A luminescent material free of rare earth elements was prepared from a partially Ag⁺ exchanged zeolite X. One gram of a commercially available zeolite X (Na⁺ form) was mixed with 100 mL of AgNO₃ aqueous solutions of 2.0 to 50 mmol/L. The mixtures were shaken for 24 h, then the solid products were separated and dried at 50°C. Some of the products were heated at 100 to 800°C in atmospheric air. Luminescence was observed from the products with Ag loadings of 0.5 mmol/g or higher. These products showed yellow luminescence under UV light excitations of 254 and 312 nm. The luminescent products showed two excitation bands with peak maxima at 271 and 311 nm, and a single emission band at 550 nm. The luminescence intensity was low for the 0.5 mmol/g Ag loaded sample, but it significantly increased with the increasing amounts of Ag⁺ up to 1.0 mmol/g loading, then a quenching occurred with a further increased Ag⁺ loading. Heating of the Ag-loaded zeolite X decreased the luminescence intensity. Heating the Ag loaded zeolite X at 800°C resulted in a low blue luminescence intensity due to collapsing the zeolite X structure into an amorphous phase. This study suggested that a luminescent material free of rare earth elements can be fabricated from Ag-exchanged zeolite X without any heat treatment. The highest luminescence intensity was attained at the Ag loading of 1.0 mmol/g, along with a measured internal quantum efficiency of 20.8% (λ ex. = 311 nm).

©2016 The Ceramic Society of Japan, All rights reserved.

Key-words : Zeolite X, Luminescence, Ag loading, Excitation, Emission

1. Introduction

Zeolites are crystalline hydroxy-aluminosilicates consist of silicon, aluminum, and oxygen atoms, showing unique properties due to the presence of channels or cavities in their crystal structure.⁵ Along with the isomorphous replacement of Si by Al, negative charges are generated, thus zeolites have a capacity to absorb metal cations.² Zeolites have adsorption capacity for heavy metals adsorption such as copper³ and lead,⁴ as well as for silver ion.⁵

Many studies were focused on silver exchanged zeolites, due to their function as catalyst, for example Ag exchanged ZSM-5 as catalyst for CO oxidation,⁶ or photocatalytic decomposition of NO into N₂ and O₂,⁷ or silver doped zeolite Y as antibacterial.⁸ In addition to those functions, luminescence phenomena were shown by some silver-exchanged zeolites, for example, some studies reported a luminescence from a dehydrated Ag exchanged zeolite A heated at 450°C,⁹-¹¹ heated Ag-exchanged zeolite Y⁹,¹²,¹³ and heated Ag-exchanged zeolite X.⁹ Those luminescences were ascribed to the presence of a silver cluster formed due to reduction of Ag⁺ ions during the heat treatment.¹⁰,¹³

Although the luminescence phenomena of the silver-exchanged zeolites were observed in those studies, but the luminescence intensities and properties were not discussed intensively. It seemed that the authors were more interested in the method to obtain a stable silver nano-cluster rather than the luminescence properties, due to the silver cluster zeolite shows catalytic properties.¹¹,¹⁶ On the other hand, luminescence intensity is an important factor for luminescence application, and strong intensity is required. Moreover, those studies reported that the luminescence was observed for the heated silver-exchanged zeolites. Our previous study indicated that a violet emission (λ = 390 nm) excited at 254 nm could be prepared from a Na-P1 zeolite by partially loading AgNO₃ solution into the Na-P1, and subsequently heating at 800°C.¹³

In this study, a luminescent material was prepared from a partially silver ion exchanged on zeolite X by a conventional cation exchange process. Different from the previous studies, in this study, a yellow luminescence was obtained from a partially Ag⁺ exchanged zeolite X without heating. The aim of the study was to find an inexpensive and strong luminescent material free of rare earth elements for industrial application such as for a sensor for counterfeiting protection.

2. Experimental

Zeolite X (zeolite F-9 powder) was purchased from Wako Pure Chemical Industries, Ltd., and was used without any purification or particle size separation. The zeolite X was a Na⁺ form. One gram of zeolite X was mixed with 100 mL of a AgNO₃ aqueous solution with various concentrations ranging from 2.0 to 50 mmol/L. The mixtures were shaken for 24 h at 25°C, then the solid phases were separated from the supernatants using a vacuum pump. The separated solid samples were dried at 50°C, then used as the Ag⁺-loaded zeolite samples. The concentration of the Ag⁺ in the supernatant was determined using atomic absorption spectrometry (Hitchi ZA 3300), in order to calculate the amount of Ag⁺ adsorbed or Ag⁺ occupancy in zeolite. To confirm the presence of the luminescence, the samples were first visually observed under UV lights (λ = 254 and 312 nm). The luminescent samples (Ag-loaded zeolite X) were then subjected

1 Corresponding author: H. Aono; E-mail: aono.hiromichi.mf@ehime-u.ac.jp
2 Preface for this article: DOI http://dx.doi.org/10.2109/jcersj2.124.P1-1

DOI http://dx.doi.org/10.2109/jcersj2.151599
for characterizations. The fluorescent signals were measured by a fluorescence spectrophotometer (Hitachi F-7000). The UV/VIS diffuse reflectance spectroscopy was done by a spectrophotometer (Hitachi U 4100). The UV/VIS diffuse reflectance spectroscopy was done by a spectrophotometer (Hitachi U 4100). The Cation exchange capacity (CEC) of the original zeolite X was determined by the K⁺ ion adsorption using a 1 M KCl solution. The CEC was determined by measurement of the K⁺ ion concentration in a desorbed and washed solution by atomic absorption spectrometry (Hitachi ZA 3300).

To investigate the effect of temperature, the samples were heated at various temperatures from 100 to 800°C for 2 h under atmospheric air. The excitation and emission spectra were measured by a fluorescence spectrophotometer (Hitachi F-7000). To investigate the change in the zeolite structure, X-ray diffraction (XRD) patterns of the heated samples were recorded using a Rigaku Rint 2000 diffractometer with Cu-Kα radiation (scanning rate = 2°/min at 40 kV and 20 mA).

Quantum efficiency was measured for a selected Ag-exchanged zeolite sample with the highest luminescence intensity. The measurement was carried out using a fluorescence spectrophotometer (Hitachi F-7000) equipped with a quantum efficiency measuring accessory, and alumina (Al₂O₃) powder was used as a reference.

3. Results and discussion

3.1 Characterization of the samples before heat treatment

Figure 1 shows the relationship between the amount of Ag⁺ added and the percent of Ag occupancy. The percent of Ag occupancy means the percentage of Ag⁺ ion from the CEC. The CEC of this zeolite X was determined to be 5.50 mmol/g. The amount of Ag⁺ occupancy linearly increased with the increasing amount of the Ag loading. The graph indicates that almost 100% of Ag⁺-loaded was adsorbed by zeolite X. This is due to the fact that among the monovalent cations, the Ag⁺ ion has the highest affinity for zeolite X, and the affinity was in the order of Ag⁺ / Ti(+) > Cs⁺ / Rb⁺ > K⁺ > Na⁺ > Li⁺.)

Figure 2 shows a photograph of some selected Ag-loaded zeolites under UV lights of 254 and 312 nm wavelengths. At a low Ag loading (0.2 mmol/g), only a very weak luminescence was observed. The bright yellow luminescence appeared at a Ag loading of 0.5 mmol/g or more, and the strongest luminescence was observed for the Ag loading of 1.0 mmol/g. From these photographs, it was clearly shown that the luminescence intensity is affected by amount of Ag loaded.

Figure 3 shows emission spectra of the Ag-exchanged zeolite X with various amounts of Ag⁺ loadings under excitation at 311 nm wavelength. The labels in the graph indicate the amounts of Ag⁺ loaded in one gram of zeolite X. For example, 1.0 mmol means 1.0 mmol of AgNO₃ solution was loaded in one gram of zeolite X. All the samples exhibited a broad emission in the visible light range from 450 to 670 nm with a maximum band at around 550 nm. It is obvious that the luminescence intensity is affected by the amount of loaded Ag⁺. The lowest intensity was for the sample with the low loaded Ag⁺ (0.5 mmol/g), then significantly increased for the Ag⁺ loading of 1.0 mmol/g. However, the intensity gradually decreased with the increasing amount of Ag⁺. The maximum intensity was attained for the Ag loading of 1.0 mmol/g. This result supports the visual observation. The highest luminescence intensity was attained for the sample with the Ag loading of 1.0 mmol/g.

Figure 4 shows the fluorescence spectrum of the sample with the highest intensity (Ag loaded = 1.0 mmol/g) plotted together with that of YAG-Ce. This figure indicated that the intensity was about 40% than the intensity of the YAG-Ce (Nemoto...
The internal quantum efficiency of this luminescence measured at the excitation wavelength of 311 nm, was determined to be 20.8%. The Ag\(^{+}\) loading for this sample was 18% of CEC. Almost 100% of the added Ag\(^{+}\) was adsorbed by the zeolite, so this zeolite contains 18% Ag\(^{+}\) and 82% Na\(^{+}\).

Figure 5 shows a 2D excitation and emission matrix of the 1.0 mmol/g Ag\(^{+}\) loaded sample, as a representative sample. The matrix clearly shows that the luminescence consists of two excitations and one emission. The excitation bands have maximum peaks at 271 and 311 nm, and the emission band is centered at 550 nm. This indicates that the loaded Ag\(^{+}\) ions on the zeolite promote two excitation energies with different levels. The other luminescent samples also have the same pattern as shown in Fig. 5.

Figure 6 shows the UV/VIS diffuse reflectance (UV/VIS DR) spectra of some selected Ag loaded zeolite samples. A spectrum of the original zeolite X was also plotted for comparison. The original zeolite X exhibits a small absorption with a maximum peak at 264 nm, indicating that zeolite X has the ability to absorb UV light. With the Ag loading of 0.2 mmol/g, almost no change was observed, and in this case, only a very weak luminescence was observed (Fig. 2). At the Ag loading of 0.5 mmol/g or higher, two absorption bands were observed around 270 and 306 nm. For the Ag loadings of 0.5 and 1.0 mmol/g and higher, the intensity of the 260 nm band increased and a new band appeared at 310 nm. This indicates that with the increasing Ag, the UV absorption increased and a new UV absorption with lower energy occurs. The presence of the two absorbance peaks may be due to the Ag\(^{+}\) ions occupying the zeolite framework at different sites.

3.2 Effect of heat treatment on the luminescence properties

The heat treatment was carried out to increase the luminescence intensity (Ag\(^{+}\) loading = 1.0 mmol/g) plotted together with YAG-Ce. The UV/VIS diffuse reflectance spectrum of Ag zeolite sample (Ag loading = 1.0 mmol/g) plotted together with its excitation profile.
Refer to this study it is considered that Ag cluster may not be responsible for this luminescence, due to the unheated Ag-exchanged zeolite showed the highest luminescence intensity. Detailed analysis using EXAFS to investigate the Ag species will be carried out and reported elsewhere.

As already mentioned, the previous study reported a luminescence from the Ag⁺-exchanged zeolite A and zeolite Y with heating treatment at 400°C or higher. However, this study proved that a luminescence could occur from the Ag⁺-loaded zeolite X without any heat treatment. The preparation of the Ag zeolite luminescence without heat treatment is the first to be reported. By this technique, a low cost luminescent material free of rare earth elements can be easily prepared from commercially available zeolite X.

4. Conclusions

This study was the first to develop a method to prepare an Ag⁺-exchanged zeolite X luminescent material by only a simple ion exchange process without any heating treatment. The highest luminescence intensity was attained at the Ag loading of 1.0 mmol/g, occupying only 18% of cation exchange site. We succeeded in developing a producing a cheap luminescent material free of rare earth elements.

Acknowledgment This study was supported by the JSPS Kakenhi Grant Number 15H04619 (N. Matsue)

References

1) T. Sun and K. Seff, Chem. Rev., 94, 858–870 (1994).
2) E. Johan, T. Yamada, M. W. Munthali, P. Kabwadza-Grner, H. Aono and N. Matsue, Procedia Environ. Sci., 28, 52–56 (2015).
3) P. Kabwadza-Grner, M. W. Moses, E. Johan and N. Matsue, Am. J. Anal. Chem., 5, 394–405 (2014).
4) P. Kabwadza-Grner, E. Johan and N. Matsue, J. Environ. Prot. (Irvine Calif.), 6, 45–53 (2015).
5) M. Akgül, A. Karabakan, O. Acar and Y. Yürüm, Microporous Mesoporous Mater., 94, 99–104 (2006).
6) E. Kolobova, A. Pestryakov, A. Shemeryankina, Y. Kotolevich, O. Martynyuk, H. J. Tizzano Vazquez and N. Bogdanchiko, Fuel, 138, 65–71 (2014).
7) S. M. Kanan, M. C. Kanan and H. H. Patterson, Curr. Opin. Solid State Mater. Sci., 7, 443–449 (2003).
8) M. M. Salim and N. A. N. N. Malek, Mater. Sci. Eng., C, 59, 70–77 (2016).
9) G. De Cremer, E. Coutiño-Gonzalez, M. B. J. Roeffaers, B. Moens, J. Ollevier, M. Van der Auweraer, R. Schoonheydt, P. A. Jacobs, F. C. De Schryver, J. Hoffken, D. E. De Vos, B. F. Sels and T. Vosch, J. Am. Chem. Soc., 131, 3049–3056 (2009).
10) G. De Cremer, Y. Antoku, M. B. J. Roeffaers, M. Siwaja, J. Van Noyen, S. Smout, J. Hoffken, D. E. De Vos, B. F. Sels and T. Vosch, Angew. Chem., Int. Ed., 47, 2813–2816 (2008).
11) H. Hoshino, Y. Sannohnci, Y. Suzuki, T. Azuhata, T. Miyana, K. Yaginuma, M. Itoh, T. Shiogno, Y. Osawa and Y. Kimura, J. Phys. Soc. Jpn., 77, 064712 (2008).
12) G. A. Ozin and F. Hugues, J. Phys. Chem., 87, 94–97 (1983).
13) H. Aono, K. Kanayama, E. Johan, Y. Itagaki and N. Matsue, J. Ceram. Soc. Japan, 124, 82–84 (2016).
14) H. Aono, K. Tamura, E. Johan, T. Yamamoto, N. Matsue and T. Henni, J. Am. Ceram. Soc., 96, 3218–3222 (2013).
15) H. S. Sherry, Ion exchange in S. M. Auerbach, K. A. Carrado, P. K. Dutta (eds.), “Handbook of zeolite science and technology”, Marcel Dekker, New York, pp. 1007–1058.
16) T. Miyana, Y. Suzuki, N. Matsumo, S. Narita, T. Ainai and H. Hoshino, Microporous Mesoporous Mater., 168, 213–220 (2013).

Fig. 8. Emission spectra of Ag zeolite (Ag loading = 1.0 mmol/g) heated at various temperatures.

Fig. 9. XRD patterns of Ag loaded zeolite (Ag loading = 1.0 mmol/g) heated at various temperatures.