

Photoluminescence in chalcogenide glasses: revisited

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Briefly reviewing photoluminescence spectra in chalcogenide glasses such as As_2S_3 , we propose a new idea for the emission spectrum peaking at around half the bandgap energy. The spectrum is connected with a Fermi level, located near mid-gaps, and a weak absorption tail, which is produced by anti-bonding states of wrong and strained bonds. In covalent chalcogenide glasses, the wrong (homopolar) bond forms more dominant gap states than those by dangling bonds.

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1. Introduction

The photoluminescence (PL) in chalcogenide glasses has been studied over a half century after pioneering work by Kolomiets et al. in 60s [1]. Cernogora et al. [2] discovered the so-called PL fatigue, i.e., luminescence weakening under prolonged excitation at low temperatures, which was later related to photoinduced mid-gap absorption and electron-spin resonance (ESR) signals [3]. These early PL studies, most of which had been performed using cw light sources and $\text{g-As}_2\text{S}(\text{Se})_3$ (g- for glassy) samples, were reviewed by Street [4]. Hereafter, for understanding some unique PL features, researchers adopted more elaborate experiments, employing pulsed lasers [5], polarized light [6], optically-detected magnetic resonance (ODMR) [6], and hydrostatic compression [7]. Relations between the three low-temperature photoinduced meta-stabilities [2, 3] have repeatedly been explored [9-12]. And, new insights into PL mechanisms have been attained using frequency-resolved spectroscopy [13, 14], Fourier-transform luminescence analyses [15], and multi-layer systems [16]. In addition, recent developments in photonics applications have highlighted the chalcogenide glass as a host for rare-earth ions [17 – 19]. Regarding this topic, Bishop et al. [20] have demonstrated the so-called broad-band excitation, i.e., excitation of rare-earth ions, not directly, but through exciting the host chalcogenide glass having a broad Urbach-edge spectrum. Despite these extensive PL studies, however, some fundamental characteristics still remain controversial [21 – 23], which should be elucidated for advancing sciences and applications of the chalcogenide glass.

Among such characteristics, the most puzzling may concern the emission spectrum of PLs. The luminescence, when excited by light with $\hbar\omega \approx E_g$ (E_g is an optical bandgap energy), undergoes a strong Stokes shift, and it appears as a broad Gaussian-shaped spectrum with a peak energy E_{PL} at $E_{\text{PL}} \approx E_g/2$ [1]. (We hereafter neglect weak

cw luminescence appearing around optical absorption edges, which has been assigned to contamination effects [24] or hot luminescence [25]). PLs in the corresponding crystals such as $\text{c-As}_2\text{Se}_3$ (c- for crystalline) and also in simple oxide glasses as $\text{Si}(\text{Ge})\text{O}_2$ seem to and may bear the same relation, as described later. Actually, we will see (in Fig. 5) that the half-gap relation applies to many materials, but why such a relation holds has not been understood (or misunderstood) for a long time.

We will consider the problem, proposing a new idea taking strained and wrong bonds [26, 27] (homopolar bonds in stoichiometric compounds) into account. In Section 2, we briefly review PL spectra in several materials, and also some models proposed so far for the half-gap PL. Section 3 devotes to the band-edge and tail states in chalcogenide glasses, since the understanding of the origins is indispensable for considering the PL spectrum. In Section 4, we present a new model for the half-gap luminescence, which can give unified explanations for many observations, including variations with temperature, pressure, excitation energy, preparation, fatigue, etc. Also given is a comment on applications to the host glass for rare-earth-ions. Section 5 briefly summarizes the present idea.

2. PL spectra

2.1. $\text{As}_2\text{S}(\text{Se})_3$

As exemplified in Fig. 1, $\text{As}_2\text{S}(\text{Se})_3$ glasses furnish good examples showing the half-gap PL, $E_{\text{PL}} \approx E_g/2$. The spectrum, when plotted in photon energy, has a broad Gaussian-shape, and its full width Δ at half maximum also scales with E_g as $\Delta \approx E_g/6$ [4, 28]. PL excitation (PLE) spectra, which are obtained by measuring PL intensity (spectrally-integrated or at $\hbar\omega \approx E_{\text{PL}}$) as a function of excitation photon-energy, also exhibit interesting features.

The shape appears fairly broad, with a peak at E_{exc} , which is located in the Urbach-edge region at absorption coefficient α of $\sim 10^2 \text{ cm}^{-1}$. We may then write the relation more accurately as $E_{\text{PL}} \approx E_{\text{exc}}/2$. Note that the PLE spectrum continues to a region of weak-absorption tail (WAT), which exists at $\alpha \leq 10^0 \text{ cm}^{-1}$ (See, Section 4.2).

Actually, 1.5 eV photons can excite the half-gap PL in As_2S_3 at 5 K ($E_g \approx 2.5 \text{ eV}$) [29]. Incidentally, PL studies for Te systems ($E_g \approx 1 \text{ eV}$) have been limited to some As(Ge)-Se-Te alloys [1, 4, 30], probably due to difficulties in luminescence measurements at $\hbar\omega \approx 0.5 \text{ eV}$.

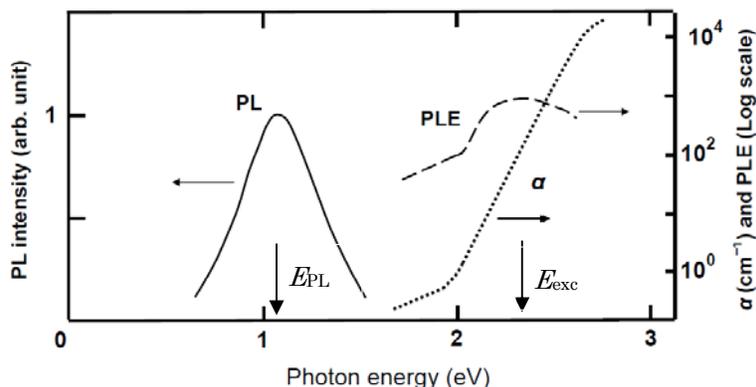


Fig. 1. PL, PLE, and absorption (α) spectra in As_2S_3 at $\sim 5 \text{ K}$ [4, 29]. PL and PLE spectra are shown, respectively, in linear (left) and logarithmic (right) scales, with the peak values being normalized to 1 and 10^3 .

2.2. $\text{GeS}(\text{Se})_2$ and $\text{Si}(\text{Ge})\text{O}_2$

PL behaviors in $\text{GeS}(\text{Se})_2$ appear to be more complicated and less reproducible than those in $\text{As}_2\text{S}(\text{Se})_3$. The reason can be sought to more stringent preparation conditions of g- $\text{GeS}(\text{Se})_2$ [31], probably arising from a large average atomic-coordination number of 2.67 and the existence of two crystalline polymorphs of

three-dimensional and layer types [19]. Actually, we see in Fig. 2, which compares reported PL spectra of GeS_2 [32–36], too big spectral discrepancies to ascribe to measuring conditions and/or experimental artifacts. As the consequence, the half-gap relation becomes vague. In GeSe_2 , spectral reproducibility becomes somewhat better, while it is still worse than those in the As-chalcogenides (see, Fig. 5).

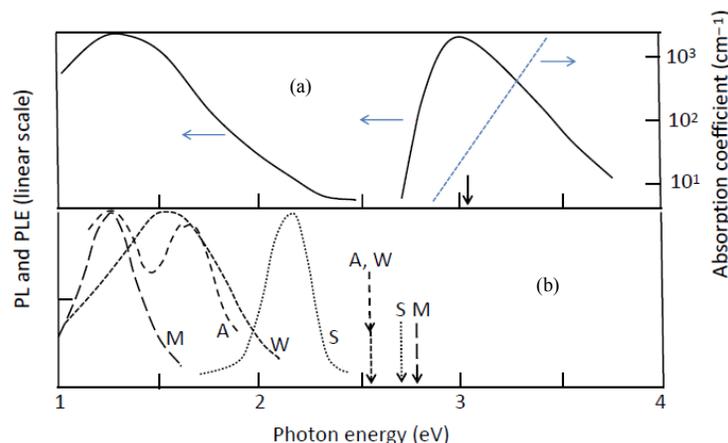


Fig. 2. PL characteristics in g- GeS_2 : (a) PL (left, under 3.1 eV excitation), PLE (left), and absorption (right, blue-shifted by 0.2 eV from a room-temperature spectrum) spectra at 80 K [36], and (b) PL spectra under single excitations at arrowed energies; A [32], M [33], and S [35] at 77 K, and W [34] at 20 K.

Here, it may be interesting to compare PL behaviors in $\text{GeS}(\text{Se})_2$ with those in simple oxide glasses. Gee and Kastner [37] have pointed out that SiO_2 with $E_g \approx 9 \text{ eV}$

also presents a half-gap PL at $\sim 4.3 \text{ eV}$, which may be emitted from Si wrong bonds [38, 39], $\equiv\text{Si}-\text{Si}\equiv$. PL in GeO_2 ($E_g \approx 6 \text{ eV}$) may follow the half-gap relation as well

[36]. However, it is known that the PL in SiO_2 appears to be sensitive to impurities such as -OH, and in addition the glass exhibits several peaks arising from a variety of Si- and O-related defects [37-39]. By contrast, the chalcogenide glass tends to exhibit only one, broad, and intrinsic peak. Accordingly, comparison of oxides and chalcogenides should be made carefully.

2.3. Elements

PL studies of pure chalcogen solids, S and Se, are limited, as summarized below. However, it should be underlined that, irrespective of crystals and glasses, PLs in these materials substantially deviate from the half-gap relation, to opposite directions; $E_{\text{PL}} > E_g/2$ in S and $E_{\text{PL}} < E_g/2$ in Se.

To the authors' knowledge, PL experiments of S have been reported only from two groups [40, 41], with the results concurring. Street et al. [40] demonstrated that c-S (orthorhombic), which consists of S_8 rings, emitted weak luminescence centered at ~ 2.5 eV (at 10 – 315 K) under a PLE spectrum peaking at 3.4 eV, which is within the fundamental absorption edge. Note that $E_{\text{PL}}/E_{\text{exc}} \approx 2.5/3.4 = 0.73 > 0.5$. On the other hand, as shown in Fig. 3, Oda et al. [41] reported that melt-quenched g-S, which is known to be composed of chain molecules, emitted at ~ 2.8 eV under pulsed 3.5-eV excitation at 300 K; i.e., $E_{\text{PL}}/E_{\text{exc}} \approx 2.8/3.5 = 0.8 > 0.5$. Oda's study, however, could not detect PLs in c-S, which they interpreted that the PL in S arises more efficiently from larger (> 8) rings, chains, and/or defects.

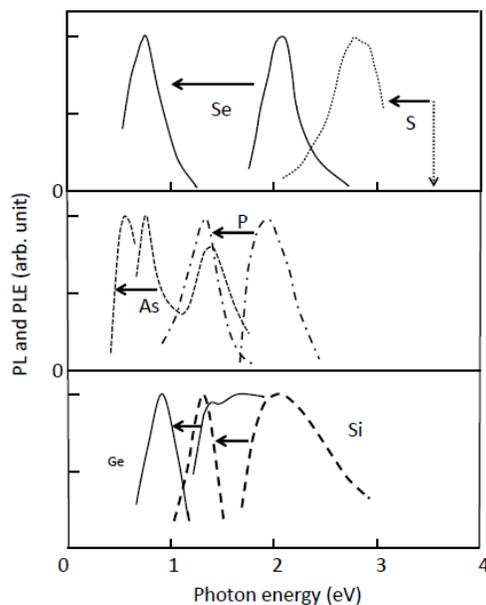


Fig. 3. PL (lower-energy sides) and PLE (higher-energy sides) spectra for (top) g-S at 300 K [41], g-Se at 10 K [4], (middle) a-P at 77 K [48], a-As at 6 K [47], (bottom) a-Ge:H at 13 K [53], and a-Si:H at 10 K [11].

For a-Se, Street et al. discovered strongly Stokes-shifted, but very weak PL [4]. Actually, it was stated to be weaker by 10 – 100 times than those in As- and Ge-chalcogenides, which may be related with hole diffusion (enhancing electron-hole separation) in a-Se, which is the highest in the chalcogenide glass [11, 19]. (In compositional studies [4, 8, 42, 43], very weak PLs have been demonstrated also in As(Ge)-Se glasses with Se concentrations higher than ~ 95 at.%) The peak appeared at ~ 0.8 eV under excitation of 2.1 eV at 10 K (Fig. 3). Clearly, $E_{\text{PL}}/E_{\text{exc}} \approx 0.8/2.1 = 0.38 < 0.5$, and this marked deviation has been reproduced in recent experiments [13, 15]. It should also be mentioned that, to the authors' knowledge, photoinduced mid-gap absorption has not been found in a-Se and the photoinduced ESR is weaker (spin densities of $\sim 10^{16} \text{ cm}^{-3}$) by one order of magnitude than those in $\text{As}_2\text{S}(\text{Se})_3$ and As [8]. In addition, it has often been reported that electronic properties and PL characteristics in a-Se are suffered from severe impurity effects of oxygen [4, 43].

Comparison of PLs in amorphous and crystalline (trigonal) forms of Se, both being composed (mostly) with chain molecules [11, 19, 44], may be valuable. Interestingly, the two PL spectra appear to be similar in shape, but nevertheless the PLE spectral shapes are very different. In the crystal, it is located at 1.8 – 1.9 eV in sharp and structured forms [45], in contrast to a single broad PLE in the amorphous [4]. Incidentally, isolated Se chains (in zeolite) exhibit distinctly different PL spectra and fatiguing behaviors [46].

It is known that elemental pnictides, a-As [8, 47] and a-red P [48-50], exhibit qualitatively the same PL behaviors, including prominently Stokes-shifted luminescence and strong fatigue, with those in the chalcogenide. Besides, the materials undergo photoinduced mid-gap absorption and ESR signals as well. These similarities manifest that the gross features of PLs and photoinduced phenomena are not unique to the chalcogenide. However, as shown in Fig. 3, PL in a-As ($E_g \approx 1.3$ eV) at 6 K is centered at ~ 0.6 eV (with a width of ~ 0.2 eV) under a PLE spectrum doubly peaking at 0.8 and 1.4 eV [47], i.e. $0.6/0.8 \approx 0.75$ and $0.6/1.4 \approx 0.43$, which makes the half-gap relation vague. Similarly, as illustrated in the figure, PL in a-red P also deviates from the relation; $E_{\text{PL}}/E_{\text{exc}} \approx 1.35/1.9 \approx 0.7$ [48].

We may also take a look on PLs in tetrahedral films. It is known that a-Si films are little luminescent [4], while hydrogenated films emit intense luminescence [51]. It is un-doubtful that non-hydrogenated tetrahedral films contain a number of neutral dangling bonds (D^0), which are likely to work as non-radiative recombination centers. (This assertion may contradict with an idea, described below, that D^0 in chalcogenide glasses works as a radiative center.) On the other hand, the hydrogenated films appear to follow the half-gap PL relation; e.g., in a-Si:H films $E_{\text{PL}}/E_{\text{exc}} \approx 1.3/2.1 = 0.62$ [11], and in a-Ge:H $E_{\text{PL}}/E_{\text{exc}} \approx 0.63/1.2 \approx 0.53$ [51] and $0.9/1.4 \approx 0.64$ [52].

3. Previous models

We may group proposed ideas for the half-gap PL spectrum into the two, which presume static and transitory gap-states [4, 11, 12, 19].

The CFO model [53] postulates static gap states, in disregard of electron-lattice coupling. The gap state tends to make a chalcogenide glass non-transparent. If some gap state exists at mid-gaps, those can be an origin emitting the half-gap luminescence. For instance, Derbidge and Taylor [28] suggest that PL in As-rich As-Se arises from As homopolar bonds. A key point of those models is, therefore, whether such intrinsic gap states really exist or not.

No static gap-state models seriously take electron-lattice interaction into account. The model assumes that a chalcogenide glass is inherently optically transparent, while the interaction produces transitory gap states [4]. One such an idea, originally proposed by Street and Mott [54], assumes that the PL arises from electron-hole recombination at neutral dangling bonds called D^0 , which can be produced from charged defects, D^+ and/or D^- , under photo-excitation. (We may regard the valence-alternation pairs model proposed by Kastner et al. [55], in which one-fold coordinated neutral chalcogen atom C_1^0 behaves as D^0 , to be conceptually the same with the dangling bond model.) A D^0 state has been assumed to be located at around the half gap, and accordingly, it could mediate the half-gap PL, the idea being repeatedly adopted in successive studies [11, 12]. Other researchers have assumed recombination of polarons, or polaronic

electron-hole pairs in deformable chalcogenide structures [56, 57]. Such ideas may also be common to those assuming bond breaking and/or alternation [54,55], since strong polaronic states are likely to accompany some bond conversions.

However, we should underline serious problems contained in these transitory gap-state models. *The assumption that D^0 states are located at the mid-gap cannot be justified in the lone-pair electron semiconductor as covalent chalcogenide glasses* [11, 19, 44, 58]. Thus, it cannot emit the half-gap light. (By contrast, in tetrahedral and pnictide materials such as Si and As, in which the conduction and the valence band are produced by σ^* and σ states, the D^0 state is possibly located at the mid gap.) Actually, a simple chemical analysis suggests that the electronic state of D^0 is located at around (or just above) that of lone-pair electron states; i.e. the D^0 state being buried in the valence band (see, also Appendix). On the other hand, for the polaron model, we cannot explain why the polaron inevitably stabilizes to energy states of $\sim E_g/2$.

4. Band-edge and -tail states

The brief review given in Section 3 reveals that the most important issue for understanding the half-gap PL is whether the gap state exists or not. We can obtain related insights into the problem from optical experiments.

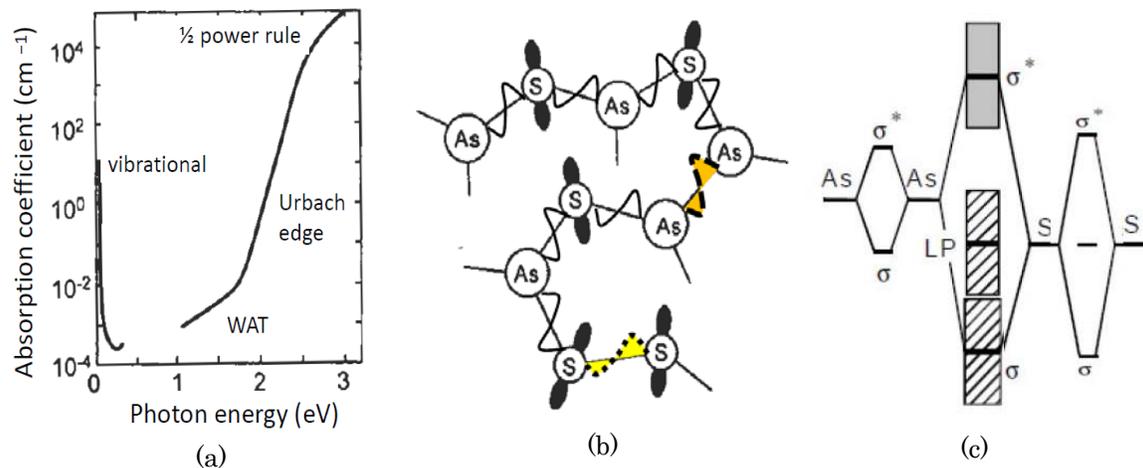


Fig. 4. Schematic illustrations for As_2S_3 glass; (a) optical absorption spectrum, (b) disordered structure including lone-pair electron wavefunctions (black lobes) of S and anti-bonding wavefunctions of As-S, As-As, and S-S, and (c) electronic structure, in which the outer-most electron energies of As(4p) and S(3p) are located at $E(As) = -7.9$ eV and $E(S) = -10.3$ eV, with the bandgap of $E_g = 2.4$ eV [19]. Similar band structures can be drawn for As_2Se_3 and $GeS(Se)_2$, with $E(Ge) = -8.4$ eV and $E(Se) = -9.5$ eV.

4.1. Urbach edge

As exemplified for As_2S_3 in Fig. 4(a), most of the amorphous semiconductors exhibit the so-called Urbach edge at $\alpha \approx 10^2 \text{ cm}^{-1}$ below the optical Tauc gap. The spectral form is exponential $\sim \exp(\hbar\omega/E_U)$ with widths of 0.2 – 0.3 eV, in which the Urbach energy E_U (~50 meV in $\text{As}_2\text{S}(\text{Se})_3$) is assumed to be governed by some kinds of structural disorder, while the “some” has not been identified. At higher temperatures [11, 19, 59] and pressures [19,60], the Urbach edge red-shifts with increases in E_U . Since the absorption spectrum is approximately written as;

$$\alpha(\hbar\omega) \sim \int D_c(E + \hbar\omega) D_v(E) dE,$$

where $D_c(E)$ and $D_v(E)$ are densities-of-states above and below the Fermi level, a problem is which density-of-state governs the Urbach edge.

We here follow the idea that an exponential density-of-state (or polaron states) just above the valence band governs the Urbach edge (see, Fig. 6(a)) [27]. An evidence is that the Urbach energy E_U is similar to a characteristic energy of a density-of-state of photoconducting carriers [61], which are known to be holes in the materials of interest. Since the valence band of covalent chalcogenide glasses consists of lone-pair electron states, it is very plausible that E_U is governed by spatially-fluctuating interaction between lone-pair electrons [62]. Such interaction may produce potential wells with varied depths of Gaussian distributions [63].

4.2. Weak absorption tail (WAT) and wrong bond

Existence of residual absorption of $\alpha \leq 1 \text{ cm}^{-1}$, called WAT (Fig. 4(a)) [64], below the Urbach edge has been demonstrated for a few materials. Since the WAT extends to mid-gap regions, the origin is of vital importance for understanding the half-gap PL. Nevertheless, due to its low absorption, which should be discriminated from light scattering in experiments, evaluations of the WAT remain laborious. In As_2S_3 [27, 64, 65], As_2Se_3 [66], and $\text{Ge}_{20}\text{Se}_{80}$ [65], the WATs appear also to be exponential, $\sim \exp(\hbar\omega/E_{\text{WAT}})$, which seem to extend to mid gaps with characteristic energies E_{WAT} of 200 – 300 meV. On the other hand, in a-Si:H, residual absorption appears as a shoulder with an absorption level of $\alpha \leq 1 \text{ cm}^{-1}$ at a spectral region of 0.8 – 1.4 eV [67], which is assumed to arise from dangling bonds. By contrast, it is not clear if g-SiO₂ [68], a-Se [27, 69, 70], and liquid S [71] possess such absorption tails. Or, ultimate transmittance ($\sim 10^{-6} \text{ cm}^{-1}$) of silica optical fibers [72] may suggest that the absorption tail does not exist in ideal SiO₂ glass.

What is the origin of the WAT? The WAT appears to be temperature-independent [59], which might imply that the tail is a manifestation of impurity states. Actually, for As_2S_3 , several researchers [19,27,73,74] have demonstrated that the WAT level correlates with the

concentration of Fe, a common impurity in glasses, which seems to act as a donor ion, Fe^{2+} . Also, Kitao et al. demonstrate that the WAT in As_2Se_3 becomes conspicuous with addition of Ag [75]. Accordingly, it might be reasonable that many works (postulating the charged defect) presume that the glass was intrinsically transparent, regarding the WAT as an impurity effect.

However, even in highly-purified samples, the WAT still remains [19, 27, 65]. In addition, in the As-S system, the WAT exhibits a non-monotonic compositional variation [76], which is difficult to be interpreted as an impurity effect. Otherwise, Street has asserted that the WAT is a predicted absorption band originating from strong electron-lattice coupling [4]. However, this idea faces difficulties in explaining the unclear WAT in a-Se [27, 69, 70], which has flexible chain structures being liable to undergo the coupling. Recently, Banik [21] and Zhugayevych and Lubchenko [23] have ascribed midgap states in semiconductor glasses to strained domain-wall regions, while its existence remains speculative.

Tanaka has proposed, on the basis of the following two ideas, that the WAT in As-chalcogenides is produced by the anti-bonding states $\sigma^*(\text{As-As})$ of =As-As= [19, 27]:

i) The WAT is produced from the tail state below the conduction band. This idea is based on the fact that the WAT does not appear in photoconductive spectra of As_2S_3 , which detects hole (and no electron) currents.

ii) This conduction-band tail can be ascribed to the anti-bonding state of As-As bonds, with the following three reasons. First, there are ample evidences, which manifest the existence of the wrong (homopolar) bond in As_2S_3 : i.e., Raman-scattering spectroscopy [77 - 81], EXAFS [82], and chemical analysis [78, 79] detect As-As bonds with concentration of a few at.%, the quantity varying with preparation procedures, i.e. melt-quenching [81] and evaporation. Second, there exists circumstantial evidence which suggests that the wrong bond is responsible for the WAT. That is, Raman-scattering spectroscopy resonantly detects As-As under excitation of WAT light [83]. Third, the energy difference of ~2.4 eV between the outermost electronic states of As and S (see, Fig. 4(c)) suggests that $\sigma^*(\text{As-As})$ states can be located below the conduction band. The electronic structure of As_2H_4 molecule [84] and the optical gaps of a-As (~1 eV [85]) are consistent with this idea. It is plausible that, due to the ionicity, an As-As bond appears to be slightly positively charged, and it behaves as an electron trap below the conduction band.

In addition, we can quantitatively connect the wrong-bond density of ~1 at.% with the WAT level lower than $\sim 1 \text{ cm}^{-1}$. As known, the transition probability of optical absorption is proportional to $|\langle \phi_f | H | \phi_i \rangle|^2$, where ϕ 's are electron wavefunctions of an initial i and a final f state and H is an electron-light interaction Hamiltonian. For the conventional band-to-band transition, e.g. in As_2S_3 , we take a lone-pair p -type electron wavefunction $\pi(\text{S})$ of S for ϕ_i and a $\sigma^*(\text{As-S})$ wavefunction for ϕ_f . The pair is located

at the nearest neighbors (see, Fig. 4(b)) with the density of $\sim 10^{22} \text{ cm}^{-3}$, which gives band-to-band absorption with an observed order of $\sim 10^5 \text{ cm}^{-1}$. On the other hand, for the WAT, the present model assumes that ϕ_i is given by the same function, while ϕ_f is given by $\sigma^*(\text{As-As})$. As illustrated in Fig. 4(b), this pair is located at the second-nearest neighbors, and a rough estimate for this wavefunction pair gives a relative transition probability smaller by $\sim 10^{-2}$ than that of $\sigma^*(\text{As-S})-\pi(\text{S})$ pairs. Accordingly, the wrong bond density of $\sim 1 \text{ at.}\%$, $\sim 10^{20} \text{ cm}^{-3}$ (smaller by two orders), is likely to cause the absorption level smaller than $\sim 10 \text{ cm}^{-1}$, in consistent with the observation.

The above proposition for the WAT origin can be extended to three directions. First, it is straightforward to apply to Ge-chalcogenides by replacing As-As to Ge-Ge, the idea being consistent with results of resonant Raman-scattering [86]. Second, we assume, taking the optical gap in a-S ($\sim 6 \text{ eV}$ [87]) into account, that S-S wrong bonds may also produce the anti-bonding states below the conduction band, as illustrated in Fig. 4(c). (In theoretical analyses [26, 35, 88, 89], the energy levels of these homopolar bonds substantially vary with calculation methods.) Lastly, we also envisage that As atoms with distorted bond angles, e.g. 120° as in the sp^2 configuration, may also produce the tail states, the detail being published elsewhere.

5. Present PL model

We assert, based on the following three facts, that the PL mechanisms of As(Ge)-S(Se) alloys and elemental Se (and probably also S) are different, as theoretically suggested by Vanderbilt [89]: First, S and Se exhibit considerably different PL characteristics, including $E_{\text{PL}} \neq E_{\text{exc}}/2$ (Fig 5, which is double-logarithmically plotted and accordingly the deviation from the $E_{\text{PL}} = E_{\text{exc}}/2$ line is apparently suppressed), remarkably weak luminescence intensity (Section 2.3), and substantially different recombination dynamics (similar to that in tetrahedral amorphous semiconductors) in a-Se [14]. As shown in Fig. 5, only the As-chalcogenides appear to accurately follow the half-gap relation. Second, as mentioned in Section 2.3, electronic properties of a-Se are, exceptionally, very sensitive to oxygen impurities [4, 19], the reason being speculative. Third, it is not clear if a-Se and liquid S possess WATs [27, 69 - 71, 76]. We may assume that PL in Se (and S) is governed by polaronic [56, 57] holes (or electron-hole pairs) in lone-pair electron states in the disordered flexible one-dimensional structure. The polaronic relaxation naturally varies with the strength of electron-lattice coupling, and accordingly, the half-gap relation is not necessarily retained. Oxides will also be excluded from the following consideration, owing to its ionic bond character [11,19].

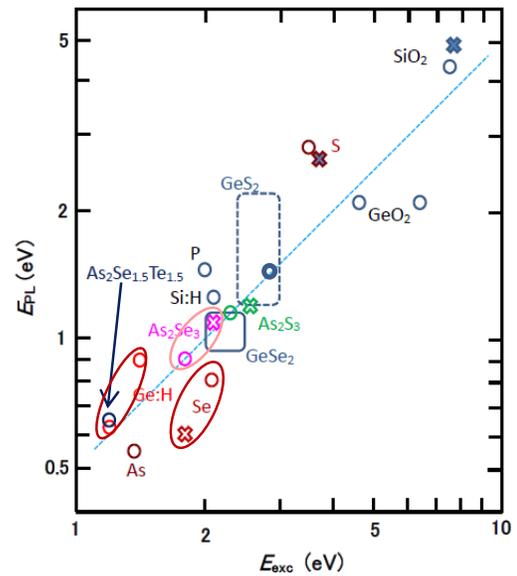


Fig. 5. PL peak energy E_{PL} as a function of PLE peak energy (or excitation energy) E_{exc} of glassy or amorphous (circles) and crystalline (crosses) materials; $g\text{-As}_2\text{S}_3$ [4], $c\text{-As}_2\text{S}_3$ [4], $g\text{-As}_2\text{eS}_3$ [4], $c\text{-As}_2\text{eS}_3$ [4], $g\text{-As}_2\text{Se}_3$ [4], $g\text{-As}_2\text{Se}_{1.5}\text{Te}_{1.5}$ [4], $g\text{-GeS}_2$ (see, Fig. 2), $g\text{-GeSe}_2$ [9, 10, 34, 42, 91 - 95], $g\text{-SiO}_2$ [37], neutron-irradiated $c\text{-SiO}_2$ [37], $g\text{-GeO}_2$ [96], $g\text{-S}$ [41], $c\text{-S}$ [40], $g\text{-Se}$ [4], $c\text{-Se}$ [45], $a\text{-P}$ [50], $a\text{-As}$ [47], $a\text{-Si:H}$ [11], and $a\text{-Ge:H}$ [51, 52].

5.1 Evolved CFO model

We propose a PL model for $g\text{-As(Ge)-S(Se)}$, illustrated in Fig. 6, which may be regarded as an evolved CFO model. As described in Section 4.2, the WAT states are produced by the anti-bonding states of As-As (Ge-Ge, S-S, Se-Se) homopolar and other (strained $\text{AsS}_{3/2}$, etc) bonds. And, the half-gap luminescence arises from radiative recombination of electrons, which are transferred to the Fermi level being located at mid-gap WAT states, and holes relaxed to Urbach-edge states at the valence-band top.

As illustrated in Fig. 6(b), plausible scenarios depend upon the excitation photon energy. i) Mid-gap excitation directly produces trapped electrons and holes, which will geminately recombine, emitting half-gap photons. ii) Bandgap and Urbach-edge excitation may produce free electrons and holes, or it may produce trapped electrons in WAT states and free holes. The free electron immediately ($\sim 10^{-12} \text{ s}$) relaxes to the conduction-band bottom, being trapped at a shallow WAT state, and then it will successively descend in WAT states through thermally-assisted tunneling toward a state near the Fermi level, which is located at mid-gap. On the other hand, a photo-excited hole may undergo strong lattice coupling, becoming a polaronic hole in an Urbach-edge state, since lone-pair electron wavefunctions are sterically flexible.

Ultimately, this pair radiatively recombines with emission of a half-gap photon. We will see below how this model can explain known observations of PL. The model will be applied also to the corresponding crystals as well.

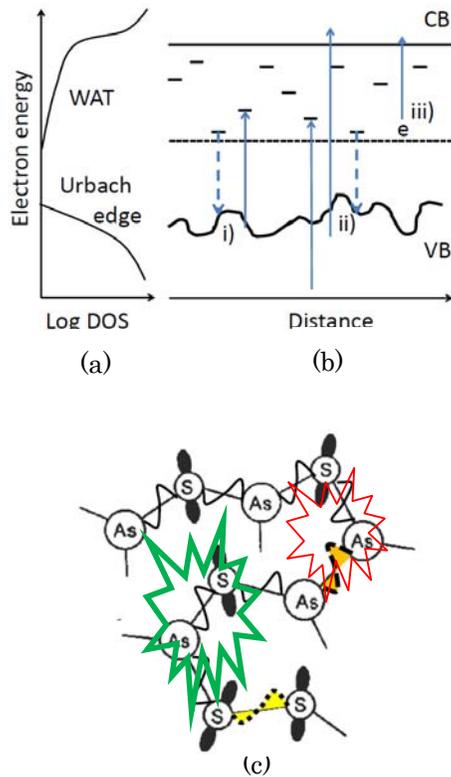


Fig. 6. Schematic representations of (a) a density-of-state DOS, (b) excitation-energy dependent PL processes in a band diagram, and (c) an atomic picture, which shows bandgap (thick green) and sub-gap (thin red) excitation. In (b), solid and dashed arrows represent absorption and recombination; i) sub-gap excitation and geminate recombination and ii) bandgap excitation and non-geminate recombination. (In this illustration, the distinction between the Tauc optical gap and the mobility gap remains vague. For instance, in As_2S_3 , the former is reported to be ~ 2.4 and ~ 2.5 eV at 300 K and 4 K [59], and the latter seems to be located at ~ 2.7 eV at 150 K [97].)

5.2. Temperature dependence

With an increase in temperature, the luminescence weakens without changing its spectral shape. Above cryogenic temperatures, it changes as $\sim \exp(-T/T_0)$ [4], where T_0 is a characteristic temperature, which also varies with excitation photon energy, as illustrated in Fig. 7; in As_2S_3 it is ~ 25 to ~ 55 K for subgap and Urbach-edge (and bandgap) excitations [29]. This exponential variation has been understood on the basis of the models that assume

thermally-assisted electron (or hole) tunneling from radiative to non-radiative recombination wells, in which T_0 is connected with the shape of related wells [4, 22, 93, 98].

In the present model, we can assume that the wells for electrons and holes are produced, respectively, by the anti-bonding state and the Urbach-edge state. However, it is not known which state is responsible for T_0 . The smaller T_0 under subgap excitation is explainable as it excites electrons (or holes) to deeper and more localized gap states.

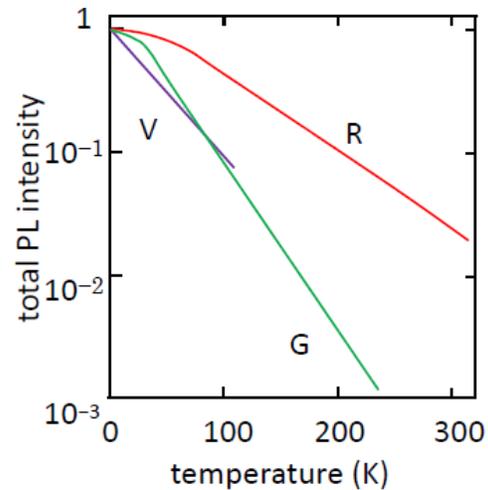


Fig. 7. Temperature variations of total PL intensity (normalized unity at 0 K) under excitations of 2.0 eV (R), 2.3 eV (G), and 2.6 eV (V) light [29].

5.3. Pressure dependence

Concerning pressure effects upon PL, only one cw study, to the authors' knowledge, has been reported by Weinstein [7]. He demonstrates for $c\text{-As}_2S_3$ and $g\text{-As}_2S_2\text{Se}$ at 13K that hydrostatic compression causes drastic PL intensity reductions and *blue-shifts* of the peaks ($\partial E_{PL}/\partial P > 0$), which tend to violate the half-gap relation, since it is known $\partial E_g/\partial P < 0$ in the crystal and the glass as well [7, 19]. For instance, in $g\text{-As}_2S_2\text{Se}$, he estimates $\partial E_{PL}/\partial P \approx +10$ meV/kbar (at ≤ 18 kbar) and $\partial E_g/\partial P \approx -17$ meV/kbar. The bandgap narrowing has been attributed to pressure broadening of the valence band (consisting of lone-pair electron states), which is induced by compression of intermolecular van-der-Waals type bonds, the covalent bond being mostly intact [7, 19]. Then, how can we interpret this puzzling, blue-shifting E_{PL} ?

The present model provides two plausible explanations. One is compression-induced conversion of wrong (As-As, S-S) bonds to heteropolar (As-S) bonds, which may be enhanced by intermolecular compression. The conversion will reduce overall WAT states, resulting

in the PL blue-shift. This idea is consistent with enhanced fatigue under compression [7], which is ascribable to efficient As-As scission under illumination and compression (see, Section 5.8). The other may be an indirect consequence of the bandgap change. Due to the drastic pressure-induced bandgap reduction, the ratio of fixed excitation energy to the bandgap energy E_{exc}/E_g increases, which will cause the PL blue-shift through dependence of luminescence spectra on excitation energy, described below. The drastic intensity decrease may also be ascribed to the gap-state reduction. (Otherwise, the weakening is caused by the bandgap decrease, which gives rise to reduction of penetration depths of excitation light.)

5.4. Excitation-energy dependence

It has been demonstrated that the PL peak energy E_{PL} increases with an increase in the excitation energy E_{exc} , which is qualitatively in line with the half-gap relation. As shown in Fig. 7, in $g\text{-As}_2\text{S}(\text{Se})_3$, E_{PL} increases typically by 0.1 – 0.2 eV [29, 99 – 102], although increasing behaviors may be a little different between in As_2S_3 and As_2Se_3 . In As_2S_3 , there seems to be a characteristic E_{PL} step at $E_{\text{exc}} \approx 2.2$ eV, which has been interpreted as a manifestation of the mobility gap [99] and a defective structure effect [102]. By contrast, As_2Se_3 may not exhibit such a step; a linear E_{PL} increase to a fixed value at $E_{\text{exc}} \geq 2.2$ eV [101]. GeSe_2 exhibits qualitatively the same variation [9]. Interestingly, as shown in Fig. 7(b), the corresponding crystal $c\text{-As}_2\text{Se}_3$ does not show excitation-energy dependence [101], which implies that the energy dependence is inherent to disordered semiconductors.

The present model interprets the excitation-energy dependence to arise from geminate and non-geminate recombination in spatially fluctuating band-edge states. Under illumination of WAT light, as illustrated in Fig. 6(b) i), an electron is excited from a valence-band edge directly to a WAT state, and it will geminately recombine with a hole. On the other hand, under bandgap illumination ii), electrons and holes are excited into the conduction and the valence band, which are composed in As_2S_3 with $\sigma^*(\text{As-S})$ and chalcogen lone-pair electron $\pi(\text{S})$ states. Otherwise, excitation may occur from bonding states $\sigma(\text{As-S})$ to WAT states as well. Excited carriers will diffuse through dissipating excess energies, with electrons and holes finally being relaxed to WAT states $\sigma^*(\text{As-As})$ and Urbach-edge states $\pi(\text{S})$, which may be separated by R . And ultimately, these undergo non-geminate recombination. The recombination energy of non-geminate electron-and-hole is higher by $e^2/(4\pi\epsilon_r\epsilon_0R)$ [11], where ϵ_r (≈ 10) is a relative dielectric constant. For $R = 1$ nm, this gives $\sim 10^2$ meV, which can explain the variation of E_{PL} in Fig. 7.

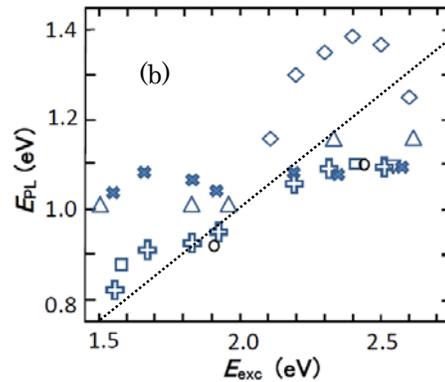
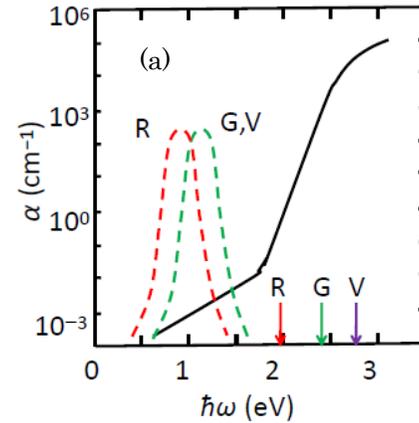


Fig. 7. Variations of PL spectra with excitation energy. (a) PL spectra under excitations of 2.0 eV (R), 2.3 eV (G), and 2.6 eV (V) light in $g\text{-As}_2\text{S}_3$ at 5 K [29]. (b) PL peak energies E_{PL} as a function of excitation energy E_{exc} for $g\text{-As}_2\text{S}_3$ (Δ [29], \diamond [99], \circ [100], \square [102]) and for $g\text{-As}_2\text{Se}_3$ (+) and $c\text{-As}_2\text{Se}_3$ (\times) [101] with a dotted line showing $E_{\text{PL}} = E_{\text{exc}}/2$. Note that the absolute peak energy is less meaningful, since it changes depending upon spectral responses of measuring systems [4], which may not be calibrated. For $E_{\text{exc}} = 1.92$ eV in As_2S_3 [100], a PL shoulder is plotted as E_{PL} .

5.5. Dynamics

When excited by pulsed light, PL in $g\text{-As}_2\text{S}_3$ decays with time constants distributing over ps – ms [1, 4, 5, 103]. Specifically, several studies, including recent frequency-resolved PL measurements [13, 14], have demonstrated that the decay consists of, at least, two processes; fast and slow, having life times of ~ 10 ns and ~ 100 μs . For the PL spectrum, several researchers had reported that, during the fast decay (~ 10 ns), the peak position red-shifted [99, 104], while Mollot [105] argued that the peak did not shift and only the spectral width became narrower. On the other hand, Murayama [106] detected a clear PL red-shift of ~ 0.5 eV from the initial (0 ns) to slow (100 μs) spectra. And, a final elucidation has not been obtained. Nevertheless, it is un-doubtful that the

slow process governs the cw PL.

The dynamics also depend upon the excitation photon energy. Murayama demonstrated for As_2S_3 at 4 K that the PL position at zero-ns delay time became to higher energies, $E_{\text{PL}} \approx 1.5 \sim 1.7$ eV, with an increase in the excitation energy of $E_{\text{exc}} \approx 2.3 \sim 2.7$ eV [106]. Aoki et al. demonstrated that, in the slow process, 1.94-eV subgap excitation relatively enhances the peak at $E_{\text{PL}} \approx 1.1$ eV [13], which is smaller by ~ 0.1 eV than that excited by 2.33 eV light [14].

The fast and slow processes have been interpreted using several ideas (terminology) [14, 102, 106, 107]. Among those, the most probable may be the recombination of singlet and triplet electron-hole pairs (excitons) in the fast and the slow process [14, 102], which is consistent with the results of PL polarization analyses [6], ODMRs [6, 101], and magnetic field effects [14]. Aoki demonstrates for As_2S_3 that the singlet excitonic state is located at a higher energy than the triplet by ~ 0.1 eV [14].

How can we compromise these ideas on dynamics with the present model? Bandgap illumination tends to excite non-geminate (distant) e/h pairs, which will relax to the band edges within \sim ps through emitting phonons. On the other hand, Urbach-edge light excites geminate pairs, which may be singlet in spin. Then, the electron will relax to $\sigma^*(\text{As-As})$ states. WAT light may excite an electron directly to $\sigma^*(\text{As-As})$, and a hole around there, which will form a kind of defect-trapped e/h pairs. During these relaxation processes at low temperatures, the singlet pairs may be converted to the triplet, due to the energy difference of ~ 0.1 eV, through hyperfine interaction with As atoms, which have nuclear spin of $3/2$, and spin-orbit interaction. Ultimately, these pairs recombine radiatively (or non-radiatively), in which the singlet and the triplet pairs contribute, respectively, to the fast and the slow luminescence process giving rise to slightly different emission energies.

We here should underline another excitation process. Bandgap light is also able to induce an electronic transition from a deep valence-band state, which may be a $\sigma(\text{As-S})$ state, to a WAT state (see, Fig. 6(b)). The hole in the deep state will relax to a valence-band top with phonon emission within ps time scales, and it may recombine with the electron in the WAT state immediately. Accordingly, zero-nanosecond delay PL spectra can have a peak at $\sim E_g/2$, as observed [106]. Polarization memory may partly be retained in such a process.

5.6. Compositional variation

PL characteristics in non-stoichiometric glasses have been studied for several alloys. For binaries, results are reported for the systems of As-S [29, 108], As-Se [4, 28], Ge-S [32 - 35], Ge-Se [9, 10, 42, 91], and P-Se [50]. Studies have also been performed for some ternary alloys such as Ag-Ge-Se [92], As-Ge-S(Se) [32, 91], Ga-Ge-S(Se) [109, 110], $\text{Bi}_x\text{Ge}_{25}\text{Se}_{75-x}$ [111], $\text{Ge}(\text{S-Se})_2$

[34, 94], and Ge-P-S [112]. It is known that, on comparison of the sulfide and the selenide system, the latter has wider glass-forming regions, which may be due to higher covalency and similar atomic sizes of cations and the anion. The wide glass-forming region is preferred to compositional studies, while bandgap energies in the As(Ge)-Se systems are nearly fixed [44].

Spectral positions of reported PLs are more-or-less reproducible. The half-gap relation seems to be satisfied, the example being shown for the Ge-Se system in Fig. 9. Roughly speaking, all the selenide glasses possess optical gaps and PLE peaks at ~ 2 eV and also PLs peaking at ~ 1 eV. In the present model, such features can be attributed to the Fermi level positioned at the gap center and defective anti-bonding tail states. However, in detail, we see some variations. For instance, as described in Section 5.4, the PL position tends to depend upon the photon energy of excitation, and accordingly, if the excitation energy is fixed, observed PL spectral shapes become complicated due to variation of $\hbar\omega/E_g$, as demonstrated for Ge-Se [9].

On the other hand, the PL intensity is less reproducible. The PL intensity in binary alloys appears to be the most intense at the stoichiometric composition, As_2S_3 [29], GeS_2 [34], and GeSe_2 (see, Fig. 8) [9, 10, 42, 91], while some controversial results have been reported for As-Se [4, 8, 28, 113]. The reason may be sought in compositionally varying PL fatigue (Section 5.8) and annealing effects [32, 91].

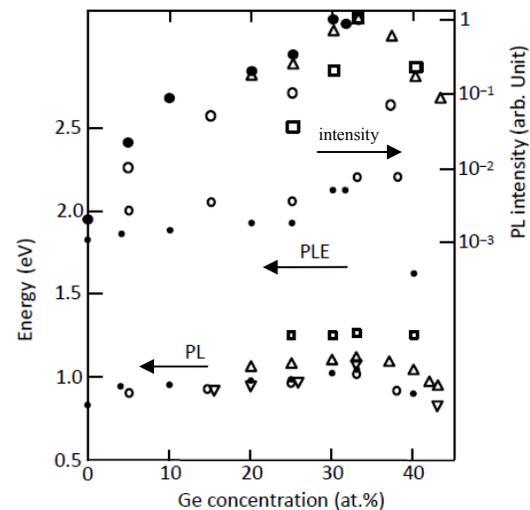


Fig. 9 Dependence of PL peak energy (lower), PLE peak energy (middle), and PL intensity (upper with right-hand side axis) on the Ge concentration in the $\text{Ge}_x\text{Se}_{100-x}$ system at cryogenic temperatures, reported in [91] (squares), [42] (open circles), [9] (triangles), [10] (solid circles), and [114] (inverse triangles).

The present model explains the most intense PL at stoichiometric compositions as follows: In the stoichiometric composition, major atomic bonds are heteropolar, as $-\text{S}(\text{Se})-\text{As}=\text{}$ in $\text{As}_2\text{S}(\text{Se})_3$, and a few wrong

bonds (=As-As= and -S(Se)-S(Se)-) produce localized states, which work as radiative recombination centers. However, with deviation from the stoichiometric composition, the density of either wrong-bond increases, or these may be clustered, which cannot strongly localize electrons, making radiative recombination efficiency smaller.

5.7. Impurity effects and preparation dependence

Impurity and doping effects have been investigated for g-As₂S(Se)₃ by several researchers. However, reported results are inconclusive, which may be due to varied experimental conditions. Kolomiets et al. [113] reported that addition of In, Zn, Sn, and Pb in to As₂Se₃ intensified the half-gap PL with small spectral changes, while Ge weakened it. On the other hand, Bishop and coworkers [43, 115] demonstrated that Cu and Tl (and also I, Ag, and In) reduced PL intensity in As₂Se₃. More recently, Babaev et al. [108] demonstrated that impurity effects appeared differently in non-stoichiometric glasses: Incorporation of Au up to 4 at.% in to As₂S₃ just slightly red-shifted the PL and PLE spectra, while the incorporation in to As₃S₇ added new PL and PLE peaks.

Despite these complicated observations, we can point out an important common feature. Doping effects are noticeable only when the dopant becomes denser than ~0.1 at.% (~10²⁰ cm⁻³). Here, only one exception is the case of Fe, which gives considerable effects upon PL intensity in As₂S₃ at ~100 ppm levels, without changing other characteristics including PL and PLE spectra, fatigue, and temperature dependence [29, 115].

Under the present model, we can understand such impurity effect as follows: First, the density of the wrong bond in As₂S(Se)₃ is estimated at a few atomic percent, which is consistent with the insensitivity of PL on impurity concentrations up to ~0.1 at.%, as noted above. Second, Cu (Ag and other cations) is known to make strong bonds with S(Se), which dramatically changes the character of the valence band, as demonstrated by photoemission studies [116]. As the result, the hole transport is substantially affected [117], while the PL spectrum is hardly influenced, since Cu-S(Se) bonds cause little effects upon the WAT state. Third, the unique effect of Fe on PL intensity can be related with the correlation between the Fe concentration and the WAT level. As mentioned in Section 4.2, Fe, which is likely to ionize as Fe²⁺, produces a donor state at around the energy level of σ*(As-As) states. The Fe seems to work as a non-radiative recombination center [115] and/or a site giving rise to concentration quenching of intrinsic PL. Otherwise, under some conditions, the atom may resonantly transfer excitation energy to the radiative recombination center [29]. Thus, PL characteristics will considerably be affected.

It is also known that PL characteristics vary in samples prepared by different procedures. For instance, in As₂S₃ [4] and GeSe₂ [118], marked differences in PL widths and intensities are observed between evaporated

films and bulk (or annealed) samples, which can be ascribed to more dense wrong bonds and fragmental structures in the films. It is also demonstrated that the PL position in g-As₂S₃ is modified with melt-quenching conditions, in accordance with the gap modification [119]. These observations are consistent with the fact that the WAT level and the wrong-bond density in As₂S₃ are markedly affected by the preparation condition [76,82,84].

5.8. PL fatigue and related photoinduced meta-stabilities

Explorations of marked PL fatigue (~1/500 in As₂S₃) and related phenomena, including photoinduced ESR and mid-gap optical absorption, have progressed through two stages [12, 19]. Pioneering studies till 1980 had demonstrated that these three low-temperature phenomena, induced in As₂S(Se)₃ by Urbach-edge light with intensity of ~1 mW/cm², were produced by photoinduced dangling bonds (D⁰) with a density of ~10¹⁷ cm⁻³ [11]. The dangling bond could be recovered thermally (at ~T_g/3) and optically (using mid-gap light). Mott and other researchers then assumed that the PL fatigue was caused by the photo-production of D⁰, which was presumed to be a recombination center as well [11, 54].

However, further investigations have revealed complicated features of defect creation-recovery processes. Mollot et al. [10] and Biegelsen and Street [120] discovered that prolonged intense (≥ 100 mW/cm²) illumination increased unpaired spin densities up to ~10²⁰ cm⁻³, ~1 at.%. Hautala et al. [121], performing detailed ESR studies, found that the induced defects in As₂S₃ were annealed through two stages, at 150–200 (~T_g/3) and ≤ 300 K (~3T_g/5); the related defects being named as type I (~10¹⁷ cm⁻³) and II (~10²⁰ cm⁻³) centers. Interestingly, the type I center and the mid-gap optical absorption undergo the same annealing behavior [121, 122]. In addition, it was discovered that photoinduced ESR spectra and densities changed with excitation photon-energy [9, 10, 123]. It was also discovered that the PL in As₂S₃ when excited by subgap light (Fig. 7) *grows*, i.e. anti-fatigues, under prolonged bandgap illumination [102, 122]. It should be mentioned here that these photoinduced changes naturally vary with glass compositions. Specifically, PL fatigues in GeS₂ are complicated and not reproducible [12, 32, 35, 124].

How can we interpret those two types of the defects? The conventional model, based on the charged defect concept, assumes that both the type I and II centers are D⁰ centers, in which I is produced from isolated D⁺ (and/or D⁻) and II from intimate D⁺D⁻ pairs or broken normal bonds. Hautala et al. [121] and Shimakawa et al. [12] proposed more detailed models that the type II centers are produced from wrong bonds (As-As and S-S). We here follow this idea, illustrated in Fig. 10(b), since the wrong-bond density is estimated at ~10²⁰ cm⁻³, which is consistent with the spin density of the type II center.

However, for the type I center of $\sim 10^{17} \text{ cm}^{-3}$, which is accompanied by mid-gap absorption and less thermally stable, we may envisage several candidates such as trapped electrons at deep anti-bonding states of $=\text{As}-\text{As}=\text{O}$ (Fig. 10(a)), which remain to be studied. Impurity effects should also be examined. Finally, it should be mentioned that what makes the understanding of the photoinduced meta-stability difficult is that the simplest material a-Se does not present clear photoinduced meta-stabilities.

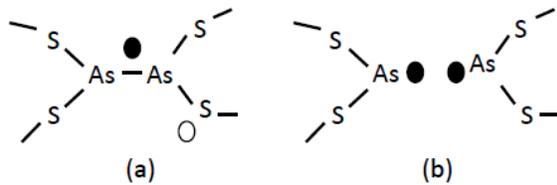


Fig. 10. Models for (a) type I and (b) II centers, with unpaired electron (\bullet) and hole (\circ).

5.9. Comparison of glass and the corresponding crystal

Comparisons of PL behaviors in glass and crystal have been performed mainly using selenides, since it is difficult to prepare single-crystalline As_2S_3 . (Instead, we can employ a mineral called “orpiment”, but the material is likely to contain impurities as Sb, which may restrict experimental reproducibility.) In addition, PL studies for c-GeS₂ have been limited [92], probably due to the wide bandgap energy of $\sim 3.5 \text{ eV}$.

Roughly speaking, PL and PLE spectra in c-As₂S₃ [1, 4, 7, 30], c-As₂Se₃ [1, 4], and c-GeSe₂ [93] resemble those in the glasses. The PL position follows the half-gap relation, and PLE spectra of c-As₂Se₃ exhibit WAT components [4], as those in g-As₂S(Se)₃. Such similar PL characteristics in the glass and crystal strongly suggest that the PLs arise from the same center. We then assume that the chalcogenide crystal also contains the wrong bond such as As-As, which remains to be investigated. Nevertheless, an estimation [26] using the bond energies predicts the existence in practical (non-ideal) crystals. It should also be mentioned that even polar semiconductor crystals such as GaAs contain Ga-Ga and As-As wrong bonds [125].

In details, however, there exist some differences between a glass and the corresponding crystal. First, the PL in the crystals appears to be blue-shifted a little and sharper, which may reflect higher and sharper optical absorption edges of the crystal [1, 4]. Second, orpiment (c-As₂S₃) exhibits stronger PL than that of the corresponding glass [1, 29], which may be ascribed to a fewer wrong bonds in the crystal, being effective to confine excited electrons. Third, the PL fatigue does not (or hardly) occur in the crystal [4], which is consistent

with no photoinduced ESR in c-As₂S(Se)₃ [8]. This observation may also be ascribed to the fewer wrong bonds. Or, we assume that the fatigue is inherent to disordered structures, since broken bonds in a crystal can immediately be recovered due to topological constraint arising from the structural periodicity. This idea is consistent with an observation by Babaev et al. [126], reporting an appreciable PL fatigue in mechanically-damaged c-As₂S₃.

6. Problems unresolved

We have emphasized the role of the WAT in the half-gap PL, while there still remain some problems. The exponential WAT form has implicitly been connected with an exponential density-of-state of $\sigma^*(\text{As}-\text{As})$ states. The broad state distribution probably arises from geometrical fluctuations of defective bonds and peripheral structures. But, why the distribution becomes *exponential* should be considered further [63].

Studies on such fundamental problems will be valuable also for the application to optical amplifiers. In the device, Ge-chalcogenide glasses, which do not contain poisonous As, may be preferred. Specifically, not covalent but ionic glasses as Ga-Ge-S have been selected for hosts which can incorporate rare-earth ions such as Pr³⁺ with high densities. The ion is likely to have excitation levels in the Urbach and WAT regions, and accordingly, resonant energy-transfer between the intrinsic states and the extrinsic rare-earth-ion states becomes of considerable importance [127, 128].

However, as summarized in Fig. 2, properties of Ge-S glasses are relatively non-reproducible. In addition, PL studies on (rare-earth undoped) ionic Ge-S glasses appear to be limited to a system Ga-Ge-S [109, 110]. It remains vague if these glasses emit the half-gap PL and/or possess the WAT. Little studies have been reported on compositional and also O [129] and Fe impurity effects. Accordingly, it remains difficult to draw a universal picture for the PL of these ionic chalcogenide glasses, which is indispensable to advancing such optical applications.

7. Conclusions

We have proposed a new model for the half-gap PL. It arises from recombination of electrons, being trapped by anti-bonding states of wrong (and strained) bonds at around the mid-gap Fermi level, and holes in Urbach-edge states at the valence-band top. The wrong bond seems to be the most dominant defect in covalent chalcogenide semiconductors such as As₂S(Se)₃, irrespective of glass and crystal, and accordingly, this model can be applied to the corresponding crystals as well. The PL fatigue, which is more prominent in the glass, may arise from momentary trapped electrons (type I) and broken chemical bonds (type II) in disordered flexible lattices. However, complete understandings of the fatigue remain difficult due to some

experimental limitations.

The negative U concept and related atomic models have appeared revolutionary fascinating, while practically the homopolar bond behaves as a more influential defect in covalent chalcogenide glasses.

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Appendix

The electronic level of a neutral dangling bond D^0 has been calculated for the simplest example, S_2 (di-sulfur) molecule. Results obtained using semi-empirical (PM7 in MOPAC2012 [J.J.P. Stewart, *J. Mol. Modelling*, **10**, 6 (2004)]) and ab-initio (GAMESS [M.W. Schmidt et al. *Comput. Chem.* **14**, 1347 (1993)] with STO-3G basis) calculations, in which the D^0 energy is taken as the p-state energy of S, are compared in Table with experimental results [B. Meyer, *Chem. Rev.* **7b**, 367 (1976)]*. The experimental HOMO energy is taken as a negative ionization energy [C.L. Liao, C.Y. Ng, *J. Chem. Phys.* **84**, 778 (1986)]**. All the energies are given in eV.

	Bond length (Å)	HOMO~LUMO gap	LUMO level	HOMO level	D^0 level
experiment	1.89*	~6 *		-8.35**	
PM7	1.83	5.7	-2.7	-8.4	-9.5
GAMESS	1.96	8.3	+0.5	-7.8	-8.9

We see in the two calculated results that the D^0 state energy is lower than the HOMO-state energy. The result suggests that, in chalcogenide glasses, the D^0 level merges into the valence band, being not located in the bandgap. It is also mentioned that the same conclusion has been obtained by comparing energy levels of S_8 rings and chains, the latter containing two D^0 's.

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