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Optical nonlinearity in glasses: The origin and photo-excitation effects

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Linear and nonlinear optical properties in oxide and chalcogenide glasses have been studied comparatively. Applying a semiconductor concept to these glasses, we show that maximal nonlinear refractive-index at optical communication wavelengths is ~10^{-4} cm^2/GW, which can be obtained in materials with bandgap energy of ~1.6 eV. It is also shown for SiO_2 and As_2S_3 that linear and nonlinear optical excitations induce different photostructural changes, which are attributable to different photo-electronic transition probabilities.

1. Introduction

With the advent of pulsed lasers and progress of optical communication technologies, the interest in optical nonlinearity in glasses is growing rapidly [1]. For instance, optical fibers with large intensity-dependent refractive index n_2 and two-photon absorption coefficient β are required for all-optical switches and intensity stabilizers [2]. In addition, laser micro-fabrications appear to be indispensable for producing waveguides and three-dimensional devices [3, 4].

However, the nonlinearity has not been elucidated in fundamental aspects. For instance, what is a maximal nonlinearity attainable at optical communication wavelengths of ~1.5 μm? We have estimated n_2 values using empirical formula such as the Boling relation, $n_2 \propto n_0 - 1$ [5, 6], or can calculate the values from bond susceptibilities [7]. However, spectral dependence has been neglected in most cases, and the maximal n_2 value cannot be predicted. On the other hand, it is still vague if linear and nonlinear optical excitations produce similar photoinduced changes. In the present work, we will focus upon these subjects, which are previewed recently [8].

2. Fundamentals

Fig. 1 shows a relation of linear and nonlinear optical properties in a framework of solid state physics [8]. Here, the basis is a non-crystalline structure in insulators and semiconductors, which is governed by constituent atoms and bonds, the latter being covalent, ionic, and/or van-der-Waals types. Then, from a known short-range structure, which may resemble a molecular structure, it is possible to draw electronic energy levels with wave-functions of φ. The levels slightly shift up and down from site to site reflecting disordered longer-range interactions, and the energy-level distribution determines an electronic density-of-state D. We then can calculate linear and nonlinear absorption coefficients, α and β, under neglect of wave-vector conservation, electron-lattice coupling, and the energy-dependent transition

probability [9] as;

$$\alpha(\hbar\omega) \propto |\langle\varphi_f|H|\varphi_i\rangle|^2 \int D_f(E + \hbar\omega)D_i(E)\, \mathrm{d}E, \tag{1}$$

$$\beta(\hbar\omega) \propto |\Sigma_n\langle\varphi_f|H|\varphi_n\rangle\langle\varphi_n|H|\varphi_i\rangle/(E_{ni} - \hbar\omega)|^2 \int D_f(E + 2\hbar\omega)D_i(E)\, \mathrm{d}E, \tag{2}$$

where H is a perturbation Hamiltonian, φ is a related electron wavefunction, in which the subscripts i, n, and f represent initial, intermediate, and final states, and Σ_n represents summation for all possible states. Under the present approximation, the absorptions are expressed as the products of a transition probability and a convolution integral, the latter being essentially common to the one-photon (1P) and two-photon (2P) absorptions, just replacing $\hbar\omega$ to $2\hbar\omega$. An optical gap E_g can then be evaluated from $\alpha(\hbar\omega)$. Next, using (non-)linear Kramers-Krönig relations;

$$n_0(\omega) = 1 + (c/\pi)\, P \int \{\alpha(\Omega) / (\Omega^2 - \omega^2)\}\, \mathrm{d}\Omega, \tag{3}$$

$$n_2(\omega) \simeq (c/\pi)\, P \int \{\beta(\Omega) / (\Omega^2 - \omega^2)\}\, \mathrm{d}\Omega, \tag{4}$$

we can calculate linear and nonlinear refractive indices, n_0 and n_2, rigorously and approximately. Fig. 1 and Equations 1–4 manifest how, for instance, the Boling relation ($n_2 \propto n_0 - 1$) is related to the atomic structure through φ and D.
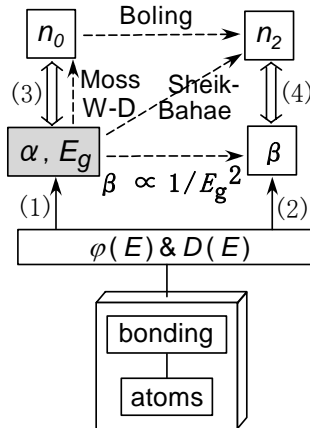

Figure 1 Relationship between atomic structure (atoms and bond), electronic structure $\varphi(E)$ and D, and linear and nonlinear absorptions (α, E_g, β) and refractive indices (n_0, n_2), with related Equations 1-4. Some useful relations, the Moss rule [10], Wemple-DiDomenico relation (W-D) [11], Bolings' relation [6], Sheik-Bahaes' relation [12], and $\beta \propto 1/E_g^2$ are also shown.

Comparing Equations 1 and 2, we can obtain valuable insights. On one hand, absolute values of α are not affected by E_g. Actually, in many insulators and semiconductors with $E_g \simeq$ 1~10 eV, we see commonly $\alpha \lesssim 10^5$ cm^{-1} [9]. A weak dependence of the linear refractive-index n_0 on E_g, the Moss rule $n_0 = 3/E_g^{1/4}$, may be obtained from Equation 3 [10]. On the other hand, β is governed by E_g through the factor of $1/(E_{ni} - \hbar\omega)^2$ in Equation 2 as $\beta \propto 1/E_g^2$ because $E_{ni} \gtrsim E_g/2 \sim E_g$. Actually, experimental results show that $\beta_{max} \propto 1/E_g^2 \sim 1/E_g^3$ and $\beta_{max} \simeq 10^0 \sim 10^2$ cm/GW [13]. This $\beta(E_g)$ dependence, when combined with Equation 4, gives a proportionality

of $n_2 \propto 1/E_g^4$, which is approximately consistent with a rigorous relation $n_0 n_2 \propto 1/E_g^4$ derived by Sheik-Bahae *et al*. [12]. In short, in contrast to the linear properties, α and n_0, the nonlinear β and n_2 strongly depend upon E_g.

3. Maximal nonlinear refractivity

When considering optical nonlinearity in homogeneous media, we should take spectral dependence into account. The spectra have been theoretically analyzed for crystalline semiconductors having direct and indirect gaps of E_g [12, 14], the results being illustrated in Fig. 2. We see that, at $\hbar\omega = E_g/2$, $\beta = 0$ and n_2 is great, the condition which is the most favorable to many nonlinear applications. Accordingly, the material with $E_g \simeq 1.6$ eV is suitable to optical devices which are utilized at the communication wavelengths of $\lambda = 1.3 \sim 1.5$ μm ($\hbar\omega \simeq 0.8$ eV). This spectral insight can be applied as a rough approximation also to non-crystalline semiconductors having non-direct gaps [9]. Specifically, since n_2 is determined by integrated β spectra, as shown by Equation 4, it is mostly irrespective of structural periodicity, which can be seen in similar n_2 values in, e.g., glassy and crystalline SiO_2 [15]. Following this idea, we can predict that Cu(Ag)-As(Ge)-S(Se) glasses with $E_g \simeq 1.6$ eV are promising for nonlinear applications, as demonstrated partially [16].
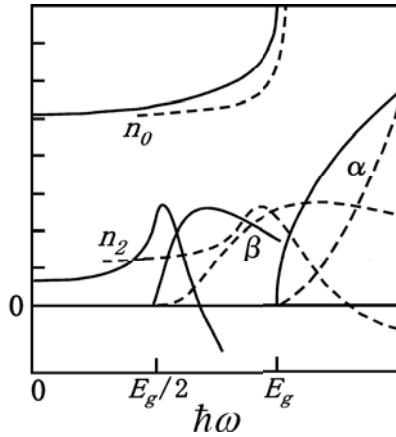

Figure 2 Spectral dependence of linear (α and n_0) and nonlinear (β and n_2) properties in direct- (solid) and indirect-gap (dashed) semiconductors with energy gap of E_g. Vertical scales are normalized.

Next, we recall a quantitative relation between n_2 and E_g. Sheik-Bahae *et al*. have theoretically derived for direct-gap semiconductors that $n_0 n_2 = KG/E_g^4$, where K (= 3. 4×10^{-8} for E_g in eV) is a constant and $G(\hbar\omega/E_g)$ represents the spectral dependence (Fig. 2) [12]. They also have demonstrated that the relation can provide good agreements, with typical data scattering of about $\pm 10\%$, for n_2 in many crystalline semiconductors including direct and indirect gaps of $E_g \simeq 1 \sim 10$ eV [12]. Recently, Tanaka has demonstrated that the relation between n_2 and E_g can be applied also to oxide and chalcogenide glasses [8], and a revised one is shown in Fig. 3, which includes some new results for As_2S_3 [17], As_2Se_3 [18], and

amorphous Si:H (at $\lambda = 1.05$ μm) (unpublished). We see in Fig. 3 that a degree of data fitting is worse, specifically in the small-gap materials $Ag_{20}As_{32}Se_{48}$ glass and amorphous Si:H, than that [12] for crystalline semiconductors, which may be inevitable in non-crystalline solids having quasi-stable disordered structures and band-tail states. Nevertheless, the Sheik-Bahaes' relation could be taken as a rough guide for n_2 in non-crystalline solids.
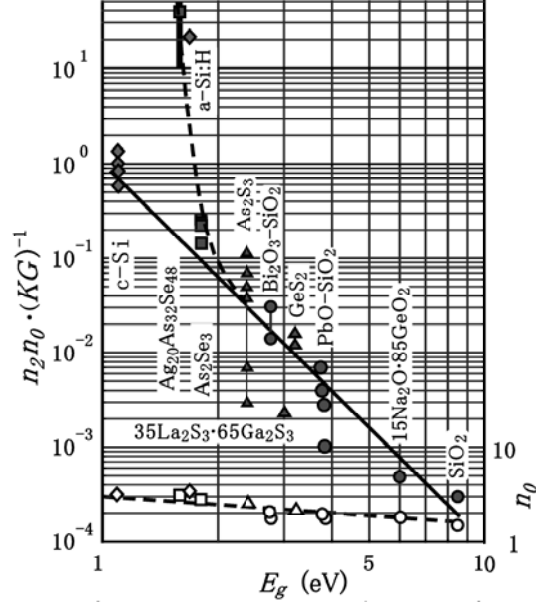

Figure 3 Relations between n_2 and E_g in oxide (circle), sulfide (triangle), selenide (square) glasses, and crystalline Si and amorphous Si:H (diamond), compared with the Sheik-Bahaes' relationship (solid line). Also shown in the lower part is the Moss rule with related data.

From these considerations, we can predict a maximal n_2 obtainable at the optical communication region of $\hbar\omega \simeq 1.6$ eV. That is, the results that a maximal n_2 is obtained at $\hbar\omega/E_g \simeq 0.5$ (Fig. 2) and at $E_g = 1.6$ eV $n_0n_2/KG \simeq 0.2$ (Fig. 3) give $n_2 \simeq 10^{-4}$ cm^2/GW. This value is smaller by two orders than those obtained for AgAsSe glass [16] and amorphous Si:H (unpublished), which can probably be ascribed to tail-state (or mid-gap) absorption, which is difficult to estimate. Probably, there seems to exist a trade-off between the absorption (α and β) and n_2. It should be underlined here that the fact that chalcogenide glasses provide greater n_2 than that in oxides such as SiO_2 at the optical communication wavelengths is just due to the appropriate, i.e. *smaller*, E_g of 1.5–3 eV.

Is this n_2 value (~10^{-4} cm^2/GW) practical for waveguide applications? Suppose an optical fiber, in which an optical path length L is 1 m and a π-radian phase-modulation is needed. Then, using $Ln_2I/\lambda = \pi$, we have $I = 10$ MW/cm^2, which corresponds to 1 W, provided that the light propagates in a core with a cross-sectional area of 10 μm^2. These conditions are now becoming a practical level of semiconductor lasers.

4. Nonlinear optical excitation

When a glass with E_g is excited by photons, a variety of photo-structural phenomena appear depending upon many factors such as photon energy, light intensity, and temperature under illumination. We here focus upon moderate exposure conditions, e.g., pulsed light with peak intensity weaker than ~1 GW/cm^2, where thermal, plasma, and multi-photon effects can be neglected. TABLE I compares photoinduced phenomena in SiO$_2$ and As$_2$S$_3$ [19]. Here, it should be emphasized that, for investigating intrinsic responses upon below-gap excitations, use of high-purity (~ppm level) samples is vitally important, which may not be satisfied in some studies.

TABLE I   Comparisons of photoinduced phenomena as a function of excitation photon energy in SiO$_2$ and As$_2$S$_3$. Core-electron excitations are excluded. The bold parts represent many studies. For abbreviations, see the text.

	SiO$_2$ ($E_g \simeq$ 9 eV)	As$_2$S$_3$ ($E_g \simeq$ 2.4 eV)
super-gap ($\hbar\omega > E_g$)	Si-Si [20], small ring [21]	photodecomposition [22]
bandgap ($\hbar\omega \simeq E_g$)	Si-Si [23]	**PD, +ΔV, +Δn (D^0 at low T) [24]**
sub-gap ($\hbar\omega < E_g$)	**-ΔV and +Δn [25] by 7.9eV** 2S excitation [26], E' centers and NBOHCs by 2P [27]	PD, +ΔV, +Δn by 2.0eV 1P excitation [28]
half-gap ($\hbar\omega \simeq E_g/2$)	**E', -ΔV and +Δn by 6.4eV photons** [25] PORs destruction by 5.0eV photons [29]	1P excitation gives no effects 2P excitation gives +Δn and As-As, but no PD [30]

Although research trends in SiO$_2$ and As$_2$S$_3$ are substantially different, reflecting different bandgap energies of ~9 eV and 2.4 eV, we can point out several interesting features. First, responses to super-gap excitations appear to resemble. It is plausible that the photons excite electrons from σ to σ^*, which can break chemical bonds such as Si-O (As-S), and exchanges of these bonds may create wrong bonds, e.g., Si-Si and O-O [20-22]. Second, bandgap excitations (Fig. 4(i)) at room temperature seem to produce markedly different effects on SiO$_2$ and As$_2$S$_3$, i.e., defect formation [23] and photodarkening (PD), respectively [24]. Hosono et al. suggest for SiO$_2$ that bandgap photons excite unstrained normal bonds ($\equiv$Si-O-Si$\equiv$), creating Si wrong bonds and interstitial oxygen as forms of peroxy-radicals (PORs, ·O-O-Si$\equiv$) and O$_2$ [31]. On the other hand, As$_2$S$_3$ exhibits the photodarkening and refractive-index increase (+Δn) and at low temperatures ($\lesssim$ 200 K) also defect (D^0) creations, which have been studied in detail [24]. However, microscopic mechanisms of the photodarkening remain speculative, because related structural modifications cannot be experimentally identifiable. There are several computer simulations, the results of which may be applicable to these excitations [32]. Interestingly, the bandgap excitations provide volume contraction (-ΔV), i.e., densification, in SiO$_2$ and expansion (+ΔV) in As$_2$S$_3$, which seems to be related with open and dense glass structures [33]. Third, for sub-gap excitations (Fig. 4(ii)), the origin of Urbach edges [9] is of

fundamental importance. Hosono and coworkers propose for SiO_2 that it is due to strained normal bonds, which are selectively excited by 7.9 eV photons and transform to pairs of E' centers ($\equiv$Si·) and non-bridging oxygen hole centers (NBOHCs, ·O-Si$\equiv$) [29,31]. In As_2S_3, intense sub-gap light (cw light of ~100 W/cm^2 with 2.0 eV) produces qualitatively the same changes as those induced by bandgap light. However, quantitatively, owing to the longer penetration depth of sub-gap light, the photoinduced volume expansion and fluidity become more prominent than those by bandgap light [28].

When a glass is excited by photons with energy of ~$E_g/2$ (half-gap excitation), we can envisage three processes [8]. These are one-photon (1P) excitation to mid-gap states (Fig. 4(iii)), which may have a functional form of Equation 1, two-step (2S) excitation, which is a successive 1P excitation through a mid-gap state, and two-photon (2P) excitation with a form of Equation 2. For SiO_2, there are many related studies using excimer lasers. For instance, several researchers suggest 5.0 eV photons provide 2P excitations on the bases of light-intensity dependence, while Kajihara *et al.* propose that the photons destroy PORs through 1P excitations [29]. However, to the authors' knowledge, no one confirms a condition for 2P excitations, $\beta I \gg \alpha$, in studies of oxide glasses On the other hand, for As_2S_3, Tanaka demonstrates that a 2P excitation, which satisfies $\beta I \gg \alpha$, increases refractive index and density of wrong bonds, but does not induce the photodarkening [30].

It should be underlined here that the half-gap excitation occurs differently in an ideal crystal and a non-crystalline solid. In the crystal, only the 2P process can occur at any places, because wave-functions extend. However, in the non-crystal, because of the existence of mid-gap states, 1P and 2S excitations occur locally at the corresponding gap states. In addition, the 2P excitation can occur resonantly and locally (Fig. 4(iv)) near the sites n which satisfy $E_{ni} - \hbar\omega \simeq 0$ in Equation 2. Accordingly, it is plausible that these half-gap excitations give rise to markedly different effects (localized and defective) from those induced by conventional 1P bandgap excitation. It should also be mentioned that these excitations have different spatial profiles in bulk samples. The 1P excitation occurs in proportion to the light intensity I, and extends to a penetration depth of ~α^{-1} from an illuminated surface. The 2P excitation is proportional to I^2 and the depth is given by $(\beta I)^{-1}$, which can produce peculiar excitation profiles, as already demonstrated in light manipulation and optical memories [2].
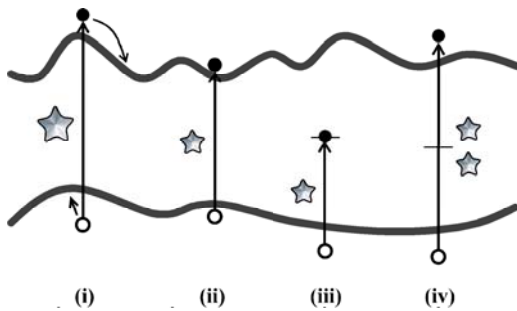

Figure 4 Schematic illustrations of (i) 1P bandgap, (ii) 1P sub-gap, (iii) 1P half-gap, and (iv) resonant 2P excitations in glasses.

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