-plumbic-silicate glass with "quartz" ($\sin \theta / \lambda \approx 0.15$ Å^{-1}) and, after treatment at $1500 – 1600$ ^{o}C, «cristobalite » (nearby 0.12 Å^{-1}) diffraction maxima on at large-angle X-ray intensity do appear.

If we analyze the data of Mackenzie [10] shown in Fig. 1 from the points of view of Brückner and Porai-Koshits it is possible to ask a question: is it impossible to estimate in glasses a configuration of "the preordered states» of quartz and cristobalite, meaning, that in quartz and cristobalite corresponding shares are equal 100 and 0 %, and in glasses they are proportional to values of density and to refraction index?
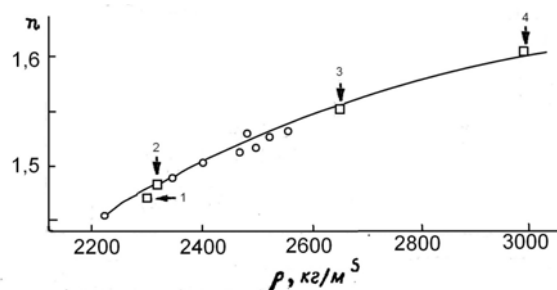

Fig.1 Correlation between refraction index and density in various silica modifications. 1- tridimite; 2 - cristabolite; 3 - quartz; 4 - coesite ○ – initial and densified glasses. [10]

Popescu (1978 [11]) mentioned for the first time the possibility to fix the ratio chain/ring in glassy selenium (a chain – structure fragments of hexagonal PM, rings – of monoclinic PM) by means of measurement of height and the area of characteristic peak (at 4.75 Å) of the radial distribution function.

In 1992 Golubkov [12]   by means of temperature dependence of small-angle X-ray scattering has found out that the sample of silica glasses can be in two various structural states: quartz-like (at T<Tg) and cristobalite-like (at T>Tg). At insufficient warming up the «mixed states» are possible.

The mixed states [13] presented in any glass at least by two polyphorms, exist obviously in the concentration ratio corresponding to the conditions of its treatment.

3. The quantitative characteristic of glass and glass forming liquid structure

Data and technique reported in Popescu work [11] can be a basis for the creation of a method of quantitative definition in glass of the ratio of «the preordered states» - a concentration ratio of polymorphoids (CRP) of various PMs.

The same can be sad about Gerber's et al. work [13] who applied a method of large-angle X-ray scattering and, has shown that in the course of increase of glassy SiO_2 density (P = 7 GPa, T = 700 °C) there is a transformation of structure with cristobalite topology into structure with quartz topology (the density increases up to ~ 15 %). The main maximum on a curve of the large-angle X-ray scattering, being for raw cristobalite-like glass received from melt (d = 2.2 g/cm^3) at s = 15.0 nm^{-1}, is displaced towards increase at consolidation of samples, reaching size of 17.4 nm for the sample with d = 2.56 g/cm^3 that is only a little less than for crystal quartz (fig. 2). The position of the main maximum and suitable glassy SiO_2 density can be interpreted in CRP (of quartz and crystobalite) as the quantitative structural characteristic of glass.
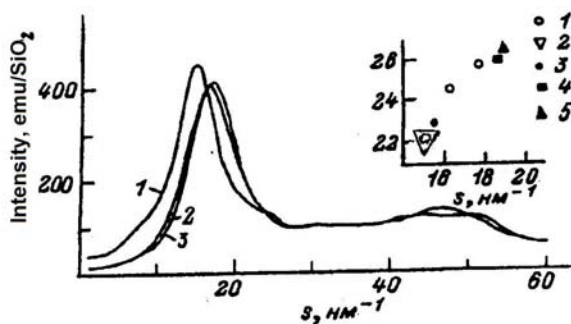

Fig.2. Large-angle scattering for vitreous SiO_2 (1) Sample is prepared from a melt (T_f ~1400 °C) at the normal pressure. Densified samples with d ($g \cdot cm^{-3}$) 2.50 (2) and 2.56 (3); s – is the scattering vector. The inset illustrates density as a function of the location of the principal maximum in the scattering curve: (1) vitreous SiO_2, (2) β-cristobalite, (3) α-cristobalite, (4) β-quartz, and (5) α-quartz. [13]

In our opinion, the method of Raman spectroscopy is especially perspective. In the work of Inoue (1987) [14] there is presented the Raman spectrum of initial and annealed glasses $GeSe_2$ (Fig. 3). At annealing below T_g ($T_{tr.n-cr}$) that equals ≈ 363 °C,   intensity of peak E, characteristic for LTPM $GeSe_2$ in which $GeSe_{4/2}$ tetrahedra are connected by corners in a three-dimensional grid (3D-form) increases. Annealing above T_g increases the intensity of peak A, connected with HTPM $GeSe_2$ where half of tetrahedra are connected by corners, and half by edges (2D-form). Thus, below T_g there is a transformation of HTPM → LTPM polymorphoids, and above T_g – return back, in full conformity with the basic theses of polimeric-polimorphoid configurations.
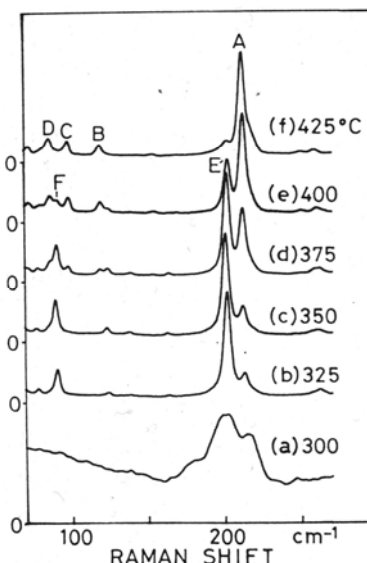

Fig.3 Raman spectra of a-$GeSe_2$ annealed at several temperatures. The annealing temperatures are shown in the figure. Lines A, B, C, and D are due to 2D form, and lines E and F are originated from 3D form. Spectrum (a) is similar to that of a-$GeSe_2$ before annealing. The spectra are normalized at the maximum peaks [14].

In Sugai work (1986) [15] the quantitative estimation of Raman spectra peak intensities for glasses Ge_xS_{1-x}, Ge_xSe_{1-x}, Si_xS_x, Si_xSe_{1-x} (x <0.33) is offered on the basis of the model of a stochastic random network. The model characterises the glass structure only by one parameter P which expresses the probability of existence of the chemical bonds connecting tetrahedra $GeSe_{4/2}$ by edges and bonds, connecting them by corners. The first one is associated with companion peak A_1^c of Raman spectrum, the second one with peak A_1. The intensity ratio of these peaks I (A_1^c)/I (A_1), changing according to the influence on glass of various factors can be related to a concentration ratio of polymorphoids (CRP) HTPM:LTPM.

Estimation of a concentration ratio of low-temperature polymorphoids and high-temperature polymorphic modifications in unicomponent glass by means of enthalpy measuring can be carried out by simple subtraction from the enthalpy of polymorphic transformation of a

crystalline state ($H_{tr.cr}$) enthalpy of glass transformations to the undercooled liquid ($H_{gl \to liq}$). The last one represents the heat of transformation of polymorphoids of low-temperature polymorphic modification of (LTPM) into high-temperature polymorphic modifications polymorphoids (HTPM). And the difference of heat corresponds to heat of transformation LTPM polymorphoids, which, in glass, are already replaced by HTPM polymorphoids. Thus the concentration ratio of LTPM and HTPM polymorphoids CRP (L:H) can be estimated by:

$$CRP(L:H) = \frac{H_{gl \to liq}}{H_{tr.cr} - H_{gl \to liq}}$$

The results of diffractometry, spectroscopy (Raman-spectrum), calorimetry and other researches of various crystal PM, glass forming liquids and glasses SiO_2, B_2O_3, GeO_2, H_2O, Se, GeS_2, $GeSe_2$, $SiSe_2$, $BeCl_2$, analysed in [1-5], allow to formulate the following thesis.

The formation of glass forming liquids at fusion high-temperature PM(HTPM) of individual chemical substance is a process of fragments formation of this PM structure, that have no long-range order (polymorphoids) and their partial transformation into polymorphoids of others low-temperature PMs (LTPMs) with the subsequent establishment of a specific CRP of different PMs [5] for each melt temperature.

The given thesis is well illustrated on an example of such glass forming liquids as H_2O. Pauling [16] wrote that transition «ice I (H_2O) → liquid » is accompanied by change of enthalpy $\Delta H ° = 6.0$ кJ • mol^{-1} that it is possible to explain by rupture of some hydrogen bands or its deformation, as, for example, in case of ice II. He consider that for liquid water both of these process are characteristic. The roentgenogram of liquid water at 4 °C is well co-ordinated with the roentgenogram, counted for a mix of microcrystals of ice Ih, ice II and ice III in the ratio 50: 33: 17.

In the work of Pavlotou and Papatheodorou (Fig. 4) [17] temperature dependence of the ratio of intensity strips I^E/I^B of the Raman-spectrum high - (328 sm^{-1}) and low-temperature (274 cm^{-1}) PM in glass and $BeCl_2$ glass forming liquids is investigated.
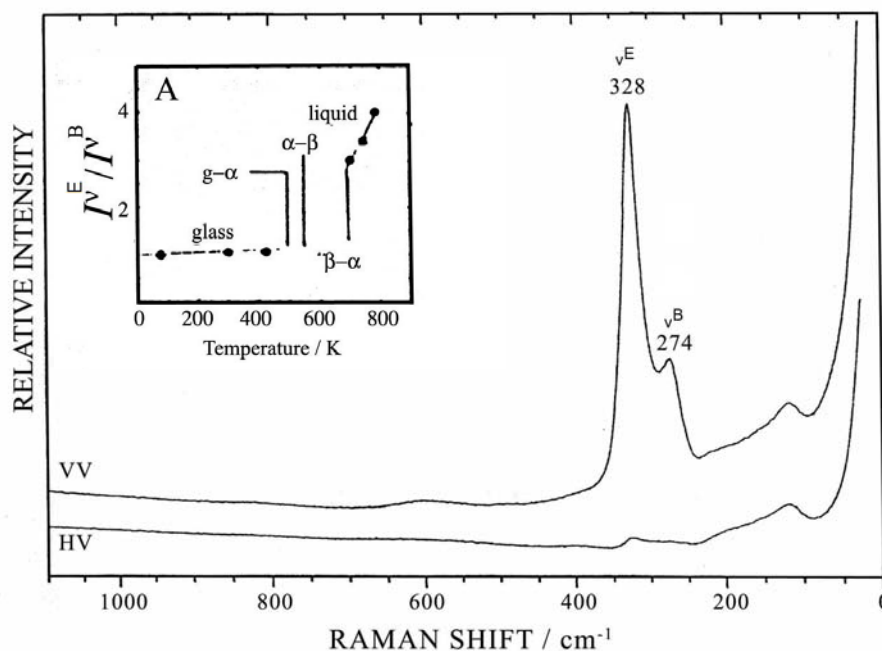

Fig.4 Raman spectra of liquid $BeCl_2$ at 470^0C. Inset A: Temperature variation of the relative intensities of stretching vibration modes of $BeCl_2$. v^E - α-PM; . v^B - (ß) - PMs [17].

This ratio in the glass equal ~1 from liquid nitrogen temperature to devitrification temperature (~ 200°C) changes slightly. At HTPM melting almost at once this ratio becomes equal ~ 3 i.e. approximately the one fourth part of a liquid forms LTPM fragments, and ¾ - HTPM. With the increase of temperature of a liquid this ratio grows to 4. At cooling of any glass forming liquid copolymerization of fragments of substance with different structures and without a long-range order (polymorphoids) takes place. Such copolymerization is the fundamental cause preventing the organization of a long-range order (crystallization) and the main feature of the glass-formation process.

4. Conclusion

As a result of comparison of the properties of glasses, glass forming liquids and crystal PMs of glass forming substances, as e.g. the characteristics of large-angle X-ray

scattering, intensity of Raman spectrum bands, the value of a thermal capacity and enthalpy, and according to other methods, already now it is possible to give a quantitative estimate of CRP of various PMs in glass, and in glass forming liquids.

For more exact definition CRP of glasses in a steady state, and also at various stages of relaxation processes (for example, glass transition) working out of the special techniques using the data on the properties and characteristics of glass, glass forming liquid and various crystal PM is necessary. It will allow to characterise quantitatively simultaneously with kinetics and thermodynamics changing structure in any process that takes place in glass forming substances, to deduce quantitative laws connecting these three approaches in glass research, to create a comprehensive theory of glass forming substances. Besides it will be possible to carry out certification and standardization of glasses on the basis of graphic and tabular dependences: CRP - property, and also the control and optimization of technological processes of glass synthesis.

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