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Two-photon optical absorption in PbO-SiO$_2$ glasses

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One- and two-photon absorption spectra in PbO-SiO$_2$ glasses have been studied comparatively as a function of the PbO content. The two spectra show different composition dependence, which can be accounted for by taking related electronic wave functions and the densities-of-states into account. This interpretation can be extended to understand high optical nonlinearity in heavy-metal oxide glasses. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1618929]

In contrast to extensive studies for crystalline materials,[1] the two-photon absorption in glasses remains to be studied further. Specifically, most previous work investigates two-photon absorption coefficients at selected wavelengths.[2–7] Spectral studies are fewer,[8–10] and interpretation of the spectra has been preliminary, taking into account only the density-of-states, while neglecting the role of transition amplitudes. However, since the transition amplitudes of one- and two-photon absorption are contrastive,[1] parallel studies on both absorptions can provide unified insights into optical absorption mechanisms, which are still ambiguous in disordered materials.[11] In addition, the study may lead to production of glassy materials having high optical nonlinearities, which will be promising for optical functional devices, such as optical power stabilizers and so forth.[12]

In the present work, therefore, we will investigate comparatively one- and two-photon optical absorption spectra of PbO-SiO$_2$ glasses. This glass system has been selected, since it has a wide glass-forming region[13] suitable for compositional studies. In addition, optical properties are relatively simple, in which the optical absorption edge is governed by electronic transitions in Pb atoms.[14,15] In addition, the glass exhibits interesting optical properties, such as marked photochromic effects,[16–18] large photosensitivity,[19] and high nonlinear refractivity[20–23] including second-order nonlinearity.[24,25] However, the origins of these phenomena have not yet been understood satisfactorily, and some fundamental insights will be valuable.

Glass ingots of $x\mathrm{PbO}\text{-}(100-x)\mathrm{SiO}_2$, where $x=38\sim68$, were prepared through the conventional melt-quenching technique. The melts with appropriate compositions were held at 700–1200 °C for 2 h, and then quenched on to an iron plate held at room temperature. The ingots were then annealed at glass-transition temperatures (380–500 °C) for 1.5 h. The annealed ingots were noncrystalline under x-ray inspection, and impurities included were less than 0.05 wt %, of which the most noticeable was Na. A photoemission measurement of the valence band using powdered samples gave spectra similar to those reported previously.[15,26,27] The ingots were sliced, and polished to a thickness of 0.5–50 mm. Optical transmittances $T(\hbar\omega)$ were measured using a spectrometer (JASCO, V-570S), and one-photon absorption spectra $\alpha(\hbar\omega)$ were calculated through the conventional procedure. On the other hand, two-photon absorption spectra $\beta(\hbar\omega)$ were evaluated using a pulsed laser system consisting of a Nd:YAG laser (Continuum, Surelite I) and an optical parametric oscillator (GMU, C-355), the details of which were reported previously.[10] A simple calculation gives $1/T = \exp(\alpha L)/(1-R)^2+[\exp(\alpha L)-1]\beta I_0/[\alpha(1-R)]$, where L is the sample thickness, R the reflectivity at sample surfaces, and I_0 the incident light intensity.[3,10] Accordingly, by measuring $1/T$ as a function of I_0, we can evaluate β.

However, special caution was needed for the present measurement. That is, as is known,[6,16–18] the glass exhibited photochromic effects upon intense light exposures. Accordingly, to obtain intrinsic spectra, which were not affected by the effect, T was measured under single or double light pulses with limited light intensity of $I_0 \leqslant 200\ \mathrm{kW}/(100\ \mu\mathrm{m})^2$. In addition, in some measurements, different positions in a sample were exposed to each light pulse. Under these procedures, it was confirmed that $1/T$ was determined as a function of I_0. In contrast, under repeated pulse exposures, $1/T$ depended upon illumination history. It should be mentioned here that no signatures of two-step absorption[10,28] have been detected.

Figure 1 shows the composition dependence of $\alpha(\hbar\omega)$ (open symbols) and $\beta(\hbar\omega)$ (solid symbols). Those of α, which are consistent with previous reports,[29] can be summarized as follows. First, the spectra are exponential at around $\hbar\omega\approx3$ eV and $\alpha\approx1\sim100\ \mathrm{cm}^{-1}$, which is referred to as the Urbach edge.[11] Second, the edge shifts nearly in parallel to lower energies with x. Third, in detail, the steepness becomes smaller at $x\approx50$, which is interpreted as a manifestation of structural disordering of glass networks,[29] which may include inhomogeneities.[30]

On the other hand, β presents different features. First, the spectra are not exponential, which is in marked contrast to those in other glasses, such as SiO$_2$ (replotted in the figure)[8] and As$_2$S$_3$.[10] With increasing x, the spectra may show a redshift. However, all the spectra seem to have a common rise at ~2.0 eV, which is more-or-less conspicuous in amorphous materials having nonsharp absorption edges. This rise suggests that two-photon transitions in all the com-

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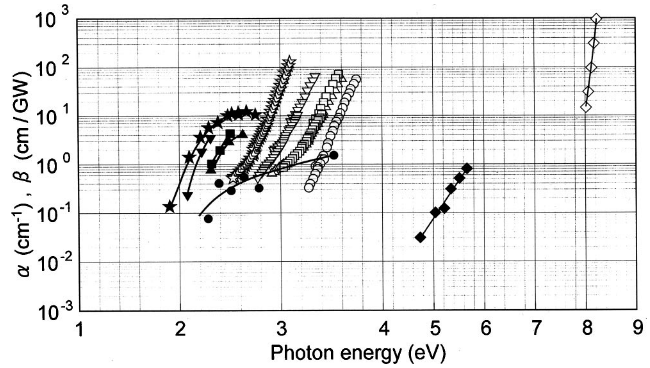

FIG. 1. One- (open symbols) and two-photon (solid symbols) absorption spectra in xPbO-$(100-x)$SiO$_2$ glasses, where $x=38$ (○), 45 (△), 54 (□), 60 (▽), and 68 (☆). As a reference, the spectra for SiO$_2$ glass are also shown (◇) (see Ref. 8). The horizontal scale at 1–4 eV is expanded to show the details, while the data for 45 and 54 overlap substantially.

positions occur between the states, which are separated in energy by more than ~4 eV. Note that this energy is substantially greater than the Urbach edges existing at ~3 eV. Second, another prominent composition change is the increase in β by an order upon increasing x by a factor of 2 (from 38 to 68). In short, these two features can be understood, roughly, as an upward spectral shift with the PbO content. Note that the present β values are mostly consistent with the ones measured at fixed wavelengths using z-scan methods.[4,6]

Theoretically, $\alpha(\hbar\omega)$ and $\beta(\hbar\omega)$ can be approximately written as

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

and

$$\beta(\hbar\omega)\propto\left|\sum_n \langle\varphi_f|H|\varphi_n\rangle\langle\varphi_n|H|\varphi_i\rangle \Big/ (E_{ni}-\hbar\omega)\right|^2 \times\int D_f(E+2\hbar\omega)D_i(E)dE. \tag{2}$$

Here, the electronic transition occurs from i to f states (via n states for β) under optical perturbation of H, in which relevant wave functions and densities-of-states are denoted as $\varphi(r)$ and $D(E)$, respectively, and $E_{ni}=E_n-E_i$. Similar to previous calculations for α in amorphous semiconductors,[11] the momentum conservation is relaxed and the transition amplitude is assumed to be independent of $\hbar\omega$. We see that, under these assumptions, the integrals including $D(E)$ have a common form in the two transitions, only the transition amplitudes being different. To evaluate $\alpha(\hbar\omega)$ and $\beta(\hbar\omega)$, therefore, we must know $D(E)$ and $\varphi(r)$.

It seems reasonable to assume that atomic levels contributing to optical absorption in PbO-SiO$_2$ glasses take place as illustrated in Fig. 2.[14,15,26,27] The broadening of the levels, which necessarily occurs in solids, is not shown for simplicity. In this model, irrespective of the PbO content, the highest occupied (HOMO) and lowest unoccupied molecular orbital states are produced mainly by Pb 6s and Pb 6p states, which are probably spatially localized in small-x glasses. When x becomes greater, similar to the situation in PbO crystals,[31] these states will form the top of valence bands and the bottom of conduction bands. Accordingly, it is straightforward to assume that the transition amplitude for α around the optical absorption edge is governed by intra-atomic $6s\rightarrow6p$ transitions in Pb, since H is an odd function. These two bands arising from Pb atoms become wider with x, due to interatomic interaction among Pb atoms, and accordingly, the broadening can cause the redshift of the one-photon absorption edge.

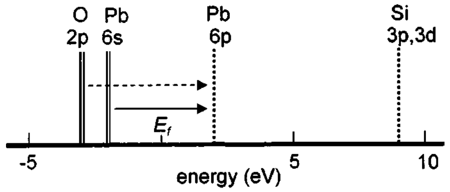

FIG. 2. Electronic structures of PbO-SiO$_2$ glasses. The solid and dashed arrows show the one- and two-photon absorption transitions, respectively.

However, the situation for the two-photon absorption is completely different. As is known from Eq. (2), the transition between s and p states in single atoms cannot occur, since the wave functions of i and f states must have the same parity. The next possibility with small photon energy is the transition from O 2p to Pb 6p states (see Fig. 2). In this case, reflecting the Pb 6p level broadening with increasing x, the two-photon absorption edge may also redshift as, shown in Fig. 1. However, the prominent increase in the two-photon absorption is puzzling. Why can the increase in x by a factor of 2 give rise to the increase in β by one order?

For the atomic structure of xPbO-$(100-x)$SiO$_2$ glasses, some structural studies[32–35] suggest the model as follows. In a wide range of compositions, structural units such as SiO$_4$, PbO$_4$, and PbO$_3$ are main constituents. In the glass with $x<50$, SiO$_4$ tetrahedral units form the glass network, which is modified by PbO$_4$ and/or PbO$_3$. In Pb-rich glasses, the roles of Si and Pb units seem to exchange. However, more detailed glass structures, specifically the bonding configuration of Pb and the inhomogeneity,[30] seem to need further study.

This structural model implies two possibilities for the prominent increase in β with x. One rests upon the characteristic change in Pb 6p states; that is, with the network formation by the Pb units, the 6p states possibly change from localized to extended states. As a result the transition amplitude $\langle \mathrm{Pb}6p|H|\phi_n\rangle\langle\phi_n|H|\mathrm{O}\,2p\rangle$ may increase substantially. The other possibility can be offered from the intermediate state $|\phi_n\rangle$. That is, when $E_{ni}-\hbar\omega\approx0$, resonant two-photon absorption can occur. In this idea, we can envisage that the resonant two-photon absorption is governed by $\langle\mathrm{Pb}\,6p|H|\mathrm{Pb}\,6s\rangle\langle\mathrm{Pb}\,6s|H|\mathrm{O}\,2p\rangle/(E_{\mathrm{Pb}\,6s,\,\mathrm{O}\,2p}-\hbar\omega)$, in which the band broadening of Pb 6s states may enhance the resonance condition. In addition the energy shift of the atomic levels is suggested,[15,27] which may also enhance the condition. Note that, since Pb 6s is an occupied state (HOMO), the two-step absorption cannot occur in the present case, which is consistent with the observations.

It is interesting to compare the one- and two-photon absorption spectra of PbO-SiO$_2$ and SiO$_2$ glasses.[8] As shown in Fig. 1, in SiO$_2$, two-photon absorption occurs at around the half photon-energy (~5 eV) of the one-photon spectrum, from which the optical band gap is estimated at ~10 eV.[8] This relation suggests that in SiO$_2$ the both transitions occur between the common two levels, that is, from O $2p$ to Si hybridized states by $3p$ and $3d$ (see Fig. 2), consistent with theoretical calculations.[36] As_2S_3 shows a similar feature,[10] and this may be a general rule in binary systems. In contrast, in PbO-SiO_2, the two-photon absorption edge (~2 eV) is located at ~2/3 of the Urbach edge (~3 eV). This is because the transitions occur in a three-level system (O $2p$, Pb $6s$, and Pb $6p$), as discussed earlier. A similar model may be applied to Bi_2O_3-B_2O_3 glasses.[9] Note that, in ideal crystals, all the electronic states in the vicinity of band edges are extended, and accordingly, a simple band theory can apply[1]—a situation which is completely different from that in disordered materials.

Since the two-photon absorption governs the intensity-dependent refractive index through nonlinear Kramers–Krönig relations,[37] the consideration just discussed predicts what kind of glass can show high optical nonlinearities. The best candidate will be the glass in which the two-photon absorption can occur between electronic states having the same parities in single atoms. However, it may be difficult to find such examples. The next is the glass in which the transition occurs between the nearest-neighbor atoms, as shown in the present work. In this case, the extension of wave functions and the resonance condition seem to have decisive roles. In any case, however, one-photon absorption should be kept small for practical usage, since it gives undesired light attenuation.

In summary, we have demonstrated that the one- and two-photon absorption spectra in PbO-SiO_2 glasses can be understood satisfactorily taking the density-of-states and the transition amplitude into account. Similar treatments can be applied to nonlinear transitions in other disordered materials. The large optical nonlinearity in the present glass seems to arise from a three-level electronic structure.

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