

WRONG BOND IN GLASSES: A COMPARATIVE STUDY ON OXIDES AND CHALCOGENIDES

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Optical absorption and electrical conduction of typical group VI glasses, such as SiO_2 and As_2S_3 , have been studied in comparison with those in the corresponding crystals. Among these materials, only the chalcogenide glass exhibits weak absorption tail and hole conduction. Origins of these features can be ascribed to wrong bonds, which are inherent to covalent compound glasses. Mobility gap and Urbach edge are also considered.

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1. Introduction

The electronic structure of disordered materials has been the one of long-standing problems in solid-state science [1-3]. At present, on the basis of Ioffe-Regel rule, we can predict gross electronic structures, which are governed by short-range atomic structures. The existence of bandgap is believed to be confirmed. However, a theoretical foundation for glasses as the Bloch theory for crystals has not yet been obtained. In addition, it remains to be studied if several concepts such as the mobility gap and the negative U defects, although being frequently employed, can be applied to real materials. To get some more insights, comparative studies may be valuable.

Among the materials shown in Fig. 1, oxide and chalcogenide glasses, typical examples being SiO_2 and As_2S_3 , have many similarities [1,4,5]. For instance, the atomic coordination numbers of the group VI atoms, O and S, are two. And, as is demonstrated by Phillips, both of these glasses are stable with the average coordination number of 2.4 [6,7]. Photoinduced phenomena are observed, which have been extensively studied.

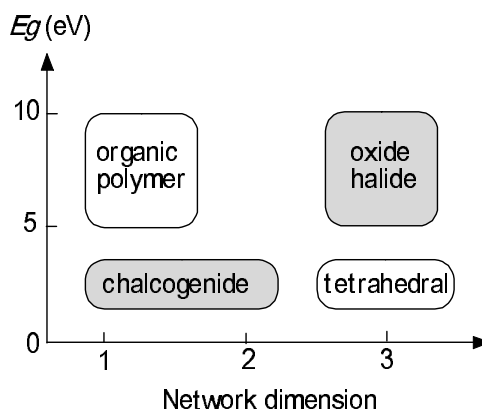


Fig. 1. Classification of amorphous insulators and semiconductors by the network dimension of medium-range atomic structures [2] and the bandgap energy E_g .

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Also, substantial differences can be marked for these glasses. For instance, SiO_2 has an energy gap of ~ 10 eV [1,8-10], and electrically insulating. For excited carriers, electrons are more mobile than holes [1,11,12]. The glass is optically transparent to an ultimate level [13]. On the other hand, As_2S_3 has a gap of 2.4 eV, which is a typical value of semiconductors [1-5]. In addition, the chalcogenide glass exhibits the *so-called* p-type conduction [1], and its optical transparency is limited by residual absorption [1].

In the present work, to get some unified insight into the nature of group VI glasses, we will study comparatively some fundamental properties of glassy and crystalline materials. Specifically, SiO_2 and As_2S_3 are focused with two reasons. One is that the compositions are stoichiometric, and the corresponding stable crystals are one kind, hexagonal SiO_2 (α -quartz) and layer-type As_2S_3 (orpiment). Such simple situations are appropriate for comparative studies of the glass and the crystal. In addition, thanks to recent optical-fiber technology, high-purity samples are available for these glasses, which are needed to obtain reproducible results governed by states in the bandgap [14]. Unresolved problems will also be pointed out.

2. Features and discussion

2.1. Structural

Fig. 2 compares the bond ionicity of oxides and chalcogenides of interests. The data are obtained from the Pauling's book, in which the bonds with Si and Ge have the same values. We see that there is a big ionicity difference between the oxides and the chalcogenides. Reminding the bond ionicity of Na-Cl to be 2.1 eV, we can regard that SiO_2 is an ionic material, while As_2S_3 is covalent. It is known that these contrastive ionicities govern short-range glassy structures [5]. These contrastive ionicities also cast a decisive effect upon defects as described below.

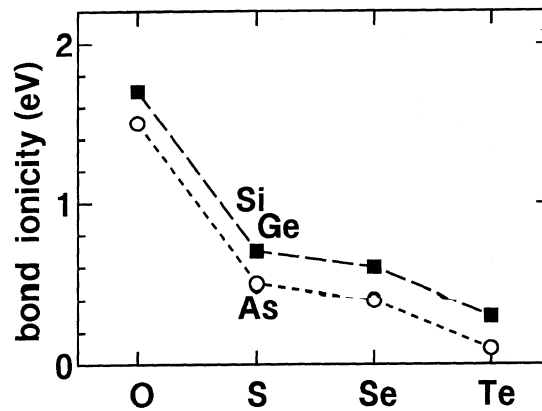
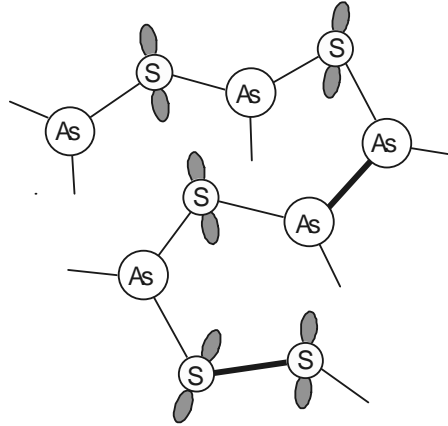


Fig. 2. Bond ionicities of Si(Ge)-O(S,Se,Te) (dashed line) and As-O(S,Se,Te) (dotted line).

As_2S_3 glass is known to contain a considerable amount of "wrong bonds", As-As and S-S (Fig. 3) [15]. Actually, structural studies such as Raman scattering, demonstrate the existence of wrong bonds with density of 0.1 - 10 at.%, which depends upon preparation procedures of the samples [16-20]. This density of wrong bonds is much greater than that proposed for the charged dangling bonds, $\sim 10^{17} \text{ cm}^{-3}$ [1]. In other words, among several candidates for defects in chalcogenide glasses [4,21], this is the defect with the highest density, which plays important roles in optical and electrical properties, as described in 2.2 and 2.3.

The wrong bond arises because of the two features. One is the low ionicity of As-S bonds. That is, the energy difference ΔE of the heteropolar bond (As-S) and the homopolar bonds (As-As and S-S) is estimated only at 0.3 - 0.4 eV [22]. The other is the quasi-equilibrium state of glasses. That is, the glass is prepared through quenching from some temperature T_q above the glass-transition temperature T_g . Accordingly, the wrong bond is included with a fraction of $\exp(-\Delta E/kT)$, where $T = T_g \sim T_q$, depending upon the quenching rate [17].

Fig. 3. Atomic structure of As_2S_3 glass.

In other materials of interest, the wrong bonds can hardly exist, because one or the both of these conditions are not satisfied. In SiO_2 glass, the wrong bonds are very rare (some orders of ppm) [23,24], reflecting the highly ionic and stable Si-O bond ($\Delta E \approx 2.6$ eV [22]). In crystals, the density could be neglected, since the crystal should have a structure with the lowest internal energy, i.e. $T = 300$ K, or in an ideal sense, $T = 0$ K.

Table. 1. Tauc optical gap E_g [1,34], Urbach energy E_U [30], steepness parameters [30] of the valence-band edge E_0^V and the conduction-band edge E_0^C , and electron and hole mobilities μ_e and μ_h at room temperature, and theoretical effective masses m_e^*/m_0 and m_h^*/m_0 (m_0 is the free electron mass). Optical gaps of crystals are evaluated as photon energies at the absorption coefficient of $\sim 10^4$ cm^{-1} . X means that no signals are obtained. Indicated references are as follows: (a) J. Stuke, Selenium, Eds. R.A. Zingaro and W.C. Cooper, Van Nostrand Reinhold, New York, 1974, p.174. (b) L.B. Shein, Phys. Rev. B, **15**, 1024 (1977). (c) S.W. Ing, Jr., J.H. Neyhart, and F. Schmidlin, J. Appl. Phys., **42**, 696 (1971); M. Burman, J. Hirsch, and T. Ramdeen, J. Phys. C: Solid State Phys., **14**, 117 (1981). (d) D.F. Blossey and R. Zallen, Phys. Rev. B, **9**, 4306 (1974). (e) A.E. Owen and J.M. Robertson, J. Non-Cryst. Solids, **2**, 40 (1970). (f) R.S. Sussmann, T.M. Searle, and I.G. Austin, Philos. Mag. B, **44**, 665 (1981). (g) J.M. Marshall, J. Phys. C: Solid State Phys., **10**, 1283 (1977); G. Brunst and G. Weiser, Philos. Mag. B, **51**, 67 (1985). (h) E. Tarnow, A. Antonelli, and J.D. Joannopoulos, Phys. Rev. B, **34**, 4059 (1986). (i) B.A. Khan, D. Adler, and S.D. Senturia, J. Appl. Phys., **60**, 2875 (1986). (j) G. I. Kim and J. Shirafuji, Jpn. J. Appl. Phys., **17**, 1789 (1978); L. Tóth, Phys. Stat. Sol. (a), **54**, K159 (1979). (k) Refs. 11 and 12. (l) Ref. 48. (m) A. N. Trukhin and P. Kūlis, J. Non-Cryst. Solids, **188**, 125 (1995). (n) Ref. 1.

Material	E_g [eV]	E_U [meV]	E_0^V [meV]	E_0^C [meV]	μ_e [cm^2/Vs]	μ_h [cm^2/Vs]	m_e^*/m_0	m_h^*/m_0
g-Se	2.0	58	26		5×10^{-3}	0.10~0.16 (a)		
c-Se(hex)	1.9				X	6~28 (a)		
c-Se(ring)	2.2				2	0.2 (b)		
g- As_2S_3	2.4	54	55		X	10^{-4} (c)		
c- As_2S_3	~2.8				1	0.1~1 (b,d)		
g- As_2Se_3	1.8	50	46		X	10^{-4} (e)		
c- As_2Se_3	~2.1(f)				1~10	X (g)	0.3	0.3 (h)
g- As_2Te_3	0.8	53	33			10^{-3} (i)		
g- GeS_2	3.2	130	100					
g- GeSe_2	2.2	73		63	0.2	0.04 (j)		
g- SiO_2	~10	~60			20~40	$< 10^{-5}$ (k)		
c- SiO_2	~10						0.3	5~10 (l)
g- GeO_2	5.8	~60 (m)						
a-Si:H	~1.8	48	42	27	0.2	0.01 (n)		

2.2. Optical

Fig. 4 compares optical absorption (or attenuation) spectra of glassy and crystalline As_2S_3 [25,26] and glassy SiO_2 [10, 27-29], Photoconduction spectra of the two glasses are also included [30-32]]. Table 1 lists some related quantities. In the following, these characteristics are considered from high to low absorption regions.

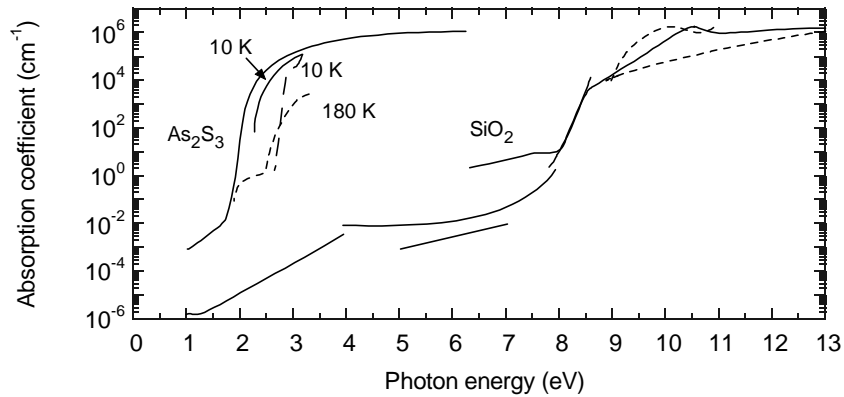


Fig. 4. Optical absorption (solid lines) and photoconductive (dotted line) spectra in As_2S_3 and SiO_2 glasses, and an optical absorption in As_2S_3 crystal (dashed line). Unless specified, the temperature is 300 K.

First, some ideas on the mobility edge can be obtained from these results. We see for As_2S_3 that the photoconduction edge of ~ 2.7 eV in the glass (at ~ 180 K) nearly coincides with the optical absorption edge of the crystal (at 10 K) [33]. It is assumed that photoconduction spectra can reflect the position of the mobility gap [1]. Accordingly, this coincidence suggests that the mobility gap in As_2S_3 glass has the same energy with the bandgap in the corresponding crystal. As reported previously [30,34], such relations can also be pointed out for other chalcogenide glasses. Therefore, it is tempting to assume that, as illustrated in Fig. 5, the mobility edges (E_{μ}^C and E_{μ}^V) of conduction and valence bands in amorphous materials, or at least in some chalcogenide glasses, are located at the band edges in the corresponding crystals. It is also mentioned in Fig. 5 that a marked energy difference exists between the positions of the photoconduction and absorption spectra in As_2S_3 glass, which can be regarded as a non-photoconducting gap [30].

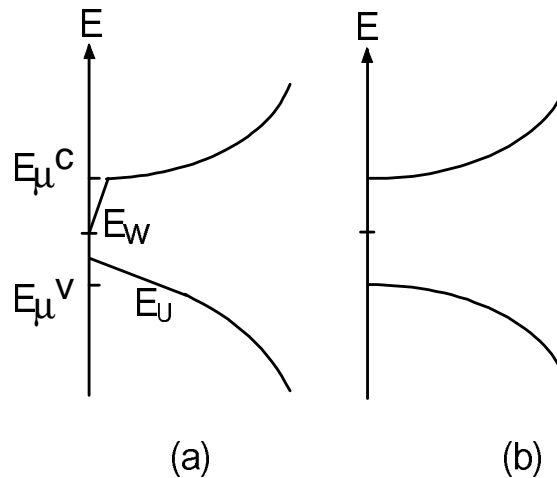


Fig. 5. Schematic density-of-states of (a) glassy and (b) crystalline As_2S_3 . The mobility edges (E_{μ}^C and E_{μ}^V) in the glass, indicated by the dotted lines, are located at the same positions with the band edges in the crystal.

Situations for SiO₂ seem to be controversial. The Tauc optical gap in the glass seems to be located at 8.5 eV [10] and that in the crystal at ~ 10 eV [35,36]. However, the photoconductive edge in the glassy films varies at 8.9 - 11.5 eV among some publications [31,32], in which electrode effects have been pointed out [37]. At the present stage, therefore, further discussion may not be fruitful. It is desired that optical and photoconductive spectra are taken for single samples.

For the Urbach edge, two features can be pointed out. One is that, for many glasses listed in Table 1, despite marked differences in E_g (2 - 10 eV), the Urbach energy E_U is similar, 50 - 60 meV [38], where E_U approximates the Urbach-edge absorption as $\alpha(\hbar\omega) \propto \exp(\hbar\omega/E_U)$. Surprisingly, amorphous-Si:H, in which chemical natures of the conduction and valence bands are totally different from those in the group-VI glasses, also shows the same E_U value [3]. This anomalous characteristic remains to be studied. The other is that, in typical chalcogenide glasses such as As₂S(Se)₃, $E_U \approx E_0^V$, where E_0^V is a characteristic energy representing the density-of-state of the valence-band edge as proportional to $\exp(-E/E_0^V)$. It is known that E_U is approximately given as a convolution integral of the densities-of-states of the valence- and conduction-band edges [1]. Accordingly, provided that the conduction-band edge being written as $\exp(E/E_0^C)$, $E_U \approx E_0^V$ suggests that the valence-band edge governs the Urbach edge [39,40]. As illustrated in Fig. 5, the conduction-band edge is assumed to be much steeper, i.e. $E_0^C \ll E_0^V$. It is reasonable to assume that this broad valence-band edge manifests spatially fluctuated inter- and intra-layer interaction among lone-pair electrons of chalcogens (see, Fig. 3) [40]. For SiO₂, no data on E_0^V and E_0^C seem to be available at present.

Optical absorption characteristics below the Urbach edges in As₂S₃ and SiO₂ glasses are contrastive. In As₂S₃, a weak absorption tail with a form of $\alpha \propto \exp(\hbar\omega/E_w)$, where $E_w \approx 250$ meV, is known to exist [1]. Previously, the weak absorption tail in As₂S₃ glasses has been attributed to impurities, typically Fe [41,42]. However, even in highly-purified samples which are synthesized for preparing optical fibers, the absorption tail still exists [26]. In optical fibers of other chalcogenide glasses, the absorption tail also seems to exist [43], and accordingly, we can assume that this residual absorption is intrinsic to the chalcogenide glass. On the other hand, in SiO₂, it is nearly of a detection limit ($\sim 10^{-6}$ cm⁻¹) at $\hbar\omega \approx 1$ eV [13]. At 5 - 8 eV, defect-related absorption appears [10,28,29], which is not considered here. Similar transparency may be pointed out in other simple oxide glasses [41,44] (and also in halide glasses [45]). Needless to say, for ideal crystals, the Bloch theory predicts the zero absorption in the photon-energy region corresponding to the bandgap (Fig. 5b).

It is therefore tempting to ascribe the weak absorption tail to a property inherent to chalcogenide glasses. The wrong bond is the most plausible candidate [40]. Actually, the antibonding states of As-As are assumed to exist below the conduction band and/or around the bottom of conduction band (see, Fig. 5a). The energy is probably distributed due to disordered circumstances and/or polaron-like structural deformations. In the present model, this energy distribution corresponds to the absorption spectrum extending to $\hbar\omega \geq 1$ eV. On the other hand, the absorption level, $\alpha \leq 10^{-1}$ cm⁻¹, of the tail may be consistent with the high wrong-bond density and a relatively small transition probability from lone-pair electron states of chalcogen atoms to the antibonding states. Precise calculations of the absorption spectrum remain.

2.3. Electrical

At the outset, a comment on terminology may be needed. It is sometimes referred to as "the chalcogenide glass is a *p-type* semiconductor", which is based on positive thermopower [1,46]. However, this is a confusing statement. The *p-type* semiconductor generally denotes the one in which $p > n$, where p and n are the densities of holes and electrons. On the other hand, the thermopower S is defined as $S = (\sigma_n S_n + \sigma_p S_p) / (\sigma_n + \sigma_p)$, where σ is the conductivity. Accordingly, if $\mu_p \gg \mu_n$ (μ : mobility), S becomes positive, provided that p and n are not much different. Actually, time-of-flight experiments demonstrate $\mu_p \tau_p \gg \mu_n \tau_n$ (τ : lifetime), which suggests $\mu_p \gg \mu_n$. In addition, as far as being known, there may be no direct evidence which shows that the Fermi level is located near to the valence band. On the contrary, a photoemission study demonstrates unambiguously that the Fermi level is located at the mid gap [47], which leads $n \approx p$. Therefore, the sentences such as "the chalcogenide glass exhibits hole conduction" or "holes are more mobile" are realistic.

As listed in Table 1, in the crystals of As₂S(Se)₃ and SiO₂, the electron appears to be more mobile. That is, $\mu_e \geq \mu_h$ has been demonstrated for the chalcogenide crystals. On the other hand, for SiO₂, a theoretical calculation predicts $m_e \leq m_h$, in which the smaller electron mass of $\sim 0.3 m_0$ at the Γ point [48] has been related with the s-orbital of Si atoms [1].

However, in the glass, the features in the oxide and the chalcogenide are contrastive. As in the crystal, electrons are mobile in SiO_2 [11,12], and also in other oxide glasses [49,50]. (Similarly, electrons are more mobile both in c-Si and a-Si:H [1].) However, holes are mobile in most of the chalcogenide glass [1], although dispersive transport frequently appears [51]

For the hole conduction in chalcogenide glasses, at least, two ideas have been proposed [52-54]. One ascribes it to disordered glassy structures [53]. That is, the structural disorder affects more strongly the antibonding states forming the conduction band than on the lone-pair electron states, and accordingly, holes can move smoothly. However, this idea may lead to the band-edge relation of $E_0^C > E_0^V$, which is incompatible with the optical result. The other idea ascribes the hole conduction to asymmetric characteristics of D^+ and D^- [52,54]. For instance, Kolobov argues that a D^0 , which is transformed from a D^- after an electron being excited, acts as an efficient recombination center for an electron [54]. Hence, holes appear to be more mobile. However, if the defects were responsible, photocurrents could be excited by subgap illumination, which is inconsistent with the photoconduction spectrum in Fig. 4 [30].

Since the hole conduction and the wrong bond appear to be inherent to chalcogenide glasses, it is tempting to connect these features. That is, since the antibonding states of As-As appear to be located below the conduction band [40], it is reasonable to assume that the wrong bonds act as deep (~ 1 eV) traps for electrons. On the other hand, holes may be trapped by shallow (~ 0.1 eV) states, which produce the Urbach edge. Accordingly, only in the chalcogenide glass, the hole conduction becomes to be prominent. Note that this model is consistent with the fact that photocurrents are excited by (super-) bandgap illumination [30,55]. This model is also consistent with the composition dependence of electron and hole mobilities in As-Se glasses [56,57]. That is, it has been demonstrated that when As is added to Se, the electron mobility dramatically decreases, despite the hole mobility being mostly intact. As-As traps may be responsible for the decrease.

2.4. Note on Se

Elemental group VI glasses, in which only Se is fairly stable at room temperature, should be excepted from the present argument. Here, all the bonds are homopolar, and accordingly wrong bonds cannot exist. In these materials, it is also known that some physical properties are exceptional. For instance, both in hexagonal Se and in a-Se, $\mu_h > \mu_e$ (see, Table 1). Holes in lone-pair electron states forming π -type orbitals may move more easily than electrons in σ^* orbitals, due to spatial overlap of the π -type wavefunctions, irrespective of order or disorder structures. In addition, there are some demonstrations that ppm-order impurities such as O drastically decrease the electrical conductivity [58-60]. Probably related with such impurity effects is if the weak absorption tail exists in a-Se not clear [26, 61]. Investigations of optical transparency using high-purity samples are desired.

3. Summaries

Through comparing some observations, we have suggested that the wrong bond causes the weak absorption tail and the hole conduction in chalcogenide glasses such as As_2S_3 . The wrong bond can exist in *covalent glasses*, which means that the energy difference between the heteropolar and the homopolar bonds is small, and that the system is in a *quasi-equilibrium* state. With these two reasons, the wrong bond becomes much more than the charged dangling bonds, and it plays decisive roles in optical and electrical properties.

In addition, we have pointed out two important characteristics. One is that the photoconductive edge in chalcogenide glasses is located at nearly the same position with the bandgap of the corresponding crystals. This coincidence implies that the mobility gap in amorphous semiconductors corresponds to the bandgap in the crystals. The other is a puzzling feature on the Urbach energy of ~ 50 meV, which is widely observed in different kinds of amorphous materials including As_2S_3 , SiO_2 , and even in hydrogenated Si.

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