Optical nonlinearity in chalcogenide glasses for near-infrared all-optical devices

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We consider tactics for attaining maximal optical nonlinearity at telecommunication wavelengths of 1.5 μm ($\hbar\omega \approx 0.8$ eV). The nonlinearity becomes greater in a material with a smaller optical gap, but it must be wider than ~1 eV for needed transparency. This trade-off makes the chalcogenide glass suitable for fiber devices (~1 m), including optical switches and intensity stabilizers. However, for waveguide devices with optical path lengths of ~1 cm, greater nonlinearity is required. We propose Se-loaded zeolites, which possess greater intensity-dependent nonlinear coefficients than those of pure Se by three orders of magnitude, is promising for this purpose.

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1. Introduction

With developments of optical fibers and peripheral devices, the optical nonlinearity in photonics glasses has attracted growing scientific and technological interests [1]. This is because the nonlinearity in glasses, though the magnitude being smaller than that in selected crystals [2], appears feasible for optical fibers due to long propagation distances. In addition, the glass has a variety of compositions with refractive indices of 1.4 - 3.2 at near-infrared wavelengths [3], from which we can select appropriate ones. Actually, in a pioneering work, Asobe *et al.* have demonstrated that As_2S_3 glass fibers with lengths of ~0.5 m work as all-optical switches [4].

Recently, our interest is shifting to nonlinear optical waveguides [5-7]. Naturally, the waveguide will afford more compact all-optical active devices, which will be integrated with passive components. In addition, if the optical path length can be shortened to 1 cm, the response time (light propagation time) becomes faster to ~100 ps, which will afford faster modulations. However, for such devices, we require a material having greater nonlinear coefficients.

We then are interested in the maximal optical nonlinearity obtainable in glasses at the telecommunication wavelengths of ~1.5 μm. What kinds of glasses exhibit high nonlinearity? Or, if the nonlinearity is insufficient for the compact devices, what are the alternatives? In the present work, we will try to find some answers to these problems.

2. Perspective

Fig. 1 shows relationships between the intensity-dependent nonlinear refractive and absorptive coefficients, n_2 and β, and needed light intensity I for complete modulations.

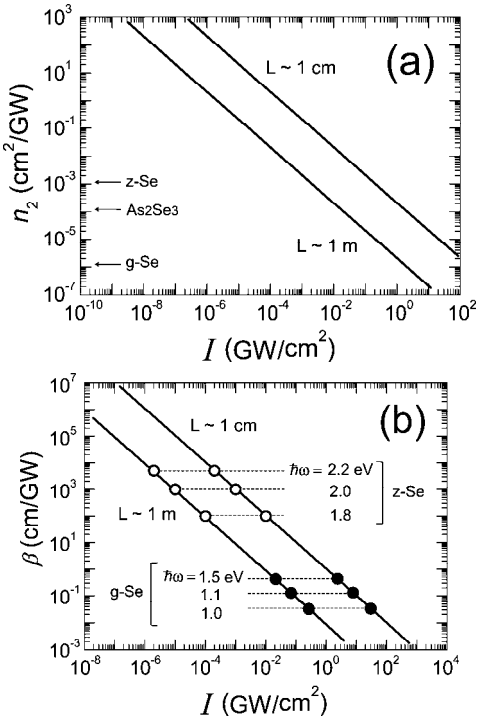

Fig. 1. Light intensities I needed for complete modulations using (a) refractive and (b) absorptive nonlinearities, with reported values of the materials indicated. The lines delineate the conditions of (a) $Ln_2I/\lambda \approx \pi$ at $\lambda = 1.5$ μm and (b) $\beta I \approx L^{-1}$ for devices having light-propagation lengths of L = 1 cm and 1 m.

In Fig.1 (a), we envisage an all-optical switch with interferometer types, for which the condition $Ln_2I/\lambda \approx \pi$ must be satisfied for the phase switching. Then, for a fiber

with a length of L = 1 m and a core cross-sectional area of 10 μm^2 and a light source with λ = 1.5 μm emitting 1 W (I = 10^{-2} GW/cm^2), which is now available using laser diodes, we need a material having $n_2 \approx 10^{-4}$ cm^2/GW. If the length is reduced to 1 cm, naturally, the material must have a greater n_2 (~10^{-2} cm^2/GW) by two orders of magnitude. In Fig. 1 (b), we envisage an intensity stabilizer which satisfies a condition of $\beta I \approx L^{-1}$. For I = 10^{-2} GW/cm^2, we need the materials of β = 10^0 ~ 10^2 cm/GW for devices with L = 1 m ~ 1 cm. How can we obtain these target n_2 and β values?

3. Results and discussion

Several semi-empirical relationships have been proposed for estimating optical nonlinearity [2]. Such relations are useful, since measurements of nonlinear optical constants are more difficult than those of linear constants.

Among the relations, the most famous may be the one derived by Boling *et al.* for (oxide) glasses [8];

$$n_2\ (10^{-13}\ \text{esu}) \approx 391(n_d - 1)/v_d^{\,5/4}, \quad (1)$$

where n_d is the refractive index at the d-line (λ = 588 nm) and v_d is the Abbe number. This relation contains only these two parameters, which can be evaluated for conventional glasses, and accordingly, it has been frequently utilized for estimations of n_2. It actually provides good approximations for small n_d glasses with $n_d \leq 1.7$ [2, 8]. However, in this equation, the glass is assumed to be transparent, and the estimated n_2 can be regarded as the value obtained at a long-wavelength limit. Consideration of the absorption and the nonlinearity is needed for finding a material working at the communication wavelength.

Sheik-Bahae *et al.* have theoretically studied the optical nonlinearity in crystalline semiconductors [9, 10]. They connect n_2 and β with the optical gap E_g;

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

and

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

where K' (≈ 0.06 cm^{2}GW^{-1}eV$^{7/2}$) and K (≈ 3100 cmGW^{-1}eV$^{5/2}$) are constants, E_p (≈ 21 eV) is the so-called Kane energy, and $G(\hbar\omega/E_g)$ and $F(\hbar\omega/E_g)$ represent spectral functions. Note that these relations have been obtained for semiconductor crystals having direct energy-gaps. For indirect-gap semiconductors, some modification, taking phonon-assisted transitions into account, is needed [11]. However, it has been demonstrated that the relations (2) and (3) give satisfactory agreements to experimental results reported for semiconductor and insulator crystals having energy gaps of 1–10 eV, irrespective of direct and indirect transitions.

Tanaka has demonstrated that Sheik-Bahaes' relations are useful also for non-crystalline solids [12], which have non-direct energy gaps [13]. The results are shown in Figs. 2 and 3, with the solid lines representing Equations 2 and 3, which include several new data [14, 15]. Here, for E_g on the horizontal axis, we take the so-called Tauc optical gap (in case it is known) or the estimated photon energy at the absorption coefficient of 10^3 cm^{-1} [12]. Figure 2 also shows that the so-called Moss rule $n_0 \approx 3/E_g^{\,1/4}$ [16] gives good approximations for the solids of interest. Using the Moss rule and Equation (2), we can estimate n_0 and n_2 only from E_g, which can be easily estimated from optical transmission spectra.

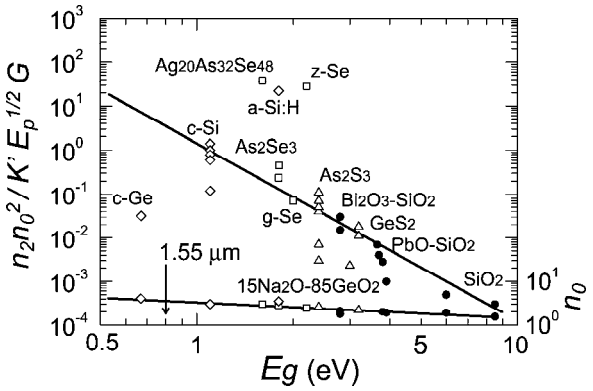

Fig. 2. Comparison of the Sheik-Bahae's relation of $n_2 \sim 1/E_g^{\,4}$ with reported data for several glasses, a-Si:H films, z-Se, c-Si, and c-Ge. The lower line with the right-hand side scale shows the Moss rule [16]. Solid circles are for oxide glasses, and triangles and squares are for sulfide glasses and for selenide glasses and Se-loaded zeolite (z-Se), respectively. Diamonds are also for crystalline silicon and germanium.

We see in Figs. 2 and 3 that the agreements between experimental data and the theoretical lines, given by Equations (1) and (2), are acceptable, but not so good as those in crystalline materials [9, 17]. The worse agreement in non-crystalline solids may be due to non-ideal bandgap structures and quasi-stable (non-equilibrium) physical properties. Specifically, the deviations of amorphous (a-)Si:H films and glassy (g-)$Ag_{20}As_{32}Se_{48}$ are appreciable. (Discussion for z-Se is given later.) A-Si:H films give substantially greater n_2 and β, which may be ascribed to effects arising from tail states, since the results are evaluated at a photon energy of ~1.3 eV, just below the absorption edge of ~1.7 eV [18, 19]. The same reasoning may be applied to g-$Ag_{20}As_{32}Se_{48}$. In addition, the Ag-chalcogenide glass is susceptible to illumination effects [20], and accordingly, practical uses will be difficult. We here note that, although the conventional chalcogenide glass as As_2S_3 also undergoes photoinduced effects upon illumination of mid-gap light [21], the effect seems to be much less than that in Ag-chalcogenides. Finally, the exceptionally small β value in g-Se in Fig. 3

may arise from the unique absorption spectrum reflecting one-dimensional atomic structures [13].

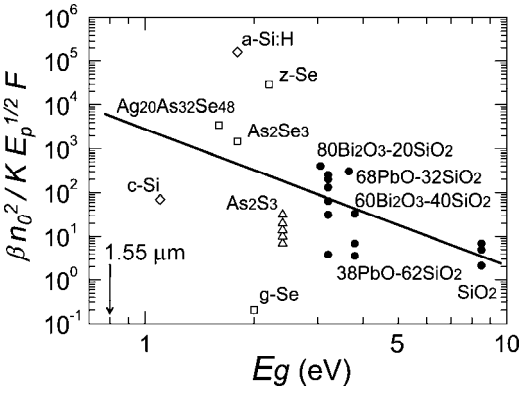

Fig. 3. Comparison of the Sheik-Bahae's relation of $\beta \sim 1/E_g^3$ with reported data for several glasses. For the symbols, see Fig. 2.

From Figs. 2 and 3, we obtain valuable insights. Under neglecting the deviated data, the maximal nonlinearity obtainable at the optical communication wavelength is $n_2 n_0^2/(K' E_p^{1/2} G) \approx 10^{-1}$, which gives $n_2 \approx 10^{-3}$ cm^2/GW. In a similar way, $\beta n_0^2/(K E_p^{1/2} F) \approx 10^3$, which leads $\beta \approx 10^4$ cm/GW. Note that these values are irrespective of atomic structures, crystalline or non-crystalline, being applicable to all homogeneous materials. Indeed, these values have been obtained in chalcogenide glasses with $E_g \approx 1.8$ eV, as As_2Se_3 [22-25] and Ge-As-Se [18, 24, 26, 27]. We here note that it seems difficult to employ tellurides such as As_2Te_3 and $Ge_2Sb_2Te_5$ as nonlinear materials at the communication wavelength, since the energy gap is smaller ($E_g \approx 1.0$ eV), thermal properties are less stable, and the glass tends to exhibits free-carrier absorption [28].

Comparing Fig. 1 and Figs. 2 and 3, we see substantial differences in magnitude. The maximal nonlinearities practically obtained, $n_2 \approx 10^{-3}$ cm^2/GW and $\beta \approx 10^1$ cm/GW, are insufficient by *one order* for fabricating nonlinear devices having a propagation length of ~1 cm operating under the irradiance of 10^{-2} GW/cm^2. Such differences may be overcome using crystalline semiconductors having sharp energy gaps of ~1 eV, as Si and InP. By contrast, it seems difficult to attain higher nonlinearity using homogeneous non-crystalline materials that are fairly transparent at the wavelength of ~1.5 μm. In addition, we should note that a material having smaller E_g is likely to be thermally unstable; *i.e.*, the glass-transition temperature in a glass and the melting temperature in a crystal becoming lower. Accordingly, the material is likely to be damaged under intense light pulses. Therefore, for producing a nonlinear waveguide, we should shift our target to inhomogeneous, heterogeneous, or structure-modulated materials such as dye-doped polymers [29], particle-doped inorganic media [30, 31], photonic crystals [32], or chalcogen-zeolite systems [14].

Among these materials, the nonlinearity of chalcogen-zeolite systems has been least studied. Nevertheless, a preliminary study by the authors for a zeolite, sub-mm size ZSM-5 crystals, has demonstrated promising features [14]. They have incorporated the three kinds of chalcogen, S, Se, and Te into ZSM-5 (abbreviated as z-S etc.) from gas phases [33], among which z-Se exhibits the most interesting properties. The reasons why they selected ZSM-5 as a host for chalcogen are two-folds. One is that recent studies produced sub-millimeter size ZSM-5 single crystals [34], which are suitable to optical applications. The other is that ZSM-5 is a relatively covalent zeolite, so that we can expect small interaction between the chalcogen and the host, which may be favorable to enhance the nonlinearity through quantum-well effects.

As plotted in Figs. 2 and 3, the obtained values are promising. We see n_2 and β in z-Se reach to 10^{-3} cm^2/GW at near infrared (λ = 1.06 μm) and 10^3 cm/GW at visible wavelengths [14, 35]. Putting these values into Equations (1) and (2), we acquire the $n_2 n_0^2/(K' E_p^{1/2} G)$ and $\beta n_0^2/(K E_p^{1/2} F)$ values, as plotted in Figs. 2 and 3. We here note that the content of Se atoms in z-Se is just ~10^{20}/cm^3 [36], which is smaller by two orders than that (~10^{22}/cm^3) in pure g-Se. In addition, z-Se shows a wider optical gap of ~2.2 eV. Despite of these features, the n_2 and β values in z-Se are greater (by three orders) than those of g-Se. (n_2 in g-Se could not be evaluated due to laser damages, which suggested a substantially smaller value.) This enhancement may be ascribed to quantum-well effects, which remain to be studied. Taking the target n_2 value (~10^{-2} cm^2/GW) shown in Fig. 1 into account, we believe that z-Se is one of the solution for nonlinear waveguides.

However, further studies are needed for developing practical uses of the nonlinearity of zeolite systems. For instance, the loading of Se into ZSM-5 crystals has not been reproducible, despite of many trials [36]. Se-loaded samples are foggy, causing substantial light scattering. And, even in a single loading reaction employing ZSM-5 crystals of ~10^3 pieces, z-Se samples showed different colors of yellow, orange and brown [14]. Corresponding to this color change, the Se content and the nonlinear absorption seemed to vary. These results may be ascribed to non-ideal ZSM-5 crystals containing minute cracks, irregular pores, impurities, and so forth. Another problem is a method of light coupling to z-Se samples. Specifically, we must device a method of coupling light from an optical fiber to the ZSM-5 crystal, which has unique external shapes [34]. In addition, studies for other kinds of zeolites will be interesting.

4. Conclusion

It has been demonstrated that the optical gap is a decisive parameter determining nonlinear optical

properties in homogeneous media. A reason why the chalcogenide glass is superior to the oxide glasses in nonlinear applications at the wavelengths of 1.5 μm can be ascribed to the smaller optical gap. Among the chalcogenides, As_2Se_3 with E_g ~1.8 eV seems to be the best choice for nonlinear optical fibers. However, for waveguides with a propagation length of ~1 cm, the nonlinearity may be still insufficient.

Se-loaded ZSM-5 can be a candidate for compact nonlinear devices. Its nonlinear optical constants are much greater than those in glassy Se. Taking the wider optical gap in z-Se than that in glassy Se, we expect that other chalcogen-zeolite systems will also exhibit promising nonlinearities.

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