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Letter to the editor

Two types of structural relaxations around the deformation temperature of $Ge_{20}Sb_{15}Se_{65}$ glass

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ABSTRACT

Chalcogenide glasses have attracted a great deal of attention for the optical elements of infrared devices. The viscosity and elasticity of glasses are important characteristics for the use of precision molding techniques. The uniaxial compression creep behavior of $Ge_{20}Sb_{15}Se_{65}$ glass was studied around its deformation temperature. The derived creep function was converted into relaxation moduli by Laplace transformation and its inversion. Analysis using a two-term Maxwell model revealed the shear relaxation modulus $G(t)$ as two distinct structural relaxation processes with short and long relaxation times on the order of 10^1 s and 10^3 s, respectively, at 313 °C. The fast relaxation with high elasticity obeyed the time–temperature superposition principle and its activation energy ΔH_1 was estimated to be 350 ± 10 kJ/mol using Narayanaswamy's relation. This energy is mainly comparable to the bond dissociation energies of Se—Se (~320 kJ/mol). The process was therefore suggested to be due to motion around these thermally broken inter-atomic bonds, as in many glassy systems. In contrast, the low-elasticity slow relaxation process had activation energy of approximately 480 ± 60 kJ/mol and was considered to represent breaking and rearrangement of heteronuclear Ge—Se and Sb—Se bonds in the glass network during pressure-induced entanglement.

1. Introduction

Chalcogenide glasses have attracted a great deal of attention for the optical elements of infrared devices such as thermal imaging cameras [1,2], chemical sensors [3], and laser knives [4]. For the fabrication of such glasses into lenses, diffraction devices or the other infrared elements in these devices, direct thermal molding of the glass would be a valuable technique with respect to mass production. The viscosity and elasticity of glasses are important characteristics for the use of precision molding techniques [5,6]. In general, the viscosity of chalcogenide glasses is sensitively dependent on the temperature around the transition temperature and these glasses are brittle compared with oxide glasses, which leads to difficulty in controlling the temperature during molding and other thermal deformation processes. Ge—Se glasses exhibit good transparency in the long-wavelength infrared (LWIR) region, are based on elements with relatively low toxicity, and have been extensively studied in terms of their glass structure and optical, thermal, and mechanical properties over the past several decades [7–10]. Ge–Sb–Se glasses have superior glass formation ability compared with simple Ge—Se systems [11–13] and have found commercial application. Koštál and Málek [14] reported that the viscosities of stoichiometric $(GeSe_2)_x(Sb_2Se_3)_{1-x}$ glasses show Newtonian behavior with a temperature dependence that can be described by a simple Arrhenius equation. Webber and Savage [15] measured the temperature dependence of viscosity for a Se-poor $Ge_{28}Sb_{12}Se_{60}$ glass using a parallel plate technique. Martinkova et al. studied the temperature dependence and fragility of a $Ge_{18}Sb_{28}Se_{54}$ glass [16]. Lee et al. [13] investigated the compositional dependence of the glass-transition temperature and softening point for over 40 samples. The structural, optical, and other properties of Ge–Sb–Se glass systems have been extensively studied [17]. However, the viscoelastic characteristics of these systems have received comparatively little attention, despite their crucial role at around the deformation temperature, especially for viscous flow under stress and recovery after the release of pressure in thermal deformation processes. The present study deals with $Ge_{20}Sb_{15}Se_{65}$ glass. The viscoelastic behavior of this material around its deformation temperature was examined using uniaxial compression creep tests. A two-term Maxwell model was applied to the relaxation elastic moduli derived from the creep function according to linear viscoelasticity theory. The structural relaxation process, which is expressed by the elastic and viscous terms of the model, is discussed in conjunction with the glass structure.

2. Experimental procedures

Commercial $Ge_{20}Sb_{15}Se_{65}$ glass (KG-1, Opto Create Co., Ltd.) was

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Table 1
Glass-transition (T_g) and deformation (A_t) temperatures, density (ρ), ultrasonic wave velocities of the longitudinal (v_L) and transverse (v_T) waves, instantaneous Young's modulus (E_0), instantaneous shear modulus (G_0), Poisson's ratio (ν), and bulk modulus (K_0) calculated from the velocities at room temperature.

$Ge_{20}Sb_{15}Se_{65}$	T_g	A_t	ρ	v_L	v_T	E_0	G_0	ν	K_0
(KG-1)	°C	°C	kg/m^3	m/s		GPa	GPa		GPa
Measured	245 ± 1	282 ± 2	4699 ± 1	2296 ± 40	1279 ± 40	19.59 ± 0.10	7.68 ± 0.10	0.275 ± 0.001	14.53 ± 0.10
Nominal	280		4720			19.1		0.27	

used in the uniaxial compression creep tests. The glass-transition (T_g) and deformation (A_t) temperatures were determined by thermomechanical analysis (TMA/SS-6300, Seiko Instruments Inc.) with a load of 100 mN and a heating rate of 5 °C/min. The density (ρ) was determined with an error of less than ± 1 kg/m^3 based on Archimedes' principle using distilled water. The ultrasonic velocities of the longitudinal (v_L) and transverse (v_T) waves were measured at room temperature using the ultrasonic pulse-echo method. A 10 MHz longitudinal transducer and a 5 MHz transverse transducer were used with a pulse transmitter/receiver (DPR300, JSR Ultrasonics). The Young's modulus (E_0), instantaneous shear modulus (G_0), bulk modulus (K_0), and Poisson's ratio (ν) were determined using these velocities with an error of less than ± 0.1 GPa for E_0, G_0 and K_0. The measurement and calculation of E_0 have been described in detail elsewhere [18–20]. Table 1 shows a comparison between the observed fundamental values for the studied glass and the typical standard values stated by the manufacturer. The observed values were also used for the calculation of the creep function and the relaxation modulus in the analysis of the creep test results [20–22].

For the creep tests, the glass sample was cut into a cylindrical shape with a diameter of 5.5 mm and a height of 5.5 mm. Both sides of the cylinder were polished to optical grade. The uniaxial compression creep tests were conducted using a precision pressing machine (GMP-311 V, Toshiba Machine Co., Ltd.) equipped with two flat parallel plates over a duration of about 8000 s. After reaching the test temperature, a constant load of 420 N was applied to the glass cylinder under a nitrogen atmosphere. The sample height at each time point was recorded to an accuracy of 1.0 μm. The period of the recording was varied from 5×10^{-3} to 1 s depending on the deformation rate. The measurements were carried out at around the deformation temperature.

3. Results and discussion

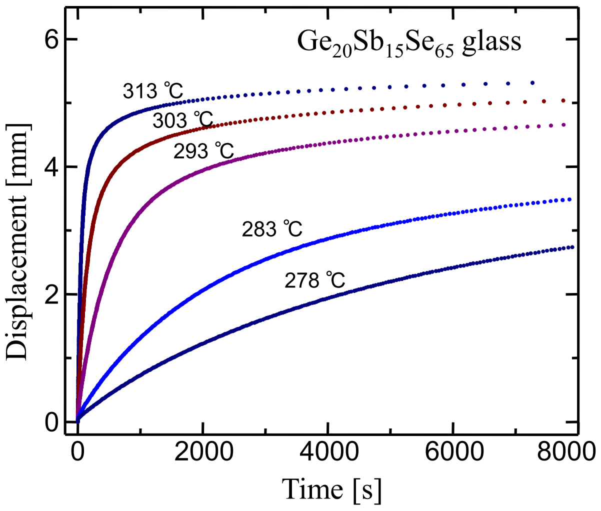

Fig. 1. Displacement histories of cylindrical sample height for the creep tests of $Ge_{20}Sb_{15}Se_{65}$ glass performed at various temperatures.

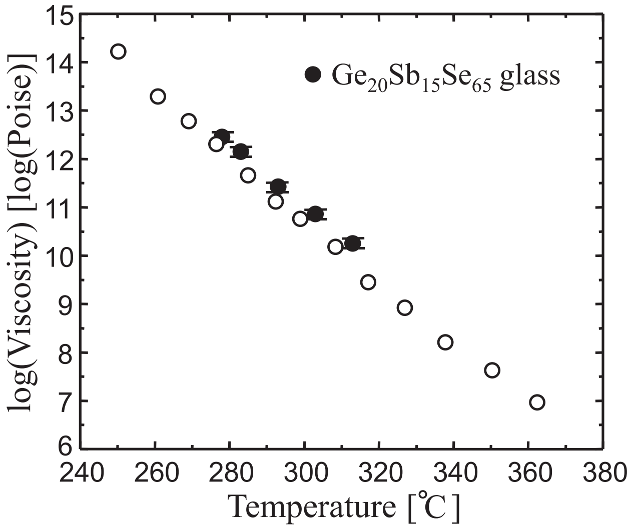

Fig. 2. Temperature dependence of viscosity for $Ge_{20}Sb_{15}Se_{65}$ glass (closed circles), alongside the literature data [14] for $(GeSe_2)_{0.7}(Sb_2Se_3)_{0.3}$ glass (open circles).

Fig. 1 shows the displacement histories derived from the creep tests performed at various temperatures. As seen in the curves recorded at higher temperatures, the displacement proceeded quickly in the early stage and then continued more slowly over an extended period. The viscosity (η) of the glass can be calculated from the displacement rate using the standard parallel plate method according to the following equation, where V is the sample volume, h is the sample height, M is the mass, and g is the acceleration due to gravity [23,24]:

$$\eta = \frac{2\pi M g h^5}{3V(\mathrm{d}h/\mathrm{d}t)(2\pi h^3 + V)} \tag{1}$$

Fig. 2 shows the temperature dependence of η for $Ge_{20}Sb_{15}Se_{65}$ alongside the previous data for $(GeS_2)_{0.7}(Sb_2Se_3)_{0.3}$, a glass with a similar chemical composition [14]. The Fulcher equation [15] was optimized to give $\eta = -5.05 + 4253/(T[°C] - 35.29)$.

Furthermore, to analyze the displacement that exceeded 10% of the initial height as shown in Fig. 1, true stress and true strain were introduced as follows to calculate the creep function $J(t)$, according to Arai's method [20,21] based on linear viscoelasticity theory:

$$J(t) = \frac{1}{E_0} + \sum_{i=1}^{10} a_i t^i. \tag{2}$$

Fig. 3 shows the $J(t)$ of the studied glass sample at various temperatures. The $J(t)$ increased almost linearly over time at lower temperatures and increased in a curved manner at higher temperatures. The creep function $J(t)$ was fitted using a ten-term power function to calculate the relaxation moduli $G(t)$ and $E(t)$ using the Laplace transformation and its inverse [22]. The instantaneous creep function J_0 at $t = 0$ was assumed using the reciprocal Young's modulus $1/E_0$ in this calculation. The details of the calculation can be found elsewhere [20,21]. Fig. 4 shows the $G(t)$ of the glass obtained using the transformation. As the time evolution of $E(t)$ was fundamentally the same as that of $G(t)$, only the latter is discussed here. It is apparent that the