

# **Estimations and implications of the mean binding energy and the fluctuation between the structural units in chalcogenide glasses**

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## **Abstract**

The mean binding energy and the fluctuation between the structural units in chalcogenide glassy systems are estimated by using the Bond Strength-Coordination Number Fluctuation (BSCNF) model. Chalcogenide glasses can be considered to be formed by an agglomeration of structural units. For this kind of glasses, the structural units are connected to each other by weak intermolecular forces. From the results obtained in the present study, it is suggested that the binding energy estimated by the BSCNF model corresponds to the intermolecular forces between the structural units. The analysis by the BSCNF model also suggests that the viscous flow or the structural relaxation results by breaking the weaker parts of the bonds in the intermolecular connections. This picture of the viscous flow is in agreement with the structural model of covalent glasses and the photoinduced properties in chalcogenide glasses proposed by other authors.

*Keywords:* chalcogenide glasses; binding energy; fluctuation; intermolecular force

## 1. Introduction

During the last decades, glassy chalcogenide semiconductors have attracted much interest for their technological applications such as optical fibers and other photo-related materials [1, 2]. From a fundamental point of view, such kinds of materials have been studied extensively to verify the different theories. Among these, the bond constraint theory, originally proposed by Phillips [3] and further extended by others [4,5], have provided a basis for understanding the composition dependence of the physical quantities, in particular, the transformations occurring at the average coordination number per atom,  $\langle r \rangle = 2.4$  (floppy-rigid transition) [3,4] and 2.67 (topological transition) [5]. Another example is the finding of a good correlation between the glass transition temperature  $T_g$  and the overall mean bond energy  $\langle E \rangle$  for various kinds of chalcogenide glasses, which has been found by using the covalent bond approach proposed by Tichý and Tichá [6]. This approach has found a wide field of application in the study of chalcogenide glasses [7-9]. The theoretical methods mentioned above have provided insightful understanding on nanoscale phenomena that occur accompanied by the composition variation in chalcogenide glasses. It should be noted however, that although large number of studies have been performed focusing on the concept of ‘mean values’ of the physical quantities, less attention has been paid to the ‘fluctuation.’

In this paper, chalcogenide glassy materials are characterized from a chemical bond point of view. Specifically, it is shown that the mean binding energy and the fluctuation of the structural units in some chalcogenide glasses can be estimated by using the Bond Strength-Coordination Number Fluctuation (BSCNF) model originally proposed by one of the authors [10]. The aims of the present study are to provide a method to estimate the values of the binding energy and the fluctuation between the structural units, and to gain a clue to understand the composition dependence of material properties in chalcogenide glasses.

## 2. The mean binding energy and the fluctuation between the structural units

### 2.1. The BSCNF model and its application to chalcogenide systems

The BSCNF model describes the temperature dependence of the viscosity in terms of the mean values of the bond strength  $E_0$ , the coordination number  $Z_0$ , and their fluctuations  $\Delta E$ ,  $\Delta Z$ , of the structural units that form the melt [10]. The BSCNF model is written as

$$\eta = \frac{\eta_0}{\sqrt{1-Bx^2}} \exp \left[ \frac{Cx + Cx^2 \left[ \left\{ \ln \left( \frac{\eta_{T_g}}{\eta_0} \right) + \frac{1}{2} \ln(1-B) \right\} \frac{(1-B)}{C} - 1 \right]}{1-Bx^2} \right], \quad (1)$$

where

$$B = \frac{(\Delta E)^2 (\Delta Z)^2}{R^2 T_g^2} \quad \text{and} \quad C = \frac{E_0 Z_0}{RT_g}. \quad (2)$$

Here,  $x$  is the inverse temperature normalized by  $T_g$ ,  $x=T_g/T$ .  $\eta_0$  and  $\eta_{T_g}$  are the viscosities at the high temperature limit and at  $T_g$ , respectively ( $\eta_0 = 10^{-5}$  Pa·s and  $\eta_{T_g} = 10^{12}$  Pa·s).  $R$  is the gas constant. The BSCNF model was constructed by considering that the melt is formed by an agglomeration of structural units as shown in Fig. 1. The information on structural connectivity which is reflected in the medium range structure is also incorporated in the BSCNF model [10,11].

In the analysis based on the BSCNF model, the glass forming materials are characterized with the quantities  $B$  and  $C$  defined above. The values of  $B$  and  $C$  are determined by fitting the experimental data of the viscosity. Intuitively,  $C$  gives the total mean binding energy per structural unit and  $B$  gives the degree of its fluctuations among the structural units against the

thermal disturbance at  $T_g$ , respectively. In the BSCNF model, the binding energy  $E$  and the coordination number  $Z$  of the structural units are introduced as independent parameters [10]. If a restricted type of material is considered,  $E$  and  $Z$  could be correlated. The relation reported by Tanaka [12], which is discussed later, is probably related with this observation. However, previous studies have revealed that the relation between  $E$  and  $Z$  in real systems does not show a monotonous variation [13]. Their relations depend on the nature of the bonding of the materials in consideration.

Fig. 2 shows the relation between  $B$  and  $C$  in  $\text{Ge}_x\text{S}_{1-x}$  system ( $x=0.3-0.44$ ). In the inset, the composition dependence of  $E_0Z_0$  and  $T_g$  or  $T_{12}$  are shown, where  $T_{12}$  is the temperature defined at which the value of viscosity reaches  $\eta=10^{12}$  [Pa·s]. It has been reported that for this  $\text{Ge}_x\text{S}_{1-x}$  system, the composition dependence of the quantities such as  $T_g$  [14] and the amount of Ag that can be photodissolved [15], exhibit a maximum at the composition  $x=1/3$ . Fig. 2 indicates that the behavior of  $E_0Z_0$  also shows a characteristic feature at the same composition. The result of  $\text{Ge}_x\text{S}_{1-x}$  shown in Fig. 2 will be considered later together with the ternary chalcogenide glasses.

In the following, we will show that the mean binding energy  $E_0Z_0$  and the fluctuation  $|\Delta E||\Delta Z|$  of the structural units can be estimated by using both,  $T_g$  and the determined parameters,  $B$  and  $C$ .

## 2.2. A relation between the mean binding energy and $T_g$

$T_g$  is known as a quantity that is related with the rigidity of the network structure. The structural property of glassy materials is attributed to some microscopic factors such as the bond arrangements and the magnitude of bond strength between the atoms. Concerning this point, an interesting study has been reported by Tichý and Tichá [6]. They have shown that for

chalcogenide glasses, there exists a good correlation between  $T_g$  and the overall mean bond energy  $\langle E \rangle$  calculated by the covalent bond approach. Specifically, it was shown that the equation given by  $T_g = 311(\langle E \rangle - 0.9)$  reproduces successfully the relation between  $T_g$  and  $\langle E \rangle$  for many kinds of chalcogenide glasses [6]. This relationship can be also written as

$$\langle E \rangle \approx 0.00322T_g + 0.9. \quad (3)$$

The units used in the above expression are  $\langle E \rangle$  [eV] and  $T_g$  [K], respectively. Eq. (3) suggests that a relationship between  $E_0Z_0$  and  $T_g$  could be derived in the light of the BSCNF model.

In our previous study [16], it has been found that  $B$  and  $C$  are mutually connected through the expression given by

$$C = \frac{2\gamma(1-B)}{2\gamma + \sqrt{B(1+\gamma^2)}} \left\{ \ln\left(\frac{\eta_{T_g}}{\eta_0}\right) + \frac{1}{2}\ln(1-B) \right\}, \quad (4)$$

where

$$\gamma = \frac{|\Delta E|/E_0}{|\Delta Z|/Z_0}. \quad (5)$$

Here,  $\gamma$  gives the ratio of the normalized bond strength fluctuation to the coordination number fluctuation. In particular, it has been found that in the case of  $\gamma=1$ , the behavior of the BSCNF model becomes identical to that of the well-known Vogel-Fulcher-Tammann equation [16]. The result of the analysis for many kinds of glassy materials [11,16] has revealed that the value of  $B$  (fluctuation) increases with the decrease in the value of  $C$  (mean value). This behavior is described by Eq. (4), and can be understood as follows. The structural units of a glassy material characterized by large value of  $B$  and small value of  $C$  are loosely connected each other. In other word, the width of the distribution  $|\Delta E|/|\Delta Z|$  around the mean value  $E_0Z_0$  becomes wide. This indicates that structural relaxation occurs cooperatively, enrolling large

number of structural units. That is, the relaxation process occurs by breaking the weaker parts of the bonds in the intermolecular connections. On the other hand, in materials characterized by large value of  $C$  and small value of  $B$ , the relaxation of structural units is more localized. In terms of the fragility concept, these differences correspond to the relaxation occurring in fragile and strong systems, respectively. The mapping of different materials in the  $(B, C)$  plane supports this observation [11,16].

In what follows, we discuss the connection between Eq. (3) and the BSCNF model. In the present study, we introduce the relation between  $E_0Z_0$  and  $T_g$  as

$$E_0Z_0 = R \ln \left( \frac{\eta_{T_g}}{\eta_0} \right) T_g + \beta. \quad (6)$$

This equation is derived from Eq. (4) by imposing  $\gamma=1$  and extracting the terms proportional to  $T_g$ . Here,  $\beta$  is given by  $\beta = -|\Delta E||\Delta Z| \ln(\eta_{T_g}/\eta_0)$ . The magnitudes of the fluctuations,  $|\Delta E|$  and  $|\Delta Z|$ , are expected to be weakly dependent on the composition. In addition, the value of  $(1/2)\ln(1-B)$ , which appears in Eq. (4), is small for the chalcogenide glasses examined in this study. Therefore, we consider that  $\beta$  takes a constant value in the present study.

### 3. Results

Fig. 3 shows the relation between  $E_0Z_0$  and the characteristic temperatures  $T_g$  or  $T_{12}$  for  $(\text{GeS}_2)_x(\text{Sb}_2\text{S}_3)_{1-x}$  ( $x=0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, 0.9$ ),  $(\text{GeSe}_2)_x(\text{Sb}_2\text{Se}_3)_{1-x}$  ( $x=0.4, 0.5, 0.6, 0.7, 0.8$ ), and  $\text{Ge}_x\text{S}_{1-x}$  ( $x=0.3-0.44$ ). The experimental data of the viscosity and  $T_g$  or  $T_{12}$  for these materials are taken from the references [17], [18] and [14], respectively. The value of  $\text{As}_2\text{S}_3$  is also indicated for comparison.

Fig. 4 shows the relation between  $E_0Z_0$  and  $|\Delta E||\Delta Z|$  for the same glasses to those considered in Fig. 3. We can see that the mean binding energy decreases with the increase in the fluctuation. It should be noted however, that for the binary  $\text{Ge}_x\text{S}_{1-x}$  system,  $E_0Z_0$  increases slightly up to  $x=0.32$ , and then decreases with the increase in the amount of Ge ( $x>0.32$ ). This trend is in accordance with the result of Fig. 3. The material trend for Ge-Sb-S systems, on the other hand, decreases with the increase in the fluctuation as a whole.

#### 4. Discussions

From Fig. 3, we can see a material trend for the ternary systems, Ge-Sb-S(Se). That is,  $E_0Z_0$  increases with the increase in  $T_g$  or  $T_{12}$ . This compositional trend indicates that the binding energy becomes stronger with the increase of the amount of Ge. This behaviour is related with the increase of the average coordination number  $\langle r \rangle$  with the concentration of Ge. According to the 8- $N$  rule, the coordination numbers for the elements Ge, Sb, and S(Se) are 4, 3, and 2, respectively. The broken lines indicated in Fig. 3 are drawn by using Eq. (6) with  $\beta = -1.01$  and  $-1.53$ . The slopes of these lines are common and are given by  $R\ln(\eta_{Tg}/\eta_0) \approx 0.00337$ . It is interesting to note that this value is close to 0.00322, which is the value of the slope given in Eq. (3).

Concerning the magnitudes of  $\langle E \rangle$  and  $E_0Z_0$ , however, we should note that there is a large difference between them. For instance, according to the covalent bond approach, the mean overall bond energy  $\langle E \rangle$  for  $\text{As}_2\text{S}_3$  is calculated to be  $\langle E \rangle \approx 2.4$  [eV] [6]. This magnitude is comparable to the bond energy calculated from the Pauling relation [19-21]. On the other hand, the magnitude of  $E_0Z_0$  for the same material is much smaller,  $E_0Z_0 \approx 0.56$  [eV]. It must be also noted that the term  $E_0Z_0$  includes the effect of  $Z_0$ . Then, what is the reason for the difference in the magnitudes between  $\langle E \rangle$  and  $E_0Z_0$ ? To which parts of the network

structure connectivity are these two bond energies related? A probable origin for this difference is the different types of bonds involved. The overall mean bond energy  $\langle E \rangle$  corresponds to that determined by the short range structure [21], while  $E_0 Z_0$  corresponds to that involving the medium range structure [10]. For the sake of comparison, the values of the parameters for some materials are shown in Table 1.

Tanaka [12] has proposed a structural model for covalent glasses. There, it has been discussed that chalcogenide glasses that follows an empirical relation  $\ln T_g \approx 1.6 \langle r \rangle + 2.3$ , consist of molecules weakly bonded each other by van der Waals (VDW) forces. The magnitude of the VDW bonding is  $\sim 0.15$  [eV], which is much weaker than the intramolecular bond energy [22]. From the point of view of the bonding nature, the activation energy for the viscosity  $E_a$  is given by [12]

$$E_a \approx \varepsilon_0 n^{\langle r \rangle - 1}. \quad (7)$$

Here,  $\varepsilon_0 \approx 0.15$  [eV] is the typical value of the VDW type bonding per atom.  $n^{\langle r \rangle - 1}$  gives the number of atoms belonging to the structural unit ( $n \approx 5$ ), and the exponent  $\langle r \rangle - 1$  reflects the dimensionality of the network connectivity within the glass.

Meanwhile, according to the BSCNF model, the activation energy for the viscosity can be written as [11]

$$E_a = (E_0 Z_0) N_B, \quad (8)$$

where  $N_B$  is the number of bonds that must be broken. Note that  $N_B$  gives also the number of structural units involved in the cooperative rearrangements of the structure which occurs accompanying the thermally activated viscous flow. We note that the physical meanings of the parameters and the expressions given in Eqs. (7) and (8) are similar. For  $As_2S_3$ , the activation energy for the viscosity at  $T_g$ , is  $E_a = \ln(10) m R T_g$  [17]  $\approx 3.4$  [eV], where  $m$  is the fragility index,

$m \approx 39$  [11]. Hence, by using Eq. (8),  $N_B$  is estimated to be  $N_B = 3.4/0.56 \approx 6.1$ . If we assume that  $E_0$  is equal to  $\varepsilon_0$ , it is possible to calculate the mean coordination number of the structural unit,  $Z_0$ . For the case of  $\text{As}_2\text{S}_3$ ,  $Z_0$  takes the value  $Z_0 \approx 1.56$ , if  $E_0 \approx 0.15$  [eV] is adopted. Actually, this value could be small, but it can take  $Z_0 \sim 2.0$  depending on the values of other parameters such as  $n$ . It is conjectured that the quantity  $Z_0$  can be related directly with the topological factor or the network dimensionality of the glasses. For the glassy Se, for instance, the average coordination number per atom,  $\langle r \rangle = 2$ , corresponds to the chain-like structure, and the network dimensionality is  $D = \langle r \rangle - 1 = 1$ . Based on this point of view, the structure of  $\text{As}_2\text{S}_3$  glass is considered to form a distorted-layer-like structure [5]. Thus, the mean value of  $Z_0 \sim 2.0$ , which is smaller than  $\langle r \rangle = 2.4$ , could be related with the connectivity of the structural units or the topological order, a characteristic that is reflected in the medium range structure. Furthermore,  $N_B$  contains information on the number of structural units involved in the segmental motions. It includes distant structural units in addition to nearest neighbor structural units. At present, no direct experimental data such as  $Z_0$ ,  $\Delta Z$  and  $N_B$  are available to verify the quantities estimated by the model. Further study is necessary on this regard. To avoid misunderstanding, in the above discussion, it should be remembered that  $Z_0$  is a quantity related with the coordination between structural units, whereas  $\langle r \rangle$  is a quantity related with the atomic mean coordination number.

The dashed line in Fig. 4 is given by the relation,  $E_0 Z_0 = -\ln(\eta_{T_g}/\eta_0)|\Delta E||\Delta Z| + 1.38$ . This relation is the same to that of Eq. (6), but modified in such a way to check the relation between  $E_0 Z_0$  and  $|\Delta E||\Delta Z|$ . From Fig. 4, we can also note that the material trend of  $(\text{GeSe}_2)_x(\text{Sb}_2\text{Se}_3)_{1-x}$  ( $x=0.4-0.8$ ) follows the dashed line. On the other hand, in Ge-Sb-S and Ge-S systems, the points deviate from the dashed line. The reason for this deviation is due to the restriction of  $\gamma = 1$  in the BSCNF model used in the present study. That is, in a real system,

it is expected that the normalized bond strength fluctuation is not equal to the normalized coordination number fluctuation,  $|\Delta E|/E_0 \neq |\Delta Z|/Z_0$ . For the case of Cu-As-Se, we have shown previously that by taking into consideration the composition dependence, the relation  $|\Delta E|/E_0 > |\Delta Z|/Z_0$  holds [13]. Analogously, for the present chalcogenide systems,  $|\Delta E|/E_0$  is larger than  $|\Delta Z|/Z_0$ , because the deviation from the dashed line in Fig. 4 indicates  $\gamma > 1$ . These observations suggest the possibility that the inequality of the normalized fluctuations, i.e.,  $|\Delta E|/E_0 > |\Delta Z|/Z_0$ , is a characteristic feature for the chalcogenide glassy semiconductors.

It is well known that chalcogenide glasses such as  $As_2S_3$  are sensitive to light illumination [23]. This fact indicates that in glassy chalcogenide materials having broad distribution of fluctuations in the bond strength, the weaker parts of bonds between the structural units are broken preferentially. This picture of weak bond disruption accompanied by the viscous flow is in agreement with the structural model of covalent glasses [12], and the model of photo-induced fluidity [22, 23]. For the later, the photo-excitation process is considered to trigger the slipping of molecular clusters [22].

## 5. Conclusions

In the present study, it was shown that for the binary and ternary chalcogenide glasses, the mean binding energy  $E_0Z_0$  and the fluctuation  $|\Delta E||\Delta Z|$  of the structural units can be estimated by using the BSCNF model. The relations between  $E_0Z_0$  and  $T_g$ , and between  $E_0Z_0$  and  $|\Delta E||\Delta Z|$ , were discussed for these chalcogenide glassy materials. It was discussed that difference in the magnitudes between the overall bond energy  $\langle E \rangle$  estimated by the covalent bond approach and  $E_0Z_0$  is large. The difference arises from the different type of interactions operating at short range and medium range distances. The model indicates that the viscous

flow is caused by breaking the weaker parts of bonds involved in the intermolecular connections of the structural units.

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### ***Figure Captions***

**Fig. 1.** Schematic representation of the connectivity of the structural units. The small open and black circles represent atoms. Large circles represent the structural units [10].

**Fig. 2.** Relation between  $B$  and  $C$  for  $\text{Ge}_x\text{S}_{1-x}$  glasses. In the inset, the relations between  $E_0Z_0$  and  $x$ , and between  $T_g$ ,  $T_{12}$ , and  $x$ , are shown. It is observed that the composition dependence of  $E_0Z_0$ ,  $T_g$ , and  $T_{12}$  change their trends at  $x=1/3$ . The experimental data are taken from ref. [14].

**Fig. 3.** Relation between  $E_0Z_0$  and the characteristic temperatures  $T_g$  and  $T_{12}$ . The materials investigated in this study are given in the inset of the figure.

**Fig. 4.** Relation between the binding energy  $E_0Z_0$  and the fluctuation  $|\Delta E||\Delta Z|$ . The symbols used are the same to those used in Fig. 3.

### ***Table Caption***

**Table 1.** Materials parameters for glassy Se,  $\text{As}_2\text{S}_3$  and  $\text{GeS}_2$ . Glass transition temperature  $T_g$ , average coordination number per atom  $\langle r \rangle$  [5], overall mean bond energy evaluated by the covalent bond approach  $\langle E \rangle$  [6],  $E_0Z_0$  and  $|\Delta E||\Delta Z|$  estimated by the BSCNF model.

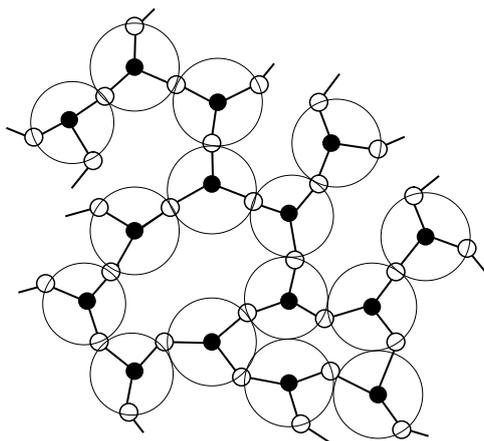


Fig. 1

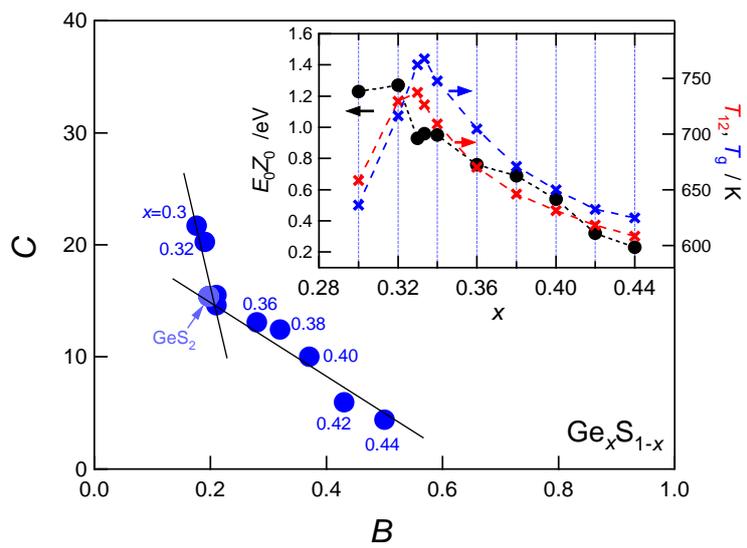


Fig. 2

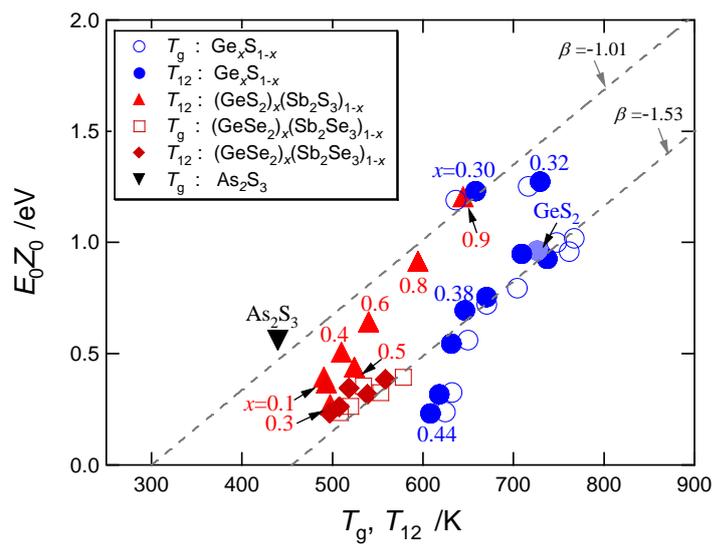


Fig. 3

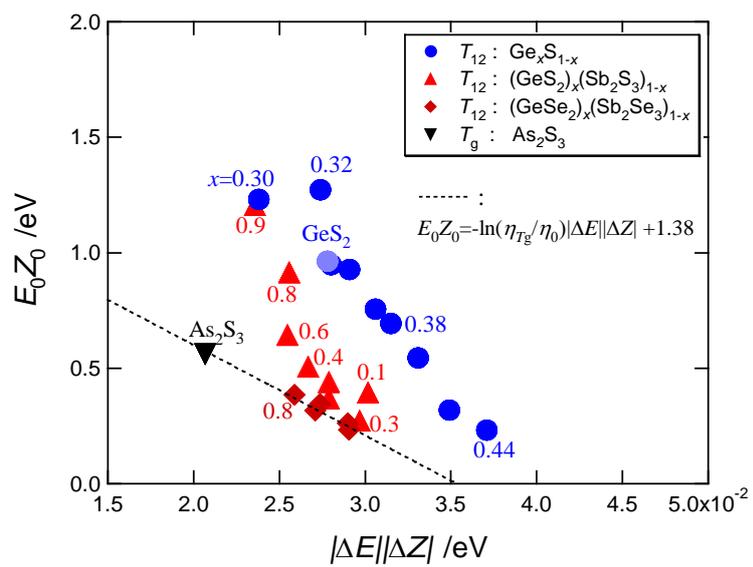


Fig. 4

	$T_g$ [K]	$\langle r \rangle$	$\langle E \rangle$ [eV]	$E_0 Z_0$ [eV]	$\frac{ \Delta E   \Delta Z }{\times 10^{-2}}$ [eV]
Se	302 <sup>[24]</sup>	2	–	0.49	2.0
As <sub>2</sub> S <sub>3</sub>	440 <sup>[12]</sup>	2.4	2.4 <sup>[6]</sup>	0.58	2.1
GeS <sub>2</sub>	750 <sup>[12]</sup>	2.67	3.3 <sup>[6]</sup>	0.96	2.8

Table 1