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WHAT ARE THE PARAMETERS THAT GLASS TRANSITION TEMPERATURE OF CHALCOGENIDE GLASSES DEPEND ON? AN OVERVIEW

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Glass transition temperature T_g is the most important parameter for characterization of any glassy material. T_g may be considered as a measure of the onset of diffusion motion and the corresponding value of viscosity is found to be a constant (10^{13} poise). Numerous studies have been done to correlate T_g of chalcogenide glasses (sulfide, selenide and telluride glasses) with various physical and chemical parameters. In these studies, it is assumed that T_g is mainly related to the heating rate, the average coordination number, the overall mean bond energy, and the relaxation process occurs from thermal history and ageing in the network. Several expressions of the relationship between T_g and these various parameters have been reviewed in this work.

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1. Introduction

Glass is often made starting from the liquid phase when the liquid could be cooled sufficiently quickly (quenched) so that crystallization could be bypassed, then the disordered structure characteristic of a liquid could be frozen-in, and a glassy solid which is spatially homogeneous, but without any long-range lattice order (amorphous) would result. Hence a glass can be defined as a solid, brittle material that has an amorphous, liquid-like structure without obvious fluidity [1]. The short-range order for the glassy state of a material is often very similar to that of the crystalline state, that is, it has a similar average nearest-neighbor distance and coordination number but, unlike the crystal, the glass has no long-range order [2].

Glasses covered wide spectrum of materials which range from those with simple structures such as the metallic and chalcogenide glasses to more structurally complex organic materials and polymers. A class of these materials is the chalcogenide glasses which include selenium, tellurium, and sulfur and their compounds. All glasses are characterized by a glass transition temperature T_g which can be defined as the temperature at which the equilibrium liquid has a viscosity of 10^{13}poise (corresponds to relaxation time in the order of 1d) [2]. This value for the viscosity is not universal; the glass transition is not an isoviscous phenomenon and some liquids have viscosities at T_g as low as 10^{11}poise [3]. Above the glass transition temperature, the system is in the rubbery state and bellow T_g, the system is in the glassy state. At T_g there are also changes in thermodynamics properties such as the specific heat, thermal expansion coefficient, and isothermal compressibility. These quantity abrupt changes from values appropriate to supercooled liquid to those typical of the crystalline solid as the temperature is lowered to T_g [2]. According to kinetic theories there is no true thermodynamic glass transition. The kinetic theories predict that the glass transition is a purely kinetic phenomenon and that it appears when the response time for the system to reach equilibrium is of the same size as the time-scale of the experiment. The nature of

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the glass transition is still uncertain and it is the subject of much current research; although, it is clear that the glass transition process is mainly one of kinetic arrest. As the temperature of the melt decreases in the supercooled regime, correspondingly its viscosity increases rapidly until the point is reached when, on the time-scale of experiment, no further structural relaxation of the melt appears to take place; the material is then glassy and behaves as a solid [1].

Glass transition temperature can be determined by different procedures. Differential scanning calorimetry (DSC) can easily used to observe glass transition phenomena. This method, which widely used for detection of T_g, is based on the measurement of the increase in heat capacity of the material as it pass from the glassy to the rubbery state upon heating. The heat capacity, C_p, of the glass increases suddenly by at least about half its original value in a very small temperature interval as the glass change to liquid and T_g is defined at the inflection point in the C_p versus temperature curve [4]. Another operation of differential scanning calorimeter is based on measurement of the thermal response of an unknown specimen as compared with a standard when the two are heated uniformly. A typical differential scanning calorimeter consists of two sealed pans; a sample pan and a reference pan (which is generally an empty sample pan). These pans are often covered by lids that act as a radiation shield. The two pans are heated, or cooled, uniformly while the heat flow difference between the two is monitored. This can be done at a constant temperature (isothermally), but is more commonly done by changing the temperature at a constant rate (non-isothermally) [5]. T_g is defined from the output DSC curves as the temperature which correspond to the intersection of two linear portions adjoining the transition elbow of the non-isothermal DSC traces in the endothermic direction [6].

Dynamic methods can also be used to detect glass transition phenomena. The dynamic mechanical thermal analysis (DMTA) measures the viscoelastic properties of the materials as a function of frequency of oscillatory deformation. In the glassy state, the material will exhibit solid-like characteristics and have a measurable shear modulus. The glass transition temperature can be detected at the temperature where the storage modulus starts to fall rapidly with increasing temperature from a very high value in the glassy state. A peak in the ratio of the loss to the storage modulus is also found at the glass transition temperature [7]. Certain models have been proposed to describe the dependence of the glass transition temperature of chalcogenide glasses on several parameters like heating rate, coordination number, overall mean bond energy, thermal history, and ageing. The aim of the present work is to study,as a review, the dependence of glass transition temperature of chalcogenide glasses on these parameters.

2. Dependence of the glass transition temperature on heating rate

In the DSC calorimetric studies, the heating rate dependence of glass transition temperature is an experimentally observed fact. The increasing of T_g on the heating rate β has been studied using different formulations like $T_g = A + B \ln\beta$ [8], $T_g = T_o + S\beta$, $T_g = T_o[\beta]^y$[9], $\frac{d\ln\beta}{d(1/T_g)} = -\frac{E_t}{R}$ [10] and $\ln\left(\frac{\beta}{T_g^2}\right) = -\frac{E_t}{RT_g} + C$ [11]. The last two equations are generally used to estimate an important quantity of the glass transition kinetics which is the glass transition activation energy E_t. This quantity is correlated with the relaxation energy and represents the amount of energy that a structure needs to jump from its quasi-stable state to another one of more stability within the glassy region. Hence, the glass with lower amount of E_t was originally formed in a local region of more stability and needs this amount of energy to relax to a stable structure and hence the least is the value of E_t, the most is the glass stable [12].

3. Compositional dependence of the glass transition temperature

Nevertheless, when the glass transition temperature is measured under standard conditions (for example calorimetrically at a fixed heating rate), attention has been brought to explain the effect of composition on glass transition temperature of the glassy system. The origin of T_g and the correlation between various physical and chemical parameters in chalcogenide glasses reveals that T_g is the thermal energy that must overcome the binding forces of the solid nature of the chalcogen materials. In other words T_g may be considered as a measure of the onset of diffusion motion and the corresponding value of viscosity is found to be a constant (10^{13} poise). In general, two approaches have been proposed to investigate the compositional dependence of various thermal parameters of chalcogenide glassy network. The first one is known as topological (or mechanical) threshold which explains the compositional variation of thermal parameters in terms of the average coordination number <z>. The second approach is known as chemical threshold which takes into consideration the effects of chemical ordering and related the thermal parameters with the overall mean bond energy <*E*> of the glassy system that can be calculated using Tichy-Ticha theory [13].

The average coordination number <z>of any glassy system can be calculated from the relation $< z >= \sum r_i a_i$, where r_i is the covalent coordination number of element i having atomic fraction a_i in the glass [14].The average coordination number is a measure of connectedness in the network and the average bond energy. The connectedness is linked with the number of bonds per atom in the network. It is assumed that T_g is mainly related to the network rigidity, the number of bonds per atom, and the bond energies between the atoms in the network [15].The dependence of the glass transition temperature T_g on the coordination number is generally expressed as a function $T_g = f(<z>)$. Different expressions were proposed as: $\ln(T_g) = 1.6 <z> + 2.3$ [16] and the famous Gibbs-DiMarzio equation $T_g = T_{g0}/[1 - \gamma(<z> - 2)]$, where T_g is the glass transition temperature of the cross-linked glass, T_{g0} is the glass transition temperature of the non-cross-linked parent chain and γ is a system constant lies in the range ($0 \leq \gamma \leq 1$) [17,18]. The idea of interpreting some physical and structural properties of glasses in terms of average coordination number <z> is an outcome of the Phillips-Thorpe theory [19], modified later by Tanaka [20]. Phillips-Thorpe theory predicts a structural transformation from floppy to rigid network at <z> = 2.4. Also, a transition from layered structure to three-dimensional (3D) network at <z> = 2.67 has been predicted by Tanaka. The nature of these critical points or thresholds may be topological or chemical. The latter is observed only at stoichiometric compositions. A structural phenomenon, such as the threshold, is often found in compositional dependences of various physical properties, particularly sensitive to the threshold phenomenon [21].

On the other hand, Tichy–Ticha covalent network model (CONM) explained the observed variation of T_g on the basis of the formation of covalent bonds between various component of the system. This model is also used for interpreting the various physical and electronic properties of chalcogenide glasses in terms of composition. In CONM, the formation of heteropolar bonds are favored against homopolar bonds and the glass structure is supposed to be made up of cross-linked structural units of stable chemical compounds and then an excess, if any, of the elements [5]. An important quantity in the Tichy–Ticha covalent network model is the overall mean bond energy <*E*> of the glassy system. The glass transition temperature is considered to be proportional to <*E*> and also several expressions for different chalcogenide glassy compounds were proposed like $T_g = 311(<E> - 0.9)$ [15], $T_g = -427 + 17.4<E>$ [22] and $T_g = 327(<E> - 1.3)$ [23].

4. Effect of ageing on the glass transition temperature

One of the most important behaviors of chalcogenide glasses (as well as any other melt-quenched disordered solids) comes from the fact that, all of their physical properties are time dependent. This phenomenon is known as physical ageing which results from the fact that the prepared glass is obtained in thermodynamically non-equilibrium state and a structural relaxation occurring in the glass. As a result, a movement of structural components toward a more energetically favorable state as a function of ageing time occurs, changing theglass transition temperature and some other properties of the glass [24]. To avoid the changes in physical properties caused by physical ageing, a material with completely saturated ageing should be used in chalcogenide-based devices. Natural physical aging requires several years at low temperaturesand the physical ageing becomes slower from year to year. However, after a very long period of time it is not possible even to know exactly whether the physical aging has completed or not. To accelerate the relaxation process, the additional external influences such as gamma-ray irradiation, photo-exposure, and thermal annealing are usually applied [24, 25]. In general, the relaxation process within the amorphous phase has several features that lack a complete explanation: the reason is of threefold: (1) in most cases, the relaxation process is non-Arrhenius in its temperature dependence; (2) it is non-exponential in its time dependence; (3) it is non-linear in its structural state dependence [26].

The effect of thermal history and ageing on DSC T_g measurements makes it difficult to compare small changes in T_g due to small compositional changes only. The theories that correlate T_g to the glass structure, such as the Tanaka relationship [16], do not normally consider the effect of thermal history and ageing in their derivations. Further, the rate of structural relaxation during ageing depends on the structure itself, hence on the composition, so that samples with different composition may not have the same ‘initial state’ even if they have been aged for the same duration [27]. There are several theoretical concepts which have been the basis for a number of phenomenological models of structural relaxation. Moynihan formalism [10] was successfully used to describe the structural relaxation in differential scanning calorimetry DSC data for a variety of thermal histories using the same relaxation parameters. This formalism is an approximation that works well only over a limited temperature range for glasses that are not too far out of equilibrium in the glass transition region. Besides, Moynihan formalism does not work well especially at a temperature far below glass transition region (like natural physical ageing at room temperature) nor for reheating at a rate slower than the cooling rate. Probing the dynamics of structural relaxation down to and below its glass transitiontemperature is, therefore, very important in the interpretation of geometrical features and some configurational motions in the glassy state. Wide classes of disordered materials have a relaxation which cannot be expressed in terms of a single decay rate (exponentially). The analysis of experimental data often leads to a Kohlrausch–Williams–Watts (K–W–W) relaxation $\phi(t) \sim \exp[-(t/\tau)^{\beta}]$ or algebraic time dependence $\phi(t) \sim t^{-\gamma}$ [28]. Probably the most frequently used approach is the Tool-Narayanaswamy-Moynihan (TNM) model $\tau = \tau_0 e^{x\Delta h^*/RT} e^{(1-x)\Delta h^*/RT_f}$ [29-31], which has been successfully used for the description of annealing effects and different thermal histories on relaxation behavior in many non-crystalline materials [32]. This model relating the relaxation time τ to the temperature and the structure (fictive temperature T_f). It includes three parameters: the pre-exponential τ_0, the apparent activation energy Δh^* and the non-linearity parameter x. The mechanism of the structural relaxation is complex, not completely understood, and still need extensive investigation.

5. Conclusions

Glass transition temperature (T_g) of chalcogenide glasses is found to depend on different parameters like heating rate, coordination number, overall mean bond energy, thermal history, and ageing. Different expressions that correlate T_g with these various parameters have been discussed in this work. The challenge in this field is to put a model that relates the glass transition temperature with all these parameters.

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