Some features of the glass transition process by the example of chalcogenide glass systems

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Based on the concept of polymer-polymorphoid structure of glass and glass-forming liquids the experimental data related to the structure and relaxation processes, in particular, the glass transition in chalcogenide and oxide and halogenide glass-forming substances are analyzed. This has been demonstrated that all the relaxation processes in liquid and glassy state have a common physicochemical nature - the mutual conversion of the structure fragments (polymorphoids) of the different crystalline polymorphic modifications without the translational symmetry (long-range order), copolymerized to a greater or lesser degree, respectively, in the vitreous or liquid state.

1. Introduction

According to Elliott (1984) [1] "the nature of the glass transition is very complex and even now is poorly understand". Boolchand et al. (2001) [2] ascertain: "the nature of the glass transition process continues to remain a subject of serious discussions". Yue (2007) [3] suggests: "the glass transition is one of the important topics for condensed matter research. Though considerable progress has been made in understanding the glass transition in general, some crucial questions still remain unanswered ".

Such a decisive and at the same time, outstanding issues include the situation of the glass transition domain (softening, conversion), the location of the glass transition temperature, the physicochemical sense of the glass transition and the glass transition temperature, the reasons for winding in the curve of "property-temperature "cooling of the melt.

The key to solve these and other crucial questions of the glass transition we regard the concept of polymeric-polymorphoid structure of glass and glass-forming liquids in the case of individual chemical substances (ICS) - elements and compounds, and within the broader concept of polymeric-nanoheteromorphous structure of glass-forming substances in the case of two- and multicomponent alloys. In this paper we consider only one component of the substance.

The concept of polymeric-polymorphoid structure of glass-forming substances appeared in the late 80-ies [4] and continues to evolve today.

The basics of the concept formulated in [5-10].The most important of these basics are listed below:

- individual chemical substance in the glassy state is a copolymer of nanofragments structure of different crystalline polymorphic modifications (polymorphoids), having no translational symmetry (long-range order) and characterized by strictly defined intermediate- and short-range order inherent in the corresponding crystalline polymorphic modifications (PM) of the substance. The structure of vitreous ICS is always presented at least two intermediate orders belonging to different PM;

- the various PM polymorphoids mutual conversion and changes in their concentration ratio (CRP) in a glass-forming ICS under the influence of external factors and time - the fundamental reason for the change of the structure and properties of non-crystalline substance in the process its relaxation, the CRP - the most important internal parameter of the non-equilibrium thermodynamic system of glass-forming substances.

2. Glass transition domain and temperature

Analyzing the glass-forming chalcogenides of silicon, germanium, phosphorus, arsenic, antimony and others Popescu (2000) [11] states that the continuous change of their properties is the fastest in the transformation domain – Fig.1 – (often in the literature uses the term glass transition interval or glass transition region). This is correct referring to other types of glass - oxides, halides.
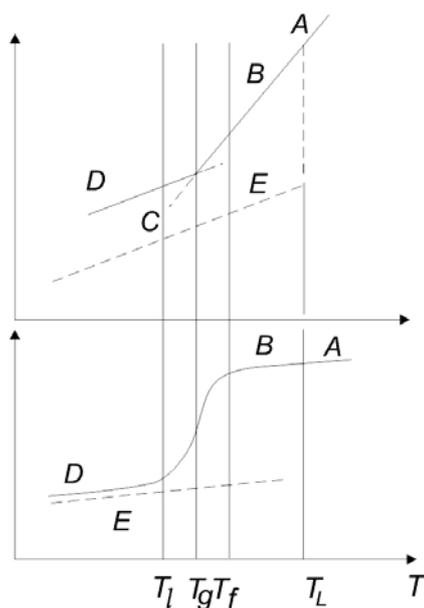
Fig. 1. The curve property – temperature for a glass; A = melt; B = undercooled melt, C = the equilibrium curve for: B; D = glass; E = crystal, T_L = the liquidus temperature, T_g = the transformation temperature (T_l and T_f are the low and high limits of the transformation domain).

The Popescu's glass transformation domain is located between the temperature T_f, separating the liquid and plastic state, and T_l - the temperature of vitrification, where the glass becomes hard and brittle (solid and fragile).

The Popescu's glass transition is essentially the same range of softening in Tamman (1933) [12] (Fig. 2), and its temperature Tl is identical in physical meaning, Tamman T_g - $T_{g (T)}$ - transformation temperature of the viscous-flow state to the solid fragile glass.

Fig. 2 shows the Tamman's ideas with Artamonova's detalizations (1983) [13].It replaces the term "range of softening," Tamman the "glass transition interval", and interprets the Tamman's data as follows.

Properties of glasses due to the variation nature in the range of the glass transition are divided into three groups. The first group includes properties P, characterizing the function of the state of matter (the internal energy E, the molar volume V, enthalpy H, the entropy S) and kinetic properties (viscosity η and resistivity ρ).Properties of the first group are changing gradually with increasing in temperature. In the range of the glass transition curve has rounded the bend (Fig. 2, curve I), which corresponds to the abrupt change in the first group of properties. The properties of the second group represent the first derivative of temperature dP/dT on the properties of the first group (the coefficients of thermal expansion - linear and volumetric, heat capacity. Curve 2 characterizes the temperature variation depending on the properties of the second group. One can see that in the range of the glass transition first derivative dP/dT has a point of winding T_W. The third group includes properties (conductivity, dielectric losses), which are the second temperature

derivatives (curve 3). The temperature dependence of d^2P / d^2T has a maximum or minimum at T_W.
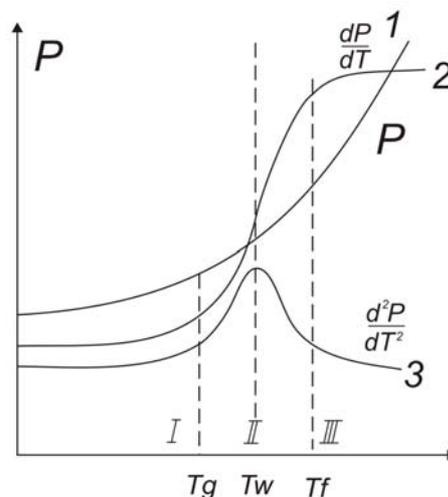

Fig. 2. The dependence of the properties P and their temperature derivatives in the glass transition range. I - solid state; II - plastic; III - liquid (melt).

Tamman temperature T_W is "in a highly viscous state" [12] and corresponds to the viscosityη= 3.10^{13}poise, $T_{g(T)}$ is the boundary between the liquid (highviscousity) and solid state.

Later, the symbol T_g was used Lindig (1959) [14] to indicate the temperature inside the glass transition interval – the temperature being determined by the intersection of tangents from property-temperature relation [15]. I.e. Lindig actually annulled Tamman's T_g and T_w and last designated as T_g. Voluntarily or involuntarily he reduce by half the glass forming range, cutting away most of the highly viscous region. The reason for this "innovation" was, apparently, the lack of Tamman explain the physicochemical sense just defined Tamman's temperature T_W and the relative closeness to its $T_{g(T)}$.Thus, Lindig actually united Tamman's T_g and T_w, taking from the first name and symbol, and from the second - the place of its temperature position. Further, we denote T_g Lindig as "T_g".

A significant part of the scientific community absolutely accept the Lindig's "innovations". Popescu [11] and Landa [15] formally accept the new Lindig's T_g, but put it in the middle of the glass transition interval, fixing at the same time, the temperature boundary between highviscosity and solid state. Popescu call this the temperature of vitrification T_l, Landa's T_B - the temperature at which a liquid becomes a glass. I.e. in fact, these authors, as well as Artamonova [13] recognized the objective point of view on the glass transition temperature of Tamman's T_g.

The glass transformation interval is uniquely associated with the most dramatic, almost straight, the increase of the logarithm of the viscosity during the cooling process of glassforming liquid (Fig. 3 [7-9, 12, 16-19]).According to Winter-Klein [16] and the authors she

cited this range lies within a 10^{7-8}- 10^{14-16}Pa·s. Nemilov [17] gives values of 10^8- 10^{15}Pa·s, Mazurin and Minko [20] - 10^{10}- 10^{15}Pa·s.

Today in spite of Tamman's "T_g" (Lindig's T_g) is characterized by a viscosity of $10^{12.3}$Pa.s.Mazurin [21] argues that the viscosity of the corresponding temperature

"T_g", obtained by heating the glass can vary up to two orders of magnitude. Viscosity of middle of glass transition region, according to Winter-Klein is 10^{12} Pa·s which is very close to the data Tamman [12] and Artamonova [13] T_W winding point (3.10^{12} Pa·s), located in the middle of the glass transition range (Fig. 2).
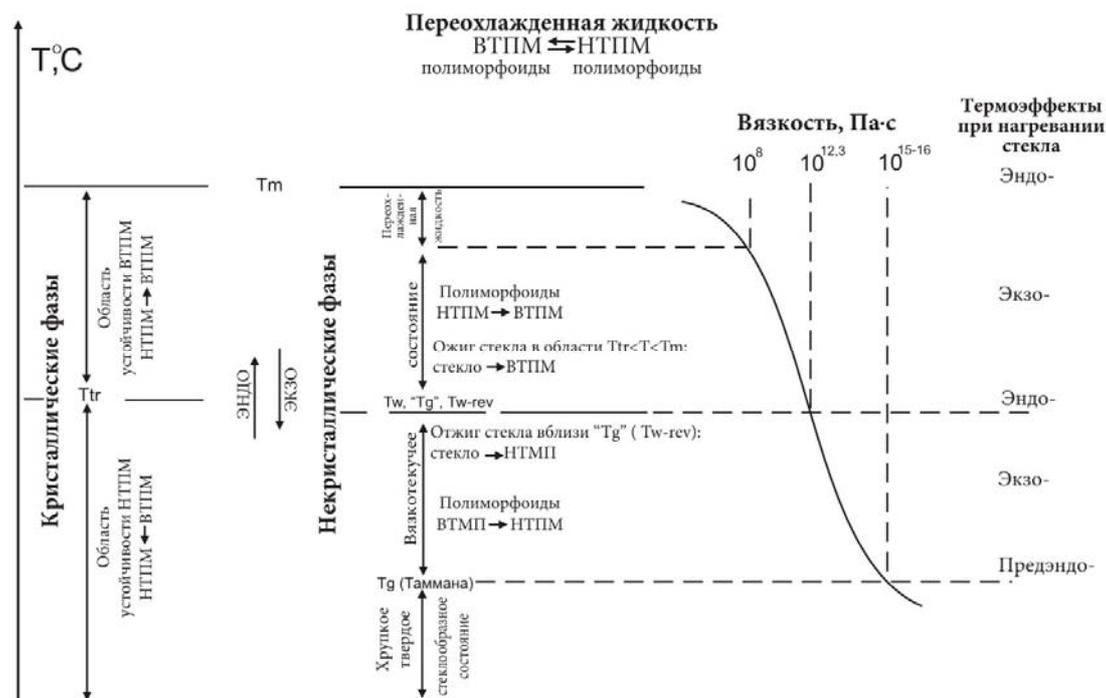

Fig. 3. A generalized scheme of the relaxation processes of the condensed glass-forming substance [12, 16-19].

During the glass heating in the temperature range at which the viscosity is 10^{15}Pa·s or less, one can see in the glass the substantial changes: the heat capacity, thermal expansion coefficient high increasing. These phenomena are associated with the fact that the atoms in the glass start oscillating erratic movements, which require more energy. These phenomena was familiar to Tamman [12].According to him they characterized temperature T_g - temperature of the loss of hardness and brittleness of glass. Next by Nemilov [17]: with increasing temperature, the intensity of vibration motions and free volume necessary to move the atoms are increasing, while the activation free energy E^*, required to move the atoms is decreasing. Conversely, the transition from viscous-flow state to a

solid glassy E^* increases. E^* value with viscosity 10^{15}Pa·s at the onecomponent substances approaches to the energy rupture of the chemical bonds that form glassy skeleton (Table 1) [17].Thus, when heating the glass at a viscosity of 10^{15}Pa.s glassy skeleton begins to break down and the glass softens. Upon cooling of viscous-flowing substance at this viscosity broken chemical bonds are restored, and forms a hard brittle glass, which is characterized at the instant of formation (as in the instant destruction of the frame) a glass transition temperature Tamman's T_g - $T_{g(T)}$.

The values of free activation energy E^* of viscous flow at transition to the brittle state in comparison with the energies of chemical bonds

Ed for simple glasses in kcal/mol [17]

Table 1.

Substance	Se	As$_2$S$_3$	As$_2$Se$_3$	GeSe$_2$ (extrapol)	SiO$_2$	GeO$_2$	BeF$_2$
E_η ,	31±1	47±1	45±2	52±1	114±10	73±4	55±3
Ed	41	61	43±3	52±3	110±5	82±3	89±1
Δ%Ed	24,5	23	4,5	0	2,5	11	38

The date of Winter-Klein [16], Nemilov [17], Mazurin and Minko [20] conclusively prove the truth of the Tamman's glass transition temperature T_g and illegitimacy of replacement Tamman's T_W - the symbol of the

temperature of the winding, in the curve of the "temperature-property" cooled melt, to the symbol T_g [22].Therefore, in the following text we denote generally

accepted today, in spite of Tamman, T_g as "T_g", and the true glass transition temperature Tamman's T_g as $T_{g(T)}$.

Cancellations Tamman's notions T_g and T_W and the replacement of the symbol the T_W to T_g did not cause serious resistance of the scientific community due to lack of information about physicochemical essence of winding on the dependence of the "property-temperature" cooled melt. This entity has been identified only in the late 90's - early 2000's [7,8] within the limits of concept of polymeric-polymorphoid structure of glass-forming substance and presented below.

3. The glass transition process and reverse temperature of interconversion direction of different PMs polymorphoids

3.1 Formation and structure of glass-forming liquids

The most important factor influencing on the glass transition process is the structure of glass-forming substance and, primarily, the structure of the liquid (melt), which is in the cooling process turning into a glass.

In accordance with [23] selenium melt slightly above the melting temperature (217°C) contains 40% monomer Se_8 (monoclinic low-temperature polymorphic modification - LTPM) and at 427°C - 25%. The rest falls on the hexagonal high-temperature PM (HTPM), by melting which the melt forms.

In [24, 25] is shown (Fig. 4, 5) that immediately after the melting HTPM $GeSe_2$ above 712°C the band intensity of the Raman spectrum at~216 cm^{-1} which characterizes the vibration mode A_1^c of edge-sharing tetrahedra (EST), is decreased and the intensity of the band at~201 cm^{-1} characterizing the vibrational mode A_1 of corner-sharing tetrahedra (CST), is increased.
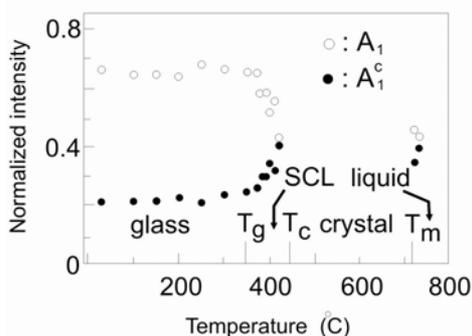
Fig. 4. Temperature dependence of phonon vibration A_1 and A^c_1 bands in glass, super-cooled liquid (SCL) and liquid $GeSe_2$. Intensity of A_1 and A^c_1 bonds normalized by the whole intensity of Ag, A_1 and A^c_1 bonds [24].

From the standpoint of the concept of polymer-polymorphoid structure of glass-forming substances this means that the polymorphoid concentration of HTPM composed in equal parts of EST and CST, decreases, and the polymorphoid concentration of LTPM composed only of CST, increases. Thus, as a result of HTPM melting in

the melt LTPM polymorphoids appears as well. A similar situation occurs for sulfur [26] and SiO_2 [27] analyzed in [6], as well as H_2O [28] and $BeCl_2$[29] analyzed in [30.10].

Thus, the structure of glass-forming liquids is constructed from the polymorphoids of the different polymorphic modifications, the concentration ratio of which (CRP) varies depending on the temperature of the liquid.

The phenomenon of the LTPM polymorphoids appearance in the melt along with HTPM polymorphoids, is of extraordinary importance: cooling of this melt at a rate above the critical value V_{cr} leads to copolymerization of various PM polymorphoids which excludes the crystallization of melt in the form of one of PM and increases the viscosity of the melt and leads to the formation of glass [8,31].

No doubt, this phenomenon is characteristic of all the glass-forming substances, and this will be confirmed in the near future.
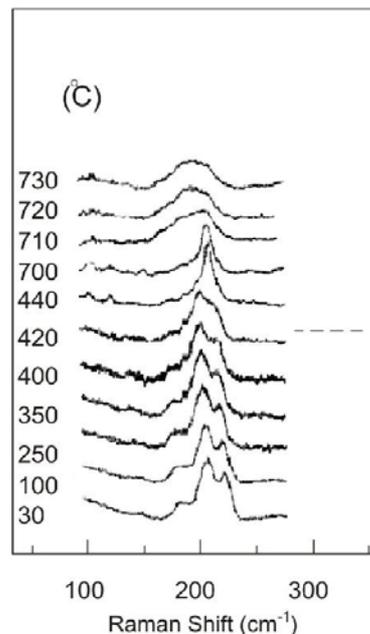
Fig. 5. Typical stokes Raman spectra for $GeSe_2$ in the glassy, crystalline and liquid state [25].

3.2 Cooling of the glass-forming melt

The glass-forming melt consisting of HTPM and LTPM polymorphoids, being cooled, passes successively the region of HTPM stability (from the melting temperature Tm to the transformation HTPM ↔ LTPM temperature T_{tr} and then the stability region LTPM (T_{tr}-$T_{g(T)}$) (Fig. 3). In the first region, the simultaneous processes of HTPM and LTPM polymorphoids copolymerization, the processes of LTPM polymorphoids depolymerization and the turning them into the HTPM polymorphoids occurs. As a result, the concentration ratio of polymorphoids (CRP) HTPM: LTPM determining the

slope of the dependence of the property - temperature increases.

The boundary between stability's areas of crystalline HTPM and LTPM characterizes by the transformation temperature T_{tr}, and the threshold enthalpy HTPM $\leftrightarrow$ LTPM conversion H_{tr}. The glass-forming melt can be characterized by the temperature and the threshold enthalpy HTPM $\leftrightarrow$ LTPM polymorphoids transformation as well. The threshold enthalpy of transformation H_{tr} in the crystalline and glass-forming substance are identical, and the temperature of transformation into a glass-forming melt varies depending on the cooling rate - increases with the rise of the cooling rate and decreases with its diminution. Upon crossing this temperature the melt during cooling appears in the region of LTPM polymorphoids stability and HTPM polymorphoids instability. At this point, the polymorphoids interconversion HTPM $\leftrightarrow$ LTPM direction reverses. Since this point the melt copolymerization is accompanied by HTPM polymorphoids decomposition and transformation them into LTPM polymorphoids. CRP HTPM: LTPM decreases, the slope of the curve depending on the property-temperature, undergoes a winding point. The temperature of this winding Tamman [12] designated as T_W (Windung (German) - the winding). Lindig [14] threw the Tamman's glass transition temperature T_g and put his a symbol T_g instead of Tamman's T_W, created in the investigation of the glass conceptual artifact, which more than half a century inhibited this investigation.

We hope that after the papers of Artamonova [13], Popescu [11], Landa [15] and series of Minaev studies [7-10], revealing the physicochemical essence of the winding in the curve of "property-temperature" this artifact will be forgotten by the scientific community and for the temperature of winding (T_w, "T_g") on the "property-temperature" curve will be assigned a symbol T_{w-rev} - symbolizing the Tamman's pioneering role in establishing this winding and physicochemical nature of the winding – direction reverse of HTPM $\leftrightarrow$ LTPM polymorphoids transformation.

"T_g" or T_{w-rev} is usually determined by the differential thermal analysis (DTA) or by the differential scanning calorimetry (DSC), often during the sample heating. Due to the existence in the heated glass both the LTPM polymorphoids, and HTPM polymorphoids with greater enthalpy, the glass enthalpy is always greater than the crystal LTPM enthalpy. Therefore, the enthalpy reaches the threshold H_{tr} at a lower temperature than crystal LTPM (Table 2).

Thus, as noted in [32] the genetic intercommunication between the crystalline, liquid and glassy states exists. The temperature interconversion HTPM $\leftrightarrow$ L PM in the crystalline substance (T_{tr}), which has no relationship to the process of glass transition, is closely related with the temperature of the direction reverse of different PM polymorphoids interconversion in high-viscosity glass-forming substance T_{w-rev} ("T_w").

Accepted today "T_g", or T_{w-rev} and T_{tr} – the transformation temperature of crystalline polymorphous modifications [9,18].

Table 2.

Substance	"T_g", или T_{w-rev}, °C	T_{tr},°C
Se	27…37	70
GeS$_2$	495	497
GeSe$_2$	370	Crystallization of glass LTPM – 325, HTPM- 425
P$_4$Se$_4$	180	192
As$_2$S$_3$	175	175…180
P$_2$O$_5$	380	>378 (active stage)
Zn(PO$_3$)$_2$	445…520	Crystallization of glass LTPM+ HTPM – 550

Below the T_{w-rev} the glass-forming melt copolymerization and polymorphoids conversion HTPM LTPM continues up to $T_{g\ (T)}$, when (viscosity $\eta \sim 10^{15}$ Pa·s), the melt becomes hard and brittle [12].

Nemilov [17] says that during the glass heating, just after the $T_{g(T)}$ 10^{15} Pa·s the glass heat capacity, the thermal expansion coefficient and the refractive index are sharply changed. These phenomena are associated with the fact that the atoms in the glass start oscillating erratic movements, which require more energy - free energy of activation E*.

We regard the above described phenomena (Tamman said the same [12]) associated with the absorption of heat, as the physicochemical essence of the phenomenon called predendoterm or predendoeffect [33], detected by DSC for rapidly quenched phosphate and silicate glasses, (Fig.3).

Above the predendoeffect in the glass-forming Se, GeS$_2$, GeSe$_2$, As$_2$Se$_3$, As$_{50}$Se$_{50}$, H$_2$O, Ca(PO$_3$)$_2$, etc. the exoeffect is observed, which analyzed in [34]. Physicochemical essence of this effect is the transformation of the HTPM polymorphoids with higher enthalpy to the LTPM polymorphoids with lower enthalpy. Following the exoeffect endothermic effect at T_{w-rev} ("T_g") is caused due to the reverse (LTPM HTPM) polymorphoid's transformation in high-viscosity liquid.

Finally, the exothermic effect above T_{w-rev} ("T_g") is associated with HTPM crystallization (Fig.3), above which the LTPM melting endoeffect observed.

And the last question arises: why both fragments of high-temperature PM and fragments of low-temperature PM, found out in a glass, are present in liquid?

The one PM to another PM conversion mechanism during the solid dispersion is proposed in [35] and is consistent with the data [36]. Here we propose to extend this mechanism for the glass-forming liquids too.

On dispersion of a substance, both solid and liquid, the sizes of its separate fragments decrease. In associated liquids to which belong glass-forming liquids such as Se, As$_2$S$_3$, As$_2$Se$_3$, GeSe$_2$, SiO$_2$, BeCl$_2$, H$_2$O, etc., there are the separate associates partially tied up among themselves constantly breaking off and reforming (already between other parts of these associates) chemical bonds.

When the temperature of the fused substance increases associates decrease in sizes and in the part which is not connected at that time with other associates there is a surface tension, trying to reduce a free surface of the associate up to the least possible limits at the given volume

of the associate, which causes certain excessive pressure inside the associate. The higher the level of associates' dispersion the higher the pressure. The increased intrinsic pressure is the main reason for associates' transformation which does not have a long-range order, that is, polymorphoids of one polymorphic modification into polymorphoids of other PM.

For silica this is transformation of crystobalite polymorphoids into polymorphoids of more dense quartz (see Gerber's experiment, etc. [7]) and to some extent coesite, for H_2O- polymorphoids of usual ice I (d=0,92g·cm^{-3}) in polymorphoids of more dense ice II (d=1,18g·cm^{-3}) and ice III (d=1,15g·cm^{-3}) [28,30].

The proposed mechanism reveals the physicochemical nature of the anomalous density increase with increasing temperature in those glass-forming liquids like SiO_2 and H_2O [37, 38].

4. Summary

1. ICS in a glassy state is a copolymer of nanofragments of various crystalline polymorphic modifications (polymorphoids) without translational symmetry. Interconversion of these polymorphoids in various PMs and their CRP change under the influence of external factors and time - the fundamental reason of the structure and properties of the glass-forming substance changes in its relaxation process.

2. It is shown the illegitimacy of the cancellation of the T_g and T_w notions proposed by Tamman (where T_g is the temperature of the transformation of viscous-flow state to the solid fragile state, T_w is the winding temperature in the curve "property-temperature").

3. It is identified the incorrect application of the symbol T_g and of its physicochemical value - the glass transition temperature - instead of Tamman's T_w, which is situated in the middle of the glass transition area.

It is also shown that T_w in a glassforming matter (mistakenly called "T_g") is an analogue of interconversion temperature T_{tr} of high- and low-temperature polymorphic modifications of crystalline substance. T_w is the temperature of the reverse of interconversion direction of polymorphoids HTPM and LTPM in the viscous-flow ($\eta \approx 10^{12,3}$ Pa·s) glass-forming substance.

4. It is proposed to replace the incorrect symbol "T_g" for the symbol T_{w-rev}, which reflects the pioneering role of Tamman in establishing the phenomenon of the winding on the "property-temperature" dependence, as well as physicochemical nature of this winding.

It is also proposed to consider the glass transition temperature as a temperature of transformation of the viscous-flow liquid ($\eta \approx 10^{15-16}$Pa·s) to solid, fragile state, as T_g, proposed by Tamman. And in order to avoid confusion it must be called $T_{g(T)}$.

5. The formation mechanism of LTPM polymorphoids along with HTPM polymorphoids in glassforming liquid is proposed.

The presence in the melt of different PM polymorphoids excludes crystallization of a substance and it is the true cause of the glass formation.

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