

Atomistic Observation of Light-induced Vector and Scalar Effects in a Chalcogenide Glass

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The interaction of solid systems with light leads to a number of important chemical reactions and physical phenomena in nature as well as in modern technology e.g. photography, xerography, holography, photopolymerization, photosynthesis of plants, etc. In general, light interacts with a solid through its electronic states, which depend upon the constituent atoms and structure of the material. Light-induced change in the atomic structure involving displacement of atoms is unusual, except in special cases of disordered materials including polymers and glasses. Such changes, when they occur, are expected to depend on the intensity and wavelength of light. However, recently light-induced mass transport [1], photo-crystallization [2], and an opto-mechanical effect [3] have been reported on glassy chalcogenide films, which imply a change in the atomic structure that depends also on the *polarization* of light. Thus, in the opto-mechanical effect, for example, the glass film reversibly photo-expands or photo-contracts *depending upon the direction of the electric field vector of the incident light*. Salimnia et al. [1] reported mass transport in a chalcogenide glass film, which depended on the polarization of the incident laser beam. These so-called *vector* effects (because they depend on the direction of the electric field vector of light) are particularly intriguing because the starting structure of the unirradiated films is amorphous and isotropic. A variety of technological applications for these surprising effects are proposed, yet there is little atomistic, element-specific, experimental evidence about such processes of photo-structural rearrangement in any glassy system.

To obtain element-specific insight into the light-induced changes in a glassy material and also to establish the origin of the newly discovered vector effects, we have investigated, at beamline X18B at the NSLS, the local atomic structure of amorphous $\text{As}_{50}\text{Se}_{50}$ using extended

X-ray absorption fine structure (EXAFS) analysis around Se as well as As atoms. For observing a vector (or anisotropic) property the probe should also be anisotropic. This condition is readily fulfilled by the synchrotron radiation, where X-rays are polarized in the plane of the ring (i.e. the electric field (\mathbf{E}_x) of the X-rays is parallel to the ground plane). The EXAFS spectra were obtained for two configurations, with the polarization of the laser beam being either perpendicular or nearly parallel to that of the X-rays (see Fig. 1): (a) horizontal polarization, HP: \mathbf{E}_L (laser) nearly $\parallel \mathbf{E}_x$ (X-rays), and (b) vertical polarization, VP: \mathbf{E}_L (laser) $\perp \mathbf{E}_x$ (X-rays). Since the photo-induced changes can be temporary and/or permanent, it was important to determine the structure under *in situ* conditions [4,5]. The intensity of the laser beam ($\approx 100\text{mW}/\text{cm}^2$) was insufficient to cause any significant increase in sample temperature [6]. The Se and As K-edge EXAFS data were collected in transmission as well as fluorescence mode on a stack of thin films of $\text{As}_{50}\text{Se}_{50}$. The volume of sample probed by X-rays is much larger than that affected by the laser

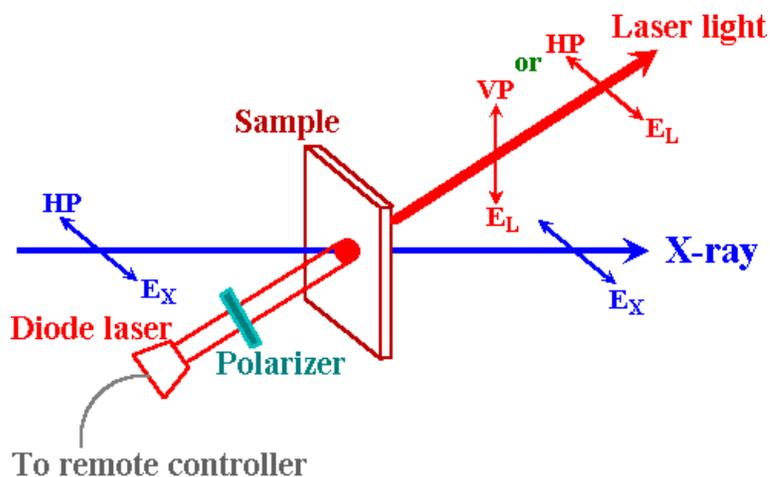


Figure 1. In situ experimental set-up for studying laser-polarization-dependent photostructural changes. The sample is irradiated with light of approximately bandgap energy from a laser diode ($\lambda = 660\text{ nm}$) and simultaneously observed by X-rays from the synchrotron. A polarizer controls the polarization of the laser beam. HP: horizontal polarization. VP: vertical polarization.

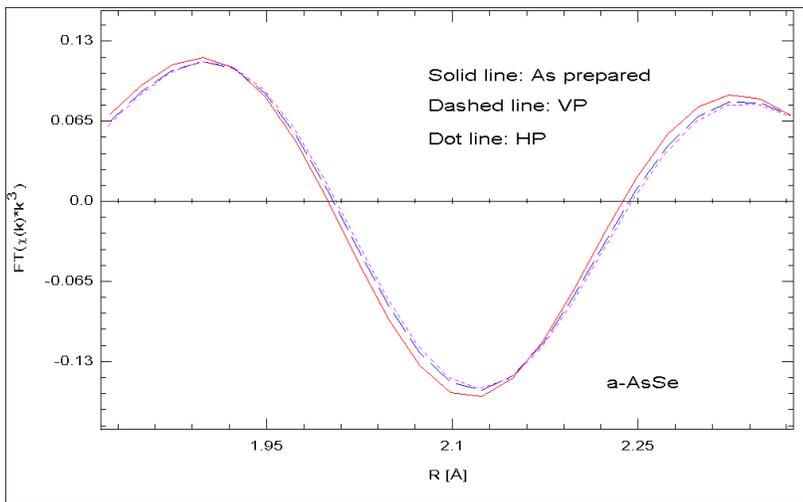


Figure 2. Real part of the Fourier transform of raw data of Se K-edge EXAFS oscillations for as prepared and laser irradiated AsSe samples.

irradiation, and often the light-induced effects are confined to certain defect sites [7]. Hence, the changes reported here are the lower limit of actual changes around a particular atom.

An example of the effect of light polarization on the EXAFS data is shown in Figure 2. The highlight of the results obtained from the analysis of these data is shown in Figure 3, for three conditions of the sample: Stage 1 - as prepared, unirradiated sample; Stage 2 - sample in the presence of polarized laser light; and Stage 3 - sample after exposing the film to laser light for 1 hour. Thus any difference in the parameters between stages 1 and 2 represents light-induced changes, both tran-

sient and permanent. The difference between stages 2 and 3 indicates recovery of the transient effect that occurs only when the light is present. Finally, a difference between stages 1 and 3 indicates a permanent change in the structure of the sample. The error bars in the figures represent actual scatter when the experiment was repeated at least four times for a given condition at the same spot on the sample.

Figure 3(a) shows that on average the nearest-neighbor distance, R , from the Se atoms increases as the sample is illuminated. This expansion of structure is permanent as the value of R remains about the same when the light is turned off. The variation of R around As parallels the expansion around Se. The combined increase of R for both the el-

ements provides an atomistic explanation for the photo-expansion observed in these materials [8]. The difference between the data for Se under two polarizations is a striking feature in Fig. 3(a). It is the first atomistic observation of a light-induced vector expansion in any material. The local structure expands significantly more when the \mathbf{E} vectors of the X-rays and the laser are parallel to each other than when the two are perpendicular. Such an anisotropic expansion also means a polarization-dependent driving force for mass transport from illuminated region to the unirradiated region.

To characterize the effect of light on the disorder around a given atom, we have evaluated the mean

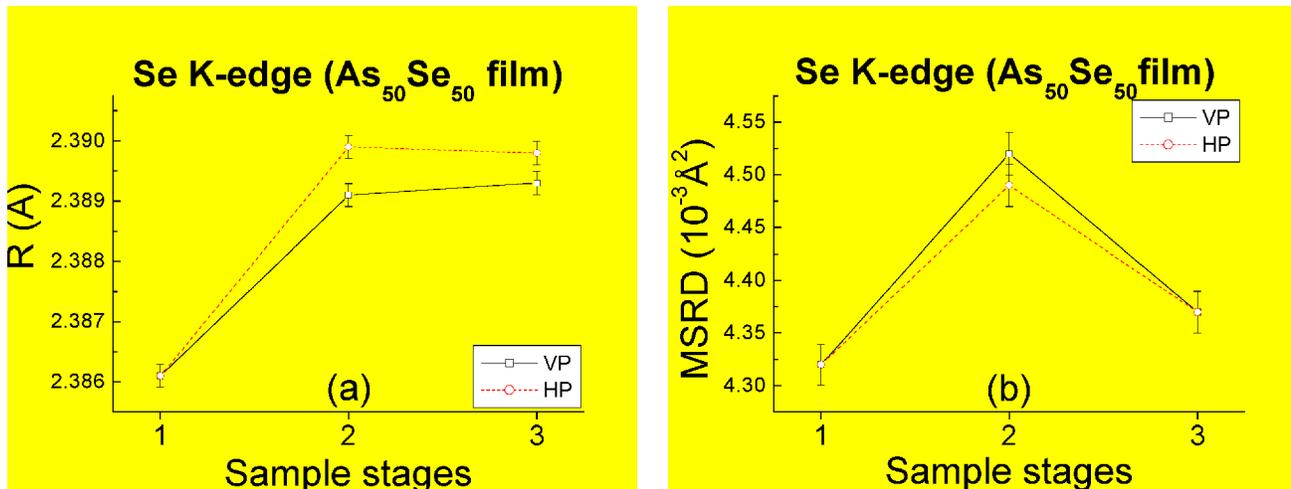


Figure 3. The change in the local structure around Se atoms in amorphous $As_{50}Se_{50}$ when an as-prepared sample (stage 1) is exposed to polarized laser light (stage 2), and after the light is turned off (stage 3). The polarization of the laser light is either parallel (HP) or perpendicular (VP) to that of the X-ray probe beam: (a) nearest-neighbor distance and (b) mean square relative displacement.

square relative displacement (MSRD), keeping the coordination number fixed. Since the polarization-dependent changes in the structure could be quite small, a separate evaluation of these two factors would have been less meaningful due to the additional uncertainty from the data analysis. The variation of MSRD in Fig. 3(b) emphasizes the temporary or transient aspect of the light-induced structural changes, where the disorder around Se increases on exposure to light, but much of it is recovered when the light is turned off. The level of disorder in stage 3 is somewhat higher than in stage 1, indicating a small, permanent increase in this disorder. These results confirm similar observations on Se and As_2Se_3 [4,5], and demonstrate the relative ease with which readily reversible changes occur in the structure around the chalcogen atoms.

In contrast to Se, the disorder around As *decreases* with exposure to light and shows no effect of the light polarization. After the light is turned off, it decreases further. The opposite permanent changes in the disorder around Se and As are in agreement with our observations of the chemical environment by X-ray photoelectron spectroscopy, where the Se-3d core level peak becomes broader but the As-3d peak becomes narrower as a result of laser irradiation [9].

The microscopic mechanism of the above reported changes is incompletely understood. Nonetheless, based on available information we propose tentatively the following explanation (see Figure 4). The absorption of approximately bandgap light promotes electrons to low-lying unoccupied conduction-band (antibonding) states, which can cause bond breaking [10,11,12]. The *permanent* photostructural changes observed by EXAFS of $\text{a-As}_{50}\text{Se}_{50}$ are associated particularly with the excess As-As bonds (such as in As_4Se_3 clusters), arising from the non-stoichiometry of this material. The absorption of light preferentially breaks such highly strained As-As bonds (present in a triangular configuration in the As_4Se_3 molecule), resulting in the formation of heteropolar As-Se bonds with excess Se atoms in the glassy matrix. As a consequence the structural disorder around As decreases. This bond breaking and reformation occurs in random orientations, so that there is little light-polarization dependence of the change in disorder around As atoms, as observed.

However, the low coordination, and consequent structural flexibility, of the Se atoms allows a bond re-

orientation for them to take place, so that the newly formed As-Se bonds are along the \mathbf{E} field of the laser light. The transformation of homopolar bonds (As-As and Se-Se) to heteropolar bonds by light excitation is energetically preferred. Such a reaction is expected to increase the average nearest-neighbor distance of Se atoms and decrease that of As atoms, as observed. Note that photoelectrons (from X-ray absorption) are preferentially scattered along the direction of \mathbf{E} (X-rays), making the detection of the nearest-neighbor distance around Se for the HP condition more likely than for the VP configuration. Incidentally, in parallel to our work, Kolobov et al. [13] have also performed a similar experiment in Japan on amorphous Se. Their observa-

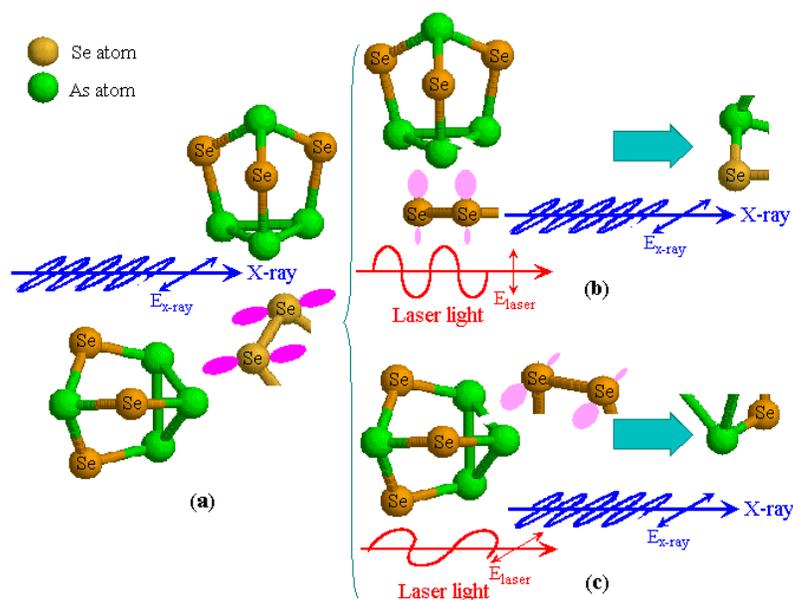


Figure 4. (a) As-rich (As_4Se_3) and Se-rich regions exist in as-prepared $\text{As}_{50}\text{Se}_{50}$ films. (b) Vertically polarized laser light breaks As-As bonds, excites and reorients the lone pairs of Se atoms to form vertical As-Se bonds. (c) Horizontally polarized laser light breaks As-As bonds, excites and reorients the lone pairs of Se atoms to form horizontal As-Se bonds.

tion that the polarization of the light can affect the orientation of Se clusters in amorphous Se is consistent with our observations. However, they did not find any polarization-dependent change of R in Se, but then their data from fluorescence detection have an inherently larger uncertainty.

In conclusion, we have made the first direct observation of polarization dependent, light-induced, permanent expansion and a transient disorder of local atomic structure around Se in amorphous $\text{As}_{50}\text{Se}_{50}$. Such vector changes around As are not experimentally discernible, which is consistent with the flexible, two-fold coordination of Se compared to the three-fold coordination of As in the structure. Our observations provide an ato-

mistic view of several novel light-induced vector and scalar effects in chalcogenide glasses.

Acknowledgement

We thank F. M. Alamgir for help with the EXAFS experiments, and the US National Science Foundation under Grants DMR 00-74624 and DMR 00-81006 for supporting this work. MV thanks support from MSMT Czech Republic under Grant ME471. Research carried out in part at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences, under Contract No. DE-AC02-98CH10886.

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