NANOHETEROMORPHOUS STRUCTURE AND RELAXATION
OF GLASSFORMING As$_2$S$_3$[♣]

V.S. MINAEV[a,b*], S.P. TIMOSHENKOV[b], V.V. KALUGIN[b], V.P. VASSILIEV[c],
D.ZH. MUKIMOV[b]
[a]*State Unitary Enterprise "Scientific-production center "Spurt", Russia*
[b]*Moscow Institute of Electronics Engineering (Technical University), Russia*
Lomonosov Moscow State University, Russia

The structure of arsenic sulfide As$_2$S$_3$, melting and glass transition process, as well as relaxation of the glass at heating are considered within the concept of polymeric nano-heteromorphous glass structure and glass-forming liquid and its particular case for the individual chemical substance (ICS) - conception of polymeric polymorphoid structure of non-crystalline substance proposed by V. Minaev [1]. ICS in non-crystalline state is a fragment's copolymer of different structures crystal polymorph modifications (PM), without translational symmetry (long-range order) which is characterized by strictly defined intermediate- and short-range orders inherent to one of the PMs taking part in glass formation. The glass transition process of As$_2$S$_3$ is a twofold process of copolymerization-depolymerization: copolymerization of formed in liquid polymorphoids of high(α)- and low-temperature(β) PM (HTPM and LTPM) and depolymerization of polymorphoids LTPM above T_g ($\sim$ 175°C) and HTPM below T_g. Changes in the external conditions of the glass transition process (cooling rate, temperature and time of glass annealing, etc.) are changing the concentration ratio of polymorphoids (CRP) of different PMs. The concentration ratio HTPM:LTPM can be estimated, for example, by comparing the Raman spectra band intensity of glass and crystal HT- and LTPM. CRP is an internal parameter of a thermodynamic system of non-crystalline substance and determines the structure and all properties of substance. A continuum of combinations of the CRP, resulting from changes of external conditions and time, defines the continuum of properties of the non-crystalline substance. This glass is a continuum of metastable states [1].

1. Introduction

Arsenic sesquisulphide As$_2$S$_3$ is widely used in industry as material of inorganic photo resistors, IR-transmitting glasses and elements of integrated optics, optical and holographic recording, photo thermoplastic, radiometry, acoustic-optical devices, ion-sensitive electrodes, etc. [1,2].

The functional parameters of devices and systems are closely related to the properties of the materials they used. Material properties are the function of their chemical composition, structure and dispersion [3,4]. Knowledge of the structure of vitreous substance, ability to manage its changes, and on this basis to predict the properties of substance, depending on the conditions of synthesis, the subsequent heat treatment, the impact of external factors (temperature, pressure, irradiation, etc.) allow for optimizing the functionality of the developed devices and systems.

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[*] Corresponding author: Viktor118@mail.ru

Information about structure of crystalline and vitreous As_2S_3 are summarized in the monographs [5, p.160; 6, p.282; 7, 8 p.34]. The effect of pressure on the polymorph transformation temperature of As_2S_3 from HTPM (α) to (β) is shown in Figure.1 [9]. It can be seen from the figure that polymorph transformation $\alpha \rightarrow \beta$ at the pressure of 1 atm. occurs at the temperature of 170-175ºC. In paper [10] information is shown about the polymorph transformation in As_2S_3 at 175ºC.
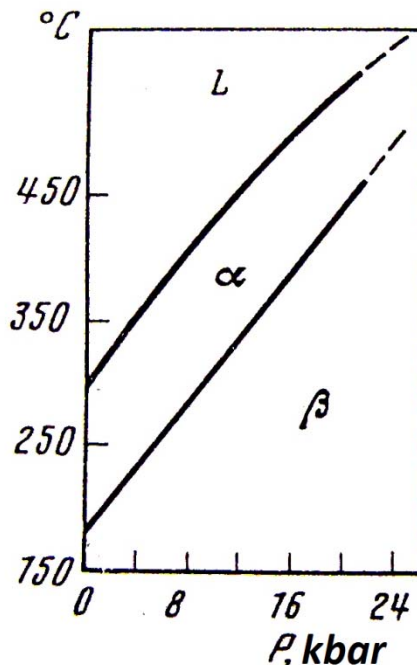

Fig.1.Temperatures of melting and polymorphic transformation of As_2S_3 vs. pressure [9].

In the crystalline state at normal pressure, As_2S_3 is characterized by the monoclinic system (space group $P^2_{1/n}$ — C^5_{2h}). We have not found any information about the structure of β- and γ-modifications. Vitreous As_2S_3 (v-As_2S_3) was described for the first time in 1870 [11]. The structural units in v-As_2S_3 are connected to with each other directly through the sulfur atoms, forming irregular rings of various sizes [12]. Authors [13], on the basis of Raman spectra of v-As_2S_3, concluded that the participation of the formation of the glass structure of the structural groupings, is connected by ribs. The structure of vitreous substance, in our case v-As_2S_3, will be considered from the position of conception of polymeric-nanoheteromorphous glass and the glass-forming liquid structure and its particular case for ICS – concentration of polymeric-polymorphoid structure proposed by Minaev [1], because the Zhachariasen concept of a continuous random network, and the crystallite concepts of Frankengeim, Lebedev, Goodman and other concepts analyzed in the monograph [1] do not explain many facts related to the structure of glass and the glass transition process.

1.1 Main theses of the conception

Nano-geteromorphism is a concurrent existence in non-crystalline substance of structurally different fragments of nanometric dimensions without long-range order.
- ICS in glassy state is one-, two-, and three-dimensional (spatially-structured) or mixed copolymer of nanometric fragments of structure from different crystal polymorph modifications (polymorphoids) without translational symmetry (long range order) but is characterized by strictly defined intermediate and short-range orders inherent to one PM. ICS's structure always presents more than two intermediate orders of different crystal PM;

Different PM's polymorphoid interconversion and its concentration ratio change in none-crystal ICS under the impact of external influences and time is the fundamental reason the none-

crystal substance structure and properties change.

$$A_k+B_l+C_m+\dots Z_x \equiv A_p+B_q+C_r+\dots Z_y \qquad (1)$$

where A, B, C …. Z are polymorphoids of different PMs of substances which concentrations k, l, m …p, q, n … x, y are changed depending on conditions (temperature T, pressure P, irradiation Ph, electrical field E, magnetic field H, etc.) in the range from 0 to 100% (Minaev V.S. [1,14-16]).
CRP is the most important internal parameter of the none crystalline substance's nonequilibrium thermodynamic system [15]:

• Polymeric-polymorphoid model of non-crystalline substance structure, like Zakhariasen's model (1931) [17], represents a grid model that is distinguished from the Zakhariasen's grid which connects accidentally located polyhedrons with short-range order, and copolymerized polymorphoids with intermediate-range orders of different crystalline PMs.

Nature of vitreous state cannot be known without analyses of crystalline (in different PM's) and fluid states.

2. Formation of glass-forming liquids. Glass transition.

Though considerable progress has been made in understanding the glass transition in general, some crucial questions still remain unanswered» [18].

Results of diffractometric, spectroscopic (Raman spectrum), calorimetric and other studies of different PMs glass-forming liquids and glasses SiO_2, B_2O_3, GeO_2, H_2O, Se, $GeSe_2$, $SiSe_2$, $BeCl_2$, (Bernal and Fowler (1933), Mackenzie (1960), Pauling (1970), Bruckner (1970), Johari (1987), Gerber et al. (1988), Porai-Koshits (1990), Golubkov (1992), Wang et al (1996), and Pavlotou and Papatheodorou (2000)) analyzed in [1,14-16] allow us to describe the most common features of ICS glass transition.

The process of glass-forming liquid at melting of high PM (HTPM) of individual chemical substances is the process of the structure fragments formation of this PM, without long-range order (polymorphoids) and partial conversion into polymorphoids of other (low temperature) PM (LTPM) followed by the establishment of the characteristic for each melt temperature with a definite concentration ratio of various PM polymorphoids.

Relaxation processes in the condensed state of vitreous arsenic sesquisulphide As_2S_3 are shown schematically in Fig. 2. T_{tr} is the temperature of polymorphous transformation LTPM ↔ HTPM. The principal feature of this transformation is that the transition from low temperature to high temperature PM is accompanied by the endothermic effect and the reverse transition by the exothermic effect [19]. T_g is the common glass transition temperature and presents a salient point in the melt cooling graph. Relaxation processes in glass are completely determined by the genetic relationship of structure and properties of all three types of condensed matter: the crystalline, liquid and vitreous [20]. Also interrelated temperatures T_{tr} and T_g: T_{tr} are kind of the prototype of T_g [14]. The value of T_g is always close to the value of T_{tr}. According to [7] the values for As_2S_3 are equal to 170-180ºC and 175ºC respectively and the melting temperature of As_2S_3 is 327ºC.

The copolymerization of nano-heteromorphous (various structures at the nanometer level) fragments of various PMs without translational symmetry of crystal (polymorphoid) occurs during cooling of the melt. This occurrence is the fundamental cause of glass formation, which excludes the possibility of organization long-range order (crystallization).

Glass transition of individual chemical substances is a process consisting of two indissobly united parts: copolymerization of polymorphoids of various PM and depolymerization of the resulting copolymer due to the decay of unstable above T_g LTPM polymorphoids, and unstable below T_g HTPM polymorphoids [14,21,22].
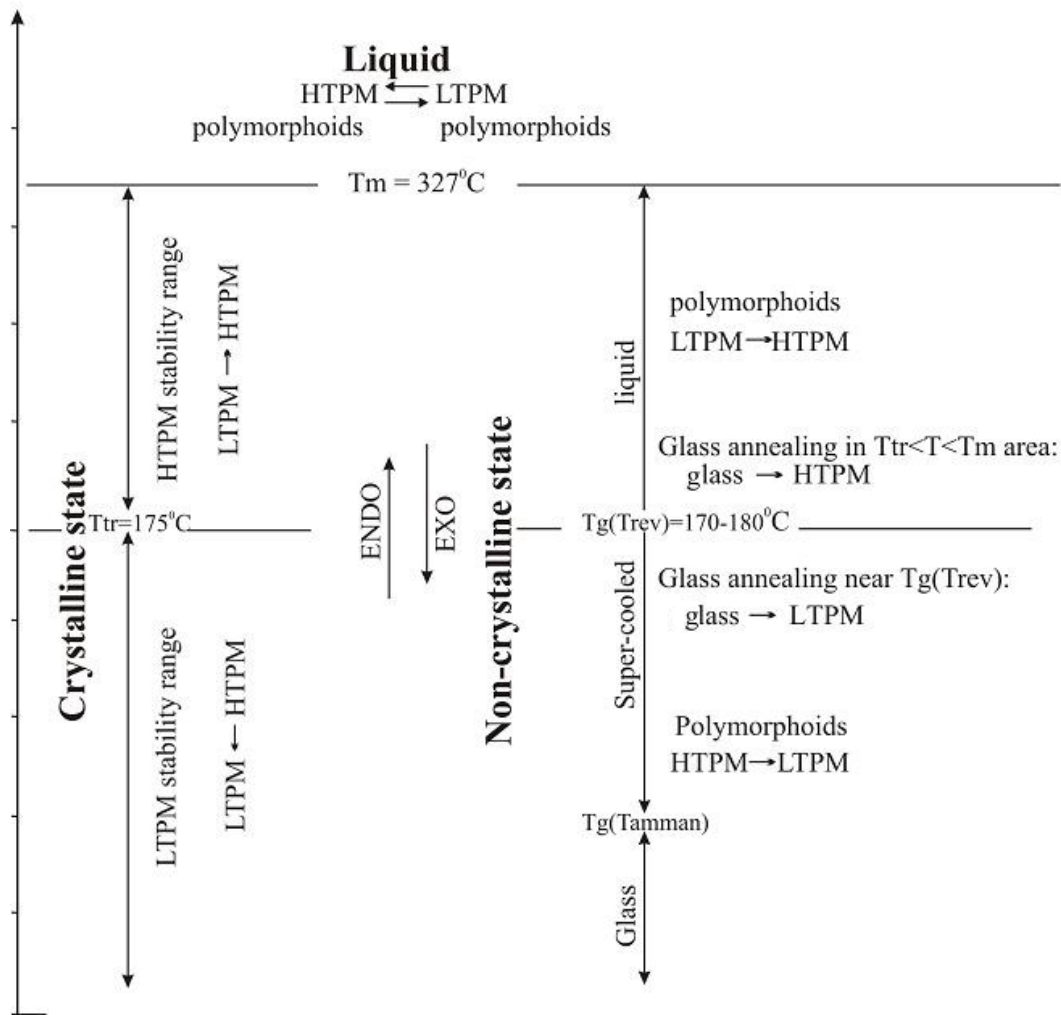
Liquid

HTPM ⇄ LTPM
polymorphoids   polymorphoids

$Tm = 327^{o}C$

Crystalline state

HTPM stability range   LTPM → HTPM

$Ttr=175^{o}C$

LTPM stability range   LTPM ← HTPM

ENDO ↑ ↓ EXO

Non-crystalline state

liquid

polymorphoids
LTPM→HTPM

Glass annealing in Ttr<T<Tm area:
glass → HTPM

$Tg(Trev)=170-180^{o}C$

Super-cooled

Glass annealing near Tg(Trev):
glass → LTPM

Polymorphoids
HTPM→LTPM

Tg(Tamman)

Glass

Fig. 2. Schematic representation of relaxation processes in the condensed v-As₂S₃. Tₘ - melting temperature, Tₜᵣ - temperature of polymorphous transformation in the crystalline substance. Tg - common (contrary to Tamman) glass transition temperature, it is also named temperature of the direction Trev reverse of polymorphoids interconversion HTPM ↔ LTPM.

The first stage of glass transition is carried out in the temperature range «melting temperature Tm - the conventional glass transition temperature T_g» (Fig. 3) and ends when the viscosity of the substance, equal to ~ $10^{12.3}$ Pa·s. It is area of the low- and high-PM polymorphoids copolymerization and the transformation of unstable polymorphoids of LTPM in stable polymorphoids of HTPM, accompanied by increasing concentration of the latter.

The second stage of the glass transition is when a reverse process of polymorphoid transforming (HTPM → LTPM), takes place below T_g. This stage covers the range of viscosity of glass-forming substances ~ $10^{12.3}$ -10^{16} Pa·s. 10^{16} Pa·s is the lower boundary of the 10^{14}-10^{16} Pa·s viscosity interval, above which the temperature curve of viscosity undergoes a break corresponding to the transition to the brittle state (Winter-Klein, 1953) [23]. This position is correlated with data on the activation energy of viscous flow that is approaching the energy gap of the chemical bonds at viscosity 10^{15} Pa·s (Nemilov, 1969) [24].

The temperature of the viscous-flowing liquid transition in a fragile state first described by Tammann (1933) [25]. He named it the glass transition temperature and gave it the symbol - T_g. Thus, the glass transition temperature of Tammann, T_g (T), is the lower bound of the interval of glass transition at viscosity ~ 10^{15}Pa·s, where the temperature curve, of viscosity undergoes fracture and the viscous-flow state of substance turns into a brittle solid state, which is associated

with a decrease in internal energy of matter below the level of energy required to break chemical bonds.

Generally accepted (in spite of Tamman) T_g is the temperature at which the bend of the temperature dependent on the properties takes place. This bend associates with the direction reverse of polymorphoids HTPM ↔ LTPM intertransformation [14,20,21]. The result is that this temperature T_g, approximates the middle of the glass transition interval ($\eta = 10^{12,3}$ Pa·s) [23], therefore, we should not call this the glass transition temperature but the temperature of reverse direction interconversion of polymorphoids with different PMs of the substance - T_{rev} [21].
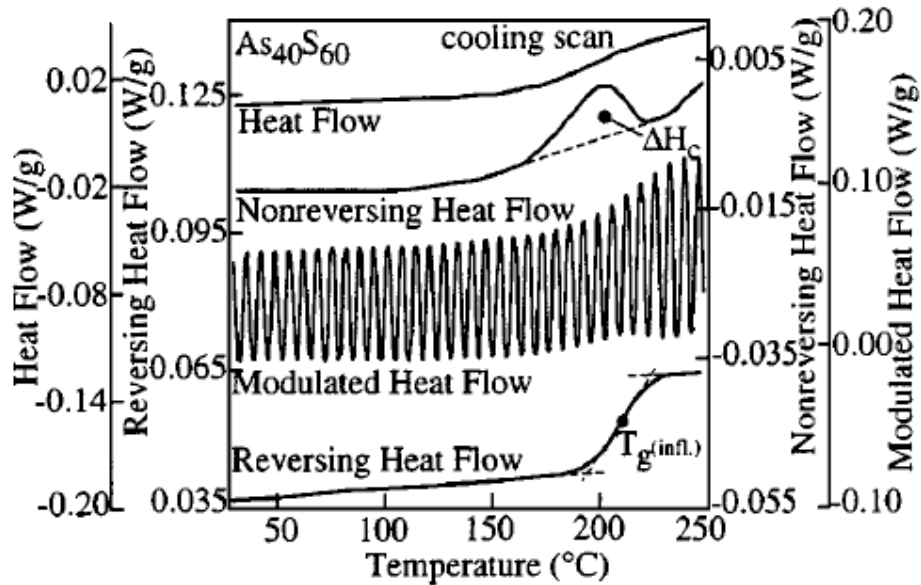

Fig. 3. Typical conventional DSC (HF) and MTDSC (MHF, NHF and RHF) results during a cooling scan. NHF shows a relaxation peak which is separated out from MHF by subtracting RHF.

The process of polymorphoids transformation (HTPM into LTPM) beginning at liquid cooling below the generally accepted T_g(T_{rev}), is accompanied, as in the case of the transformation of crystal HTPM into LTPM in [19], by the exothermic effect. This effect is observed for $As_{40}S_{60}$ on cooling curves obtained by the modulated-temperature differential scanning calorimetry (MTDSK) in the experiment (Fig.3), held in [26].

MTDSC measures the amplitude of instantaneous flow and average or total heat flow HF. HF in MTDSC divides into irreversible and reversible components - nonreversible heat flow (NHF) and reversing (backward) heat flow (RHF). Changing of total and separated heat flows on cooling As_2S_3 (Fig. 3 [26]) fixes the glass transition temperature T_g (in our interpretation - the polymorphoid intertransition HTPM↔LTPM temperature - T_{rev}), affiliated with the exothermic effect - the loss of enthalpy ($\Delta H_{cooling}$) in substance as a result of polymorphoids transition HTPM → LTPM. This transformation is analogous to the polymorphic transformations in crystalline material flowing at T_{tr} ([14], Fig.2).

Cooling liquid below the generally accepted today T_g in accordance with the data above is continuing a two-fold process of glass transition. Glass forming liquid is depolymerizing here cause of unstable HTPM decay. It's fragments rearranges and turn stable in T_g(T_{rev}) polymorphoids of LTPM. They are copolymerizing with indicated HTPM polymorphoids and embedding into the glass structure. (It should be observed that in the paper [26] the quantity of T_g at heating is ~211ºC and at cooling ~209ºC i.e. far different from the [7] (175ºC), which is connected with the experiment's method and purity of As_2S_3.

The same situation (exo-effect) is observing on the DSC bond on the process of the fluid selenium cooling [27]. This was interpreted in [21] as exothermic effect of HTPM to LTPM polymorphoids transition process. The temperature of the end of exoeffect lying within the

temperatures from ~120ºC (nonreversible heat flow) to 140ºC(heat flow), is the end of the second – below $T_g(T_{rev})$ – stage of the viscous-flow liquid glass forming process and its transformation in to brittle glassy solid state. This is Tamman's glass forming temperature $T_g(T)$. This assumption should be experimentally proved.

3. Relaxation of glass-forming arsenic sesquisulphide (As₂S₃) at heating

Relaxation is the process of establishing thermodynamic equilibrium in macroscopic physical systems [28]. Relaxation process involves system into spontaneous "movement" from some conditions of its existence in other conditions different from those in which system was before process of relaxation. They study relaxation of glass-forming substances usually from the point of view of its movement in changing temperature conditions. For example most common case is melt cooling in order to obtain the glass. To understand the structure of glass-forming substances and processes occurring in it, it is equally important to consider relaxation processes occurring on heating of substance. Obviously, in this case the equilibrium state will be determined by the final temperature of heating. While heating at temperature elevation substance always relaxes to potential equilibrium determined by temperature of substance on this moment [29].

The study of heating process (with DSC at a rate of 10 K/min) of vitreous As_2S_3 as a target for sputtering film obtained by ultrafast laser deposition (ultrafast laser ablation method) and films annealed at 140 , 150, 160, 180 and 200ºC for 15 hours (Fig. 4) was scrutinized.

The authors define position of the minimum in the area of 200ºC on DSC curve as T_g. For the target (monolithic glass As_2S_3 with stoichiometric structure) T_g is 213ºC, for freshly deposited film broad area of glass transition starts at 158ºC and reaches a minimum at 204ºC. It is assumed that this film is heterogeneous, composed from clusters of various sizes and, possibly, combinations. After annealing at different temperatures endothermic transition becomes less extended. In our point of view $T_g (T_{rev})$ is characterized not by a maximum of endoeffect, but by its onset (at a lower temperature), by beginning of polymorphoid transformation LTPM→ HTPM.

Authors analyze T_g dependence of the annealing temperature (T_a) of the film. Increasing the annealing temperature T_a, up to 170ºC leads to increasing T_g, but with further increase of annealing temperature, T_g «saturates» and then slowly decreases.
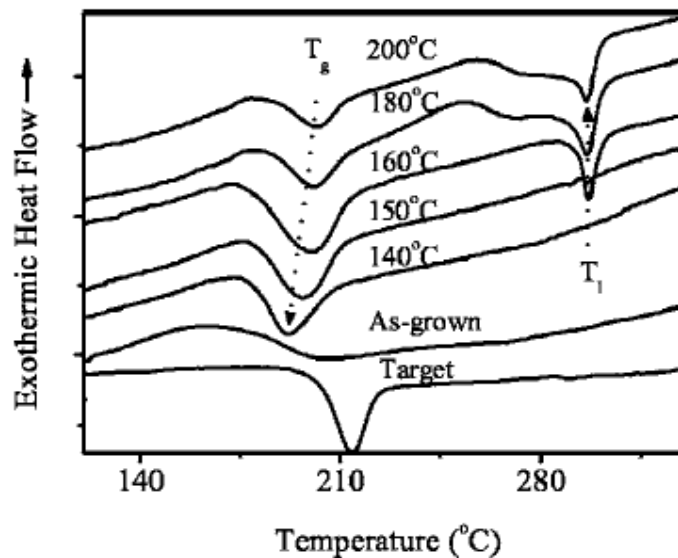

Fig. 4. Glass transition temperature Tg of target, as-grown film, and films annealed at different temperatures for 15 h. Liquidus temperature Tl can be found in some DSC curves as marked by the arrow. The curves are upshifted for clarification [30].

What is the reason for such behavior of As_2S_3 films? The authors following [31] believe that reason of this dependence is relaxation flowing in the film. The physicochemical essence of the processes occurring during annealing below Tg and endoeffect (at heating) clearly derives from the concept of polymeric-polymorphoid structure of glass and glass-forming liquid [1, 14, 21]. There is a transformation of HTPM polymorphoids to LTPM at $T < T_g$ (T_{rev}) (Fig.2). The higher temperature of glass annealing (not exceeding Tg!), the more HTPM polymorphoids are transforming into polymorphoids of LTPM. Their accumulation reduces the total enthalpy of glass. The lowest enthalpy has the glass annealed at a temperature closest to the temperature of polymorphous transformation LTPM $\rightarrow$ HTPM in a crystalline substance, which characterizes the threshold level of enthalpy H_{thr}, at which begins this transformation. The smaller pre-threshold enthalpy glass the higher temperature the endothermic effect beginning, physicochemical essence of which is endothermic transformation of polymorphoids of LTPM to HTPM in glass. This transformation is genetically related to the endothermic transformation of LTPM $\rightarrow$ HTPM in the crystalline material (left side of figure 2).

Annealing above 170ºC leads to reverse process: polymorphoids LTPM transform to polymorphoids HTPM - enthalpy of the glass increases, and the transformation temperature of LTPM $\rightarrow$ HTPM in glass (i.e., T_g (T_{rev})) decreases because of more rapid achievement of a threshold level of enthalpy, H_{thr}. Thus, the structure of vitreous As_2S_3 and relaxation processes in it, both on cooling and on heating, are in full compliance with the theses of the concept of polymeric-polymorphoid structure of glass and glass-forming liquids.

Acknowledgements

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