

Photo-Induced Phenomena of AsS and As₂S₃ Microclusters Encapsulated in Zeolite

Yoshinori Katayama^a, Kenji Maruyama^b, Makoto Yao^c and Hirohisa Endo^d

^aDepartment of Physics, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Yokohama 223, Japan.

^bDepartment of Chemistry, Faculty of Science, Niigata University, Igarashi, Niigata 950-21, Japan.

^cDepartment of Physics, Graduate School of Science, Kyoto University, Kitashirakawa, Kyoto 606-01, Japan.

^dFaculty of Engineering, Fukui Institute of Technology, 3-6-1 Gakuen, Fukui 910, Japan.

Photoacoustic spectroscopy (PAS) and EXAFS measurements have been carried out on As₂S₃ and As S microclusters encapsulated in cages of zeolite Y. PA spectra show that the optical gap of Y-As₂S₃ is almost same as that of crystalline As₂S₃ whereas that of Y-AsS is wider than that of crystalline AsS. The absorption edges for both microclusters shift to lower energy by illumination with light having energy above the optical gap at low temperature. EXAFS data reveal that there appear changes in the correlations of bonding atoms and non-bonding atoms by illumination. The observed photo-induced phenomena for these microclusters are discussed in connection with the changes in the local structures.

1. INTRODUCTION

It is well known that wide variety of physical and chemical properties of chalcogenide glasses are altered by exposing a sample to near band-gap light[1-4]. These photo-induced phenomena are observed as either irreversible or reversible changes, depending on the sample conditions. One of the most prominent changes is the reversible photodarkening effect; a shift of the optical absorption edge to lower energy by irradiation with band-gap light and a reversal of the shift by thermal annealing near the glass transition temperature. This change is attributed to the modifications of atomic configuration. For the last two decades, many works have been done to understand the origin of the photo-induced phenomena because they not only reveal interesting characteristics in the disordered states but have potential technological importance as well. In spite of those efforts, however, the microscopic mechanism responsible for these changes is not well

understood yet.

The structural disorder and the presence of chalcogen atoms play an important role in these changes. The two-fold coordinated arrangements of chalcogen atoms result in a non-bonding p character on the top of the valence band and a high degree of structural flexibility. The degree of flexibility is expected to be increased when the sample is formed by fine clusters. Hence the structural and optical properties of chalcogen clusters are supposed to be modified under light irradiation. This has been shown to be true for Se, S and Se-S mixed chains isolated in mordenite[5,6] and CdS clusters grown in zeolites[7].

In this study we have carried out EXAFS and photoacoustic spectroscopy measurements on As₂S₃ and AsS clusters encapsulated in zeolite Y to discuss the correlation between structural changes and the photodarkening phenomena.

2. EXPERIMENTAL

2.1. Sample Preparation

The zeolite used in the present study is synthetic Na zeolite Y ($25\text{Na}_2\text{O}_3 \cdot 25\text{Al}_2\text{O}_3 \cdot 142\text{SiO}_2$) supplied by the Tosoh Manufacturing Co., Ltd. Zeolite Y consists of interconnected sodalite cages (about 5 Å in diameter) and supercages (about 13 Å in diameter). The zeolite samples containing As_2S_3 and AsS (Y- As_2S_3 and Y-AsS) were prepared by the following way. First As_2S_3 and AsS alloys were prepared by quenching the molten mixture. The zeolite powder was washed by distilled water and dehydrated at 500°C for 3 hours under vacuum below 10^{-4} Pa. Dehydrated zeolite powder and corresponding alloy were sealed in a Pyrex glass tube. The tube was heated up to 500°C to expose zeolite powder to vapor of the alloy. The sample was kept at 500°C until it became homogeneous in color. It was cooled down slowly to room temperature.

2.2. EXAFS measurements

EXAFS measurements were performed with a spectrometer installed at BL-10B of Photon Factory in the National Laboratory for High Energy Physics. The zeolite sample was packed in an airtight copper holder with acrylic resin windows under He atmosphere to prevent hydration. X-ray absorption spectra near As K-edge were measured at 80K. The energy range was from 11.6 keV to 13.1 keV. A 500 W Xe arc lamp equipped with an UV-33 filter was used for light irradiation experiments. Further details of experimental procedure and data analysis were described in the previous paper[5,8].

2.3. PAS measurements

Photoacoustic Spectroscopy (PAS) was employed to study optical absorption of the cluster encapsulated in zeolite because the samples were powder. The details of the experimental setup were described in the previous paper[5]. The PA spectra were obtained in the wavelength range 250-1600 nm. The measurements were carried out at room temperature and 70 K using a PAS cell equipped with a N_2 continuous flow cryostat. The samples were transferred to sample chamber under He atmosphere. A Xe arc lamp and a monochromator in the spectrometer were also used for light irradiations.

3. RESULTS AND DISCUSSION

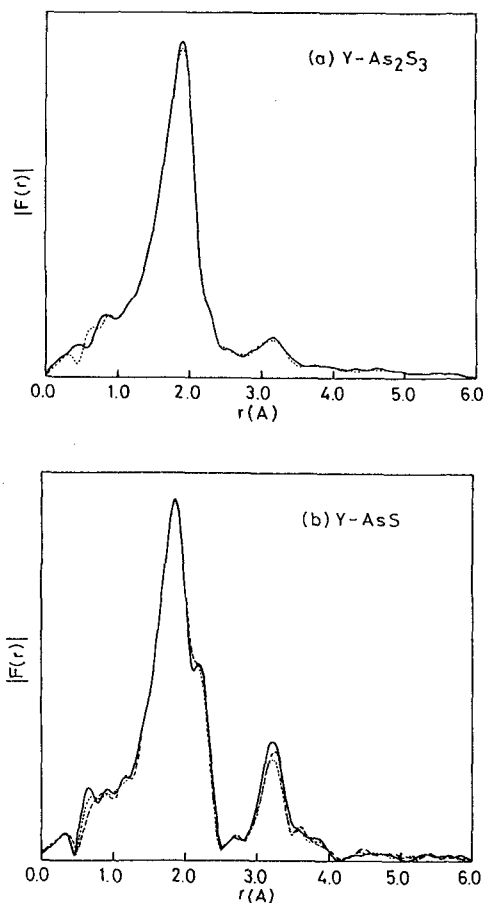


Figure 1: The radial distribution function $|F(r)|$ around As atom at 80 K. (a)Y- As_2S_3 . (b)Y-AsS. See text for details.

3.1. EXAFS measurements

The basic structural unit in crystalline As_2S_3 (c- As_2S_3) is an infinite layer-like structure of covalently bonded arsenic and sulfur atoms, whereas that of crystalline AsS (c-AsS) is covalently-bonded As_4S_4 molecule[9]. We carried out EXAFS measurements to see the structure of the clusters in the zeolite cage.

Fig.1(a) shows radial distribution function $|F(r)|$ around As atom which is obtained from Fourier transform of EXAFS function $\chi(k)$ weighted by k for Y- As_2S_3 at 80 K. The solid line represents $|F(r)|$ before light irradiation. It is found that the first peak is almost identical to that of c- As_2S_3 , which suggests that the three As-S bonds forming AsS_3 pyramidal units

are preserved in the clusters. On the other hand, the second peak is found to be much smaller than that of crystal, indicating that there is large disorder in the correlation between second nearest As-As atoms.

Fig.1(b) shows $|F(r)|$ around As atom for Y-AsS. The solid line represents $|F(r)|$ before light irradiation. The main peak consists of two peaks, the first one is due to the contributions of two As-S bonds and the second one is due to the contribution from one As-As bond. The second peak around 3 Å is due to contributions from non-bonding As-S and As-As correlations. Since the atomic distances obtained from a parameter fit analysis on the first and second peaks are very close to the intra-molecular atomic distances for c-AsS, we suppose that the As_4S_4 molecular units are preserved in the clusters in zeolite cages. The intensity of the second peak around 3 Å is less than half of that for crystal, though the main peak is almost identical to that of c-AsS[10]. The decrease of the intensity of the second peak may be arised from deformations of the molecule and/or decrease of inter-molecular correlation.

3.2. Room temperature PA spectra

Fig.2(a) shows Photoacoustic (PA) spectra of Y- As_2S_3 together with that of c- As_2S_3 . The position of absorption edge of Y- As_2S_3 is almost the same as that of c- As_2S_3 . On the other hand, the position of the absorption edge of Y-AsS shown in Fig.2(b) is in higher side, compared with that of c-AsS. The blue shift of the absorption edge is also observed for the CdS clusters grown in zeolites and for the isolated Se chains in mordenite[5-7]. The blue shift is attributable to the narrowing of the electronic band structure, which is commonly seen in semiconductor microclusters[11]. No photodarkening effect was observed at room temperature.

3.3 Photodarkening effect

Fig.3.(a) shows PA spectra of Y- As_2S_3 at 70 K. The dashed line represents the spectrum before light irradiation and the solid, chain and dotted lines represent those after light irradiation with photon energy shown in the figure. The duration of the irradiation was 60 min. By the irradiation, the absorption edge shifts towards lower energy and the slope of the edge becomes small. The

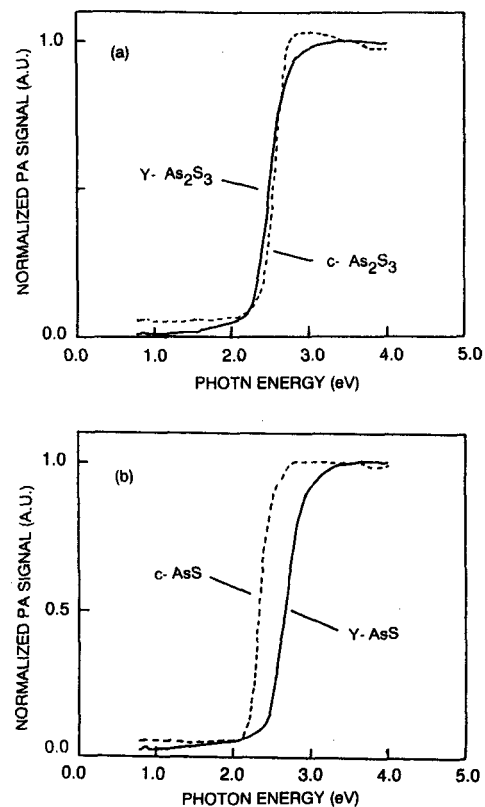


Figure 2: The PA spectra at room temperature. (a) Y- As_2S_3 and c- As_2S_3 . (b) Y-AsS and c-AsS.

amount of the shift depends on the energy of the light. These shifts are restored by the annealing at room temperature.

The photodarkening effect of Y-AsS shown in Fig.3(b) is larger than that of Y- As_2S_3 . It is worth pointing out that no photodarkening effect is observed for amorphous AsS. Geometrical or chemical modifications of clusters in zeolite cages may play an important role in the photodarkening effect. The shifts are restored by annealing at room temperature. Similar photodarkening effects are observed in the isolated chalcogen chains and the CdS clusters[5-7]. The changes in PA spectra of chalcogen chains and CdS clusters consist of many absorption bands, however the changes observed in Y- As_2S_3 and Y-AsS have less structure.

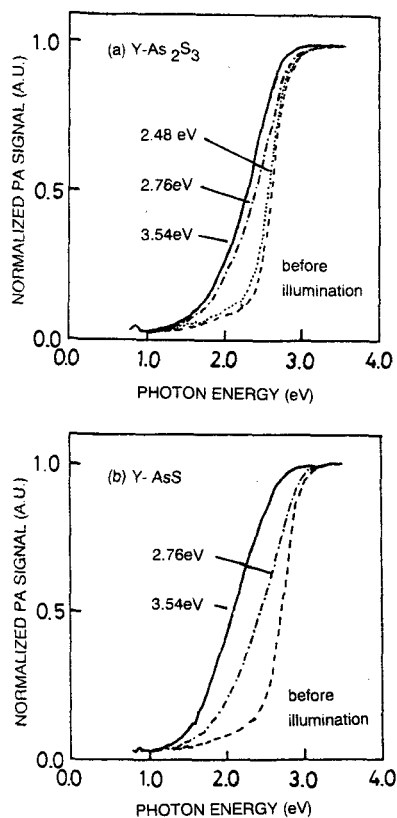


Figure 3: The Photodarkening effect at 70K. (a)Y-As₂S₃. (b)Y-AsS.

3.4 Photo structural change

The dotted line in Fig.1(a) represents $|F(r)|$ for Y-As₂S₃ after light irradiation at 80 K. The intensity of first peak slightly decreased after light irradiation. This change was not restored by the annealing at room temperature. The possible origins of the change are increase of fluctuation in bond length and the decrease of the As-S coordination number due to bond breaking. The decrease of the first peak was observed in light-irradiated amorphous Se and the isolated Se chains[5].

The dotted line in Fig.1(b) represent $|F(r)|$ for Y-AsS measured after light irradiation at 80 K. The peak at the higher r side of the main peak moves toward lower r -direction. Since this part is due to the contributions from As-As bond, it indicates shortening of the As-As bond. In addi-

tion the intensity of second peak decreased with light irradiation. This decrease is ascribed to the increase of the fluctuations in the correlation between non-bonding atoms. These changes were partly restored by the annealing at room temperature, as shown by the dashed line. Similar decrease of second peak in $|F(r)|$ was reported for light-irradiated amorphous As₂S₃ [12]. In addition, increases of disorder in intermediate range order was reported by a recent anomalous x-ray diffraction study on photo structural change in amorphous As₂S₃ [13]. The reversible structural change in Y-AsS may have relation to the photodarkening effect.

In summary we found various photo-induced changes in Y-As₂S₃ and Y-AsS. These changes are similar to those observed in CdS clusters in zeolites and isolated Se chains in mordenite as well as those in amorphous As₂S₃.

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