Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 27 Oct 2006

To cite this article: Tetsuya Kodaira & Takuji Ikeda (2000): Optical Transitions of Agi and Agbr Clusters in Zeolite Fau, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 341:2, 441-446

To link to this article: http://dx.doi.org/10.1080/10587250008026179

Mol. Cryst. and Liq. Cryst., 2000, Vol. 341, pp. 441-446
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Optical Transitions of AgI and AgBr Clusters in Zeolite FAU

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(In final form July 7, 1999)

AgI and AgBr clusters are both incorporated into the cages of zeolite FAU. The absorption spectra of these clusters, whose loading densities varied from dilute to four AgI and AgBr molecules per supercage, are discussed. In both samples, the lowest absorption band shifts to the lower energy side with increasing loading density. The large blue shift in AgI clusters compared to the bulk can be qualitatively explained by the model of strong quantum confinement of the photoexcited electron-hole pair. In the sample of AgBr clusters with four molecules per cage, however, the energy of the lowest absorption band is close to that of the lowest direct transition of AgBr in bulk. This apparently weak quantum confinement in the photo-excited state seems to originate from the singular band structure in the bulk, *i.e.*, AgBr is the indirect gap material.

Keywords: zeolite FAU; AgI; AgBr; cluster; absorption spectra; indirect transition

INTRODUCTION

Bulk silver halides have attracted the attention of scientists because of their unique physical and chemical properties, *e.g.*, photosensitivity, superionic conductivity, and so on. From the viewpoint of modifying these properties by reducing the size of the silver halides, we have attempted to incorporate AgI clusters into zeolite cages[1, 2]. In the case of stabilizing AgI clusters in zeolite LTA where the α-cages are connected in a simple cubic structure, a notable blue shift of the lowest absorption band was observed compared to the exciton energy of the bulk AgI, and superlattice reflections were observed in the X-ray powder diffraction (XRD) pattern.

In the present study, AgI and AgBr clusters are each incorporated into zeolite FAU whose framework structure is shown in Fig. 1. The framework consists of Si, Al and O atoms. Supercages with an inner diameter of 13 Å are arrayed in a diamond structure. The alkali-metal cations in the space of the framework are not displayed in this figure. We report how the optical spectra of the silver halide clusters depend on the type of halogen atoms when substituting iodine

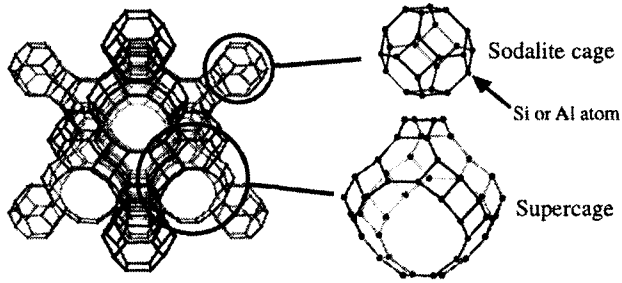

FIGURE 1 Framework structure of zeolite FAU viewed from the [110] direction (left), and its building units, sodalite cage and supercage (right).

for bromide. The bulk AgBr is well known as an ionic crystal with an indirect band gap[3]. The optical properties of AgBr microcrystals have been reported[4-8]. We expect to obtain some new information on the quantum confinement of the photo-excited state of the AgBr clusters.

EXPERIMENTAL

Na-type zeolite FAU with an *Si/Al* ratio of 1.3, which we abbreviate as Na-FAU hereafter, was dehydrated at 450 °C for 2 h in a vacuum, and then sealed in the glass tubes with AgI or AgBr in bulk. The silver halides were adsorbed on the Na-FAU through the gas phase by heating the glass tubes to 420 °C.

Diffuse reflection spectra were measured at room temperature, and were transformed into absorption spectra using the Kubelka-Munk function, $(1-r)^2/2r$, where r is the diffuse reflectivity. Although both AgI and AgBr in bulk are photosensitive materials, no photochemical reaction occurred in these stabilized clusters. The XRD pattern of the AgI-loaded Na-FAU was also measured in a vacuum.

RESULTS AND DISCUSSION

The absorption spectra of AgI-loaded Na-FAU (AgI/Na-FAU) and merely dehydrated Na-FAU (broken line) are shown in Fig. 2. Loading density increases in the order of curves (a) - (g), and the baselines for curves (c) -(g) are shifted. In curve (g), the loading density of the AgI molecule per supercage is four, which is a saturated one. In curves (a) and (b), notable absorption band can be seen at 5.6 eV. The weak band at 6.4 eV in curve (a) originates from the transition of Na-FAU itself. In curves (c) - (g), bands at 4.1 and 4.7 eV appear at the loading density of the AgI molecule per supercage exceeding unity, and grow with invariant relative

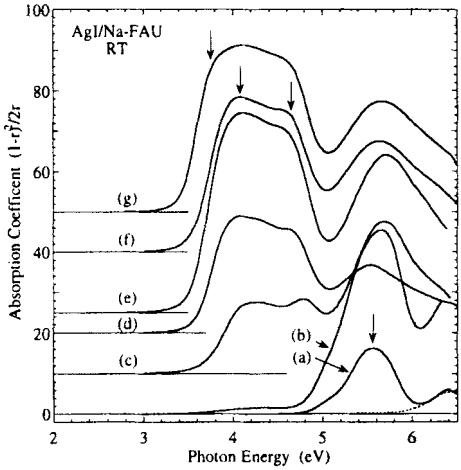

FIGURE 2 Absorption spectra of Ag loaded Na-FAU. Loading densities of AgI molecule per supercage are (a): 0.3, (b): 1.0, (c):1.2, (d): 2.0, (e): 2.9, (f): 3.5 and (g): 4.1. The broken line is the spectrum of dehydrated Na-FAU.

intensity. This behavior indicates that these two bands originate from AgI clusters with the same size. In curve (g), a band appears at 3.7 eV. In all spectra, the band at 5.6 eV, which is observed in the dilute loading density, remains.

It is experimentally and theoretically well known that the photoexcitation energy increases (decreases) with decreasing (increasing) size of the microcrystal because of the quantum confinement of an exciton or a photoexcited electron-hole pair[9]. In Fig. 2, the energy of the lowest photoabsorption band decreases accompanying the increase in the loading density of AgI. This means that larger clusters are formed with the increase in the loading density. When the loading density is less than unity, the intensity of the band at 5.6 eV merely depends on the density. This means that this band originates from the AgI molecule which is the smallest unit to be stable in the supercage. The energy of this band assigned to the AgI molecule is quite high compared to that in the gas phase[10]. The interaction between the alkali-metal cations and the guest AgI molecules are not negligible and induces an Ag^+ ion-like transition[11].

The obtained XRD pattern of AgI/Na-FAU with four AgI molecules per supercage shows reflections with the same indexing condition as the original Na-FAU. The space group $Fd\bar{3}$[12] of the Na-FAU is conserved with the AgI loading. The number of AgI molecules in each supercage is uniform, because

each supercage is equivalent in this space group. Therefore, in this sample, four AgI molecules are loaded in each supercage, and the largest cluster in one supercage is $(AgI)_4$. The band at 3.7 eV originates from these clusters. Compared to the exciton energy of the AgI bulk, 3.0 eV[13], the blue shift of this band is of an eV order. At the intermediate loading density, the bands at 4.1 and 4.7 eV seem to correspond to $(AgI)_3$ clusters, because the intensity of these two bands with the same origin increases even if the loading density exceeds two. The reason why the $(AgI)_2$ clusters are not observed has not been definitely determined. The doublet structure at 4.1 and 4.6 eV may be from the spin-orbit splitting of the iodine, although the splitting width is relatively smaller than that of an iodine atom, $\Delta_{s\text{-}o} = 0.94$ eV[14]. The band at 5.6 eV at high loading may be due to the intra-transition of the Ag^+ in the cluster, or some AgI molecules in one supercage do not participate in the formation of the cluster.

The absorption spectra of AgBr in Na-FAU (AgBr/Na-FAU) are shown in Fig. 3. With increasing loading density, absorption bands at 5.6(5.9), 4.5, and 4.1 eV appear in this order. The shape of the spectra is roughly the same as that of the spectra for AgI/Na-FAU. Therefore, we can postulate that larger AgBr clusters are formed with increased loading density. The band at 5.6 eV is from the AgBr molecule accompanying an interaction with the zeolite. The bands at 4.5 and 4.1 eV seem to be from $(AgBr)_3$ and $(AgBr)_4$ clusters, respectively, similar to the

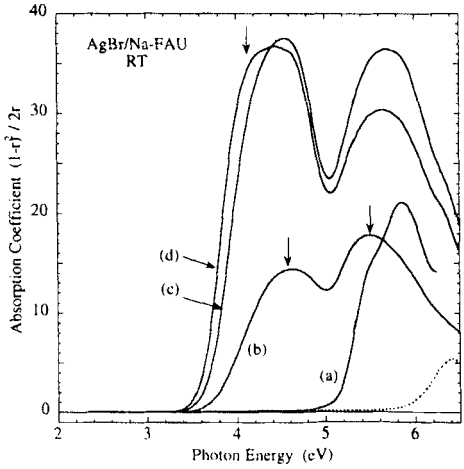

FIGURE 3 Absorption spectra of AgBr loaded in Na-FAU. Loading densities of AgBr molecule per supercage are (a): 0.8, (b): 2.0, (c): 3.0, and (d): 4.0. The broken line is the spectrum of dehydrated Na-FAU.

manner discussed for AgI/Na-FAU. Based on a more detailed study, however, there are some differences in the spectra between the AgI and AgBr clusters. In curve (a) of Fig. 3, a doublet structure, *i.e.*, 5.6 and 5.9 eV, is observed. Even if the loading density is reduced to less than unity, the relative intensity of these two bands does not change. This means that the origin of the two bands is from the AgBr molecules. At the intermediate loading density, *i.e.*, curves (b) and (c), no doublet but a singlet band is at 4.5 eV. A qualitative interpretation suggests that the spin-orbit splitting of the bromine atom, $\Delta_{s\text{-}o} \approx 0.46$ eV[14], which is smaller than that of iodine atom, seems to make difficult to observe the splitting of the two bands. Finally, for the saturated loading sample, *i.e.*, curve (d), the lowest excitation band from the $(AgBr)_4$ clusters is at 4.1 eV which is higher than the case of AgI/Na-FAU. This is qualitatively interpreted as follows.

It is observed and theoretically calculated that the luminescence from the indirect exciton of AgBr microcrystals shifts its energy to the higher energy side and increases its intensity as their sizes decrease[4-8, 15]. The luminescence originates from the recombination of the electron and the hole at the Γ- and L-points, respectively[3]. In the present study, we are discussing the absorption spectra. The strong oscillator strength is from the direct electronic transition between the valence state and the conduction state. Therefore, for the simple consideration, it is better to make a comparison to the direct transition, $\Gamma_{8v}^- \rightarrow \Gamma_{6c}^+$ in bulk, where the effective mass of the electron at Γ_{6c}^+ is positive, and that of the hole at Γ_{8v}^- depends on the direction of the wave vector k, *e.g.*, $m_h < 0$ for the [100] direction[3]. The direct transition energy of AgBr is 4.276 eV in the bulk[16]. The (0, 0) transition energy is 3.87 eV in the gas phase AgBr molecule[10]. Apparently, it seems that there is a very weak quantum confinement effect on the photoexcited state of the AgBr microcrystal compared to the bulk. This can be explained as follows.

We can qualitatively consider the behavior of the excitation energy of the microcrystal (E^*) compared to the energy of the inter-band transition (E_g) in bulk under an effective mass approximation, although this approximation is not a good model for a quantitative discussion. According to Brus' theory[9], the energy shift ΔE ($=E^* - E_g$) can be described as,

$$\Delta E = E^* - E_g = \frac{\hbar^2 \pi^2}{2R^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \frac{1.8e^2}{\varepsilon R}, \qquad (1)$$

where R is the radius of the microcrystal which is smaller than the exciton Bohr radius, m_e and m_h are the effective masses of the conduction electron and the valence hole, respectively, and ε is the dielectric constant of the bulk crystal. In Eq. (1), the image charge effect is not included for simplicity. The first term

describes the enhancement of the kinetic energies of the electron and the hole. The second term, which reduces the blue shift, is due to the Coulomb attractive force between the electron and the hole. If the mass of the hole has a negative value, ΔE does not increase so much by the first term. Therefore, from the analogy of this consideration, the excitation energy of the $(AgBr)_4$ cluster in Na-FAU seems to be close to the direct transition energy in the bulk. A similar behavior is observed for 25 Å AgBr microcrystals[4]. The lowest absorption band at *ca.* 3.9 eV seems to correspond to the direct transition with no blue shift. On the contrary, AgI in bulk has the direct band gap. Therefore, a blue shift of an eV order is observed in the AgI clusters compared to the bulk exciton energy.

SUMMARY

AgI and AgBr clusters are incorporated into the zeolite Na-FAU. By increasing the loading density, the cluster size becomes larger and the lowest photoexcitation band shifts to the lower energy side in both cases. The energy shift can be qualitatively interpreted by the quantum confinement model of the photoexcited state. The small blue shift in the lowest absorption band for the AgBr cluster seems to be related to the singular band structure, *i.e.*, indirect band gap in the bulk.

ACKNOWLEDGEMENTS

T. K. thanks R. Tadenuma for her experimental assistance. This work is financially supported by CREST (Core Research of Evolutional Science and Technology), JST.

References

[1] T. Kodaira, T. Ikeda, and H. Takeo, Chem. Phys. Lett. **300,** 499(1999).
[2] T. Kodaira, T. Ikeda, and H. Takeo, Euro. J. Phys. D, in press.
[3] Ladolt-Börnstein, New Series **17b,** Springer, Berlin (1982).
[4] M. I. Comor, and J. M. Nedeljkovic, Chem. Phys. Lett. **299,** 233(1999).
[5] H. Vogelsang, H. Stolz and W. von der Osten, J. Lumin. **70,** 414(1996).
[6] S. Pawlik, H. Stolz and W. von del Osten, Mat. Res. Soc. Symp. Proc. **358,** 289(1995).
[7]] Y. Masumoto, T. Kawamura, T. Ohzeki and S. Urabe, Phys. Rev. **B46**, 1827(1992).
[8] H. Kanzaki and Y. Tadakuma, Solid State Commun. **80,** 33(1991).
[9] L. E. Brus, J. Chem. Phys. **80,** 4403(1984).
[10] B. A. Brice, Phys. Rev. **38,** 658(1931).
[11] T. Kodaira, to be submitted.
[12] D. H. Olson, Zeolites **15,** 439(1995).
[13] M. Cardona, Phys. Rev. **129**, 69(1963).
[14] C. E. Moore, "Atomic Energy Levels" National Bureau of Standards Reference Data Series Vol. 35, U.S. Government Printing Office, Washington D.C. (1971).
[15] T. Takagahara and K. Takeda, Phys. Rev. **B46,** 15578(1992).
[16] N. J. Carrera and F. C. Brown, Phys. Rev. **B4,** 3651(1971).