A Model for the Temperature Dependence of the Viscosity

in Cu-As-Se system

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Abstract

The microscopic bonding behavior of amorphous $Cu_x(As_2Se_3)_{1-x}$ (x=0.00, 0.01, 0.05, 0.10 and 0.20) is studied from the point of view of the viscosity. The model used in this analysis describes the temperature dependence of the viscosity in terms of the mean bond strength E_0, the mean coordination number Z_0, and their fluctuations ΔE, ΔZ of the structural units that form the melt. The model reproduces quite well the temperature dependence of the viscosity of $Cu_x(As_2Se_3)_{1-x}$ observed experimentally. According to the theory, the fragility of the system increases as the fluctuation of the total bond strength increases. It is shown that the viscous flow is accompanied by the cooperative movements of the structural units and occurs by breaking selectively the weaker parts of the bonds between the structural units. This notion is related to the concept of Cooperatively Rearranging Region (CRR) in the theory of Adam-Gibbs. By analyzing the model, the fluctuation of the total bond strength in Cu-As-Se system is evaluated quantitatively, and the composition dependence of the fragility is discussed in terms of bond strength and the coordination number between the structural units. The analysis

suggests that in the $Cu_x(As_2Se_3)_{1-x}$ system, there must be a strong composition dependence in the bond strength and a weak composition dependence in the fragility and coordination number fluctuation.

Keywords: chalcogenide glasses, fragility, viscosity, cooperatively rearranging region

1. Introduction

It is well known that chalcogenide glasses exhibit a wide variety of photoinduced phenomena [1-4]. In addition to the photoinduced properties, the chalcogenide glasses containing silver or copper exhibit also ionic conduction [4-6]. Furthermore, it is known that chalcogenide glasses containing a small amount of such metals exhibit anomalous behaviors in their physical properties [7-10]. For instance, the photodarkening which is normally observed in chalcogenide glasses are suppressed by the addition of small amount of Cu [7,8]. In addition, compared with the number of experimental studies that have been done, theoretical studies on mass transport and mechanical relaxation phenomena in these chalcogenide glasses is scarce despite their fundamental importance in glass science. The results of microscopic events are reflected in the macroscopic quantities such as viscosity. In this study, the microscopic bonding behavior of liquid Cu-As-Se system is investigated from the point of view of the viscosity.

The temperature dependence of the viscosity (or relaxation time) for various glass forming materials is often shown by the so-called Angell's plot [11]. By plotting the logarithm of the viscosity η as a function of the reduced inverse temperature T_g/T, where T_g is the glass transition temperature, curves with different degrees of non-Arrhenius behavior may be systematized. In order to evaluate quantitatively the behavior, a quantity called fragility has been proposed [12]. It gives the gradient of Log η against T_g/T at T_g. For strongly covalent bonded glass formers such as SiO_2, an Arrhenius behavior in the Log η vs T_g/T plot is

observed. These types of materials exhibit small values of fragility and are called strong systems. On the other hand, for systems such as ionic or organic glass forming liquids, a large deviation from the Arrhenius behavior is observed. These types of materials exhibit relatively higher values of fragility and are called fragile systems.

A large number of models have been proposed to describe the temperature dependence of the viscosity in the supercooled liquid region. Among these, the Vogel-Fulcher-Tammann equation [13] and the Adam-Gibbs theory [14] have been very successful and are often cited in the literature. Some years ago, one of the authors has proposed a model for the fragility to describe the temperature dependence of the viscosity in glass forming liquids [15]. The model has been used to investigate the viscosity of many kinds of materials such as covalent, ionic, metallic and molecular systems [16]. According to the model, the temperature dependence of the viscosity is described in terms of the mean bond strength, mean coordination number and their fluctuations of the structural units that form the melt. It was shown that the model can reproduce quite well the experimental results. Moreover, from the model, it is possible to extract some important microscopic bonding characteristics of the system such as the condition of occurrence of the viscous flow [16].

In this contribution, the model is applied to study the viscosity of $Cu_x(As_2Se_3)_{1-x}$ (x=0.0, 0.01, 0.05, 0.10 and 0.20). The application is interesting, because the system exhibits unusual composition dependence in their physical properties [8,17] whose origin is not clarified at all. Viscosity study may give some information to understand better the properties of this system. By extending the previous model [15,16], the fluctuations of the bond strength $|\Delta E|/E_0$ and the coordination number $|\Delta Z|/Z_0$ are evaluated quantitatively. From the results, some notions regarding bonding connectivity in glass forming system are obtained from the microscopic

point of view. The connection between the present model and the concept of cooperatively rearranging region (CRR) in the theory of Adam-Gibbs and other models are also discussed.

2. Theory

2.1 MODEL OF THE MELT AND VISCOSITY

The glass forming melt is formed by an agglomeration of structural units. When the temperature of a supercooled liquid is lowered below its glass transition temperature, the spatial distribution of the constituent elements is frozen retaining its random connectivity. The constituent elements are considered as clusters or structural units that retain its local short range structure. In our model, the structural units are bound to other structural units by a certain bond strength E which is denoted as

$$E = E_0 + \Delta E, \tag{1}$$

where E_0 is the average value and ΔE is its fluctuation. Concerning the coordination number, each structural units is surrounded by a certain number of other structural units and the coordination number of the structural units Z is denoted as

$$Z = Z_0 + \Delta Z, \tag{2}$$

where Z_0 is the average value and ΔZ is its fluctuation.

According to the model, the viscous flow occurs when the structural units move from one position to another by breaking the bonds connecting the structural units. It is important to recognize however, that for the occurrence of viscous flow, there is no necessity to break all the bonds pertaining to a structural unit. Partial breaking and bond twisting may also lead to viscous flow. In the course of this structural relaxation, it is quite probable that the network structure remains effectively the same as have been observed in some systems [18, 19].

Concerning this point further discussion will be given later. Based on this picture, the temperature dependence of the viscosity has been described as [15]

$$\ln\left(\frac{\eta}{\eta_0}\right) = \frac{Cx + Cx^2\left\{\left[\ln\left(\frac{\eta_{Tg}}{\eta_0}\right) + \frac{1}{2}\ln(1-B)\right]\frac{(1-B)}{C} - 1\right\}}{1 - Bx^2} - \frac{1}{2}\ln(1 - Bx^2) \ , \tag{3}$$

where

$$B = \frac{(\Delta E)^2(\Delta Z)^2}{R^2 T_g^2}, \qquad C = \frac{E_0 Z_0}{RT_g}, \qquad x = \frac{T_g}{T} \ . \tag{4}$$

Here, η_0 and η_{Tg} are the viscosities at the high temperature limit and at the glass transition temperature, respectively. R is the gas constant. As usually, the values $\eta_0 = 10^{-5}$ Pa·s and η_{Tg} $= 10^{12}$ Pa·s are adopted. The expression of the viscosity, Eq. (3) is written in terms of physically intuitive quantities B, C and x. C gives the mean total bond strength and B gives the degree of its fluctuation between the structural units, respectively.

The fragility index m is defined as [12]

$$m = \lim_{T \to Tg} \frac{\mathrm{d} \operatorname{Log} \eta}{\mathrm{d}(Tg/T)} \ . \tag{5}$$

This quantity has been used widely to characterize the properties of glass forming liquids. According to the model, the fragility index m can be expressed as

$$m = \frac{1}{\ln(10)}\left\{\frac{B - C + 2\left[\ln\left(\frac{\eta_{Tg}}{\eta_0}\right) + \frac{1}{2}\ln(1-B)\right]}{1 - B}\right\} \ . \tag{6}$$

Our basic picture for the occurrence of viscous flow is due to bond breaking and bond twisting between the structural units which are activated thermally. In our model the activation energy for the viscous flow is determined by the mean values of the bond strength

energy and the coordination number between the structural units [15]. The concept of the model has similarity with other models. For instance, in a model proposed by Avramov *et al*., a quantity denoted as dispersity of the probability of appearance of energy barrier σ is used [20]. This quantity embodies similar physical ideas with the parameter B in our model. By changing the chemical composition of the system, the way to interconnect the structural units changes, resulting in the lubricant effect [21] or the change in the entropy which is quantified by the parameter σ. In our model, the same effect is denoted as fluctuation in the bond strength energy and the coordination number fluctuations. This picture also connects with a model of fragility proposed by Naumis [22]. There it is suggested that the heat capacity jump or the fragility in chalcogenide system is controlled by the number of floppy modes or the average coordination number. In this connection, it will be convenient to mention once again that the parameters in our model, B and C, depend on both, the bond strength and the coordination number, which vary depending on the chemical species that form the system and on their composition ratio. Experimentally it is known that the fragility of some materials changes in a complex way by changing the chemical composition. For instance, in the Ge-Sb-Se system, the fragility determined from viscosity takes a minimum value when the average coordination number of the system is 2.67 [23]. In our model, such a behavior is described by changing the values of B and C.

2.2 VISCOUS FLOW AND COOPERATIVELY REARRANGING REGIONS

Concerning the viscous flow, it is possible to discuss the condition for the occurrence of viscous flow by using the activation energies for viscosity E_a and the mean total bond strength E_0Z_0. A quantity defined as $N_B=E_a/(E_0Z_0)$ [16], provides a measure for the amount of bonds that must be broken for the occurrence of viscous flow. It is expressed as

$$N_{\mathrm{B}} = \frac{B - C + 2\left[\ln\left(\dfrac{\eta_{Tg}}{\eta_0}\right) + \dfrac{1}{2}\ln(1 - B)\right]}{(1 - B)C} \quad . \tag{7}$$

Here, it must be noted that it is not necessary to break all of bonds pertaining to a particular structural unit to observe the viscous flow. In Fig. 1, the behaviour of m (broken lines) and N_B (full lines) are shown as functions of B and C. It is known that the structural relaxations near the glass transition temperature are related to the cooperative movement of molecules and clusters. In a fragile system, an abrupt increase of the viscosity is observed when the system approaches the glass transition temperature. In terms of the concept of Adam-Gibbs theory [14], the increase of the viscosity is related to the increase of the Cooperatively Rearranging Region (CRR). In addition, it is reported that the CRR increases with the increase in the fragility [24-26]. However, concerning the number of particles involved in CRR, there seem to be no convincing theories at the present [27-29].

From Fig. 1, we can see that N_B increases accompanying the increase of m. That is, the number of bonds that must be broken for the occurrence of viscous flow increase with the increase in the fragility. This implies that in the viscous flow of a fragile system, large numbers of structural units are involved. This notion is in harmony with the picture that is extracted from the CRR concept.

In a previous study, it was shown that the values of B and C determined for various classes of materials are interrelated [16]. The trends between the parameters B and C is shown by shaded area in Fig. 1. From Fig. 1, we can note that when the total bond strength C increases, its fluctuation B decreases, and vice versa. It must be also noted that in the area where B takes higher values, N_B becomes also larger. This observation suggests that the viscous flow occurs when the weaker parts of bonds between the structural units are broken selectively. Therefore, the number of structural units that rearrange collectively (or the number of molecules in the CRR) will be large in more fragile systems.

2.3 THEORETICAL RELATION BETWEEN B AND C

In the previous subsection 2.2, we mentioned that the values of B and C determined for various classes of materials are interrelated as shown by the shaded area in Fig. 1. In the course of the derivation of Eq. (3), the following relation is obtained.

$$\frac{1}{2RT_g}\left\{Z_0\frac{(\Delta E)^2}{E_0}+E_0\frac{(\Delta Z)^2}{Z_0}\right\}=\left[\ln\left(\frac{\eta_{Tg}}{\eta_0}\right)+\frac{1}{2}\ln(1-B)\right]\frac{(1-B)}{C}-1 \quad . \tag{8}$$

From this equation, the theoretical relation between B and C can be written as

$$C=\frac{2\gamma(1-B)}{2\gamma+\sqrt{B}(1+\gamma^2)}\left[\ln\left(\frac{\eta_{Tg}}{\eta_0}\right)+\frac{1}{2}\ln(1-B)\right] \quad , \tag{9}$$

where

$$\gamma=\frac{|\Delta E|/E_0}{|\Delta Z|/Z_0} \quad . \tag{10}$$

Here, γ gives the ratio of the normalized bond strength fluctuation to the coordination number fluctuation. The behaviour of Eq. (9) is shown in Fig. 2 for the cases of $\gamma=1$ (dashed line) and $\gamma\neq1$ (solid line), respectively. It is noted that the curve for the case of $\gamma\neq1$ deviates from that of $\gamma=1$ in the intermediate region of B. The line where the fragility takes a constant value is also shown. The set of values (B,C) for a particular compound can be determined by using the data of viscosity measurements. On the other hand, Eq. (9) indicates that the point of intersection between $C(B,\gamma)$ and the line of constant fragility index m can be determined uniquely, provided we know the fragility index m and the ratio of the fluctuation γ. However, it is rather difficult to obtain the values of both, $|\Delta E|/E_0$ and $|\Delta Z|/Z_0$, simultaneously. This situation can be overcome by using the definition given in Eq. (4) and by writing γ as

$$\gamma=\frac{\sqrt{B}}{C\left(\frac{|\Delta Z|}{Z_0}\right)^2} \quad . \tag{11}$$

Then, from Eqs. (9) and (11) we obtain

$$C = -\frac{1}{\delta} + \sqrt{\frac{(1-B)}{\delta^2} + \frac{2(1-B)}{\delta}\left\{\ln\left(\frac{\eta_{Tg}}{\eta_0}\right) + \frac{1}{2}\ln(1-B)\right\}} \quad , \qquad \delta = \left(\frac{|\Delta Z|}{Z_0}\right)^2 \quad . \tag{12}$$

This equation indicates that the relation between B and C can be written if the fluctuation $|\Delta Z|/Z_0$ is given.

3. Application to Cu-As-Se system

The temperature dependence of the viscosity obtained from the model calculation and the experimental data for $Cu_x(As_2Se_3)_{1-x}$ (x=0.00, 0.01, 0.05, 0.10 and 0.20) [30,31] are shown together in Fig. 3. We recognize that the model reproduces quite well the experimental data. The values of the fragility index m and the best-fitted parameters B and C are also indicated in the figures. It should be noted that the values of the parameters depend only on the chemical composition of the system and not on the temperature. It is quite probable that this observation is related to the retention of the structure with the change in the temperature as observed in some systems [18,19].

The main purpose of this study is to extract some microscopic knowledge for the $Cu_x(As_2Se_3)_{1-x}$ system from the viscosity behavior. The relation between B and C obtained from Eq. (12) by varying the values of $|\Delta Z|/Z_0$ is shown in Fig. 4. In the same figure, the values of B and C determined for the case of $Cu_x(As_2Se_3)_{1-x}$ (x=0.00, 0.01, 0.05, 0.10 and 0.20) from the viscosity measurements are also shown. We can see that as $|\Delta Z|/Z_0$ increases, the slope of C against B diminishes gradually. For small values of $|\Delta Z|/Z_0$, B is small and $|\Delta Z|/Z_0 < |\Delta E|/E_0$ (region denoted as ①). On the other hand, for large values of $|\Delta Z|/Z_0$, B is large and $|\Delta Z|/Z_0 > |\Delta E|/E_0$ (region denoted as ②). The case where $|\Delta Z|/Z_0 = |\Delta E|/E_0$ is given

by Eq. (9) and is shown by dotted curve in Fig. 4. The figure gives information concerning on which kind of fluctuations (coordination $|\Delta Z|/Z_0$ or bond strength $|\Delta E|/E_0$) dominate in the different parts of the B-C space. If a certain system exhibits a composition dependence in the area ①, the system is expected to show a strong composition dependence in the bond strength and a weak composition dependence in the fragility and coordination number fluctuation. On the other hand, if the system exhibits a composition dependence in the area ②, such a system is expected to show a strong composition dependence in the fragility and coordination number fluctuations and a weak composition dependence in the bond strength fluctuations. In addition, for this case, it is expected that the system would become more heterogeneous. Ediger has discussed extensively the dynamical properties of spatially heterogeneous supercooled liquids [32]. There, it has been pointed out that the heterogeneity has important consequences for the understanding of transport properties near the glass transition temperature.

Concerning the fluctuations of both $|\Delta E|/E_0$ and $|\Delta Z|/Z_0$ in the Cu-As-Se system, experimental data that give direct information on these quantities are not available. However, the analysis shown in Fig. 4 suggests that this system belongs roughly to the group ① discussed above. That is, the system is expected to show a strong composition dependence in the bond strength and a weak composition dependence in the fragility and coordination number fluctuation. According to the result shown in Fig. 4, the coordination number fluctuations take values between 0.06 and 0.1 depending on its composition. Once knowing $|\Delta Z|/Z_0$, Eq. (12) permits to evaluate the other quantities, whose results are shown in Table 1. Fig. 3 and Table 1 indicate that the fragility index m and the related quantities $|\Delta Z|/Z_0$, $|\Delta E||\Delta Z|/E_0 Z_0$ and N_B do not vary monotonically with the composition. Fig. 4 indicates that by adding 1 % of Cu into As_2Se_3, the fragility index decreases from $m \approx 40$ to $m \approx 33$ and that the total bond strength increases from $C \approx 5$ to $C \approx 15$. In this course, B decreases by a small

quantity. In other words, the network formed by As_2Se_3 becomes rigid by doping a small quantity of Cu. The exact origin of this behavior is not known. However, it is expected to be related to the anomalous behavior observed in many chalcogenide system doped with small amount of Ag or Cu [7-10,17]. For instance, the glass transition temperature T_g, a quantity related to the stiffness of the network connectivity, exhibits the minimum value at around x=5% [17]. Similar behaviors have been also seen in the composition dependence of the fragility m and the heat capacity change ΔC_p, measured by Košt'ál et al [31]. On the other hand, NQR measurements performed in $Cu_{0.15}(As_2Se_3)_{0.85}$ and $(Cu_2Se)_{0.225}(As_2Se_3)_{0.775}$ have revealed that there is a difference in the number of As-As bonds between these two compounds [33]. It is probable that this kind of difference in the local bonding originate the composition dependence of the physical properties observed in $Cu_x(As_2Se_3)_{1-x}$.

Concerning the ion transport properties, some studies have been done in the system Cu-As-Se [6]. In the parent compound Ag-As-S and Ag-Ge-S, it is reported that there exist at least three regions in the composition domains with drastically different ion transport properties [34]. Among these, it is interesting to note that the composition regime above the critical percolation threshold (0.012 - 1.2 at. % Ag, in the case of Ag-As-S), corresponds approximately to the composition range where we have found an unusual variation in the physical quantities as shown in Table 1. Therefore, it is quite probable that the viscosity of the Ag-As-S system will also show a similar behavior to that reported for the Cu-As-Se system [31].

According to the bond fluctuation model of superionic conductors [35], the superionic conduction is closely related to the bonding characteristics of the materials. For oxide glassy systems, it has been suggested that the inhomogeneity of the network structure influences largely the ion transport properties, and that the local bond fluctuation around the mobile ion

occurs efficiently within the inhomogeneous network structure [36]. It is quite probable that the unique composition dependence of the fragility shown in Fig. 4 is related to the inhomogeneity of the network and that a peculiar ion transport behavior could be observed. Concerning this last point, experimental verification is required.

4. Conclusion

In the present work, the microscopic bonding behavior of amorphous Cu-As-Se system has been discussed from the point of view of the viscosity. It has been shown that the temperature dependence of the viscosity of Cu doped chalcogenide glasses are quite well described by our model that uses the bond strength and coordination number between the structural units. From the application of the model to the Cu-As-Se system, the fluctuations of the bond strength and the coordination number, and the number of structural units involving in the viscous flow have been evaluated quantitatively. It has been shown that the fluctuation of the total bond strength exhibits a non-monotonic composition dependence by the addition of Cu. The analysis based on our model suggests that there must be a strong composition dependence in the bond strength and a weak composition dependence in the fragility and coordination number fluctuation. It has been also shown that the viscous flow is accompanied with the cooperatively rearranging movements of the structural units and that the viscous flow occurs by breaking selectively the weaker parts of bonds. The relations of the present theory with the concept of CRR in the theory of Adam-Gibbs and other models of the fragility have been also discussed.

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Figure Captions

Fig. 1: Relationship between the values of B and C determined for different materials. The behavior of m (broken lines) and N_B (solid lines) defined by Eqs. (6) and (7), are also shown.

Fig. 2: Theoretical relation between B and C as given by Eq. (9). The dashed and solid lines represent the cases for $\gamma=1$ and $\gamma \neq 1$, respectively.

Fig. 3: The temperature dependence of the viscosity in $Cu_x(As_2Se_3)_{1-x}$ (x=0.00, 0.01, 0.05, 0.10 and 0.20). The experimental data are taken from Refs. [30,31].

Fig. 4: The composition dependence of the viscosity in Cu-As-Se system. The symbols in the figure show the cases for x=0.00(●), 0.01(▲), 0.05(▼), 0.10(◆) and 0.20(♦) in $Cu_x(As_2Se_3)_{1-x}$, respectively. The behavior of Eq. (12) for different values of $\delta=(\Delta Z/Z_0)^2$ and the behavior of m defined by Eq. (6), are also shown.

Table Caption

Table 1: Composition dependence of the normalized coordination number fluctuation $|\Delta Z|/Z_0$, the fluctuation of the total bond strength $(|\Delta E||\Delta Z|)/(E_0 Z_0)$, and the amount of bonds that must be broken for the occurrence of viscous flow N_B in $Cu_x(As_2Se_3)_{1-x}$.

Fig. 1

Fig. 2

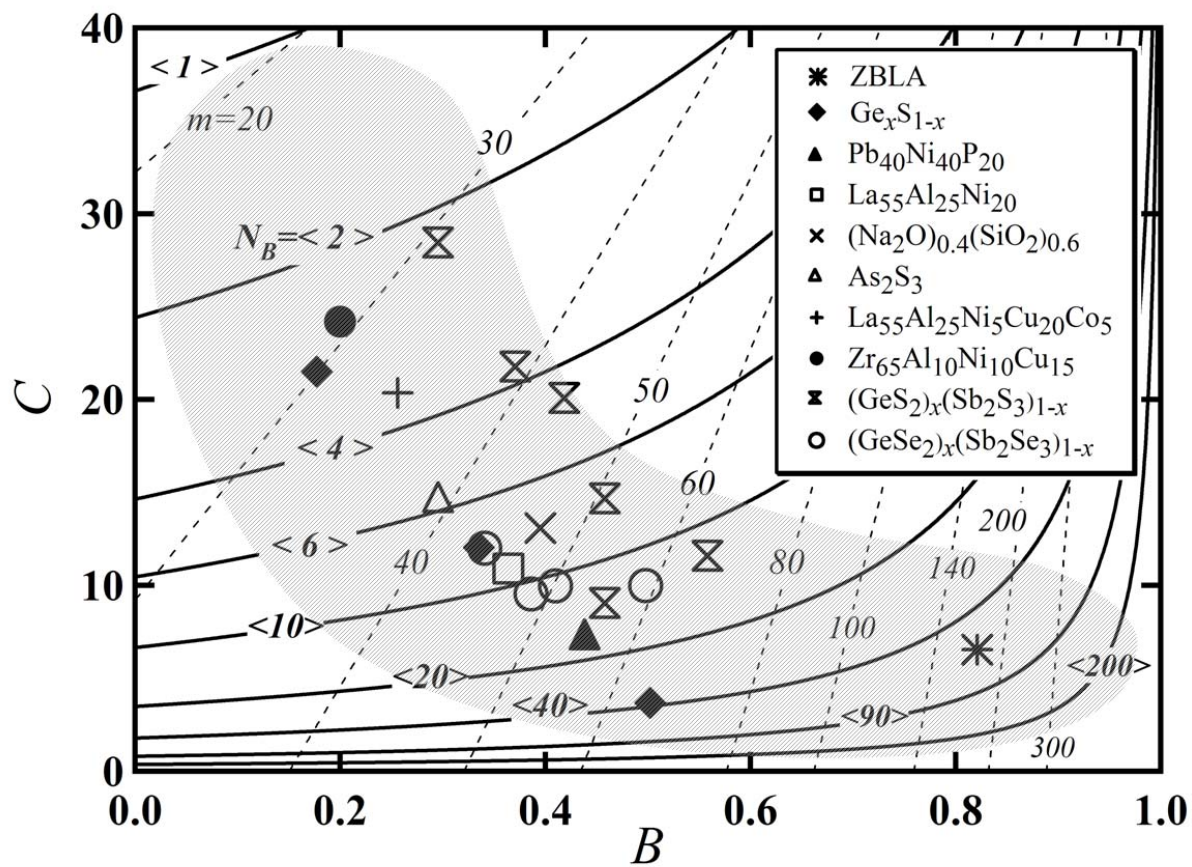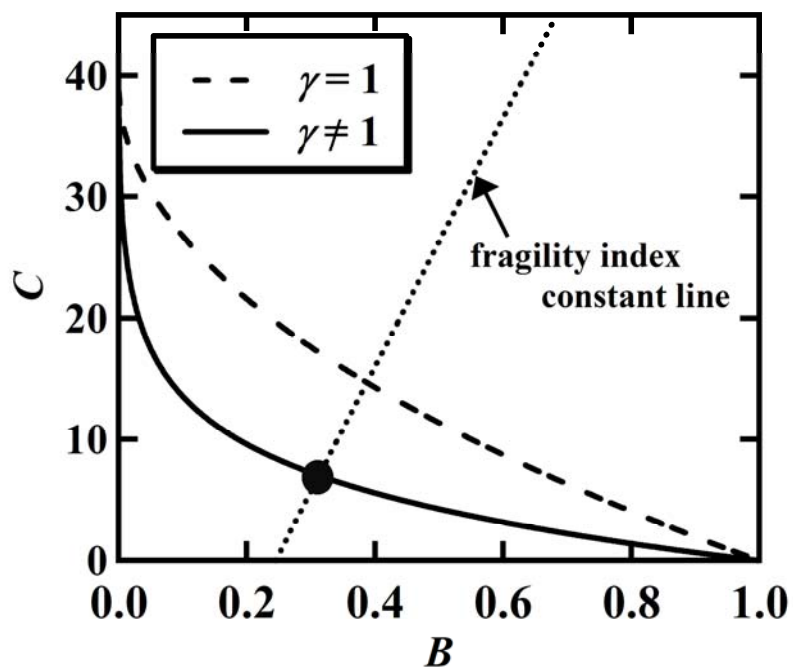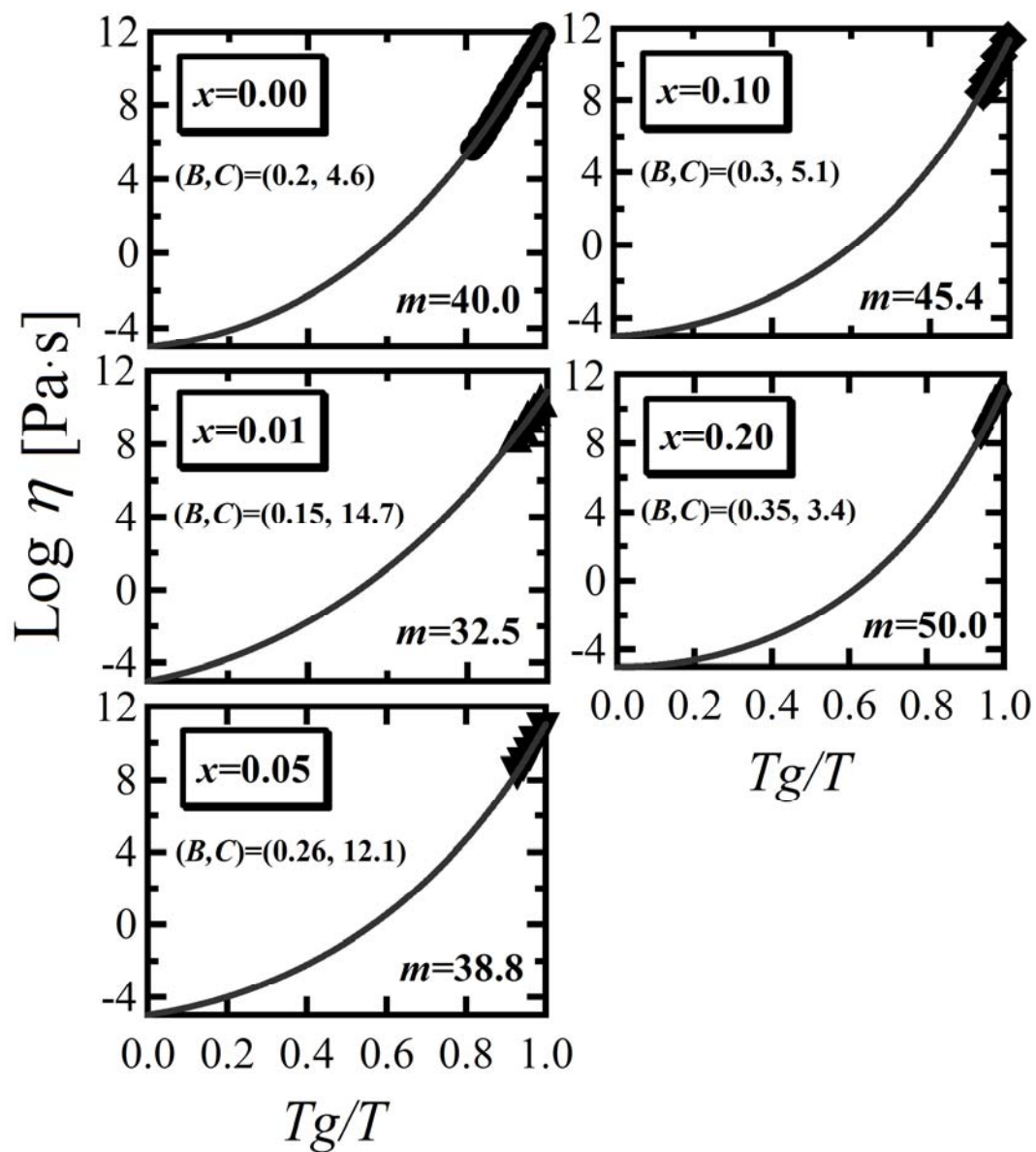Fig. 3
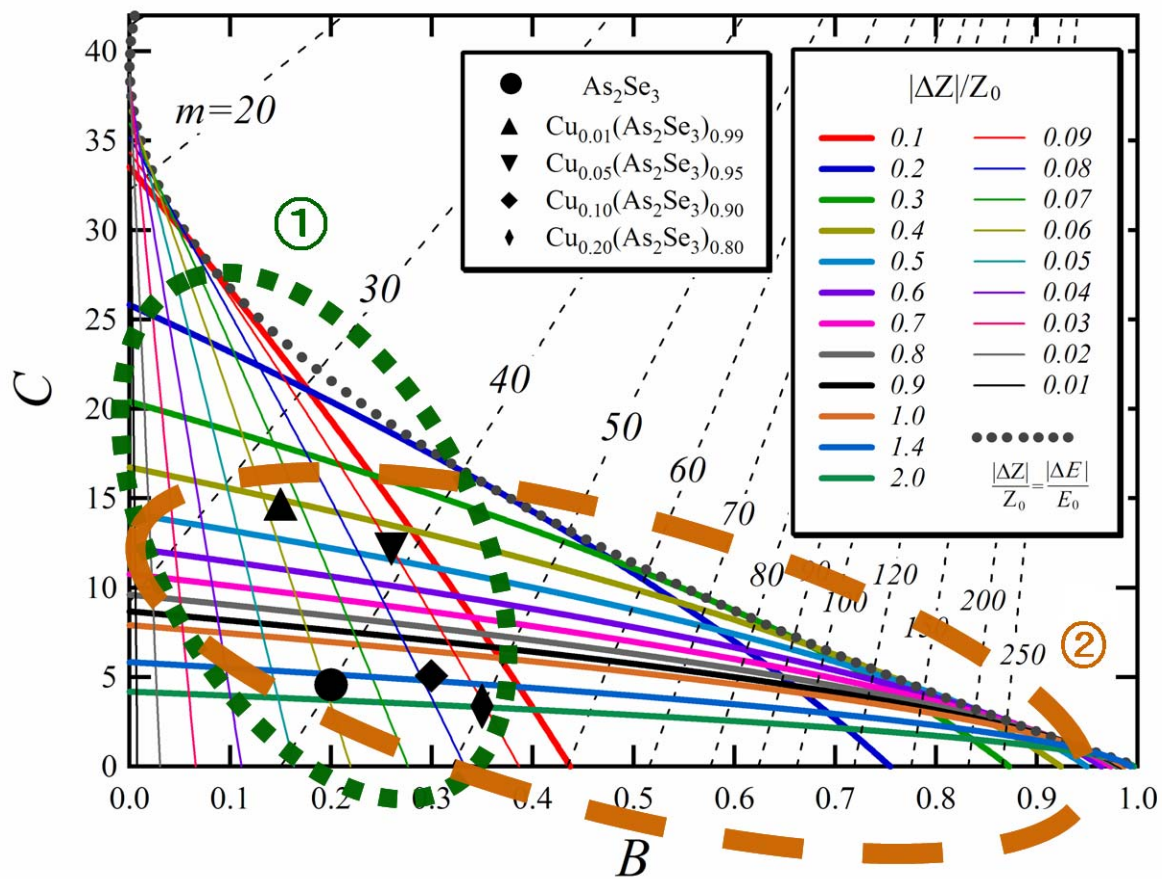
Fig. 4

x	0.00 (●)	0.01 (▲)	0.05 (▼)	0.10 (◆)	0.20 (♦)
$\lvert \Delta Z\rvert/Z_0$	0.062	0.063	0.090	0.082	0.089
$\lvert \Delta E\rvert\lvert \Delta Z\rvert/E_0 Z_0$	0.097	0.027	0.042	0.108	0.175
N_B	20.1	5.1	7.4	20.7	34.0

Table 1