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Two-photon optical absorption in PbO-SiO₂ glasses

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One- and two-photon absorption spectra in PbO-SiO₂ 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,⁹ parallel studies on both absorptions can provide unified insights into optical absorption mechanisms, which are still ambiguous in disorded 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-SiO₂ glasses. This glass system has been selected, since it has a wide glass-forming region¹³ 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 photochromatic effects,¹⁶⁻¹⁸ large photosensitivity,¹⁹ and high nonlinear refractivity²⁰⁻²³ 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 xPbO·(100−x)SiO₂, where x = 38⁻⁶₈, 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 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. Opt-
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 x, 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 (LUMO) 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 to assume that the transition amplitude for α around the optical absorption edge is governed by intra-atomic 6s→6p 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.

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 studies32–35 suggest the model as follows. In a wide range of compositions, structural units such as SiO4, PbO4, and PbO3 are main constituents. In the glass with x<50, SiO4 tetrahedral units form the glass network, which is modified by PbO4 and/or PbO3. 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 \( \langle \text{Pb}6p|H|\phi_n\rangle\langle\phi_n|H|\text{O}2p\rangle \) may increase substantially. The other possibility can be offered from the intermediate state |\( \phi_n \)\>. That is, when \( E_n-i\hbar\omega=0 \), resonant two-photon absorption can occur. In this idea, we can envisage that the resonant two-photon absorption is governed by \( \langle \text{Pb}6p|H|\text{Pb}6s\rangle\langle\text{Pb}6s|H|\text{O}2p\rangle/(E_{\text{Pb}6s,\text{O}2p}-\hbar\omega) \), 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,5,7 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 2 S 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 2 O 3 -B 2 O 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–
Kröning relations, 37 the consideration just discussed predicts
what kind of glass can show high optical nonlinearity. 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 tran-
sition 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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