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THE NEW APPROACH TO THE VITRIFICATION PROCESS

V. S. MINAEV[a,c], V. P. VASSILIEV[b*], S. P. TIMOSHENKOV[c]
[a]*Joint-Stock Company «Research Institute of Material Science and Technology», passage 4806, h.4, Zelenograd, 124460, Moscow, Russia.*
[b]*Lomonosov Moscow State University, Chemical Department, 119992 Moscow, Russia.*
[c]*National Research University of Electronic Technology, passage 4806, h.5, Zelenograd, 124498, Moscow, Russia.*

On the basis of analysis of the numerous experimental data, we have demonstrated in this paper, that the now generally accepted glass transition temperature T_g stays away from Tamman's notion. This has resulted from borrowing from Tamman's symbol T_g, which denotes the transformation temperature of a viscous-flow liquid into a solid brittle vitreous state, which should actually be the symbol T_w. Tamman's symbol T_w represents a temperature of the bend on the dependence "property-temperature" of the glass-forming substance, located above Tamman's T_g.The physico-chemical nature of the temperature of the bend T_w (now T_g) was established on the basis of the concept of polymer-polymorphoid structure of the glass-forming substance. Namely the temperature of the bend T_w is the reverse temperature of the interconversion of the structural nanofragments (polymorphoids) of the high-temperature polymorphous modification and the low-temperature polymorphous modification (HTPM↔LTPM), coexisting in the glass-forming substance. The recent discovery of the pre-endothermic effect, located as Tamman's T_g below the currently accepted T_g, confirms the validity of Tamman's T_g, which is characterized by an increasing of the specific heat of the heated glass.

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1. Introduction

The glass transition temperature (T_g) of the glass-forming substance and its position on the curve of "property - temperature" is one of the most important and at the same time, one of the most perplexing problems in the theory and practice of vitrification.

The first serious researcher of the T_g effect was, apparently, Tamman (1926, 1933) [2, 3]. Tamman does not use the term "glass transition temperature". He gives the following definitions of the T_g term:

a) Transition temperature of the supercooled viscous liquid into the brittle state (*below,* he names this state as a glassy state);

b) Glass solidification temperature.

Thus, Tammann's glass transition temperature is the transition of the viscous-flow liquid into the solid brittle vitreous state.

"Now it is difficult to reveal, Mazurin wrote in 1986 [4, p.24], who used the first Tamman's temperature with the symbol T_g, but put it in a completely new content. Nevertheless, this new definition of T_g received very wide recognition, and almost no one remembers Tamman's definition (perhaps, with a single exception of university textbook [5]. "

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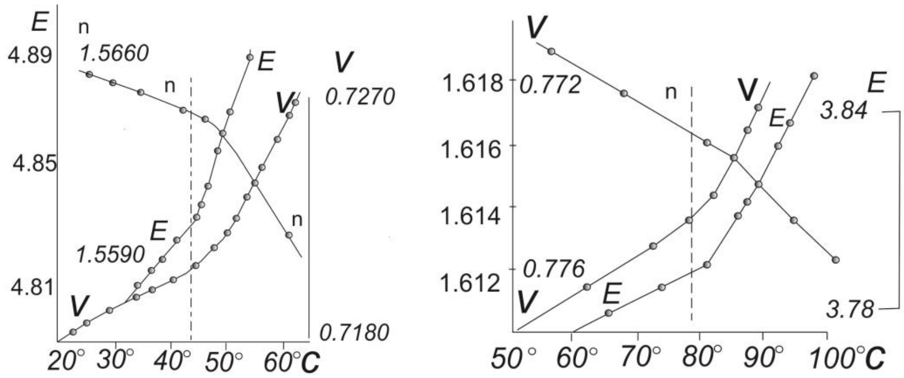
[*] Corresponding author: valeryvassiliev@yahoo.fr

One of the authors of the new content of the symbol T_g, as the glass transition temperature, was Lindig [6], (1959), according to Landa et al. [7]. Lindig used the symbol T_g to denote the temperature inside of the range of the glass transition, indicating the intersection of the tangents on the curve "property-temperature" [6].

There are also other points of view on the location and physical-chemical meaning of the glass transition temperature T_g. Thus Winter- Klein [8, 9], believes the glass transition temperature is at the beginning of the glass transition range, while Shelby [10] suggests that the glass transition temperature is at the end of this interval. Which of these points of view (including Tamman's point of view) is the most objective? The following sections of this paper are devoted to answering this question.

2. The characteristic temperatures and the Tamman's interval of conversion (vitrifaction). "The refutation" of the views of Tamman

Tamman coined the symbol T_w, which he refers to as the temperature of the bend on the curve "property - temperature" of the cooling melt ("w" is the first letter of the German word "windung", or "bend" in English). Tamman's T_g temperature is located slightly below T_w. Tamman did not reveal the physicochemical nature of the temperature of the bend on the curve" property - temperature." This apparently is (along with the close proximity of T_w and T_g) the main cause for the replacing of the symbol T_w by T_g, subsequently.



a) b)

Fig. 1The dependence of the "property – temperature" for vitreous silicin (a) and brucine (b). E – the dielectric constant, V – the specific volume, n – the refractive index. The position of the glass transition temperature T_g represented by the dotted vertical line [3].

Fig. 1 gives two examples of the relative position of T_g and T_w (vertical dashed line) for the salicin and brucine vitriforms [3].

Tamman also gives a definition of the T_f temperature. This is the temperature at which the liquid's first signs appear and begin to stretch the first threads [3]. Tamman writes further: "Between the temperatures T_g and T_f, is "an interval of conversion" or "transition "(Fig. 2 [3]). Tamman does not introduce the term "glass transition range" although it is obvious that if the glass forming material is cooled, then of course this interval may be called "the glass transition interval", and then there is an interval in which the glass transition takes place, which was eventually accepted by the scientific community [4, p.24].

Perhaps Tamman feared that after the introduction of the term "glass transition range," it was necessary to also introduce the term "glass transition temperature". And here the question arises: what temperature in this range can be called the glass transition temperature? At the start, end, or in the middle? After all, virtually any temperature in the range of T_f -T_g is the temperature of a certain part of the vitrification process. Didn't Tamman foresee the possibility of creating confusion on this issue?

When giving his definition of T_g, Tamman meant the final temperature of the process of transformation of liquid into glass and calls it T_g, where the index «g» is an abbreviation of the word «glass». It is therefore logical to identify this temperature as the glass transition temperature, and of course, to avoid any confusion, add the name of Tamman ($T_{g\,(T)}$). Tamman paid much attention to the variations of the physical properties in the temperature range of the glass softening $T_{g\,(T)}$ -T_f or, as is customary to say now, in the range of the glass transition, T_f - $T_{g(T).}$

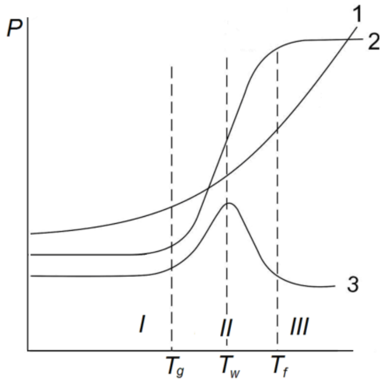


Fig. 2. The temperature dependence of the physical properties (P) in the interval softening.
Curve 1- P, Curve 2 – dP/dT, Curve 3 – d^2P/dT^2*; the designations are contained in the text [3, 5].*

These variations are shown in Fig. 2, [3, p. 23], wherein Artamonova [5] mentions later, using dashed lines and numerals, the areas allocated by Tamman: I - glass (for $T < T_g$), II - viscous state ($T_g > T > T_f$), III - liquid ($T > T_f$). The author [5] also made a notation for T_g and T_f, from Tammans monograph [3]. Tamman divides the properties of glass in the interval of softening of the three groups.

The first group includes the properties (P), which characterize the function of state internal energy (E), molar volume (V), enthalpy (H), entropy (S) and kinetic properties: viscosity (η) and resistivity (ρ). The properties of the first group increase progressively with the increasing temperature (Fig. 2, curve I).

A second group of properties (P): the coefficients of thermal expansion (linear and volumetric), and heat capacity represent the first derivative of the temperature dP/dT. In this group there is an inflection point T_w in the range of vitrification. So, Curve 2 characterizes the temperature dependence on the second group's properties.

The third group includes the properties (P) as thermal conductivity and dielectric loss. These properties are second derivatives with respect to the temperature of state functions. They are represented by the curve 3. The temperature dependence of d^2P/d^2T has a maximum or minimum at T_w.

Tamman's temperature T_w is higher than $T_{g\,(T)}$ "in a highly viscous state" [3, p. 25] and corresponds to the viscosity $\eta = 3.10^{12}$ Pa·s, so $T_{g\,(T)}$ is the boundary between the liquid (viscous flow) and the solid state.

Tamman writes [3, c.37, 49] that the $T_{g\,(T)}$ temperature corresponds to the beginning of softening, where there is a rapid increase of the heat capacity. The increase of the molecular motion requires a new quantity of energy. The separation of molecules from each other is associated with a new amount of the energy expenditure. Obviously the $T_{g\,(T)}$ temperature is associated with an endothermic effect.

Lindig [7] (1959), mentioned above, annulled, in fact, the Tamman's temperatures T_g and T_w, and he defined the T_w, as T_g temperature. So, voluntarily or not, he reduced the interval of vitrification by about half, cutting off the most viscous part. The reason for this "innovation" was, apparently, the lack of Tamman's explanation in regard to the physiochemical sense of inflection on the "property - temperature" curve and the relatively close location of T_w and $T_{g\,(T)}$. Lindig actually united Tamman's temperatures T_g and T_w , by taking the name and symbol of the first term and putting it in the place of the Tw temperature. However, the T_g symbol was used before

Lindig by Jones (1956) [11] and Kobeko (1952) [12] instead of the Tamman's T_w inflection temperature.

3. The facts and arguments in favor of the Tamman view

However, the refutation of Tamman's position associated with the T_g temperature (transition temperature of a supercooled liquid into a solid brittle vitreous state) and T_w (the temperature of inflection on the "properties – temperature" curve) did not succeed.

Kobeko [13, p. 22] (in 1933) was close to Tamman's conception. In particular, Kobeko used the top (T_f) and lower (T_g) limits of the softening temperature T_g and defined it as the vitrification temperature. Above the (T_g) temperature, the heat capacity is increased, and it is associated with an additional quantity of heat, "which is spent for the softening of complexes."

Shelby [10] almost completely shares Tamman's viewpoint: "the temperature range between the limits, one of which corresponds to the enthalpy of the fluid equilibrium and the other to the enthalpy of substance in the frozen solid state, is called the glass transition region". Shelby determines T_g as the temperature "at which the supercooled liquid passes into the solid state or vice versa: at which a solid turns into a viscoelastic state", which actually echoes Tamman.

On the basis of numerous experimental data, Winter Kline drew the conclusion (1953) that within the region of viscosity 10^{16}-10^{14} Pa.s, the curve of viscosity shows a bend corresponding to the transition of the viscous-flow liquid into the solid state [8, 9]. Thus, Winter-Klein actually revealed the viscosity of a glass-forming substance at Tamman's T_g, that is the «transition temperature of a supercooled liquid into the fragile state" [3]. She also revealed that "the transformation area," or Tamman's softening interval, or the modern term "glass transition range," lies in the range 10^7-10^{14} Pa · s. Shelby [10] gives the value for this interval 10^8-10^{13} Pa·s, Mazurin and Minko [14] give 10^{10}-10^{15} Pa·s, and Nemilov [15] proposes the values 10^8-10^{15} Pa·s. Thus, the viscosity at Tamman's $T_{g\,(T)}$ for various glasses lies in the range 10^{13}-10^{16} Pa·s.

The viscosity of the average transformation region (vitrification) is 10^{12} Pa·s, according to Winter-Kline [9]. This value is very close to Tamman's data for the inflection point T_w, where it equals $3{\cdot}10^{12}$ Pa · s [3], which again confirms the illegitimacy of the replacement of Tamman's T_w on T_g. The actual used T_g temperature, with a viscosity of ~10^{12} Pa·s [16, 17] is also located in the middle of the interval of softening (vitrification) and is close to the T_w. In an effort to vitrify the viscous fluid having a viscosity of 10^{12} Pa · s, the additional cooling and increasing of the viscosity to about 2-3 orders of magnitude is required. We conclude that the "modern» T_g [16, 17] is not the actual vitrification temperature or, in other words, the transformation temperature of viscous-flow liquid into the glassy state is Tamman's T_g temperature with a viscosity of ~10^{13}-10^{16} Pa·s.

At present, the usage of the T_g symbol and its interpretation as a "glass transition temperature" provoke contradictions with the objective experimental data. The most important of these contradictions is this "glass transition temperature". Moreover, the 'primary' glass transition ends at this non-Tamman's T_g and the "secondary" glass transition [4] begins, with a non-known ending temperature. In addition, it has been argued that there is a glassy state below T_g [16, p. 12]. Whence it follows that the process of secondary vitrifaction continues, but not in the viscous-flow liquid, like Tamman [3], but in the glass, whose structure is frozen, and does not depend on the temperature and the time change [4, p. 20]. Thus, taking into account the above contradictions, it is clear that the innovative T_g is not a glass transition temperature.

The glass area is characterized by a viscosity of substance lying, with the greatest probability in the range 10^8-10^{15} Pa · s [15]. At the same time the viscosity at T_g temperature is ~10^{12} Pa · s [16, 17]. Consequently, the glass-forming substance is not yet vitrified in the range of ~10^{12} -10^{15}, and the viscosity value ~10^{12} Pa · s characterizes not glass, and not glass transition temperature, but the viscous-flow liquid temperature whose viscosity is approximately 3 order magnitude less than the viscosity of the glass. Only this fact is sufficient to bring back Tammann's T_g symbol to his transformation temperature of the viscous-flow liquid into a solid brittle glassy state.

The revealed contradiction can be eliminated if we take Tamman's transformation temperature of viscous-flow liquid into a solid brittle glassy state (T_g) [3] as the glass transition temperature. Appen [18] almost fully shared Tamman's matter in question. He writes “it should be considered the beginning of the disappearance of the brittleness temperature T_h as the lower boundary of the glass softening under heat. Then, the upper temperature limit will be such when the last solid signs disappear, for example, the residual ability to the reverse deformation at low loads (flow point T_f)”.

The only dissimilarity from Tamman is that Appen [18] uses his own symbol Th instead of Tamman's T_g, and renames Tamman's T_f temperature, when the “first signs of liquid state appears”, as “the temperature, when the last vestiges of solid state disappear”.

Nemilov [15, 19] supports well-reasoned Tamman's position on the process of softening the glass. A significant change is observed in the glass when it is heated at the temperature with a viscosity of 10^{15} Pa·s or less. Under these conditions, there is a sharp increase of heat capacity and a thermal expansion coefficient. According to [15], the intensity of the vibrational motions and free volume increase with the increasing of temperature, and the free energy of activation of the viscous flow E^*_η, required for moving atoms, decreases. And, conversely, E^*_η increases during the transition from the viscous-liquid state to solid glass. The value E^*_η for the viscosity of 10^{15} Pa·s in simple substances is close to the dissociation energy of chemical bonds, which form a glassy frame (Table1) [19].

Table 1. The free activation energy of the viscous flow at the transition into the brittle state in comparison with the energy of chemical bonds E_d for the simple glass in kcal / mol [19]

Substance	Se	As_2S_3	As_2Se_3	$GeSe_2$ (extrapolation)	SiO_2	GeO_2	BeF_2
E^*_η	31±1	47±1	45±2	52±1	114±10	73±4	55±3
E_d	41	61	43±3	52±3	110±5	82±3	89±1
$\Delta\%\ E_d$	24.5	23	4.5	0	2.5	11	38

Thus we can conclude that the glassy frame receives an additional quantity of heat (endoeffect) and starts to break down when the heated glass, with a viscosity of 10^{15}Pa·s, softens. Conversely, the broken chemical bonds are restored at the same viscosity and the brittle solid forms under the cooling of a glass viscous-flow substance, i.e. Tamman's glass transition (softening) temperature $T_{g(T)}$ is the characteristic point, both at the moment of formation and fracture of the frame.

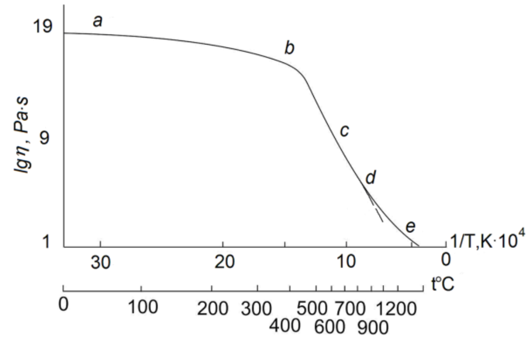


Fig. 3. The temperature dependence of viscosity of glass $Na_2O·CaO·6SiO_2$ [15]

Nemilov’s results are given in Fig. 3 for the viscosity of the glass composition $Na_2O·CaO·6SiO_2$ *vs* temperature [15]. The viscosity changes slightly at low temperatures to the beginning of glass softening (section ab). The sharpest drop of the viscosity occurs at the heating in the area $(10^{15}\text{-}10^8)\pm1$ Pa·s, (bc), and then the slope of the line decreases (cde). The viscosity area (10^{15}-10^{8} Pa·s) characterizes the "softening interval "of glass (Tamman's terminology), or "glass transition interval" (modern terminology).

The number of researchers recognizing the new Tg, located on the site of Tamman's temperature T_w (point of inflection "property - temperature") can not get out from under the influence of Tamman's idea relating to his T_g temperature (point of turning of viscous-flow liquid into a solid brittle glassy state).

The possibility is not excluded that some of these researchers were not familiar with the concept of Tamman's $T_{g,}$ but their experimental data led them to conclusions similar to the findings of Tamman.

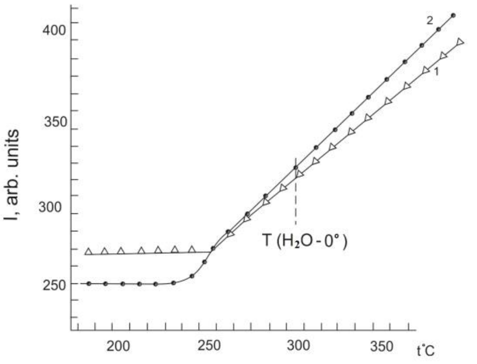


Fig. 4. Dependencies of the SAXS intensity of the B_2O_3 samples on the temperature: 1, 2 – I (400'), and I (40') respectively for the «dry» sample in the equilibrium state [20]

So, Golubkov [20] established some features of structural changes for dry and hygroscopic B_2O_3 samples, during the study of temperature and time dependencies, using the small angle X-ray scattering intensity (SAXS) method. We can see in Fig. 4 [20], the intensity of the X-ray scattering of the dry B_2O_3 samples at the scattering angles 400' and 40' decrease linearly with decreasing temperature to 250 ° C; the T_g temperature is not detected in this experiment. The curvature of the intensity *vs.* temperature has a place in the range of 240-260°C in the case of a dry (without H_2O impurity) sample, i.e. "the sample remains in the supercooled liquid state" up to ~ 250 ° C. Below this temperature the structure is frozen, reaching a particular state in which structural changes are impossible. The temperature, corresponding to this condition, is indicated in [20] as T_p.

The transition from the supercooled liquid state into a solid glassy state occurs at temperature $T_p \pm 10$ ° C [20]. According this work, there is a rule: the differenceT_g–$T_p \approx 50$°C is performed for the dry and hygroscopic B_2O_3 samples. Hygroscopic samples have a lower T_g and T_{const} temperatures. In fact, Golubkov's T_p is analogous to Tamman's $T_{g\ (T)}$, which completely confirms the validity of Tamman's $T_{g\ (T)}$. Golubkov extends the findings of his work [20] relative to the sodium borate [21] and sodium borosilicate [22] glass.

Submicroheterogeneous structure (regions of inhomogeneity of ~15 angstrom in size) arises in the supercooled liquid state of glassforming B_2O_3 [20]. Further, the author [20] says: the submicroheterogeneous structure completely disappears during the transition from supercooled liquid to the glassy state (below 250˚C B_2O_3).

We cannot agree with the last proposition. The submicroheterogeneous structure does not disappear with the transition from supercooled liquid to the glassy state, but, as the author [20] writes, there is a process of freezing of this structure. That is, the submicroheterogeneous structure ceases to change; the intensity of SAXS becomes constant.

According to Popescu [23], the region of glass transition is located between the T_f temperature (which separates the liquid and plastic state) and the vitrification temperature (T_l), when the glass becomes solid and brittle. The vitrification region [23] is significantly similar to Tamman's softening region [3], and the T_l temperature is identical to the physical meaning of Tamman's T_g; $T_{g\ (T)}$ is a transformation temperature of a plastic state to a solid brittle glass.

Landa et al. [7] formally recognize the “new” T_g, but also as Popescu [23], they placed it in the middle of the glass transition range ($T_a – T_b$). Here the T_a is the least temperature of an equilibrium liquid state and T_b is the temperature at which the liquid becomes a solid glass; in fact, here the authors of [6] come to Tamman’s formulation of the temperature conversion of a viscous-flow liquid into a solid brittle glassy state.

The data [5, 7, 9, 15, 18, 19, 21-23] and others conclusively prove the truth of Tamman’s glass transition temperature $T_{g(T)}$, and the illegitimacy of the replacement of Tamman’s T_w, (where T_w is a symbol of the temperature bend in the curve of the "temperature-property" of a cooled melt) by symbol T_g.

4. Polymer-polymorphoid structure of glass-forming substance and physical and chemical nature of inflection on the "property-temperature" curve

The cancellation of Tamman’s notions T_g and T_w and the replacement of the T_w symbol by T_g did not cause any serious resistance from the scientific community due to the lack of information on the physico-chemical nature of the inflection on the "temperature-property" curve of the cooled melts. This entity has been identified only at the end of the 1990s and early 2000s within the concept of polymer polymorphoid structure of glass-forming substances [24-26]; at the same time the illegitimacy of the replacement of T_w by T_g symbol was shown. Below we give some background on this concept, as well as an analysis of the physical and chemical nature of the said inflection.

The process of the formation of the one-component glass substance is a process of occurrence, interconversion and copolymerization of (the structural nanofragments) (polymorphoids) of different polymorphous modifications of the substance into crystalline disordered (at the level of the long-range order) polymer-polymorphoid structure of glass (tangle of chains, belts, etc).

Polymorphoid is a fragment of a crystal structure, which consists of a group of atoms connected together by chemical bonds, according to the rules of stereometric ordering inherent to one of the crystalline polymorphic modifications. The polymorphoid does not have translational symmetry of the crystal. Polymorphoid has no long-range order (LRO) even the minimum value, that is consisting of two neighboring unit cells of the structure of the crystalline substance capable of a mutual translation. The term "polymorphoid" directly connects to the notions of short-range and intermediate-range orderings (SRO and IRO), which are applicable to both a crystalline and non-crystalline substance.

Glass is a copolymer of structural nanofragments of the crystal lattices of different polymorphic modifications (PMs) with no long-range order (polymorphoids). The interconversion of polymorphoids of the different PMs and their copolymerization (or depolymerization) occurs in glass-forming liquids and glass under external influences. The structure and properties of the glass are determined by the concentration ratio of polymorphoids (CRP) of the various PMs inherent to the glass, and depending on the state of the initial material, preparation conditions and processing of the glass-forming material. Between glassy, liquid and crystalline states, there is a genetic relationship expressed in the likeness of the character of physical and chemical processes occurring in the material in different states.

The structure of a glass-forming substance, and, above all, the structure of the liquid (melt), which transforms into glass due to the cooling process, is the most important factor of glass-forming. According to [27], the selenium melt contains up to 40% of the Se_8- monomers of monoclinic low temperature polymorphic modification (LTPM) at the temperature which is slightly higher than the melting point of selenium (221°C). The concentration of the Se_8 monomers is reduced to 25% at 427°C. The rest belongs to the hexagonal high-temperature PM (HTPM), by melting, the melt forms. The presence of the structural nanofragments (polymorphoids) of HTPM and LTPM is stated for the sulfur [16], and SiO_2 [28, 29] melts, as well as for H_2O [30] and $BeCl_2$ [31], on the basis of the analysis in [25, 29, 32, 33].

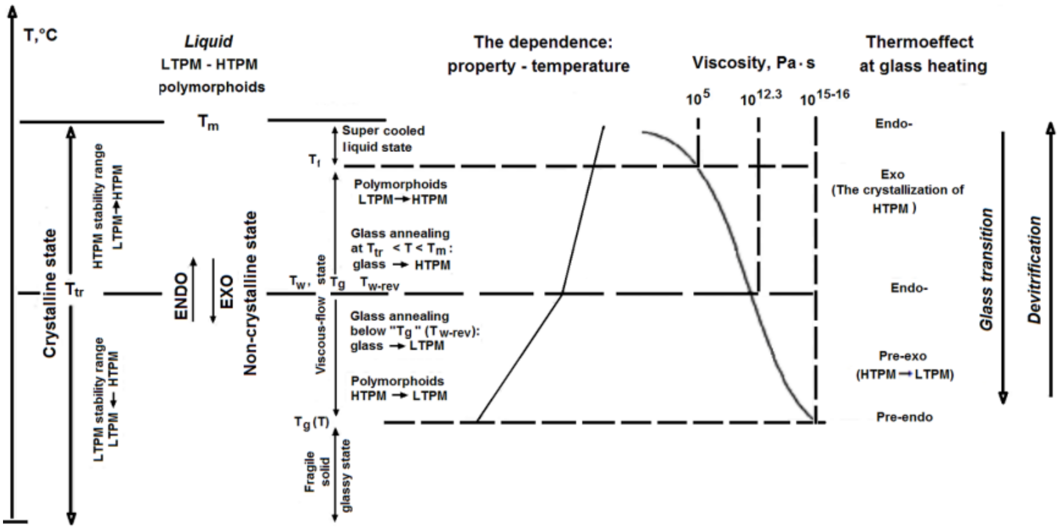


Fig. 5. The generalized scheme of structural relaxation processes of the condensed glass-forming substances [3, 8, 19, 24, 25]

During the cooling, the glass forming melt (consisting of the HTPM and LTPM polymorphoids) successively passes the stability region of HTPM from the melting temperature T_m to the transformation temperature T_{tr} (HTPM □ LTPM), and then it passes the stability region of LTPM (T_{tr} - $T_{g\ (T)}$) (Fig. 5) [25]. In the first region, there is a process of polymorphoid copolymerization of the HTPM and LTPM. At the same time there is the process of LTPM polymorphoid depolymerization and their transformation into HTPM polymorphoids. As a result, the concentration ratio of polymorphoids (CPR) HTPM: LTPM increases, which determines the slope on the curve “property – temperature”.

The border between the region of stability of crystalline polymorphic modifications HTPM and LTPM is characterized by the temperature T_{tr} and by the threshold enthalpy of the transformation (H_{tr}) of the HTPM ↔ LTPM process [22, 25]. The threshold enthalpy and temperature of the HTPM □ LTPM polymorphoid conversion $T_{w\text{-}rev}$ T_w, T_g) (Fig. 5) [25] are also characteristic of the glass-forming melt. The symbol $T_{w\text{-}rev}$ [25] represents the pioneer role of Tamman in setting this temperature of inflection (“w” – Windung (German)) of the curve “temperature – property”, and physico-chemical nature of this inflection: “rev” – reverse of direction of mutual transformation of HTPM↔LTPM polymorphoids. Upon cooling the melt enters the region of stability of the LTPM and instability of the HTPM polymorphoids at the intersection of this temperature. The reverse of direction of the HTPM↔LTPM polymorphoids interconversion is made at that moment.

The copolymerization of melt is accompanied now by the decomposition of the HTPM polymorphoids and turning them into the LTPM ones. The relation CRP (HTPM : LTPM) decreases, and the slope of the curve “property- temperature” experiences an inflection [22].

The temperature $T_{w\text{-}rev}$ (or T_g) is usually determined by differential thermal analysis (DTA) or differential scanning calorimetry (DSC), used most often with the sample under heating. In the glass, along with LTPM polymorphoids, there are HTPM ones with greater enthalpy. As a result the enthalpy of the glass is always greater than the enthalpy of the crystalline LTPM. Therefore, the threshold value of the glass enthalpy H_{thr} is achieved at a temperature less than the transformation temperature of crystalline LTPM into HTPM (Table 2) [34].

Thus, as already mentioned in [35], between the crystalline, liquid and glassy states there is a genetic intercommunication. The interconversion temperature (T_{tr}) of the HTPM ↔ LTPM in a crystalline substance is closely related to the reverse direction interconversion temperature of polymorphoids of different PMs $T_{w\text{-}rev}$ (T_w) in a high-viscosity glass-forming substance.

Table 2. Commonly-accepted T_g (or $T_{w\text{-}rev}$) in some one-component substances [34]

Substance	T_g (or $T_{w\text{-}rev}$), °C	T_{tr},°C
GeS_2	495	497
$GeSe_2$	370	Crystallization from a glass: LTPM – 325, HTPM– 425
P_4Se_4	180	192
As_2S_3	175	175…180
P_2O_5	380	>378 (active process)

The copolymerization of the glass-forming melt and transformation of the HTPM □LTPM polymorphoids continues below the $T_{w\text{-}rev}$ temperature up to $T_{g(T)}$, (viscosity □ □$10^{13\text{-}15}$ Pa · s) at which the melt is transformed into a hard and brittle glass-forming substance [3, 9, 13].

5. Tamman’s T_g and pre-endothermic effect

As mentioned above, Tamman [3] and other authors [8, 9, 15] observed in a heated glass at T_g of Tamman ($T_{g\,(T)}$) (viscosity ~10^{15} Pa · s) a sharp increase in the heat capacity and the change in other properties of glass-forming substances.

These phenomena are characteristic of the pre-endoeffect (pre-endotherm, endothermic pre-peak, sub-T_g peak, or "shadow" peak) [36, 37, 38], which was opened in the 80s and located in the data [20, 38] on 10-70 °C below the temperature of the “modern” T_g (i.e. T_w of Tamman). The presence in the glass of this endoeffect confirms once again the fact that the true glass transition temperature is the temperature of the interconversion of glass-forming liquids and glass, which is actually the temperature of Tamman's T_g($T_{g\,(T)}$). The pre-endoeffect, during the glass heating, precedes the exothermic effect (polymorphoids transformation of the HTPM into the LTPM) and the subsequent endoeffect of polymorphoids conversion LTPM → HTPM at $T_{w\text{-}rev}$ temperature (Tamman's T_w, or "modern» T_g) of the glass-forming substance (Fig. 5) [25].

The pre-endoeffect was observed in the B_2O_3 glass [36], in glass-forming systems Ge-Se, As-Se, Ge-As-Se [38], as well as in metallic, silicate and phosphate glasses and glassy water [39].

Chen and Kurkjian [36] were among the first researchers who discovered the pre-endothermic peak by scanning calorimetry during the heating of the glass forming samples B_2O_3 previously annealed for various lengths of time below T_g = 583 K: 1 hour, 3 hours, 10 hours, 30 hours. The annealing was carried out at a temperature T_a = 460 K (Fig. 6).

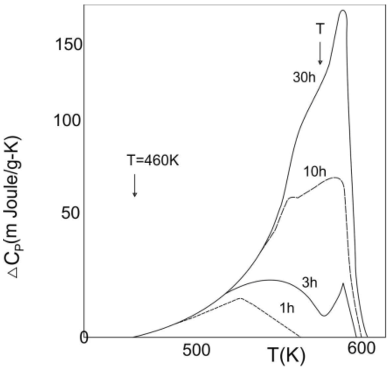


Fig. 6. Endothermic specific heat, ΔC_p, of B_2O_3, as a function of annealing time t_a, at t_a = 460K [36]

If the annealing time is less than 2 hours (for example, when t_a = 1 hour) the B_2O_3 sample the shows sub–T_g (the heat capacity peak ΔC_p) appearing near the annealing temperature T_a =

460K and disappearing below T_g. Upon annealing, which takes three hours, the sub–T_g peak increases and is overlaps the endothermic peak T_g, which increases with an increasing annealing time. As stated above, this peak reflects the transformation process of the LTPM polymorphoids accumulated as a result of the annealing into the HTPM ones, having the greater heat capacity. The longer the glass is annealed at T_a = 460K (3 hours, 10 hours, 30 hours), the greater the quantity of LTPM polymorphoids accumulating on the glass; and the greater the quantity of heat during the passage of the temperature T_g ($T_{w\text{-rev}}$) as we have shown in [25]. The increasing of the B_2O_3 heat capacity is similar to the increasing of the selenium heat capacity [40] with a time increment after synthesis at temperatures below T_g, where, in accordance with the concept of polymer-polymorphoid glass structure, at T_g ($T_{w\text{-rev}}$), the polymorphoid transformation~~s~~ of the monoclinic LTPM into polymorphoids of the hexagonal HTPM modification also occurs [41]. The sub-T_g endotherms for the chalcogenide glass systems (Ge-Se, As-Se, Ge-As-Se) were presented in [38].

The results of the modulated differential scanning calorimetry (MDSC) of a chalcogenide glass $As_{37,5}Se_{62,5}$, tempered in cold water and aged for 8 years as well as the same glass, rejuvenated by heating above T_g and subsequent cooling are shown in Fig. 7 [38].

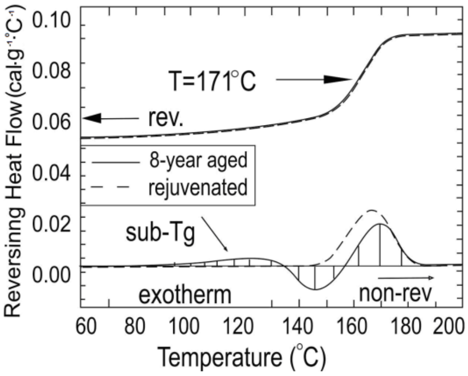


Fig. 7. MDSC scan of sample $As_{37,5}Se_{62,5}$ (water-quenched and aged in a laboratory environment, and rejuvenated) [38]

The aged sample is characterized by a pre-endothermic peak around 120 °C, then by a subsequent exothermic peak with a maximum at about 145 ° C and at the end of an endothermic peak at 171 °C ($T_{w\text{-rev}}$ (T_g)). The authors [38] attribute sub-T_g endotherm to the compaction of the flexible part of the network upon long term aging, and pre-T_g exotherm, and they relate them to the nanoscale phase separation in the glass.

From the standpoint of the concept of the polymer polymorphoid structure of glass, the endothermic peak fixes the processes associated with Tamman's T_g, at which there is an increasing of molecular motion, a separation of molecules from one another and an increase of the heat capacity [3].

According to the concept of polymer-polymorphoid glass structure [24, 33], the pre-Tg-endoeffect always presents itself in one-component glass because it is a manifestation of the conversion process of solid glass into a viscous-flow liquid, which is accompanied by the rupture of a large part of the chemical bonds forming the frame of the glass [3, 8, 19].

This effect is negated by its opposite exothermic effect under certain conditions of glass synthesis, in particular, with the rapid cooling of the melt. Quickly tempered glass consists essentially of HTPM polymorphoids since these polymorphoids, during rapid quenching, have no time to be transformed into LTPM polymorphoids at temperature lower then Tw-rev [14, 26]. When a solid glass is transformed into a viscous-flow liquid at the temperature Tg (T), the endothermic effect of the cleavage of chemical bonds leads to the formation of HTPM polymorphoids. These polymorphoids are not stable at a temperature below Tw–rev. As a result, the conversion reaction of the HTPM into the LTPM polymorphoids proceeds with exothermic effect. This exothermic effect neutralizes the endothermic effect of chemical bond cleavage and at a sufficient number of the HTPM polymorphoids (at a sufficient fast rate of cooling of the melt) reduces the endothermic effect to zero. As a result, the temperature of the endothermic effect of $T_{g\,(T)}$ or Tamman's temperature in a rapidly quenched glass is not detected by differential scanning calorimetry.

The author of the article [42] lists a number of criteria, which determine the appearance and behavior of the sub-T_g peak. The author does not explain the physico-chemical essence of the mechanism of action of the listed criteria.

We list below some of these criteria and show (in parentheses) from the standpoint of the concept of polymer-polymorphoid structure of glass-forming substances, the causes of the phenomena appearing in the glass as a result of these criteria in the action.

A. Annealing of glass is necessary for observing sub-T_g peak in a heated glass.

(The exothermic reaction of the transformation of the polymorphoids HTPM into polymorphoids LTPM occurs below T_g ($T_{w,}$ $T_{w\text{-}rev}$). During the annealing of the glass below T_g this reaction is almost finished and has no effect on the endothermic reaction taking place during the sub-T_g endoeffect. In the absence of glass annealing the above-mentioned exothermic reaction neutralized endothermic reaction of the glass softening during the sub-$T_{g,}$ and endoeffect is missing).

B. An increase in the annealing time, t_a, at a fixed temperature T_a increases the height, area and temperature of the sub-T_g peak.

(The more the annealing time is, the fewer HTPM polymorphoids remain in the glass, which neutralizes the sub-T_g endoeffect by their exothermic conversion below T_g in the LTPM polymorphoids).

C. The increase of the annealing temperature, T_a, at a constant time of annealing, t_a, increases the height and size of the sub-T_g peak.

(The higher the annealing temperature, the more active the transformation of the HTPM polymorphoids into the LTPM polymorphoids flows that below T_g is. The fewer HTPM polymorphoids the glass contains, the lower the neutralization of sub-T_g endoeffect is during the heating of the glass).

D. Glass does not crystallize quickly in the field of sub-T_g peak.

In this area owing to a low temperature the process of the HTPM polymorphoids transformation into the LTPM polymorphoids is too low. Namely, this process eventually leads to the crystallization of the glass in the form LTPM.

E. The sub-T_g peak is absent if the sample contains more than 0.2% of the matter in the crystalline state.

(The crystalline part is LTPM polymorphoids formed during the cooling of the glass below T_g. It initiates the process of further transformation of HTPM polymorphoids into LTPM polymorphoids. This process occurs with exothermic effect, neutralizing the endothermic effect of the glass softening (sub-T_g peak).

From the standpoint of the concept of the polymer-polymorphoid structure of glass [24, 33, 43, 44] pre-T_g the exotherm is linked with the tempering of glass and with preservation of a large number of the polymorphoids of high temperature polymorphic modification (HTPM), which are stable only above the generally accepted (non Tamman's) T_g. The HTPM polymorphoids transform here into the stable LTPM ones, as a result of slow heating during the scanning with a release of excessive heat (exoeffect). The majority of the HTPM polymorphoids transforms into LTPM ones, in slowly cooled rejuvenated glass. As a result, the heat does not occur at subsequent heating during the scanning. The exoeffect is absent.

We can regard the DSC curves in Fig. 6 [36] and Fig. 7 [38] as illustrating the conditions of the manufacturing of glass samples (quenching rate, temperature and time of the annealing, scan speed of heating):

a) all three characteristic effects: pre-T_g endotherm, pre-T_g exotherm and T_g-endotherm (Fig. 7, solid line),

(b) the first two of these effects, characterize the annealing of the glass for 3 hours (Fig. 6),

c) only the pre-T_g endotherm (the curve which characterizes the annealing of glass for an hour (Fig. 6)),

d) only T_g-endotherm, or the more contemporary, $T_{w\text{-}rev}$ endotherm, of the transformation of the LTPM into the HTPM polymorphoids, characterizing the rejuvenated glass, i.e. the glass, heated above $T_g(T_{w\text{-}rev})$ and then cooled below pre-T_g (Fig. 7, dashed curve).

6. Conclusion

Tamman's T_g ($T_{g(T)}$) is the transition temperature of the viscous-fluid liquid to solid brittle glassy state. During the heating of the glass at this temperature, there is a rapid increase of the specific heat. Tamman's T_f is the temperature at which the first signs of a liquid state appear in the glass. Between Tamman's T_g and T_f temperatures there is an "interval of conversion" or "transition". During post-Tamman's period, this interval was called the "transformation area glass transition", and according to the average data [8, 9, 10, 14, 15] it is in the range of viscosity $10^{7\text{-}10}$-$10^{13\text{-}15}$ Pa · s. Thus Tamman's T_g is characterized by a viscosity of ~ $10^{13\text{-}15}$ Pa · s. In addition, the listed researchers provide further facts, confirming Tamman's point of view.

Also Tamman introduced the T_w temperature i.e. the inflection temperature on the "property-temperature"curve, characterized by a viscosity of $3 \cdot 10^{12}$ Pa · s. The T_w is located at a higher temperature than Tamman's T_g temperature; it is close to the temperature of the "middle transformation region" according [9] at 10^{12} Pa · s.

Tamman's T_g and T_w were forgotten until the mid-twentieth century, and the T_g symbol replaced Tamman's T_w, and was presented as the temperature within the range of the vitrifaction denoted by the intersection of the tangents on the dependence "property-temperature" [6, 7]. The currently used T_g is characterized by a viscosity ~ 10^{12} Pa · s [16, 17], which is from one to three orders of magnitude less than the viscosity at Tamman's T_g .

Some researchers formally recognize this T_g temperature, but they set it in addition to the existence of the transformation temperature of the viscous-flow liquid into a solid brittle glassy state, which is below T_g [5, 6, 18, 20, 25]. The author [5] is in total agreement with Tamman's point of view on his T_g .

Starting from the 80s of the last century, the researchers have been actively investigating the so-called pre-endoeffect (pre-endoterma, endothermic pre-peak, sub-T_g peak), located at 10-70 °C lower than the currently used T_g, i.e. in region Tamman's $T_{g\,(T)}$. The pre-endoeffect is identical to Tamman's T_g on its physico-chemical essence: in both cases there is an increase of the heat capacity of the heated glass.

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