HOKKAIDO UNIVERSITY

Title	Nonlinear optics in glasses : How can we analyze?
Author(s)	Tanaka, Keiji
Citation	Journal of Physics and Chemistry of Solids, 68(5-6), 896-900 https://doi.org/10.1016/j.jpcs.2006.11.035
Issue Date	2007-05
Doc URL	http://hdl.handle.net/2115/28800
Type	article (author version)
File Information	JPCS68-5-6.pdf

Instructions for use

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

NONLINEAR OPTICS IN GLASSES: HOW CAN WE ANALYZE?

Keiji Tanaka
Department of Applied Physics, Graduate School of Engineering, Hokkaido University,
Sapporo 060-8628, Japan

Maximal optical nonlinearity obtainable in amorphous materials at telecommunication wavelengths of ~1.5 μm is predicted. Applying a semiconductor concept, we suggest that nonlinear properties become greater in the materials with smaller optical gaps. This trend makes the chalcogenide glass such as As_2Se_3 promising for fiber devices (~1 m) including optical switches, intensity stabilizers, and stimulated Raman amplifiers. However, for integrated devices with optical path lengths of ~1 cm, greater nonlinearity is needed.

E-mail; keiji@eng.hokudai.ac.jp
Postal address; as written above
Fax number; 81(0)117166175

1. Introduction

The advent of optical-fiber communication networks progressively requires faster functional devices [1]. And, such requirements have stimulated extensive studies on all-optical devices including optical switches [2,3] and intensity stabilizers [4]. These devices, which should operate on ps time scales, need materials having high nonlinear refractive index n_2 or absorption β at optical communication wavelengths of ~1.5 μm. In addition, all-optical amplifiers need wider-band operations [5]. For such devices, amorphous materials including glasses have some advantages, since long fibers and homogeneous films with tunable compositions can be produced relatively easily. However, because of this compositional tunability, we need some guiding principles for selecting suitable nonlinear materials.

So far many empirical relations have been proposed for optical nonlinearities [2,6,7], which may be divided into two categories. In treating the glass as an insulator, the most famous is the Bolings' relation, $n_2 \propto (n_0 - 1)/\nu^{5/4}$ [2,8], which connects n_2 to the linear refractive index n_0 and the Abbe number ν. On the other hand, chemical-bond relations have also been proposed; e.g., $n_2 \propto \alpha_c^5 (5\alpha_p^2 - 1)$, where α_c and α_p are covalency and polarity of

atomic bonds [6]. In addition, several kinds of computer calculations have been performed recently [9,10].

However, alternative ideas may be valuable, since most of these treatments neglect spectral dependence and some are computational. In addition, n_0 is relatively difficult to measure. Relations including the bandgap energy E_g, which can be estimated easily from transmission measurements, will be more useful.

In the present work, therefore, we apply a concept developed for crystalline semiconductors by Sheik-Bahae and coworkers [11,12] to non-crystalline solids. It is shown that the concept can work as rough approximations in these materials as well. The result suggests that the maximal n_2 and β at communication wavelengths, ~1.5 μm, in transparent solids are ~10^{-4} cm^2/GW and ~10^1 cm/GW, which are obtained in As_2Se_3 glass. We will discuss if these values are practically sufficient to nonlinear devices. Stimulated Raman-scattering is also considered.

2. Theoretical background

Figure 1 shows spectral dependences of optical properties in direct- (solid lines) and indirect-gap (dashed lines) crystalline semiconductors with energy gap of E_g. The linear absorption α shows the known spectral dependence approximately proportional to $(\hbar\omega - E_g)^\delta$, where δ is 1/2 and 2 for direct- and indirect-gap semiconductors. The absorptions then give dispersion spectra of linear refractive index n_0, which can be calculated using a Kramers-Krönig relation. On the other hand, nonlinear absorption β and refractive-index n_2 spectra can be calculated in similar ways [2,11-14]. We see that the overall shapes appear to be similar to those of the linear, while the horizontal positions shift to ~ $\hbar\omega/2$ regions of the linear spectra. Here, the factor of 1/2 manifests that both β and n_2 are governed by two-photon absorption. We also see that β and n_2 give broad peaks at around $\hbar\omega \approx 0.7E_g$, and, at $\hbar\omega \approx E_g/2$, $\beta = 0$ and n_2 is great (or nearly maximal in direct-gap semiconductors).

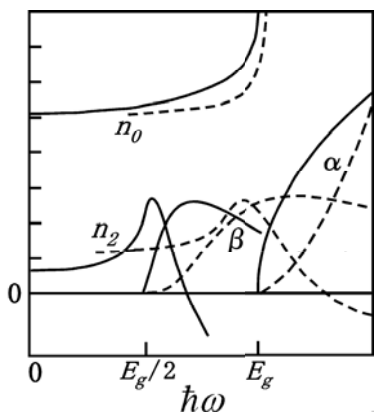

Fig. 1. Spectral variations of linear (n_0 and α) and nonlinear (n_2 and β) absorptions (α and β) and refractive indices (n_0 and n_2) in direct- (solid lines) and indirect-gap (dashed lines) crystalline semiconductors with energy gap of E_g. Vertical scales are arbitrary.

Similar spectral features can be assumed for amorphous semiconductors. As is known, α in most of amorphous semiconductors having non-direct gaps shows also spectral dependence of $\delta = 2$ [15], which resembles that in indirect-gap semiconductors. Here, static disorders in amorphous semiconductors and phonons in indirect-gap semiconductors appear to exert similar influences upon photo-electronic excitation. Accordingly, it is tempting to assume that amorphous semiconductors and disordered insulators possess similar linear and nonlinear spectra to those in the crystals. That is, the following idea will be applied to all the insulators, in which photo-electronic absorptions are governed by valence and conduction bands, not by molecular or atomic levels. Rigorous analyses remain.

Sheik-Bahae and coworkers have derived universal relationships for optical nonlinearities in direct-gap semiconductors with E_g [11,12]. That is,

$$n_2 = K' E_p^{1/2} G/(n_0^2 E_g^4), \quad (1)$$

$$\beta = K E_p^{1/2} F/(n_0^2 E_g^3), \quad (2)$$

where K' (= 0.06 cm^2· GW^{-1}· eV$^{7/2}$), K (= 3100 cm· GW^{-1}· eV$^{5/2}$), E_p (≈ 21 eV, Kane energy), and spectral functions $G(\hbar\omega/E_g)$ and $F(\hbar\omega/E_g)$, are all material-independent and uniquely determined. Material properties appear only in n_0 and E_g. In deriving these equations, basic assumptions they made are quantum-mechanical formulations, Kramers-Krönig relations, and simple band structures for crystalline semiconductors. We see that both n_2 and β are strongly dependent upon E_g as $n_2 \propto 1/E_g^4$ and $\beta \propto 1/E_g^3$. Effects due to n_0 (≈ 1.5~3) are secondary. Or, upon inserting the Moss rule, $n_0 \approx 3/E_g^{1/4}$ [16] (see, Fig. 3a), in to these equations, the nonlinearity is determined completely by E_g.

Sheik-Bahae and coworkers have also demonstrated good agreements, with accuracy of ~50%, between these theoretical results and experimental data for direct- and indirect-gap crystalline materials with $E_g \simeq$ 1~10 eV [11,12]. This agreement, obtained also in the indirect-gap semiconductors, suggests that detailed electronic structures do not affect gross features of the nonlinearity. It is then tempting to apply these relations to non-crystalline solids.

Here, it is interesting to mention the following two: One is that the linear properties, α and n_0 values, do not exhibit such strong dependences ($n_2 \propto 1/E_g^4$ and $\beta \propto 1/E_g^3$) upon E_g. For instance, $\alpha \lesssim 10^6$ cm^{-1} in both SiO_2 ($E_g \simeq$ 9 eV) and As_2Te_3 ($E_g \simeq$ 0.8 eV) [15]. And, as shown in the Moss rule [16], n_0 is weakly (-1/4) dependent upon E_g. The strong dependence of the

nonlinear properties on E_g is attributable to the second-order transition probability, since the convolution integrals of densities-of-states have nearly common forms in linear and nonlinear absorptions [14]. The other is that similar strong dependences ($\chi^{(3)} \propto 1/E_g^6$) of optical nonlinearity upon E_g are pointed out also for series of organic molecules [17].

3. Comparison

Fig. 2 compares the theoretical nonlinear spectra, G and F, with reported n_2 and β values [18-33] for non-crystalline solids. For some materials, data obtained at different $\hbar\omega$ are included. Here, for E_g on the horizontal axis, we take the so-called Tauc optical gap [15] in case it is known or (estimated) photon energy at $\alpha \simeq 10^3$ cm^{-1} when the gap being unknown, which is the conventional way [15]. We see that the experimental data are located at around the theoretical curves, which manifests semi-quantitative agreements. That is, the semiconductor concept seems to be applied as a rough approximation to glasses and amorphous films.

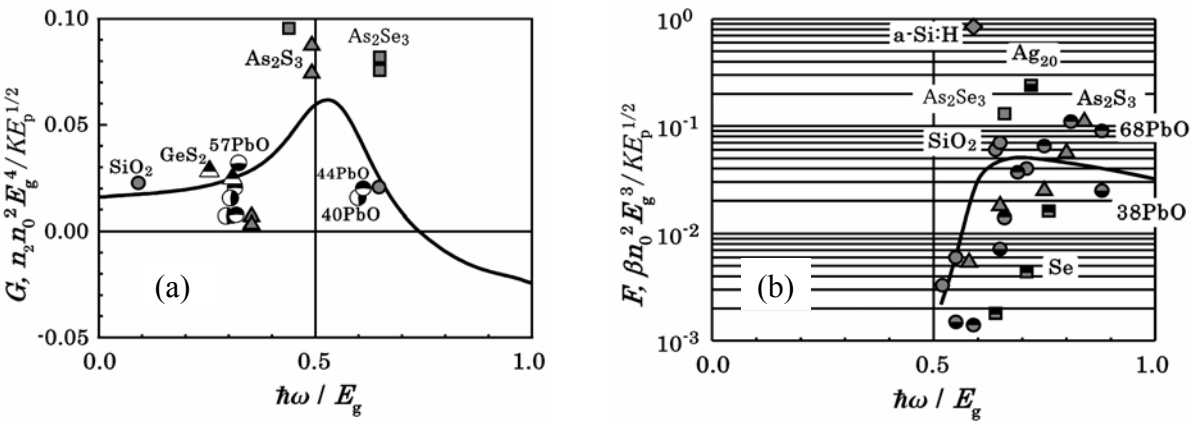

Fig. 2 Comparisons between theoretical spectra (solid lines), (a) $G(\hbar\omega/E_g)$ and (b) $F(\hbar\omega/E_g)$, and experimental data, (a) $n_2 n_0^2 E_g^4/(KE_p^{1/2})$ and (b) $\beta n_0^2 E_g^3/(KE_p^{1/2})$, in oxide (circles), sulfide (triangles), selenide (squares) glasses, and amorphous Si:H. xPbO-(100-x)SiO_2 and $Ag_{20}As_{32}Se_{48}$ glasses are abbreviated as xPbO and Ag_{20}.

Fig. 3 compares the Sheik-Bahaes' relations, $n_2 n_0^2/(KE_p^{1/2}G) = 1/E_g^4$ and $\beta n_0^2/(KE_p^{1/2}F) = 1/E_g^3$, with experimental data for non-crystalline solids [18-33]. Here, for most of the materials with $E_g \gtrsim 2$ eV, we see rough agreements. In specific, n_2 shows better agreements, which is reasonable since the refractive index is governed by total absorption, being relatively insensitive to detailed absorption spectra. However, we also see some marked deviations. Amorphous Si:H and Ag-As-Se with $E_g \approx 1.7$ eV give substantially greater n_2 and β, which

can be ascribed to tail-state effects, since these results are evaluated at a photon energy of $\hbar\omega \approx 1.3$ eV, just below the absorption edges [25,32]. Also in (b), Se shows appreciably smaller β [33], which may be attributable to the one-dimensional molecular structure [15]. It should be mentioned here that, as shown in the lower part of (a), the Moss rule $n_0 \approx 3/E_g^{1/4}$ [16] is satisfied in the solids of interest.

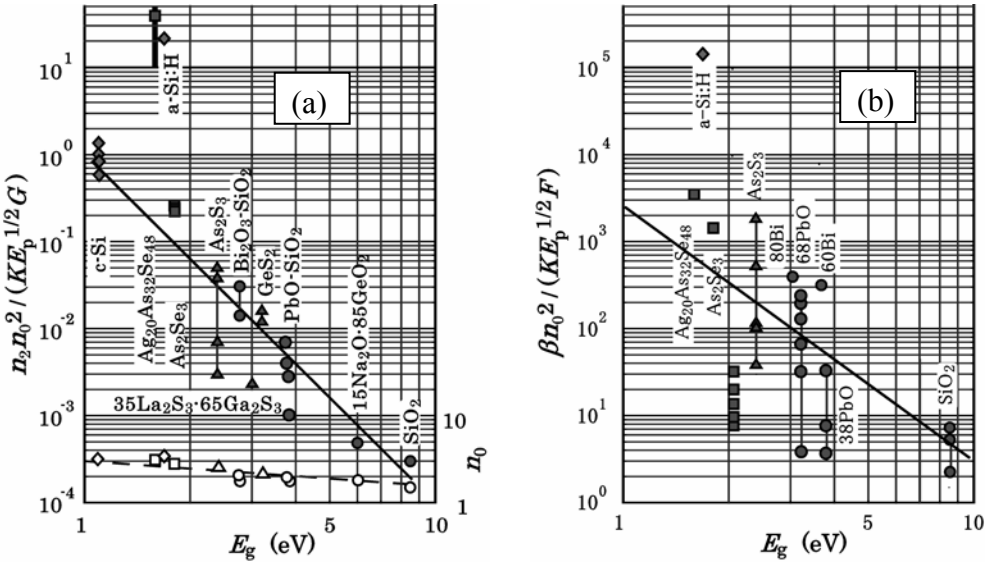

Fig. 3. Comparisons of the Sheik-Bahaes' relations (solid lines), (a) $n_2 \sim 1/E_g^4$ and (b) $\beta \sim 1/E_g^3$, with reported data for several glasses and a-Si:H and. As a reference, results [34-36] on crystalline Si are also included in (a). Several data points for single materials come from different references and/or wavelengths. In (a), lower open data with the right-hand side scale show the Moss rule.

4. Maximal nonlinearity

From Figs. 1 and 3, we can estimate maximal nonlinear values obtainable at optical communication wavelengths. Since the spectral peaks appear at around $0.5E_g$ - $0.9E_g$ (Fig. 1) and these peaks should be located at the wavelengths of ~1.5 μm (~0.8 eV) for nonlinear applications, we expect that the materials with $E_g \approx 1.0$~1.6 eV are suitable. However, in many applications, materials with slightly wider gaps (~1.8 eV) seems to be preferred, since tail states tend to limit optical transparency in non-crystalline solids [15]. Then, Fig. 3(a) suggests that the nonlinear refractivity in such materials satisfies $n_2n_0^2/(KE_p^{1/2}G) \approx 10^{-1}$, which gives $n_2 \approx 10^{-4}$ cm^2/GW. In a similar way, we see that $\beta n_0^2/(KE_p^{1/2}F) \approx 10^3$, which leads to $\beta \approx 10^1$ cm/GW. These values have been obtained in chalcogenide glasses with $E_g \approx 1.8$ eV, such as As_2Se_3 [22,24-26] and Ge-As-Se [22, 27-29].

Are these nonlinear values practical? Suppose an all-optical switch with Mach-Zehnder

type interferometers [3] consisting of optical fibers, in which an optical path length L is 1 m and a π-radian phase-modulation is needed for switching. Then, using $Ln_2I/\lambda = \pi$ and $n_2 \approx 10^{-4}$ cm^2/GW, we have I = 10 MW/cm^2, which corresponds to 1 W for a fiber with a core cross-sectional area of 10 μm^2. This light intensity is now becoming an attainable level of semiconductor lasers. On the other hand, under this light intensity and $\beta \approx 10^1$ cm/GW, we obtain $\beta I \approx 0.1$ cm^{-1}, which can produce in a 1-m fiber an intensity-dependent absorption of $\exp(-10) \approx 10^{-5}$, which may be sufficient for intensity stabilizers. These results suggest that chalcogenide-glass fibers are promising for nonlinear devices at ~1.5 μm.

These nonlinear values, however, may be insufficient for applications to optical integrated circuits. Since light propagation lengths in such devices are limited to, at most, ~1 cm, we need materials having greater nonlinearities by two orders. Fig. 3 may suggest that candidates for these devices are smaller gap materials (1.6-1.8 eV), a-Si:H films and Ag(Cu)-As(Ge)-Se glasses. However, these materials exhibit appreciable linear absorptions of 1-10 cm^{-1} at ~1.5 μm, which arise from *intrinsic* tail states [15,37]. It is plausible that the tail states affect also the nonlinear properties through resonant two-photon and two-step absorptions [14]. Therefore, when designing real device structures and performances, evaluations using several kinds of figure-of-merits [14] will be required for respective materials. Alternatively, we may utilize inhomogeneous systems such as particle-doped materials or photonic crystals, for which further studies are needed for obtaining high and fast-response nonlinearities at the wavelength of ~1.5 μm.

5. Stimulated Raman-scattering

Stimulated Raman-scattering [38] appears to be promising for wide-band optical amplifications [39-41]. Since Raman scattering is also a two-photon process as the two-photon absorption, the transition probability can be calculated following the conventional perturbation theory. In addition, for obtaining high amplifying gain, which is governed by Raman-scattering efficiency, resonant Raman-scattering is favored, which has a cross section approximately proportional to $1/(E_g - \hbar\omega)^\gamma$, where $\gamma \approx 1 \sim 3$ depending upon types (deformation potential or Frőhlich) of electron-lattice interactions [42].

This resonant Raman-scattering can provide an explanation to known observations. That is, the chalcogenide exhibits greater Raman gain by 2-3 orders of magnitude than that of silica glasses [39-41]. This gain ratio can be interpreted as a power of bandgap ratio, $(9eV/1.8eV)^3 \approx 10^2$, using the optical gaps of SiO_2 and As_2Se_3 [15] and temporally $\gamma = 3$. In short, we can assume that the chalcogenide glass is useful also to the Raman amplifier.

6. Summary

It has been demonstrated that the optical gap is a decisive parameter determining nonlinear optical properties in non-crystalline solids. A reason why the chalcogenide glass is superior to the oxide and halide glasses for nonlinear applications at the wavelengths of ~1.5 μm can be ascribed to the smaller optical gap. Among the chalcogenide, As_2Se_3 and Ge-As-Se with $E_g \approx 1.8$ eV seem to be the best choices for nonlinear fibers. For optical integrated devices with optical path lengths of ~1 cm, further studies are needed for obtaining higher nonlinearities. For practical applications, however, suppression of light reflections between chalcogenide devices and silica fibers by some means [43] is necessary.

The author would like to thank Dr. A. Saitoh for critical reading of this manuscript.

References

1. T. Kamiya and M. Tsuchiya, Jpn. J. Appl. Phys. 44 (2005) 5875.
2. R.W. Boyd, Nonlinear Optics 2nd Ed. (Academic Press, San Diego, 2003).
3. B. Bureau, X. H. Zhang, F. Smektala, J.-L. Adam, J. Troles, H.-L. Ma, C. Boussard-Plèdel, J. Lucas, P. Lucas, D. Le Coq, M. R. Riley and J. H. Simmons, J. Non-Cryst. Solids 345-346 (2004) 276.
4. Y.P. Sun and J.E. Riggs, Inter. Rev. Phys. Chem. 18 (1999) 43.
5. M.R.E. Lamont, M. Rochette, D.J. Moss, and B.J. Eggleton, IEEE Photonics Technol. Lett. 18 (2006) 1185.
6. V. Dimitrov and S. Sakka, J. Appl. Phys. 79 (1996) 1741.
7. H. Tichá and L. Tichý, J. Optoelectron. Adv. Mater. 4 (2002) 381.
8. N.L. Boling, A.J. Glass, and A. Owyoung, IEEE Quantum Electron. QE-14 (1978) 601.
9. D. Hobbs, D. Weaire, S. McMurry, and O. Zuchuat, J. Phys.: Condens. Matter 8 (1996) 4691.
10. S. Suehara, T. Konishi, and S. Inoue, Phys. Rev. B 73 (2006) 92203.
11. M. Sheik-Bahae, D.J. Hagan, and E.W. Van Stryland, Phys. Rev. Lett. 65 (1990) 96.
12. M. Sheik-Bahae and E.W. Van Stryland, in Semiconductors and Semimetals, eds. E. Garmire and A. Kost (Academic Press, San Diego, 1999) Vol. 58, Chap. 4.
13. M. Dinu, IEEE J. Quantum Electron. 39 (2003) 1498.
14. K. Tanaka, J. Mater. Sci. 16 (2005) 633.
15. N.F. Mott and E.A. Davis, Electronic Processes in Non-Crystalline Materials (Clarendon Press, Oxford, 1979).
16. T.S. Moss, Optical Properties of Semi-conductors (Butterworths Science Publisher, London, 1959) p. 48.
17. H. Kishida, K. Hirota, T. Wakabayashi, H. Okamoto, H. Kokubo, and T. Yamamoto, Appl. Phys. Lett. 87 (2005) 121902.
18. S.R. Friberg and P.W. Smith, IEEE J. Quantum Electron. QE-23 (1987) 2089:
19. Y. Watanabe and T. Tsuchiya, J. Non-Cryst. Solids 210 (1997) 55.
20. K.S. Bindra, H.T. Bookey, A.K. Kar, B.S. Wherrett, X. Liu, and A. Jha, Appl. Phys. Lett. 79 (2001) 1939.
21. A. Jha, X. Liu, A.K. Kar, and H.T. Bookey, Curr. Opinion Sol. St. Mater. Sci. 5 (2001) 475.
22. J. Troles, F. Smektala, G. Boudebs, A. Monteil, B. Bureau, and J. Lucas, Opt. Mater. 25 (2004) 231.
23. A. Dragonmir, J.G. Mclnerney, and D.N. Nikogosyan, Appl. Opt. 41 (2002) 4365.

24. J. Requejo-Isidro, A.K. Mairaj, V. Pruneri, D.W. Hewak, M.C. Netti, and J.J. Baumberg, J. Non-Cryst. Solids 317 (2003) 241.
25. K. Ogusu, J. Yamasaki, S. Maeda, M. Kitao, and M. Minakata, Opt. Lett. 29 (2004) 265:
26. L. Fu, A. Fuerbach, I.C.M. Littler, and B.J. Eggleton, Appl. Phys. Lett. 88 (2006) 81116.
27. J.M. Harbold, F.O. Ilday, F.W. Wise, and B.G. Aitken, IEEE Photonics Technol. Lett. 14 (2002) 822.
28. J.T. Gopinath, M. Soljacic, E.P. Ippen, V.N. Fuflyigin, W.A. King, and M. Shurgalin, J. Appl. Phys. 96 (2004) 6931.
29. A. Zakery and M. Hatami, J. Opt. Soc. Am. B 22 (2005) 591.
30. K. Tanaka, Appl. Phys. Lett. 80 (2002) 177.
31. K. Tanaka and N. Minamikawa, Appl. Phys. Lett. 86 (2005) 12112.
32. N. Minamikawa and K. Tanaka, Jpn. J. Appl. Phys. 45 (2006) L960.
33. Tanaka, unpublished.
34. H.K. Tsang, C.S. Wong, T.K. Liang, I.E. Day, S.W. Roberts, A. Harpin, J. Drake, and M. Asghari, Appl. Phys. Lett. 80 (2002) 416.
35. G.W. Rieger, K.S. Virk, and J.F. Young, Appl. Phys. Lett. 84 (2004) 900.
36. H. Yamada, M. Shirane, T. Chu, H. Yokoyama, S. Ishida, and Y. Arakawa, Jpn. J. Appl. Phys. 44 (2005) 6541.
37. K. Tanaka, J. Optoelectron. Adv. Mater. 4 (2002) 505.
38. R.W. Hellwarth, Phys. Rev. 130 (1963) 1850.
39. J. Bromage, J. Lightwave Technol. 22 (2004) 79.
40. R.E. Slusher, G. Lenz, J. Hodelin, J. Sanghera, L.B. Shaw, and I.D. Aggarwal, J. Opt. Soc. Am. B 21 (2004) 1146.
41. S.D. Jackson and G. Anzueto-Sànchez, Appl. Phys. Lett. 88 (2006) 221106.
42. R.M. Martin, Phys. Rev. B 4 (1971) 3676.
43. C. Grillet, C. Smith, D. Freeman, S. Madden, B. Luther-Davis, E.C. Magi, D.J. Moss, and B.J. Eggleton, Opt. Exp. 14 (2006) 1070.