

Correlation between the nonlinear optical constants and the structural relaxation parameters in chalcogenide glasses

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Abstract

It is well known that chalcogenide glasses exhibit high values of nonlinear optical constants in addition to the widely studied photostructural changes. However, the relations between these properties are not sufficiently understood. On the other hand, according to the bond strength-coordination number fluctuation (BSCNF) model proposed by one of the authors, the viscous behavior is described in terms of the average bond strength, coordination number, and their fluctuations of the structural units that form the system. In the present study, the interrelation between the nonlinear optical constants and the structural relaxation parameters defined from the BSCNF model has been investigated for the case of chalcogenide systems. It is found that the third order nonlinear optical susceptibility increases with the fluctuations of the structural relaxation parameters. The correlation found is discussed based on the BSCNF model and the average electronegativity.

Keywords: Chalcogenide glasses; Nonlinear optical constants; Viscosity; Structural relaxation; Average electronegativity

1. Introduction

The concept of fragility introduced by Angell characterizes the temperature dependence of the viscosity of glass-forming liquids [1]. Many researchers have discussed about the correlation between fragility and other physical properties such as bulk modulus and shear modulus [2]. The existence of correlation between these

quantities is understandable, because both quantities are related to mechanical properties of the system. However, concerning the relation between viscous behavior and optical properties, the subject is not so obvious. As far as the authors are informed, no systematic study has been done till now. Clarifying this point is interesting, because, there are numerous studies reporting the light induced structural modification phenomena. In particular, in amorphous chalcogenide systems, phenomena such as photodarkening, photodoping, photoinduced phase transition, photoinduced fluidity, and high nonlinear optical constants, etc. have been reported [3-6]. Therefore, studying the physical background that is behind the optical properties and structural relaxations will be of considerable interest from both, fundamental science and materials development point of views. In the present contribution, a study on the correlation between the nonlinear optical constants and the structural relaxation parameters is reported.

2. The BSCNF model

Numerous models that describe the temperature dependence of the viscosity of the melt have been proposed till now. Among these, the VFT and the free volume theory are well known. In our study, the Bond Strength-Coordination Number Fluctuation (BSCNF) model, proposed by one of the authors will be used [7]. This model has been used successfully to study the viscous behavior of many kinds of materials. According to the BSCNF model, the viscous flow occurs when the structural units that form the melt move from one position to another by breaking or twisting the bonds connecting them. In the BSCNF model, the bond strength E between the structural units is described as $E=E_0+\Delta E$, where E_0 is the average bond strength and ΔE is its fluctuation. The coordination number Z of the structural units is denoted as $Z=Z_0+\Delta Z$, where Z_0 is the average coordination number and ΔZ is its fluctuation. By using these quantities, the following expression for the temperature dependence of the viscosity has been derived [7].

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

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

where T_g is the glass transition temperature and R is the gas constant. $\eta_0 = 10^{-5}$ Pa·s

and $\eta_{T_g} = 10^{12}$ Pa·s are the viscosities at the high temperature limit and at the glass transition temperature, respectively. The quantities B and C defined in Eq. (1) have the following intuitive meanings. C gives the mean total binding energy per structural unit and B gives the degree of its fluctuations among the structural units against the thermal disturbance at T_g . In the present study, B and C are used as fitting parameters.

Previous studies have shown that strong systems such as SiO_2 are characterized by large value of C and small value of B . On the other hand, fragile systems such as polymeric systems are characterized by small value of C and large value of B [8]. This observation indicates that the BSCNF model catches the essence of the viscous properties of the materials. In the present study a new parameter Y defined as

$$Y = \frac{\sqrt{B}}{C} = \frac{\Delta E \Delta Z}{E_0 Z_0}, \quad (2)$$

is introduced to analyze the viscosity behavior of chalcogenide systems. The temperature dependence of the viscosity for different values of Y is illustrated in Fig. 1. We recognize that the fragility increases with the increase of Y .

3. Correlation between the nonlinear optical constants and the structural relaxation parameters

Chalcogenide glasses exhibit many photoinduced phenomena. Among these, there are properties such as photoinduced structural changes, photoinduced mass transport, photoinduced fluidity, etc., that are related with the viscous behavior discussed in the previous section. Concerning the photoinduced mass transport such as photodoping, its relation with the superionic behavior has been suggested [9]. On the other hand, according to the bond fluctuation model of superionic conductors [10], good ionic conductors should have high electronic polarizability. This conjecture has been verified in recent studies [11]. These observations prompt us to investigate the interrelation between viscous behavior and optical properties, in particular, the interrelation with the nonlinear optical constants.

Fig.2 shows the relation between the structural relaxation parameter Y defined by Eq. (2) and the third order optical susceptibility $\chi^{(3)}$ in some chalcogenide glasses. The values of Y have been determined by fitting Eq. (1) to reported experimental data of viscosities [12-14]. The values of $\chi^{(3)}$ for $(\text{Sb}_2\text{S}_3)_x-(\text{GeS}_2)_{1-x}$ glasses are taken from [15]. For the other glasses, the values of $\chi^{(3)}$ have been estimated by applying the Wemple formula [16] and the Miller rule [17] to the data reported in [18,19]. The

evaluation method of $\chi^{(3)}$ applied here have been used quite frequently in the literature and the evaluated values exhibit good agreement with the measured values [18]. We have adopted this method of evaluation, because the reported experimental values of $\chi^{(3)}$ depend on the frequency range used in the measurement. From Fig. 2, we note that the nonlinear optical constant increases with the increase of Y . The figure indicates clearly that the thermo-mechanical and optical properties of chalcogenide systems considered here are interrelated. Although the correlation studied has been guided by the bond fluctuation model and the BSCNF model, the result shown in Fig. 2 is surprising, because it connects two quantities pertaining to different time and space extent regimes. Concerning the time regime, $\chi^{(3)}$ and Y are dominated by fast and slow processes, respectively. Concerning space extent, in these materials the optical susceptibility arises mainly from bond susceptibilities. That is, it is a short-range structure related quantity. On the other hand, the structural relaxation parameters are medium-range structure related quantities. Elucidating the physics that is behind this correlation is a challenging problem. The authors believe that this correlation has much in common with the observation that the vibrational properties of glasses well below the glass transition temperature are correlated with the fragility value [20].

The number of data points in Fig. 2 is limited. This is due to the fact that there are only few compounds where data of the both quantities, the optical susceptibility and temperature dependence of the viscosity are available. To increase the impact of the results shown in Fig. 2, the accumulation of data is desirable. It is hoped that result shown in Fig. 2 will motivate further studies.

4. Discussion

In a previous study, we have shown that the ionic conductivity in some oxide glasses such as $M_2O-B_2O_3$ ($M=Ag, Rb, Cs$) correlates with the third order optical susceptibility [21]. The origin of such a correlation can be understood from the point of view of bond fluctuation model of superionic conductors [10]. Briefly, according to this model, the ionic motion is accompanied by local or short ranged change of the chemical bond. This local fluctuation of the bonding triggers the movement of other ions that surround the bond fluctuating site, which results in the correlated motions of ions and high ionic conductivity. Note that, fluctuations of the chemical bond imply that the susceptibilities of the bonds connecting the atoms are large, which result in the high nonlinear optical constant. That is, the ionic conductivity and the

optical susceptibility are not independent of each other, though these two quantities are properties of the materials observed at quite different frequency regimes.

The above observation provides a hint to understand the result shown in Fig. 2. The quantity Y gives the degree of the fluctuation between the structural units that form the system. If the interconnection between the structural units is rigid and strong, the degree of the fluctuation Y is small. Strong interconnections are maintained by rigid interatomic bonds. That is, in this case the bond susceptibility is low. In other words, since $\chi^{(3)}$ reflects the magnitude of bond susceptibility, materials having strong degree of interconnection (small Y) have low value of $\chi^{(3)}$ as observed in Fig. 2.

In order to confirm the above discussion, an analysis based on the average electronegativity is given. If the chemical formula of a glass is written as $A_xB_yC_z \dots$, where A, B, C, ...are the elements and x, y, z, \dots are their stoichiometric participation, the average electronegativity is given by [10]

$$\chi_m = \left(\chi_A^x \cdot \chi_B^y \cdot \chi_C^z \cdot \dots \right)^{1/(x+y+z+\dots)}. \quad (3)$$

This expression of the average electronegativity has a generalized form of the principle of electronegativity equalization proposed by Sanderson [22]. Although simple, the above definition of the average electronegativity has been used successfully to systematize the composition dependence of many properties. Recently, it has been applied to study the chemical trends of the medium range structure [23] and the third-order susceptibility of superionic glasses [11].

Fig. 3 shows the relation between the average electronegativity χ_m and the total bond strength C . We note that for each system, C increases with the increase of χ_m . This observation is in accord with our expectation. χ_m gives the average electron attracting power of each element within the compound. That is, χ_m scales with the magnitude of relative bond strength of the system. From the figure, we can recognize how the values of χ_m and C vary with the chemical composition. For instance, for the case of $(\text{Sb}_2\text{S}_3)_x-(\text{GeS}_2)_{1-x}$, by increasing the concentration of (Sb_2S_3) , χ_m and C decrease. This observation is useful from the point of view of prediction of materials' properties. For instance, for the above system, if we need a glass with $C = 25$, its chemical composition should be $(\text{Sb}_2\text{S}_3)_{0.17}-(\text{GeS}_2)_{0.83}$. From the chemical trend of Fig. 3, it is also predicted that the value of C for Sb_2S_3 should be small than $C = 8.4$.

Fig.4 shows the relation between the average electronegativity χ_m and the fluctuation of the structural units B . For this case, we observe that B decreases with

the increase of χ_m . The origin of this behaviour is obvious, because weak interatomic bond strength (small χ_m) results in large fluctuations of the structural units (large B). Analogous to the case of C , one can predict the value of B from chemical composition through the evaluation of χ_m defined in Eq. (3). An important point that should be noted here is that B increases with the decrease of C and vice versa. This behaviour is reflected in the strong-fragile classification of glass forming materials as discussed previously [8].

Fig.5 shows the relation between χ_m and Y . It indicates the general trend, Y decreases with the increase of χ_m . The behaviour is easily understandable, because C and B increases and decreases with the increase of χ_m , respectively. That is, the increase and decrease of the total bond strength C and its fluctuation B , respectively, results in the decrease of the fluctuation Y . In other words, this behaviour indicates that strong systems have small values of Y . For the sake of comparison, the values of Y and χ_m evaluated for SiO_2 is shown in the figure. We note that it is in accord with our expectation.

The results shown in Figs. 3 to 5 and their discussion confirm that the strength of the structural unit connectivity C , and its fluctuations B , are closely related with the interatomic bond strength. These reinforce the interpretation given for Fig. 2 concerning the relation between structural relaxation parameters and the nonlinear optical constants.

5. Conclusion

The correlation between the third order optical susceptibility and the relaxation parameter determined from viscosity in some chalcogenide glasses has been presented. The result indicates that the susceptibility increases with the fluctuation of the structural units. The result is interesting, because, in these materials the optical susceptibility is expected to arise mainly from bond susceptibilities. That is, it is a short-range structure and high frequency related quantity. On the other hand, the structural relaxation parameters are medium-range structure and low frequency related quantities. The origin of the correlation has been discussed based on the BSCNF model of viscosity and the average electronegativity.

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Figure Captions

Fig. 1. Temperature dependence of the viscosity described by the BSCNF model.

Fig. 2. Correlation between the third order susceptibility $\chi^{(3)}$ and the structural relaxation parameter Y . The representative magnitude of the error bar is indicated for the case of As_2S_3 .

Fig. 3. The relation between the average electronegativity χ_m and the structural relaxation parameter C . The representative magnitude of the error bar is indicated for the case of As_2Se_3 .

Fig. 4. The relation between the average electronegativity χ_m and the structural relaxation parameter B . The representative magnitude of the error bar is indicated for the case of As_2Se_3 .

Fig. 5. The relation between the average electronegativity χ_m and the structural relaxation parameter Y . The representative magnitude of the error bar is indicated for the case of SiO_2 .

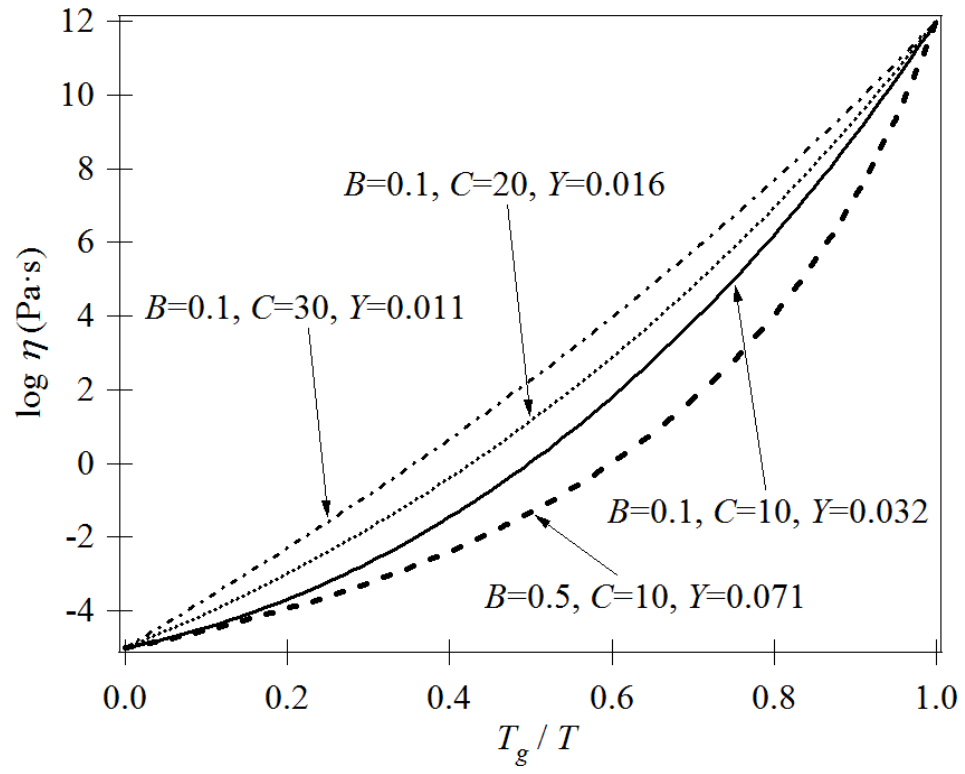


Fig.1

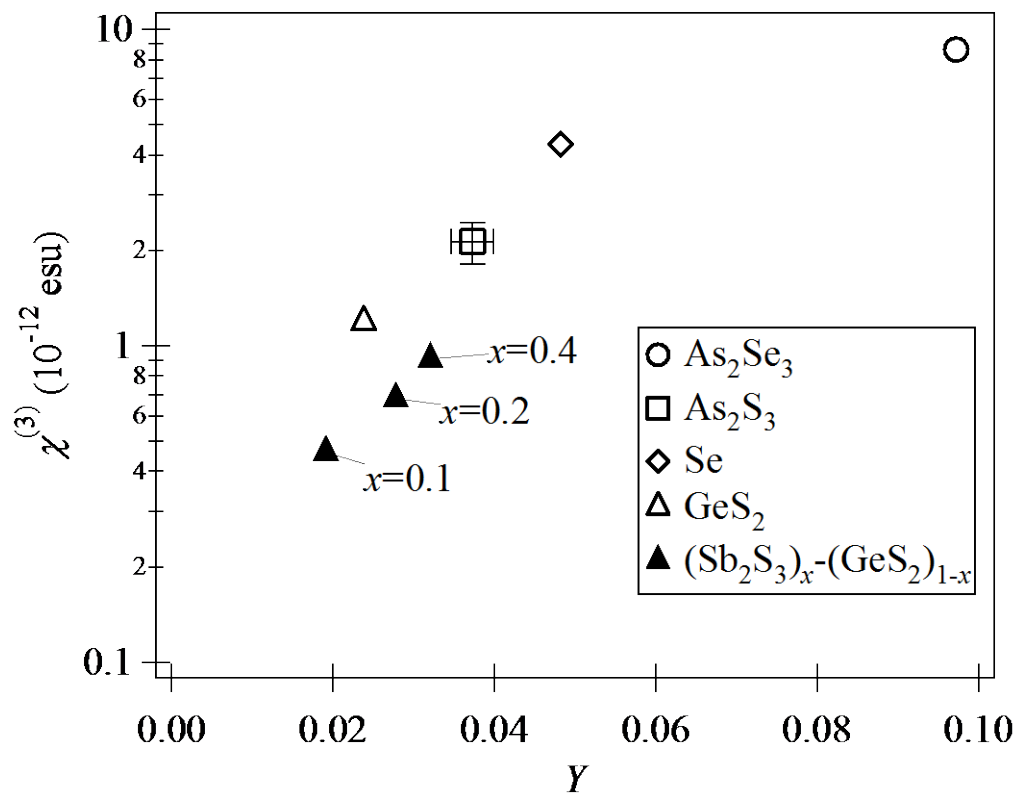


Fig.2

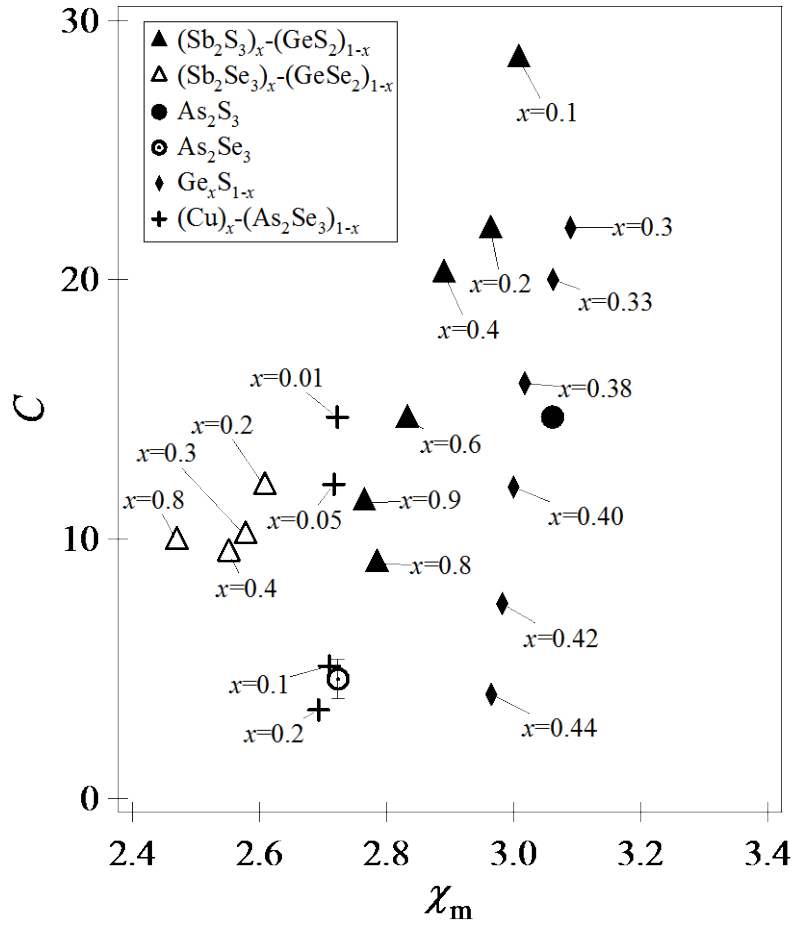


Fig.3

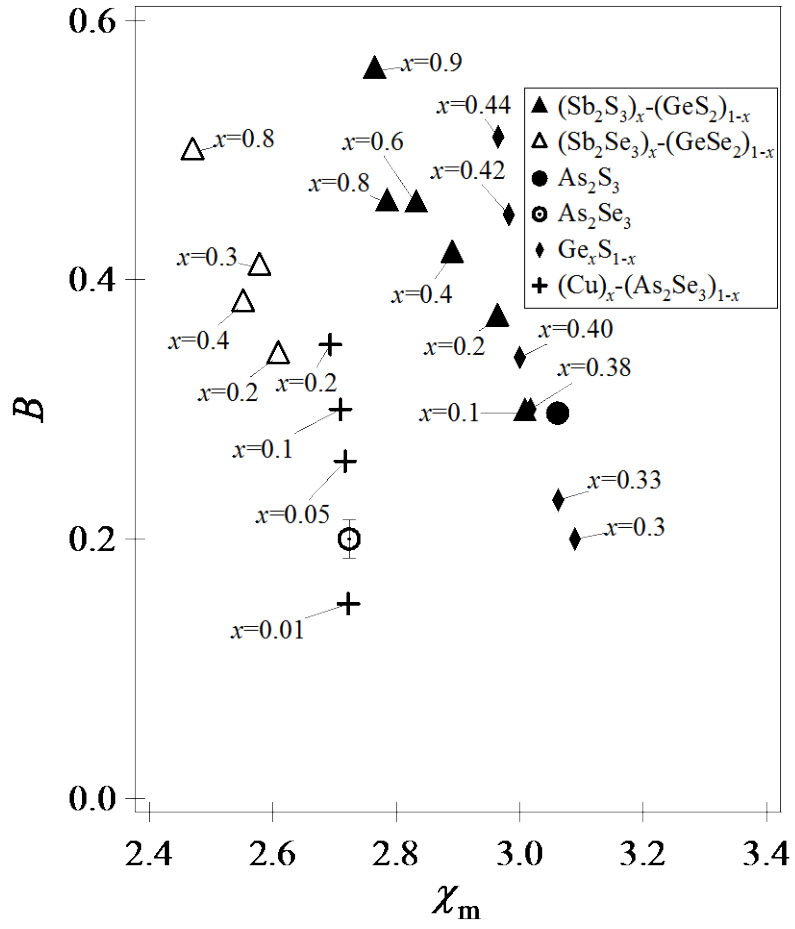


Fig.4

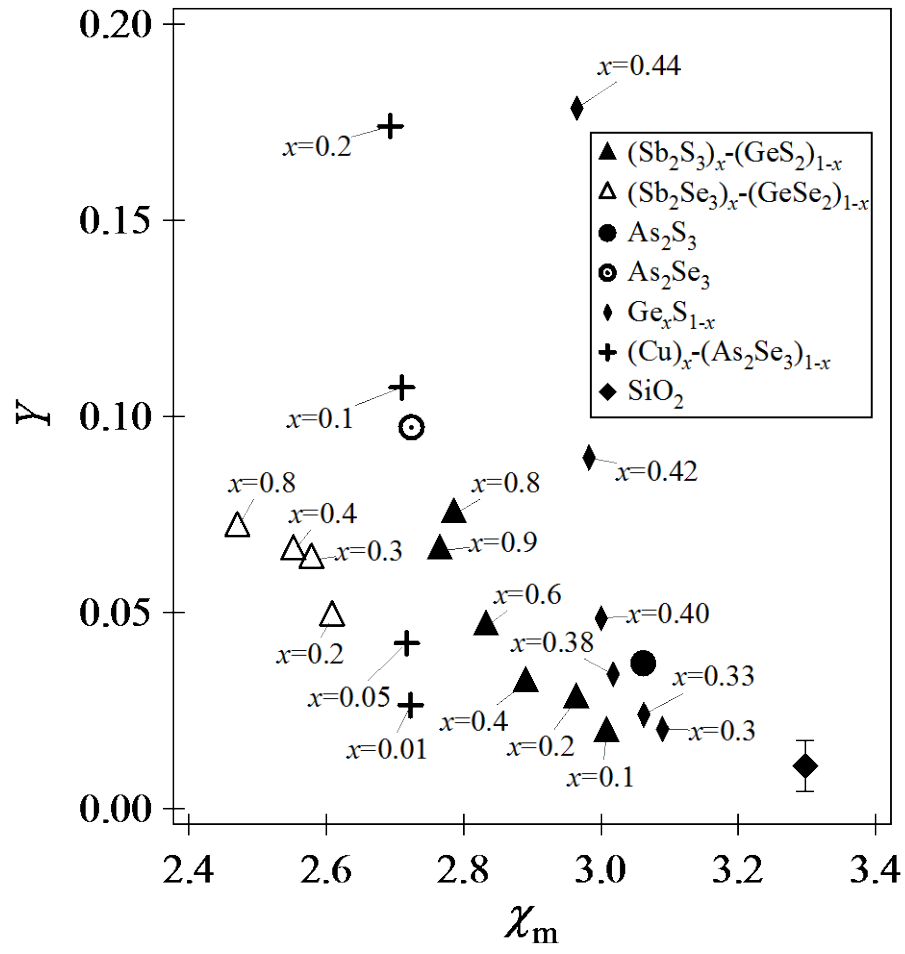


Fig.5