Optical nonlinearity in $PbO-SiO_2$ glass: Kramers–Kronig analyses

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Relationship between nonlinear refractivity and two-photon absorption has been studied for $PbO-SiO_2$ glasses using a nonlinear Kramers–Kronig relation. Nonlinear refractive indices, which are determined with *z*-scan measurements, are consistent with those which are calculated using the relation from two-photon absorption spectra. This consistency suggests that large intensity-dependent refractivity in this glass system arises from resonant two-photon electronic transitions from oxygen 2*p* to lead 6*p* states. © *2005 American Institute of Physics*.
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With developments of optical fibers and devices, nonlinear properties in photonic glasses have attracted growing interests. This is because the optical nonlinearity in glasses, which may be smaller than that in crystals, appears in substantial magnitudes in fibers,[1,2] waveguides,[3–5] and microspheres[6] due to long propagation distances. In addition, the nonlinearity can be continuously changed by varying glass composition.[7–9] The nonlinearity can be induced at selected positions.[5] In some cases, the nonlinearity is responsible for photoinduced phenomena.[10] Because of these features, several applications such as all-optical switches, optical limiters, and waveguide formation have been extensively explored.[4,11]

However, the optical nonlinearity in glasses remains to be studied. Specifically, fundamental mechanisms of the intensity-dependent refractivity n_2 $(n=n_0+n_2I+\ldots)$ in glasses have been less-well understood than those in simple systems such as two-level atoms[12] and crystalline semiconductors.[13] For glasses, only empirical or semiempirical relationships have been proposed,[14] most of which cannot provide spectral dependence. It seems to be very difficult to predict the magnitude of n_2 in glasses from an expectation value of polarization which is formulated quantum mechanically.[12]

Here, another way to grasp the intensity-dependent refractivity is to relate it with nonlinear absorption. That is, we start with the absorption, which can be connected with photoelectronic transitions between some electronic energy levels. Then, using a nonlinear Kramers–Kronig relation,[15] we can derive the nonlinear refractivity explicitly. Such a procedure has provided satisfactory understanding for crystalline materials.[13] It should also be noted that this procedure has an experimental advantage, since absorption spectra can be obtained more easily through transmittance measurements than refractivity spectra. To the authors' knowledge, however, such a procedure has not been applied to glasses.

To obtain a unified insight into the optical nonlinearity in glasses, we explore the above method in the present work. As an example, a PbO system is taken, which is known to be a kind of heavy-metal oxide glasses. We measure the nonlinear refractivity n_2 using *z*-scan measurements, and compare the results with those derived by applying a nonlinear Kramers–Kronig relation to nonlinear absorption spectra. Since the absorption spectra can be directly connected to an electronic structure of the glass, we will obtain a unified microscopic picture of the optical nonlinearity in glasses.

$PbO-SiO_2$ glass ingots were the same as those previously employed for investigating the one- and two-photon absorption spectra.[16] The ingots were polished to thin flakes with thickness of 80–100 μm. Nonlinear refractive indices n_2 at wavelength of 1.06 μm ($\hbar\omega=1.17$ eV) were evaluated through the conventional *z*-scan method[17] using a pulsed Nd:YAG laser (~5 ns), which was also previously employed,[16] an aberration-corrected focusing lens with a focal length of 10 cm, a fast-response photodiode, and a digital oscilloscope. Note that this lens had a diffraction length of 150 μm, being greater than the sample thickness, which is needed for applying an approximated analysis assuming small wave-front distortion.[17]

Figure 1 shows a typical *z*-scan profile for $68PbO-32SiO_2$ glass. Experimental results were fitted with a theoretical curve,[17] shown by the solid line, through the least-squared-error method. From a fitted parameter, n_2 has been calculated as described in Ref. 17.

Figure 2 summarizes absorption and refractivity spectra for the $68PbO-32SiO_2$ glass. The one-photon absorption spectrum $\alpha(\hbar\omega)$ shown by open circles in (a) is replotted from Ref. 16, and a refractive index n (≈1.9) at $\hbar\omega=1.17$ eV in (b) is estimated from linear reflectance. As a preliminary check of numerical calculations, we first apply the conventional Kramers–Kronig relation:[15]

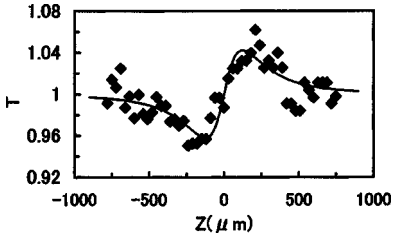

FIG. 1. Typical *z*-scan output, normalized transmittance *T* as a function of the axial position *Z*, obtained for a $68PbO-32SiO_2$ sample under an irradiance of 50 GW/cm^2. The solid line shows a theoretical fit.

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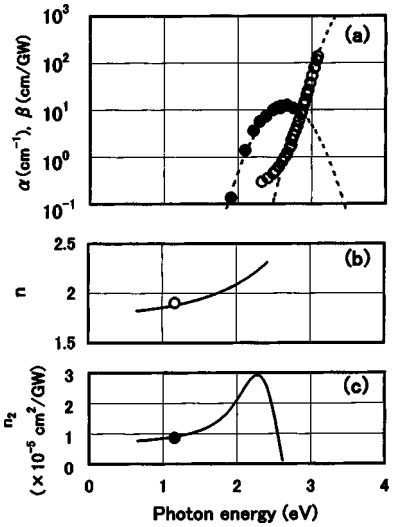

FIG. 2. Linear and nonlinear optical spectra in $68PbO-32SiO_2$ glass: (a) shows one-photon (open circles) and two-photon (solid circles) absorption spectra, $\alpha(\hbar\omega)$ and $\beta(\hbar\omega)$; (b) shows refractive index n experimentally determined (open circle) and the spectrum $n(\hbar\omega)$ (solid line) calculated from $\alpha(\hbar\omega)$; and (c) shows nonlinear refractive index n_2 experimentally obtained (solid circle) and the spectrum $n_2(\hbar\omega)$ (solid line) calculated from $\beta(\hbar\omega)$.

$$n(\omega) - 1 = (c/\pi)\wp \int [\alpha(\Omega)/(\Omega^2 - \omega^2)]d\Omega, \tag{1}$$

to these results, where the integration should be carried out from zero to infinite frequencies. However, since the measured absorption is limited to an energy region of 2.3–3.1 eV, we extrapolate the spectrum with a Gaussian distribution $A\exp[-(\hbar\omega - E_0)^2/\sigma^2]$, where $A = 10^4$ cm^{-1}, $E_0 = 4$ eV, and $\sigma = 0.45$ eV, a part of which is shown in (a) by a dashed line. Note that this distribution is compatible with the experimental $\alpha(\hbar\omega)$ and also with an electronic band structure, in which optical absorption is assumed to occur from Pb 6*s* to Pb 6*p* states.[16,18] A calculated $n(\hbar\omega)$ is shown in (b) by a solid line, which is in agreement with the experimental refractive index of ~1.9.

Having obtained a satisfactory agreement in the linear properties, we now apply a nonlinear Kramers–Kronig relation to the two-photon absorption spectrum $\beta(\hbar\omega)$. The relation is expressed as[15]

$$\Delta n(\omega;\zeta) = (c/\pi)\wp \int [\Delta\alpha(\Omega;\zeta)/(\Omega^2 - \omega^2)]d\Omega, \tag{2}$$

where $\Delta\alpha$ is a nonlinear absorption induced by an optical excitation at Ω and a perturbation at ζ. Note that this relation is derived for nondegenerate cases such as two-beam experiments with different photon energies, Ω and ζ. Accordingly, its application to a two-photon absorption spectrum obtained through degenerate experiments, as in the present case, is provisional. However, if calculated $n_2(\hbar\omega)$ is restricted to substantially lower energy region than $\beta(\hbar\omega)$, applications of the nonlinear Kramers–Kronig relation to degenerate data may be reasonable.[19] We then insert a Gaussian spectrum of $\beta(\hbar\omega)$ with $A = 12$ cm/GW, $E_0 = 2.65$ eV, and $\sigma = 0.36$ eV, which is the best fit to the experimental data[16] as shown in Fig. 2(a), into $\Delta\alpha(\Omega)$. A numerical integration provides the smooth line shown in Fig. 2(c), which quantitatively agrees with the nonlinear refractivity n_2 evaluated from the result in Fig. 1. This agreement strongly suggests that the nonlinear

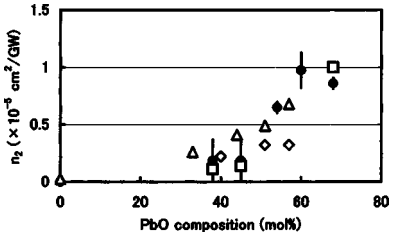

FIG. 3. Composition dependence of experimental (solid circles) and theoretical (squares) n_2 at photon energy of 1.17 eV. Previous results obtained using commercial glasses are also plotted by triangles and diamonds.

Kramers–Kronig relation can also be employed in degenerate cases, and that the nonlinear refractivity at transparent wavelengths is governed by the two-photon absorption, which is consistent with a situation in crystalline semiconductors.[13]

Z-scan measurements have been done for six compositions, and the results (solid circles) are compared in Fig. 3 with those (squares) calculated from the two-photon absorption spectra.[16] Error bars attached to the experimental data arise from *z*-scan noises (see Fig. 1), inhomogeneous glass ingots, etc. The figure also includes some previous results[7,8] at the wavelength of 1.06 μm. We see, n_2 increases with the PbO content. In detail, the increase may be more prominent when the PbO content is greater than ~50 mol %. We also see that, taking fairly large experimental errors necessarily appearing in n_2 measurements, the present and previous[7,8] values agree more-or-less satisfactory with those derived from the two-photon absorption spectra using the nonlinear Kramers–Kronig relation.

This agreement provides an explanation for the large n_2 in this glass system. In the previous studies,[16,20] it has been suggested that the two-photon absorption in PbO glasses is governed by electronic transitions from O 2*p* to Pb 6*p* states, which are resonated by Pb 6*s* states. This resonance seems to be enhanced with an increase in the PbO content. Since n_2 is governed by the two-photon absorption, as we have seen above, the large n_2 in this glass can therefore be ascribed to this resonant photoelectronic transition. In other words, the large n_2 is a manifestation of the specific electronic structure (O 2*p*, Pb 6*s*, and Pb 6*p*) in this glass system. Such a conclusion may be generalized to heavy-metal oxide glasses such as Bi-containing glasses.[21,22]

In summary, we have demonstrated that the intensity-dependent refractivity in $PbO-SiO_2$ glasses can be quantitatively connected to the two-photon absorption through the nonlinear Kramers–Kronig relation. The large nonlinear refractivity in this heavy-metal oxide glass seems to be a manifestation of resonant two-photon absorption from oxygen 2*p* to heavy-metal 6*p* states. The present work provides a unified and principal scheme for understanding the nonlinear optical properties in glasses, since the absorption spectrum can be connected more directly with an electronic structure, which is determined by atomic energy levels and bonding structures.

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