

Study of Polarized Absorption Spectra of Se Chain Incorporated into Zeolite AFI

T. Kodaira^{a,b}, M. S. Ivanova^{a*}, Y. Kiyozumi^{a,b}, H. Takeo^{a,b}, T. Yamamoto^c and V. V. Poborchii^{d+}

^a National Institute for Advanced Interdisciplinary Research, 1-1-4 Higashi, Tsukuba, Ibaraki 305, Japan

^b National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305, Japan

^c Advanced Technology Laboratory, Kubota Corp., 5-6 Koyodai, Ryugasaki, Ibaraki 301, Japan

^d Institute for Materials Research, Tohoku University, Katahira, Aoba-ku, Sendai, Miyagi 980-77, Japan

Se atoms were successively loaded into one-dimensional channels of zeolite AFI with several number density. Optical properties of these samples were studied by polarized microoptical absorption spectra. When Se loading density is high, large anisotropy was observed in the spectra. From the anisotropic property and the energy of absorption edge, it is elucidated that one Se chain is formed in each channel. On the contrary, no anisotropy was observed in case of low loading density. This indicates that Se₂ molecules and/or Se rings are randomly oriented in the space of the channel.

1. INTRODUCTION

Clusters in nano-size cages of zeolites have been attracted much attention because of their newly created interesting properties which originate from mutual interaction between them[1]. Many different framework structure type is well known, such as not cage type but channel one. The latter one will be the fascinating host for stabilizing quantum wires with high density and homogeneous diameter. Quantum wires is predicted to have a large anisotropy in their electronic properties, because electron can move only in one-direction. Therefore, studies of quantum wires should be performed under considering the anisotropy of them.

Zeolite AFI is a good candidate to stabilize one dimensional system, since it has nano-size cylindrical channel. Furthermore, large size single crystal over 100 μm is relatively easy to be synthesized at AFI. The framework of AFI is shown in Figure 1. Ideal

chemical formula of AFI is Al₁₂P₁₂O₄₈. Al and P atoms site alternately across O atoms. The cylindrical channels with inner diameter 7.3 Å array parallel to *c*-axis and are completely isolated each other. In an unit cell, one channel exists and lattice constant of *c*-axis is 8.4 Å. AFI has no cation which exists in alumino-silicate type zeolite. Adsorption potential of AFI for guest materials, such as organic molecules and semiconductors, seems to be mainly supplied by the permanent dipole of Al and P atoms. This means that guest materials will be loaded by this physisorption potential, and the arrangement of them is expected to obey the periodicity of the framework.

Selenium (Se) is one of the suitable material to incorporate into AFI and to study its properties, because;

(1) Se will form chain or rings by changing dihedral angle to suit the size and shape of the channels or cages.

Present address;

* Pskov State Pedagogical Institute, Pskov, 180760, Russia, ⁺ Ioffe Physico-Technical Institute, St. Petersburg 194021, Russia

(2) Se will be easily loaded into zeolites through vapor phase, and is stable even if it is treated at atmospheric condition.

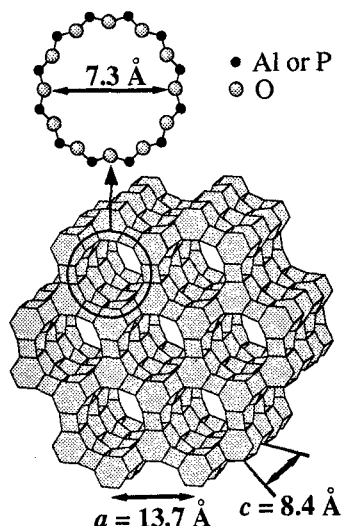


Figure 1 Illustration of AFI framework. Inner diameter of the channel which is parallel to c -axis is 7.4 \AA .

Praise *et al.* reported photo absorption and EXAFS spectra of Se loaded AFI (Se/AFI) powder sample[2]. They obtained a result of the formation of Se chains in the channels. In their sample, loading density of Se atoms were fixed only to *ca* 3 per unit cell. It is necessary to study the samples with various Se loading densities, because the electronic properties and structures of Se species may depend on them. Furthermore, optical properties of highly orientation with anisotropic structure should be studied by using the polarized probe light and large single crystal sample.

In this study, polarized optical absorption spectra of Se/AFI single crystal with various Se loading density were measured. It is made clear that one Se chain is formed in a channel at high loading density. However, at low loading density, Se chain is not formed.

2. EXPERIMENTAL

AFI single crystals were synthesized by the procedures that Finger *et al.* [3] and Demuth *et al.* [4] reported with some modifications. Hexagonal rod-

like crystals with maximum size of *a*. 120 and $50 \mu\text{m}$ along and across c -axis, respectively, were obtained. Chemical formula of obtained AFI was $\text{Al}_{11}\text{Si}_2\text{P}_{11}\text{O}_{48}$ determined by Inductively Coupled Plasma (ICP) spectroscopy. It is checked by powder X-Ray Diffraction (XRD) that the crystals have AFI structure, even if Al and P atoms are partly substituted by Si atoms.

After sealing bulk Se and dehydrated AFI in a vacuumed glass tube, Se atoms were loaded into AFI through vapor phase by elevating temperature to 400°C . Loading density of Se was controlled by changing the heat treatment time. Saturated sample was prepared by keeping temperature at 400°C for long enough until the color of crystal did not change any more. Loading density of Se was determined by ICP spectroscopy or energy-dispersive X-ray analysis. All the samples are homogeneously colored from light to dark orange with increasing the Se loading density.

Polarized absorption spectra were measured at room temperature by using a microoptical apparatus. Polarization of incident light was fixed at $E // c$ and $E \perp c$.

3. RESULTS AND DISCUSSION

Figure 2 shows the absorption spectra of Se/AFI at room temperature. Loading densities of samples from *a* to *d* are 0.1, 0.6, 1 and 6 atoms per unit cell, respectively. In sample *a*, absorption bands at 3.5 and 4.6 eV are observed without showing any anisotropy. With increasing Se loading density, anisotropic behavior becomes notable especially at the absorption edge. As a result, a strong band at 2.75 eV is observed at spectrum of $E // c$ of sample *d*. Compared with spectra of $E // c$, spectral shape of $E \perp c$ have slight change with increasing loading density. The observation of high anisotropy for saturated sample *d* indicates the formation of Se chain in a channel as already reported[2]. The bulk trigonal Se (*t*-Se) crystal parameters support this conclusion, since the inner diameter of the channel is large enough to stabilize an Se chain in it. Optical transition at the absorption edge originate from electron excitation between lone pair (LP) state and σ^* state of $4p$

between lone pair (LP) state and σ^* state of 4p electron, respectively. Energy of LP state is disturbed by the interaction with neighboring chains[7]. Therefore, energy of absorption edge give us information of inter-chain interaction.

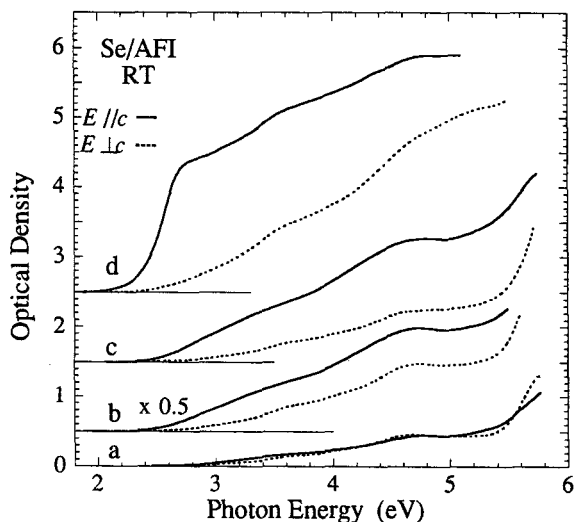


Figure 2 Polarized absorption spectra of Se/AFI at room temperature. Density of loaded Se atoms are $a:0.1$, $b:0.6$, $c:1$, $d:6$ per unit cell.

Results of formation of Se chains in other channel type zeolites, MOR[5] and LTL[6], should be compared with above result to discuss more details of the form of the chain. MOR has elliptic channel whose inner size is $7.0 \times 6.5 \text{ \AA}$. LTL has channels of one-dimensionally connected spherical cages with window size of 7.1 \AA . Fig. 3 is the spectra at absorption edge of Se loaded LTL (Se/LTL), MOR (Se/MOR) and AFI at room temperature. Absorption spectrum of Se/LTL is obtained by transforming diffuse reflection spectrum. From transmission electron microscope observation, it is elucidated that one Se chain exists in a channel of MOR[7]. Absorption edge of Se/LTL is red shifted compared with Se/MOR. This shift is interpreted by the model that plural Se chains in a channel interact each other[6]. Therefore, it can be concluded that one Se chain exist in each channel of AFI as in MOR from the coincidence of the absorption edge of Se/AFI and Se/MOR. However, detailed structure of Se chain in

AFI will differ from that in MOR[5].

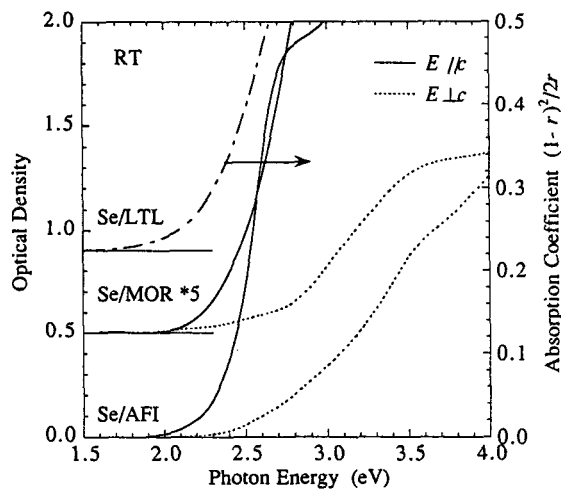


Figure 3 Absorption spectra of Se/LTL, Se/MOR and Se/AFI at room temperature.

In AFI, Se chain may locate along wall of the channel, because inner wall of the channel gives homogeneous physisorption potential as mentioned before. A Se chain of *t*-Se has three-fold spiral structure. To saturate the channel of AFI by Se atoms, it seems that Se chain has spiral structure, because, this structure of a Se chain has the most highest packing density geometrically. If the periodicity of the Se chain and the channel commensurate, the chain may have six-fold symmetry, because the space group of AFI framework is P6cc and loading density of Se atoms at sample *d* is six per unit cell. Four-axes XRD study of Se/AFI single crystal was carried out to confirm this speculation. We could only obtain the information of lattice constant of AFI framework before and after loading Se as, $a=13.75 \text{ \AA}$, $c=8.43 \text{ \AA}$ and $a=13.79 \text{ \AA}$, $c=8.40 \text{ \AA}$, respectively. This means that, by loading Se atoms, inner diameter of the channel becomes slightly larger and this distortion leads to the decrease of lattice constant of *a*-axis. In Se/MOR system, from the result of Raman scattering measurement, it is concluded that Se chain has characteristic spiral structure [5].

No anisotropy observed in dilutely loaded AFI sample *a* indicates two possibility. One is that

anisotropic Se species randomly orient in the channel. The other is that Se species themselves have no or very small anisotropic electronic state. In the gas phase selenium, several allotropes, such as Se_n ($n=2, 3, 5-8$) molecules or rings, are known. All these allotropes seem to have anisotropic electronic state. If these species are the adsorbents in the channel, the smaller these species are, the easier to orient randomly. Here, ring type structures with small number of atoms are most probable, because dangling bond should be avoided. In case of loading BiI_3 molecules dilutely into channel of AFI, very small anisotropy was observed in the polarized absorption spectra, too[8]. It is interpreted that isolated BiI_3 molecules are arrayed randomly despite of effective size of BiI_3 molecule is slightly larger than inner diameter of the channel. It may be requested for guest materials to show anisotropic properties that they should be loaded into the channels with high density to form chains of covalent bond, or array each other through permanent dipole of a molecule or hydrogen bonding, as the arrangement of *p*-nitroaniline[9, 10], because channels of AFI is constructed only by six membered rings, and has no sub-channels or side pockets which will be the trigger of the orientation.

In intermediately loaded sample *b* and *c*, the gradual increase of the anisotropy indicates the gradual formation of Se chain. With increasing Se loading density, polymerization of Se species will occur and form short Se chains, because average distance between Se species becomes smaller. As a result, in the intermediately loaded sample, short Se chains and Se rings will coexist. Under this discussion, there is an unclear behavior of the spectra. Spectra of $E \perp c$ has small dependence on Se loading density. If the Se chain becomes longer, electronic state should be modified. This will be discussed with actual structure determined by XRD in future.

4. SUMMARY

Se atoms are successfully loaded into the channels of AFI single crystal with various loading density, from dilute to saturated one. Structures of formed species of Se in the channel is discussed from polarized absorption spectra. It is made clear that

one Se chain is formed in each channel at high Se loading density. It seems that these chains are formed by the polymerization of Se molecules or rings with increasing the number density of these species.

5. ACKNOWLEDGMENT

The authors would like to thank to Prof. Y. Nozue of Tohoku University for using microoptical apparatus which is constructed by him. They also thank to Dr. J. Akimoto of National Institute of Materials and Chemical Research for the measurement of four-axes XRD.

REFERENCES

- 1 Y. Nozue, T. Kodaira, S. Ohwashi, T. Goto and O. Terasaki, Phys. Rev. B48(1993) 12253
- 2 J. B. Parise, J. E. MacDougall, N. Herron, R. Farlee, A. W. Sleight, Y. Wang, T. Bein, K. MoMoller and L. M. Moroney, Inorg. Chem. 27(1988) 221.
- 3 G. Finger and J. Kornatowski, Zeolites 10(1990) 615.
- 4 D. Demuth, G. D. Stucky, K. K. Unger and F. Schuth, Microporous Matt. 3(1995) 473.
- 5 V. V. Poborchii, M. S. Ivanova and S. S. Ruvimov, Stud. Surf. Sci. Catal. 84(1994)2285
- 6 Y. Nozue, T. Kodaira, O. Terasaki, K. Yamazaki, T. Goto, D. Watanabe and J. M. Thomas, J. Phys.:Condens. Matter 2(1990)5209.
- 7 O. Terasaki, K. Yamazaki, J. M. Thomas, T. Ohsuna, D. Watanabe, J. V. Sanders and J. C. Barry, Nature 330(1987) 58.
- 8 Y. Ikemoto, Y. Nozue, S. Qiu, O. Terasaki, T. Kodaira, Y. Kiyozumi and T. Yamamoto, to be published in Matt. Engin. A
- 9 S. D. Cox, T. E. Gier and G. D. Stucky, Chem. Mater., 2(1990) 609
- 10 F. Marlow, K. Hoffmann, G.-G. Lindner, I. Girmus, G. van de Goor, J. Kornatowski and J. Caro, Microporous Mater. 6(1996) 43.