

IR and XAFS Studies of Photoluminescent Ag-type Zeolite-A

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Abstract

We examined the relation between the zeolite framework, Ag clusters, and properties of photoluminescence (PL) using in-situ infrared spectroscopy (IR) and X-ray absorption fine structure (XAFS). The Ag clusters are generated in the cavity of Ag-type zeolite-A that is cooled to room temperature after heating at 500°C for 24 hour under vacuum or in atmosphere. The Ag clusters in the zeolite cavity break down when air is introduced. According to the formation and breakdown of the Ag cluster, the infrared spectrum of the zeolite framework changed slightly. Then, this change was compensated by irradiation of the excitation light. Results suggest that the structural change in the zeolite induced by the formation and breakdown of the Ag clusters is a key point of the PL mechanism.

Keywords: Ag-type zeolite-A, Ag clusters, photo luminescence, infrared spectroscopy, XAFS

1 Introduction

Zeolites are crystalline aluminosilicates exhibiting unique properties because of the presence of cavities (cages) in their structure [7, 10, 11, 18]. Because of their micro-porosity, zeolite have very high surface area. They have been widely used in applications such as catalysis, ion exchange, and separation [2, 4, 13, 17]. In addition, zeolite is an inexpensive material. A promising property of Ag^+ exchanged zeolite is photoluminescence (PL). In fact, Ag-zeolite is a luminescent material despite having no rare earth metal constituent. Recently, many researchers have explored the emissive behavior of silver-exchanged zeolite [3, 5, 9, 16]. Various reports have explained that the photoluminescence of Ag-zeolite derives from Ag clusters formed in the zeolite framework. However, in the study of PL, the presence of Ag clusters has only been confirmed indirectly. In a recent study, we took PL and XAFS measurements simultaneously to ascertain the relation between the PL band and the local structure of the Ag cluster [14]. Results confirmed that the Ag clusters are formed during heat treatment processing. Then Ag clusters are broken down when cooled to room temperature (RT). The unheated XAFS spectrum and the cooled spectra are very similar in XAFS measurements. No PL band from unheated Ag-zeolite-A is observed, but strong PL bands are exhibited from the heat-treated sample. From XAFS measurements, no difference was observed between the heat treated state (PL was observed) and the unheated state (PL was not appeared).

Vibrational spectroscopy has gained wide recognition for its capability for determining the chemical nature of materials. Particularly, infrared spectroscopy (IR) has achieved high sensitivity at high resolution. For Ag-zeolite measurements, XAFS is useful to observe the local structure around the Ag, observing the framework in IR. Consequently, when measuring Ag-zeolite, the combination of IR and XAFS is a superior means of obtaining complementary information. As described in this paper, we combined three techniques (PL, IR, and XAFS) to investigate the PL mechanism from the perspectives of the zeolite framework and the Ag local structure. In addition, we describe the effects of laser radiation on IR spectra.

2 Experimental

Fully Ag-exchanged zeolite-A (hydrated 12Ag-A) powder samples were prepared using ion-exchange method. The Ag-type zeolite-A was heated at 500°C under atmosphere or vacuum to produce the Ag cluster. Then PL measurements were taken using a UV-VIS spectrometer (SPM-002; KLV Co. Ltd.) and a 405 nm violet laser (SU-61-405; Audio-Technica Corp.) light source. The Ag-type zeolite-A was set in the in-situ infrared, photoluminescence, and XAFS measurement high vacuum chamber (RVX-3 [14]) in which the sample can be heated to 600°C in vacuum and atmosphere. All measurements were performed at RT. The IR light absorption spectra were obtained at normal incidence of radiation. The measurements were taken using a spectrometer (MB-100; ABB Bomem) equipped

with DTGS detector at 4 cm^{-1} resolution with 128 interferometric scans.

X-ray absorption spectra of *K*-edge of Ag (25 keV) were measured at NW10A at the Photon Factory at KEK with transmission mode. XANADU code and FEFF 8.10 were used for XAFS analyses.

Ag-type zeolite-A was heated at 500°C for 24 hr in atmosphere or vacuum to produce Ag clusters [6]. For vacuum processing, they were cooled to RT; then air was introduced. Furthermore, we have conducted observations of the framework change because of UV-laser irradiation. Experimental details are presented in reports of several earlier studies [6, 12, 14].

3 Results and Discussion

Fig. 1 shows PL spectra of Ag-zeolite for unheated and heat-treated conditions excited by 405 nm. Before heat treatment processing at 500°C (unheated sample: dashed line), photoluminescence was not observed. We have already confirmed that Ag-zeolite-A does not emit luminescence in a vacuum even after heating. After exposure to air, the strongest intensity of the PL band around 2.1 eV was observed

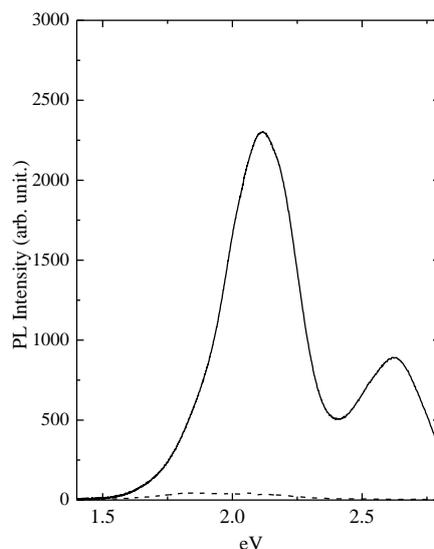


Fig. 1: PL curves for unheated (dashed line) and heat-treated (solid line) Ag type zeolite-A measured in air

(solid line). Even in the case of heat-treated in air, a strong PL band was observed at ca. 2.1 eV from Ag-zeolite-A. Results show that PL of Ag-zeolite-A is independent of the heating environment. However, it is necessary that the atmosphere coexist at the time of measurement. It is important that the air coexists when measuring luminescence.

Figure 2 shows the Ag-K EXAFS $k^2 \chi(k)$ spectra for the unheated Ag-type zeolite-A at RT in atmosphere (solid line), at RT in vacuum after heated (dashed line), and after air was introduced (dotted line). Results show that the structure changed around 3.5 \AA^{-1} after heating, which is a characteristic feature of generating the Ag clusters [6]. After air was introduced, the structure returned to its initial state around 3.5 \AA^{-1} . This change in $k^2 \chi(k)$ spectra indicates the crumbling of the Ag clusters.

Results of the curve fittings [14] are presented in Table 1. When the sample was evacuated, the *coordination number of Ag* (N_{Ag}) increased from 1.12 to 1.98, which indicates production of Ag clusters. Then it was observed that the Ag clusters were grown by heat treatment ($N_{\text{Ag}} \sim 2.58$). After cooling to RT, they remain ($N_{\text{Ag}} \sim 1.93$). After air was introduced, the strong PL band was observed as presented in Fig. 1. After introducing air, the Ag clusters disappeared. The *inter-atomic distances of Ag-Ag* (r_{Ag}) and N_{Ag} are nearly equal to those at the RT in atmospheric pressure. The air engenders breakdown of the Ag clusters. Judging from the results of the PL and the XAFS, the existence of the Ag clusters is not necessary to produce the strong PL band.

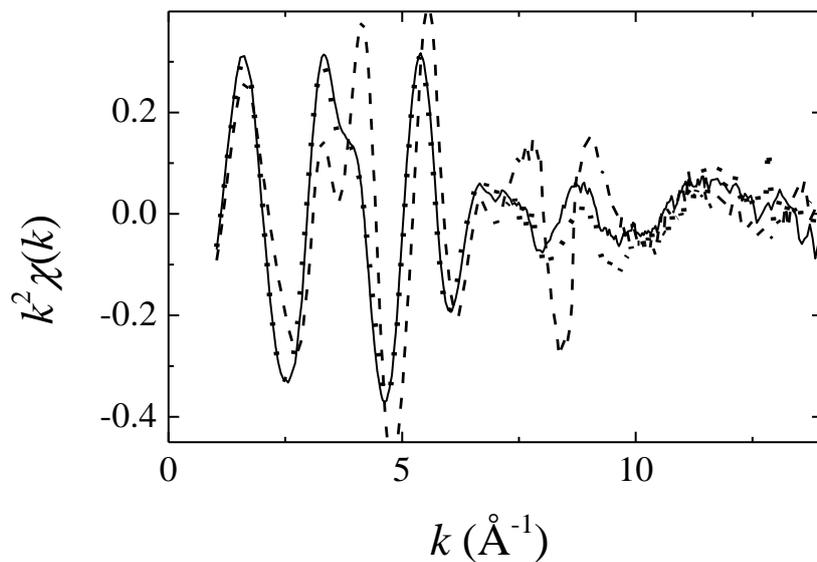


Fig. 2: EXAFS $k^2 \chi(k)$ spectra for Ag-zeolite-A at RT in atmosphere (unheated, solid line) and at RT in vacuum after heating (dashed line) and after air was introduced (dotted line)

Table 1. Structural parameters: r and N for various conditions

	r_{O1} (Å)	N_{O1}	r_{O2} (Å)	N_{O2}	r_{Ag} (Å)	N_{Ag}
unheated at RT	2.38	5.51	2.85	3.92	2.88	1.12
in vacuum at RT	2.30	3.70	2.82	3.89	2.83	1.98
in vacuum at 500°C	2.29	3.40	2.74	3.49	2.80	2.58
in vacuum at 500°C after 24 h heated	2.29	3.10	2.74	3.20	2.80	2.55
in vacuum at RT after 24 h heated	2.29	3.14	2.81	3.61	2.81	1.93
air introduced	2.38	4.57	2.86	2.96	2.86	1.40

Figure 3 presents the IR result obtained for the Ag-zeolite-A. The solid line shows

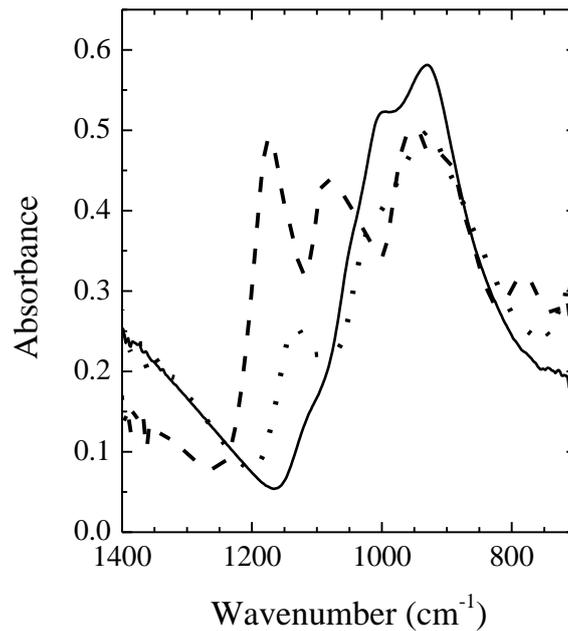


Fig. 3: IR absorbance spectra of Ag type zeolite-A unheated (solid line) after heating to 500 °C in vacuum (dashed line) and when air was introduced after heating in vacuum (dotted line)

the IR transmission spectrum of the unheated Ag-zeolite. Because zeolite has a complicated structure, the various Si-O and Al-O bands are superimposed. It is extremely difficult to discern one from the other. Therefore, assignment of the absorp-

tion band around 1000 cm^{-1} region is represented as $\nu(\text{T-O})$ ($\text{T} = \text{Si}$ or Al) [15]. Bands appearing at a high wavenumber are assigned to the ν_{as} mode, and in the lower wavenumber region are assigned to ν_{s} mode. The dashed line presents a spectrum of the Ag-zeolite cooled to RT after heating for 24 hr at $500\text{ }^{\circ}\text{C}$ in vacuum (measured in a vacuum). Compared to the unheated spectrum, the absorption band has been changed drastically. Although the individual band assignment is not known, as described above, considering the XAFS results, it is reasonable to infer that the change occurred because of Ag cluster formation. For cluster formation, it is necessary that Ag^+ ions (at least partially) be reduced to Ag^0 . Also Ag is to be aggregated away from the site at which Ag^+ ion was located. Reduction of ions and changing their position also affect vibration of the framework in each case. Differences in the distance Ag atoms from frameworks can perturb the vibration of the T-O, as can differences in the electrostatic attraction of Ag atom and Ag^+ ion. In other words, IR is probably a technique that is sensitive to such a change. The dotted line is the spectrum obtained after introducing air into zeolite-At RT after heating in vacuum. This spectrum greatly changed again, approaching much closer to the unheated spectrum shown as a solid line. However, although the spectra coincide substantially with the state air intake after heating and unheated is obtained for XAFS, in the case of IR, they are similar but do not match completely. In XAFS, the spectrum after introducing the atmosphere substantially coincides with the spectrum of the unheated. In the case of IR, they do not coincide completely.

A distinct band appeared at 1140 cm^{-1} . The strength of the main band of $1000\text{--}900\text{ cm}^{-1}$ has decreased slightly. In a state where the excitation light is illuminated (the state in which PL is expressed), the main band intensity increases and the intensity of 1140 cm^{-1} band decreases (Fig. 4(a)). The cause of this change is not apparent.

As the cause of this change, considering that almost no change in XAFS is observed, the following two hypotheses might be tested.

- (1) Oxygen deficiency is generated in the framework by treatment such as heating in vacuum.
- (2) After a cluster collapse, Ag^+ cannot be located at a stable site. Rather it is "caught" at a metastable site near a stable site. This metastable site must be a shift of the slight position that cannot be determined using XAFS.

Because Ag loading into zeolite occurs in solution for a sufficient time, Ag^+ ions can be positioned at the stable site. In contrast, disintegration after cluster formation occurs in atmosphere at RT and might not exceed a potential barrier existing between the stable site and metastable sites.

Figure 4(b) portrays difference spectra between excitation light irradiation and non-irradiation. When these are compared with the difference spectra obtained before and after heat-treatment shown in Figure 4(c), it is clear that change by the excitation light irradiation is the change to suppress the change caused by heat treatment. For these reasons, the spectral change by heat treatment is related directly to the PL. Changes in 1070 cm^{-1} of spectra have increased by both of heating and excitation light irradiation. This change is currently under investigation.

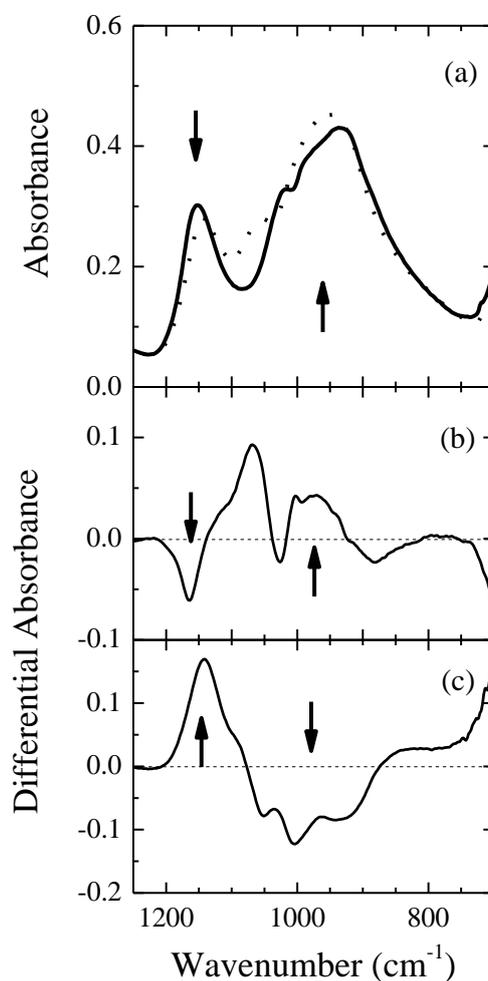


Fig. 4:

- (a) IR absorbance spectra of Ag type zeolite-A before laser irradiation (solid line) and during irradiation (dashed line).
(b) Differential IR absorbance measured before and after laser irradiation.
(c) Differential IR absorbance for unheated, and after air was introduced after heating in vacuum

4 Conclusion

We studied in-situ IR and XAFS to assess structural changes of zeolite framework and Ag cluster after heat treatment and introduction of air. Results show that the Ag clusters were formed by heat-treatment and were then broken when air was introduced. Along with the formation and breakdown of the Ag cluster, the infrared spectrum of the zeolite framework changed slightly. Then, this change was compensated by irradiation of the excitation light.

Results suggest that the change of the zeolite framework after heat-treatment and introduction of the air plays an important role of expression of the strong PL band. Ag clusters might not be direct species for the PL. We infer the possibility that the slight site change of Ag⁺ ion in the zeolite cavity induced by the formation and breakdown of Ag clusters is a key point of the PL mechanism.

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References

- [1] H. Aono, K. Kanayama, E. Johan, Y. Itagaki, N. Matsue, Amorphous materials prepared by heat treatment at low temperature for partially Ag-exchanged Na-P1 type zeolites and their photoluminescence properties, *J. Ceram. Soc. Japan*, **124** (2016), 82-84. <http://dx.doi.org/10.2109/jcersj2.15140>
- [2] A. Carvalho, M. Carvalho, J. Pires, Degree of crystallinity of dealuminated offretites determined by X-ray diffraction and by a new method based on nitrogen adsorption, *Zeolites*, **19** (1997), 382-386. [http://dx.doi.org/10.1016/s0144-2449\(97\)00101-2](http://dx.doi.org/10.1016/s0144-2449(97)00101-2)
- [3] G.D. Cremer, E.C. Gonzalez, M.B.J. Roeffaers, B. Moens, J. Ollevier, M.V. der Auweraer, R. Schoonheydt, P.A. Jacobs, F.C. De Schryver, J. Hofkens, D.E. De Vos, B.F. Sels, T. Vosch, Characterization of Fluorescence in Heat-Treated Silver-Exchanged Zeolites, *J. Am. Chem. Soc.*, **131** (2009), no. 8, 3049-3056. <http://dx.doi.org/10.1021/ja810071s>
- [4] R.S. Gomez, X. Li, R.L. Yson, H.H. Patterson, Zeolite-supported silver and silver-iron nanoclusters and their activities as photodecomposition catalysts, *Res. Chem. Intermed.*, **37** (2011), 729-745. <http://dx.doi.org/10.1007/s11164-011-0313-z>
- [5] E. C-Gonzalez, W. Baekelant, D. Grandjean, M.B.J. Roeffaers, E. Fron, M.S. Aghakhani, N. Bovet, M.V. der Auweraer, P. Lievens, T. Vosch, B. Sels, J. Hofkens, Thermally activated LTA(Li)-Ag zeolites with water-responsive photoluminescence properties, *J. Mater. Chem. C*, **3** (2015), 11857-11867. <http://dx.doi.org/10.1039/c5tc02723c>
- [6] H. Hoshino, Y. Sannohe, Y. Suzuki, T. Azuhata, T. Miyanaga, K. Yaginuma, M. Itoh, T. Shigeno, Y. Osawa, Y. Kimura, Photoluminescence of the Dehydrated Ag-type Zeolite A Packed under Air, *J. Phys. Soc. Japan.*, **77** (2008), 064712. <http://dx.doi.org/10.1143/jpsj.77.064712>

- [7] Y. Kim, K. Seff, The octahedral hexasilver molecule. Seven crystal structures of variously vacuum-dehydrated fully silver(1+)-exchanged zeolite A, *J. Am. Chem. Soc.*, **100** (1978), 6989-6997. <http://dx.doi.org/10.1021/ja00490a035>
- [8] A.S. Kuznetsov, V.K. Tikhomirov, M.V. Shestakov, V.V. Moshchalkov, Ag nanocluster functionalized glasses for efficient photonic conversion in light sources, solar cells and flexible screen monitors, *Nanoscale*, **5** (2013), 10065. <http://dx.doi.org/10.1039/c3nr02798h>
- [9] S.H. Lee, Y. Kim, K. Seff, Weak Ag⁺-Ag⁺ bonding in zeolite X. Crystal structures of Ag₉₂Si₁₀₀Al₉₂O₃₈₄ hydrated and fully dehydrated in flowing oxygen, *Microporous and Mesoporous Mater.*, **41** (2000), 49-59. [http://dx.doi.org/10.1016/s1387-1811\(00\)00270-5](http://dx.doi.org/10.1016/s1387-1811(00)00270-5)
- [10] T. Miyanaga, H. Hoshino, H. Endo, Local structure of silver clusters in the channels of zeolite 4A, *J. Synchrotron Radiation*, **8** (2001), 557-559. <http://dx.doi.org/10.1107/s0909049500012668>
- [11] T. Miyanaga, H. Hoshino, H. Endo, H. Sakane, XAFS study of silver clusters in zeolites, *J. Synchrotron Radiat.*, **6** (1999), 442-444. <http://dx.doi.org/10.1107/s0909049599000631>
- [12] T. Miyanaga, Y. Suzuki, N. Matsumoto, S. Narita, T. Ainai, H. Hoshino, Formation of Ag clusters in zeolite X studied by in situ EXAFS and infrared spectroscopy, *Microporous Mesoporous Materials*, **168** (2013), 213-220. <http://dx.doi.org/10.1016/j.micromeso.2012.09.013>
- [13] R.M. Mohamed, L.A. Mkhallid, M. Abdel Salam, M.A. Barakat, Zeolite Y from rice husk ash encapsulated with Ag-TiO₂: characterization and applications for photocatalytic degradation catalysts, *Desalin and Water Treat.*, **51** (2013), no. 40-42, 7562-7569. <http://dx.doi.org/10.1080/19443994.2013.775671>
- [14] A. Nakamura, M. Narita, S. Narita, Y. Suzuki, T. Miyanaga, In-situ XAFS study of Ag clusters in Ag-type zeolite-A, *J. Phys.*, **502** (2014), 012033. <http://dx.doi.org/10.1088/1742-6596/502/1/012033>
- [15] S.A. Rodrigues, Vibrational spectroscopy and structural analysis of Na-Y zeolite, *Vib. Spectroscopy*, **9** (1995), 225-228. [http://dx.doi.org/10.1016/0924-2031\(94\)00082-r](http://dx.doi.org/10.1016/0924-2031(94)00082-r)
- [16] R. Seifert, R. Rytz, G. Calzaferri, Colors of Ag⁺-Exchanged Zeolite A, *J. Phys. Chem.*, **104** (2000), 7473-7483. <http://dx.doi.org/10.1021/jp000905z>

- [17] H.S. Sherry, S.M. Auerbach, K.A. Carrado, P.K. Dutta, *Handb. Zeolite Sci. Technol.*, (2003), 1007.
- [18] T. Sun, K. Seff, Silver Clusters and Chemistry in Zeolites, *Chem. Rev.*, **94** (1994), 857-870. <http://dx.doi.org/10.1021/cr00028a001>

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