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<td>Author(s)</td>
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<tr>
<td>Citation</td>
<td>Applied Physics Letters, 94(24), 241905</td>
</tr>
<tr>
<td>Issue Date</td>
<td>2009-06-15</td>
</tr>
<tr>
<td>Doc URL</td>
<td><a href="http://hdl.handle.net/2115/38749">http://hdl.handle.net/2115/38749</a></td>
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<td>Type</td>
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<td>File Information</td>
<td>94-24_241905.pdf</td>
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Optical nonlinearities of Se-loaded zeolite (ZSM-5): A molded nanowire system

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(Received 14 April 2009; accepted 28 May 2009; published online 16 June 2009)

Nonlinear optical properties of Se-loaded ZSM-5 single crystals have been studied comparatively with those of glassy Se. Two-photon absorption coefficients and intensity-dependent refractive-index of the Se-zeolite are higher by three orders of magnitude than those of glassy Se. The enhancements can be ascribed to electron confinement in single Se chains. © 2009 American Institute of Physics. [DOI: 10.1063/1.3155452]

Sufficiently high third-order optical nonlinearities are being sought for fabrication of compact all-optical switches and so forth operating at the 1.5 μm communication band. For instance, a waveguide switch with a length of 1 cm and a cross section of 10 μm² operating under 1 W light needs an intensity-dependent refractive index n² of 10⁻² cm²/GW. However, it becomes to be known that such a high nonlinearity is difficult to attain using homogeneous materials that are transparent at the wavelength of 1.5 μm.¹⁻⁴ Then, our target is directed to heterogeneous media such as dye-doped polymers, particle-doped inorganic media, and photonic crystals.Ọ

We here explore nonlinear properties of a chalcogen-loaded zeolite, a kind of inorganic-dye-doped systems. This guest-host composite appears to be promising as nonlinear materials with the following reasons. It has been demonstrated that the chalcogenide glass, due to its smaller energy gap than that of the oxide, possesses higher nonlinearity of n² ≳ 10⁻³ cm²/GW.¹⁻² However, the nonlinearity is insufficient for practical uses. In addition, the glass is more damageable than the oxide due to its lower glass-transition temperature. Hence, it is intriguing to employ the zeolite, a porous silica-based crystal, as a host for incorporating the chalcogen. In addition, recent studies have produced submicrometer size zeolite single crystals, suitable to nonlinear optical measurements. This letter reports optical nonlinearity of Se-loaded ZSM-5 (z-Se) in comparison with that of glassy Se (g-Se). Fundamental properties of Se-loaded ZSM-5 have been reported elsewhere.¹³

Two kinds of samples were investigated. One was z-Se, the preparation detail being reported in Ref. ¹³. In short, ZSM-5 crystals with a typical dimension of 40×40×200 μm³ for the a, b, and c axes (see Fig. 1) were employed as matrices and 6N purity Se was thermally incorporated from gas phases in vacuum. Varied preparation conditions produced samples with colors of yellow, orange, and brown. And, the present work mostly dealt with the orange sample, for which thermal desorption measurements suggested that Se concentration in the sample was ~10¹⁴ atoms or ~10²⁰/cm³. The z-Se sample was laid on an aperture with a diameter of 25 μm, and probe light was propagated through the sample along the zeolite b-axis. Light polarization was not resolved. The other sample was g-Se, the bulk and films being prepared through the conventional melt-quenching method and vacuum evaporation.¹⁴

Optical transmission spectra of these samples were evaluated using a laser-detector system.¹³ Two-photon absorption coefficient β and intensity-dependent refractive index n² were measured using three pulsed sources: a 5 ns yttrium aluminum garnet (YAG) laser, an optical parametric oscillator (OPO), and a 0.3 ns YAG laser. Optical setups employed were two kinds. β spectra were evaluated through intensity-dependent transmittance measurements.¹¹ For measuring β and n² at λ ≈ 1064 nm, we employed a z-scan technique in combination with a profile imager, which monitored intensity patterns of transmitting light. Through fitting Gaussian curves to the patterns, which were averaged over repeated light pulses, we could evaluate the total light intensity and central peak intensity. These values correspond to the so-called open- and closed-aperture signals.¹¹ This profile-imaging z-scan method can greatly reduce noises, which is important for somewhat irregular samples as the zeolite.¹⁷

Figure 1 shows transmission spectra of pure ZSM-5 and z-Se with photographs of typical samples. ZSM-5 is transparent over wavelengths of λ ≈ 350–1064 nm with a slight

**FIG. 1.** (Color online) Transmission spectra (lines with circles) of typical ZSM-5 and z-Se. Insets give photographs of (a) ZSM-5 and (b) z-Se and an illustration of ZSM-5, with crystal axes and magnified channels.
transmission decrease at shorter wavelengths, which may reflect light scattering due to minute cracks. On the other hand, 2.0 eV in ZSM-5 is estimated at 600 nm.\textsuperscript{13} z-Se is opaque at $\lambda \leq 600$ nm.\textsuperscript{13}

Figure 2 shows a result of the imaging z-scan measurement for a $z$-Se sample at $\lambda \approx 1064$ nm, pulse width of 5 ns, and irradiance of $\sim 0.5$ GW/cm$^2$. We see for the central intensity (open circles), which corresponds to the closed-aperture signal, a valley-peak distance of $\sim 140$ $\mu$m, and a normalized valley-peak transmittance of $\Delta T_{p-v} \approx 0.3$, which gives $n_2 \approx 10^{-3}$ cm$^2$/GW with sample-to-sample variations of a half order. Dependence upon the pulse widths (0.3 and 5 ns) has been smaller than this variation. The profile asymmetry and the intensity reductions at $z = \pm 200$ $\mu$m reflect the eclipse due to the small aperture (see, the inset in Fig. 2). On the other hand, the total power, which corresponds to the eclipse due to the small aperture which possibly varies from site to site.\textsuperscript{13} Then, defining the intensity absorption coefficient $\beta$ at this wavelength is smaller than a detection limit. We also see that the Gaussian diameter of the light spot shows a peak at $z = -70$ $\mu$m, which probably reflects a beam-defocusing effect arising from the positive $n_2$.

Figure 3(a) compares linear absorption spectra of $g$-Se and $z$-Se. The linear absorption spectrum of $g$-Se is mostly consistent with previous results,\textsuperscript{14} giving an optical gap $E_g$ of $\sim 2.0$ eV. On the other hand, $z$-Se shows a less-steep absorption edge. It is plausible that this gradual slope arises from structural inhomogeneity, i.e., Se is impregnated as a form of single chains with an average chain length of 10$^2$ atoms, which possibly varies from site to site.\textsuperscript{13} Then, defining the optical gap as a photon energy at the absorption coefficient $\alpha$ of $10^3$ cm$^{-1}$, we have $E_g = 2.2$ eV, which blueshifts by $\sim 0.2$ eV from the bulk gap.

Figure 3(a) also compares $\beta$ spectra of $g$-Se and $z$-Se, which have been evaluated from intensity-dependent transmittances of light pulses emitted from the OPO.\textsuperscript{1,13} Different from the linear spectra, the $\beta$ spectra seem to have peaks at $\sim 1.5$ and $\sim 2.2$ eV in $g$-Se and $z$-Se, the positions being located between $E_g/2$ and $E_g$ in agreement with theoretical predictions.\textsuperscript{3,4} We here underline that $z$-Se shows higher $\beta$ than that of $g$-Se by approximately three orders. It should also be mentioned that a brown-color $z$-Se has exhibited a still greater $\beta$ value ($\leq 10^5$ cm/GW).\textsuperscript{18} A damage threshold of $z$-Se has appeared to be higher by an order than that ($\sim 0.5$ GW/cm$^2$) of $g$-Se.

Using these $\beta$ spectra, we can estimate $n_2$ spectra, as shown by solid curves in Fig. 3(b). In this calculation, the $\beta$ spectra have been approximated by the Gaussian curves, as shown in Fig. 3(a), which are transformed using a nonlinear Kramers–Krönig relationship.\textsuperscript{15} On the other hand, as plotted in the figure, the z-scan measurement for $z$-Se gives $n_2$ of $10^{-3}$ cm$^2$/GW at 1064 nm, which is consistent with the calculated result. $n_2$ in $g$-Se at the wavelength could not be inspected, while it is predicted to be substantially smaller, as shown in Fig. 3(b).

Why does $z$-Se give such a greater nonlinearity than that of $g$-Se? We consider four possibilities. First, it is theoretically predicted that a material having smaller $E_g$ possesses a higher $n_2$,\textsuperscript{3,4} but $z$-Se has a wider $E_g$ ($\sim 2.2$ eV) than that in $g$-Se ($\sim 2.0$ eV). Second, we may envisage some effects arising from modifications of chemical bonds. Specifically, the electron wave function of the valence band, consisting of lone-pair electron states, is likely to more localize in $z$-Se.\textsuperscript{20} However, if such a modification can explain the enhancement of the three orders is questionable. Third, it is tempting to envisage exciton-confinement effects predicted for semiconductor-doped glasses.\textsuperscript{7} Nevertheless, if the theory, which presumes spherical semiconductor particles, can be applied to the present case is not known. Actually, the exciton Bohr radius $r_B$ in hexagonal Se is reported to be $\sim 1$ nm,\textsuperscript{21} the Se chain radius $R$ is $\sim 0.3$ nm,\textsuperscript{14} and the chain length $L$ in ZSM-5 is estimated at $\sim 10^4$ nm.
In conclusion, we have demonstrated that $\beta$ and $n_2$ and in $z$-Se reach, respectively, to $10^5$ cm/GW at visible wavelengths and $10^{-3}$ cm$^2$/GW at near infrared, which are much greater than those in glassy Se. Taking the wider optical gap in $z$-Se than those in glassy Se, we suggest that the chalcogen-zeolite system is promising for fabricating compact optical devices, not only of the third-order but also of the second-order nonlinearity.\cite{Sheik-Bahae15, Tanaka92}

The authors would like to thank Dr. Y. Kiyozumi for supplying ZSM-5 crystals, Dr. V. V. Poborchii for cancrinite-Se samples, Dr. A. V. Kolobov for private correspondences, and Mr. N. Minamikawa for experimental assistance. The authors also acknowledge financial support from Nippon Sheet Glass Foundation for Material Science and Engineering.

\cite{Boyd03, Yamane92}, so that $r_B/R > 1$ and $r_B/L < 1$. Lastly, the most attractive interpretation is to follow a concept developed for one-dimensional quantum wells, in which the third-order polarizability increases in proportion to $L^3$, where $L$ is a well length.\cite{Gomez21, Rustagi22} The single Se chain may be regarded as a one-dimensional quantum well and such a length enhancement is likely to exist. Actually, a preliminary experiment for Se$_2$ anions in cancrinite\cite{Poborchii92} could not detect $z$-scan signals, which is consistent with this model. We then expect that longer Se chains in zeolite will afford practical compact all-optical switches, keeping in mind that an implicit assumption in the quantum-well model is a longer mean-free path of electrons than $L$.

\cite{Tanaka92, Saitoh08, Gomes08, Irvin08, Ganany-Padowicz09, Fedus10, Ogusa04, Bouds12, Kiyozumi05, Shimizu01, Saitoh09, Sheik-Bahae01, Sheik-Bahae09, Saitoh10, Sheik-Bahae14, Tanaka99, Roberts74, Rustagi74, Poborchii02, Werner92}