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Elastic properties and activation energy profiles of viscosity in Ge–Se system across the glass-transition range

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ABSTRACT

The relation between the temperature dependence of shear modulus $G(T)$ and viscosity $\eta(T)$ of Ge_xSe_{1-x} ($0 \leq x \leq 0.30$) system across the glass-transition range is investigated using several ideas: the Wachtman equation for G, the shoving model and the bond strength–coordination number fluctuation (BSCNF) model of viscosity. Firstly, the present study shows that the empirical Wachtman equation reproduces reasonably well the shear modulus data. Next, it is shown that the shoving model implemented with the analysis of G describes quite well the high viscosity data in the glass state. Besides, the viscosity in the supercooled liquid side, especially for Ge_3Se_7, exhibits a clear change from Arrhenius-like to VFT-like temperature dependence upon heating. From the viscosity analysis for the composition $GeSe_4$, $GeSe_3$ and Ge_3Se_7, we obtain a maximum value for the activation energy across the glass-transition range. This result implies that there is an energetic barrier that the structural units need to surmount collectively before the occurrence of the viscous flow. The temperature variation of the activation energy also suggests that in terms of the BSCNF model, the decomposition of network structure upon heating is linked with the collective excitations of the structural units, which gives a viewpoint relevant to the softening of glass.

1. Introduction

In recent years, the interest to glasses and their related phenomena such as glass transition, structural relaxation, elastic property, crystallization and melting of amorphous materials, is more and more growing [1–8]. So far, many efforts have been devoted to clarify the mechanisms and the correlations between the glass properties. However, the fundamental understanding of glasses in a unified way is still far from being complete [9].

The transition of a liquid into the glass upon cooling is accompanied by an apparent change of the activation energy for viscosity η and relaxation time τ. That is, the temperature dependence of η and τ varies systematically from non-Arrhenius to Arrhenius-like behavior [10–14], during which the translational motions of the liquid components are kinetically frozen in. It is well known that for most of the liquids, the equilibrium viscosity shows the Vogel–Fulcher–Tammann (VFT)-like temperature dependence. Exceptions to this behavior, however, are found in several glass-forming liquids such as SiO_2 and GeO_2. Meanwhile below the glass transition temperature T_g, the non-equilibrium viscosity shows an Arrhenius-like behavior [10–12]. Speaking from the Adam–Gibbs theory's point of view [15], the glass-transition in a cooling process could be related to the change of the degree of cooperativity from α- to β-process [13,14]. On the other hand, the process reverse to the vitrification, i.e. the softening of a glass into the liquid in a heating process is also an important subject to study from a fundamental point of view [4,5].

In our recent work, it was shown [16] that the viscosity behavior as described by the VFT equation is successfully explained by the bond strength–coordination number fluctuation (BSCNF) model [17,18]. Specifically, the BSCNF model reduces to a form of the VFT equation under a certain condition, namely when the fluctuation of the binding energy normalized by the mean value becomes equal to that for the coordination number of the structural units that form the melt (Hereafter we call it the VFT–BSCNF relation). According to this relation, the VFT-like pattern of viscosity is attributed to the binding energy distribution that reflects the disordered structure. Specifically, the BSCNF model suggests that the binding energy of the bonds connecting the structural units that form the melt has a distribution [17]. This picture accounts for the relation between the fragility and the cooperativity of glass-forming liquids: The more fragile the glass-forming liquids, the larger number of structural units are involved in the viscous flow [19–21]. This observation leads to the notion that the viscous flow occurs by breaking preferentially the weaker parts of bonds placed near the foot of the binding energy distribution. In other words, the structural units that are connected tightly each other are not easily broken or deformed largely by the thermal disturbance.

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The above notion derived from the BSCNF model motivates us to examine the interrelation of the viscous flow with other physical quantities such as elasticity of glasses. In the present study, we focus on the relation between the temperature-dependent shear modulus $G(T)$ and the viscosity $\eta(T)$ in germanium–selenium system. The experimental data used in this study have been reported in the literature [6,22], where the viscosity $\eta(T)$ and the elastic moduli (the shear modulus $G(T)$ and the Young's modulus $Y(T)$) for Ge_xSe_{1-x} (x=0–0.30) have been measured in the kHz frequency range. In the present study, in order to relate the viscosity η with the shear modulus G, we applied the Dyre's shoving model [23,24]. As will be shown below, the shoving model is well applicable even to the highly-viscous regimes of the Ge–Se glasses. In the high temperature region, on the other hand, particularly for Ge_3Se_7, the viscosity begins to follow the VFT–BSCNF relation. In the following sections, after showing the results based on the above analyses, we further discuss the activation energy for viscous flow and its implications to the degrees of cooperativity and softening in Ge_xSe_{1-x} ($0 \le x \le 0.30$) across the glass-transition range.

2. Relation between the shear modulus and the viscosity in Ge–Se

2.1. Application of the Wachtman equation to G(T)

The elastic properties of various glass-forming substances including the Ge–Se system have been investigated extensively [6–8,25,26]. For chalcogenide semiconducting glasses, which have attracted much attention as model of covalent glasses, the composition dependence of various physical quantities such as T_g, band gap energy, and elastic properties [6,7,22,25,26] have been discussed in terms of the bond constraint theory (BCT) proposed by Phillips and Thorpe [27,28], and further extended by Tanaka [29]. The BCT predicts that some transformations occur at the average coordination number per atom $<r>=2.4$ (the rigidity threshold) and 2.67 (the chemical threshold). These "magic numbers" on $<r>$ are obtained by counting the number of constraints per atom $N_{co}(<r>)$ (arising from the radial and angular constraints) and equalizing it with the spatial degrees of freedom (i.e., $N_{co}=3$ in the case of three-dimensional space). Interestingly, it has been demonstrated in many studies [7,25,26,29–31] that binary and ternary chalcogenide glasses such as Ge–S(Se) and Ge–Sb–S(Se) exhibit peculiar composition dependence in various physical quantities, showing extreme values at $<r>=2.4$ and 2.67.

Gueguen et al. [6] have measured the temperature-dependent elastic moduli (the shear modulus G and the Young's modulus Y) and the viscosity η in Ge–Se system across the glass transition range. In the present study, we have used their data, and analyzed firstly the shear modulus $G(T)$ using the empirical Wachtman equation [32]. Fig. 1(a) shows the temperature dependence of $G(T)$ fitted with the Wachtman equation which is given by

$$G(T) = G_0 - b^{(G)} T \exp\left(-\frac{T_W{}^{(G)}}{T}\right), \qquad (1)$$

where, G_0, $b^{(G)}$ and $T_W^{(G)}$ are constants determined by fitting the experimental data. G_0 is the zero-temperature limit of $G(T)$. Fig. 1(b) shows the temperature dependence of the Young's modulus $Y(T)$ for the same compositions to that indicated in Fig. 1(a) in addition to the Young's modulus of $GeSe_9$ and $Ge_{15}Se_{85}$ [22]. From Fig. 1(b), it is noted that by replacing $G(T)$ with $Y(T)$, the Wachtman equation given in Eq. (1) also reproduces reasonably well the experimental data of the Young's modulus excepting $GeSe_9$. For this composition, the Young's modulus data deviates from the behavior described by the Wachtman equation in the low temperature region, probably due to the influence of the excess selenium content. In selenium-rich composition ($x \le 0.15$), the temperature variation of the internal friction evaluated experimentally [22] is much sensitive than that those samples containing larger amount of germanium.

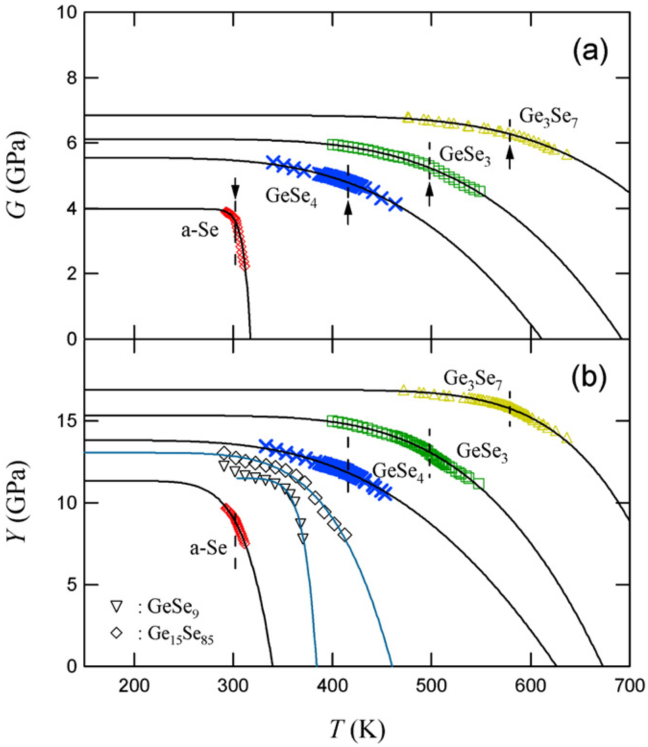

Fig. 1. (a) Temperature dependence of the shear modulus $G(T)$ for $GeSe_4$, $GeSe_3$, Ge_3Se_7 and a-Se. The solid curves are reproduced by using Eq. (1). The arrow indicates the glass transition temperature T_g. (b) Temperature dependence of the Young's modulus $Y(T)$ for the same compositions to that indicated in (a), plus, $GeSe_9$ and $Ge_{15}Se_{85}$ [22]. The solid curves are the Wachtman equation drawn by replacing $Y(T)$ instead of $G(T)$ in Eq. (1). The fitting parameters of these relations are listed in Table 1.

A theoretical foundation of the Wachtman equation was reported by Anderson [33]. Anderson showed that the empirical Wachtman equation can be derived from the Mie–Grüneisen equation of state. It was shown that the parameter $b^{(G)}$ is given by $b^{(G)} = 3R\gamma\delta/V_0$, and that $T_W^{(G)}$ is a quantity closely related with the Debye temperature. Here R is the gas constant, γ is the Grüneisen parameter, V_0 is the specific volume at absolute zero temperature, and δ is a constant independent of temperature defined by using thermal expansion coefficient and temperature-derivative of the bulk modulus, respectively [33]. In addition, Anderson has also discussed that the expression for the bulk modulus $B(T)$ reduces to the Young's modulus $Y(T)$ when the Poisson's ratio σ has sufficiently weak temperature dependence [33]. Fortunately, the derivation given by Anderson can be applied to the present study as well, since the Poisson's ratio for Ge_xSe_{1-x} (with the exception of a-Se) shows also weak temperature dependence [6]. It is well known that the Young's modulus Y and the shear modulus G are mutually interrelated through the equation, $Y=2(1+\sigma)G$. This relation justifies the applicability of the Wachtman equation to $G(T)$ as expressed in Eq. (1) and shown in Fig. 1(a). The fitting parameters of Eq. (1), as well as that applied to $Y(T)$, are listed in Table 1.

2.2. The viscosity of Ge–Se glasses across the glass-transition

Fig. 2 shows the viscosity of $GeSe_9$, $GeSe_4$, $GeSe_3$, Ge_3Se_7 and a-Se across the glass-transition range. We can see from the figure that the glass-transition temperature (or the temperature T_{12} at which the value of viscosity reaches $\eta(T_{12})=10^{12}$ Pa·s) increases with the increase of Ge content. The shift of the glass-transition temperature toward higher temperature is consistent with the results of the elasticity shown in Fig. 1. There, $G(T)$ and $Y(T)$ increase systematically with the increase of Ge content. From Fig. 2 we also note that excepting a-Se, the viscosity in the lower temperature region (i.e., $\eta \ge 10^{12}$ Pa·s) exhibit