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# Optical and X-ray diffraction study of AgI clusters incorporated into zeolite LTA

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**Abstract.** AgI clusters are incorporated into cages of zeolite LTA. The loading density of AgI is systematically changed from 0.2 to 4.0 molecules per $\alpha$-cage. The electronic states and structures of the AgI clusters, with regard to their optical absorption spectra and X-ray powder diffraction patterns, are discussed. At a dilute loading, a notable absorption band, assigned to the AgI molecule, appears at 5.6 eV. With increasing loading densities, new absorption bands appear at 4.7, 4.2, 4.1, and 3.6 eV. These bands show that $(\mathrm{AgI})_n$ $(n = 2 - 4)$ clusters with larger sizes are formed with increasing loading density. These clusters seem to exist in $\alpha$-cages. The X-ray diffraction (XRD) patterns exhibit superlattice reflections at high loading densities. The appearance of the extra reflections has a correlation with the formation of $(\mathrm{AgI})_3$ and $(\mathrm{AgI})_4$ clusters. The Ag and I atoms of the cluster seem to be situated at the position of tetrahedral-based symmetry in the $\alpha$-cage.

**PACS.** 61.10.Nz Single-crystal and powder diffraction – 36.40.Vz Optical properties of clusters

## 1 Introduction

Bulk silver halides are unique semiconductors. Their photosensitive property, i.e., the formation of silver clusters by light irradiation, has been applied to the photographic technique. Electronic band structures and the properties of conductivity significantly depend on the type of halogens, e.g., indirect transitions of AgBr and AgCl in the lowest photoexcited states, and the superionic conductivity of $\alpha$-AgI (bcc structure). If these bulk silver halides are reduced in their size to the nanometer order, differences in their properties and structures from those of the bulk are expected.

Recently, zeolites, which are microporous crystals, are used as hosts for stabilizing the nanometer size materials, e.g., clusters and quantum wires [1,2]. Furthermore, the guests will array depending on the periodicity of the zeolite cages. In this study, zeolite LTA was employed for the stabilization of the AgI clusters. The framework of the LTA is schematically illustrated in Fig. 1. Two kinds of cages, $\alpha$ and $\beta$, with inner diameters of about 1.1 and 0.7 nm, respectively, are arrayed in a CsCl-type lattice. The space group of the Na-type LTA (Na-LTA) is $\mathrm{Fm\bar{3}c}$ with a lattice constant of 2.46 nm, because of the alternative arrangement of the Si and Al atoms [3].

In a previous paper, successive incorporation of AgI clusters into the cages of LTA was confirmed from an optical absorption spectrum and an X-ray powder diffraction (XRD) pattern [4]; a large blueshift in the spectrum was compared with that of the original AgI bulk, and superlattice reflection peaks in the XRD pattern were observed. The structures and the electronic states of the clusters seem to depend on the size of the clusters. Therefore, in the present paper, the loading density of AgI is systematically changed up to saturation of 4.0 molecules per $\alpha$-cage. The optical absorption bands that originate from the $(\mathrm{AgI})_n$ $(n = 1 - 4)$ clusters are observed. The superlattice reflections are observed at the AgI loading density to be higher than 3 molecules per $\alpha$-cage. The AgI clusters seem to have a tetrahedral-based symmetry.

## 2 Experiment

The powder form of the Na-LTA was used. The dehydrated Na-LTA at 450 °C and bulk AgI were sealed together in a quartz glass tube without exposure to air. The AgI vapor was adsorbed into the Na-LTA at 420 °C. Through control of the weight ratio of Na-LTA and bulk AgI, the loading density of AgI molecules per $\alpha$-cage was systematically changed.

The diffuse reflection spectra were measured at room temperature. The Kubelka–Munk function, $A \propto (1-r)^2/2r$, where $A$ is the absorption coefficient and $r$ is the diffuse reflectivity, was used for transforming the diffuse reflec-

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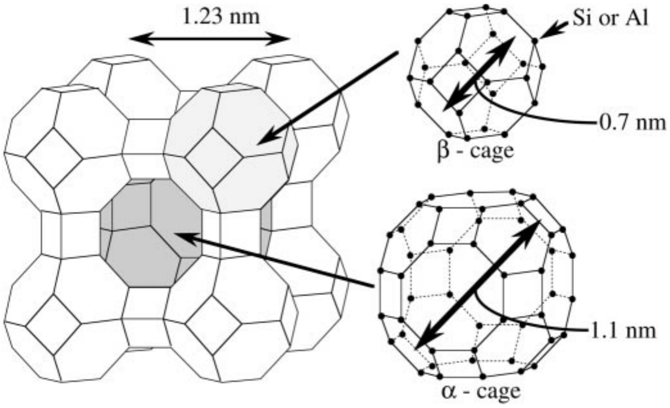

**Fig. 1.** Schematic framework structure of zeolite LTA. In the actual LTA, Si and Al atoms are alternatively arrayed, and O atoms exist between them. The O atoms of the framework and the $Na^+$ ions in the space of the framework are omitted.

tivity into the absorption coefficient. The XRD patterns were measured at room temperature using a $\theta-\theta$ configuration X-ray diffractometer with a Cu $K_\alpha$ line. So that the reaction in the atmosphere would be avoided, the samples were kept in a vacuum (about $10^{-4}$ torr) during the measurements.

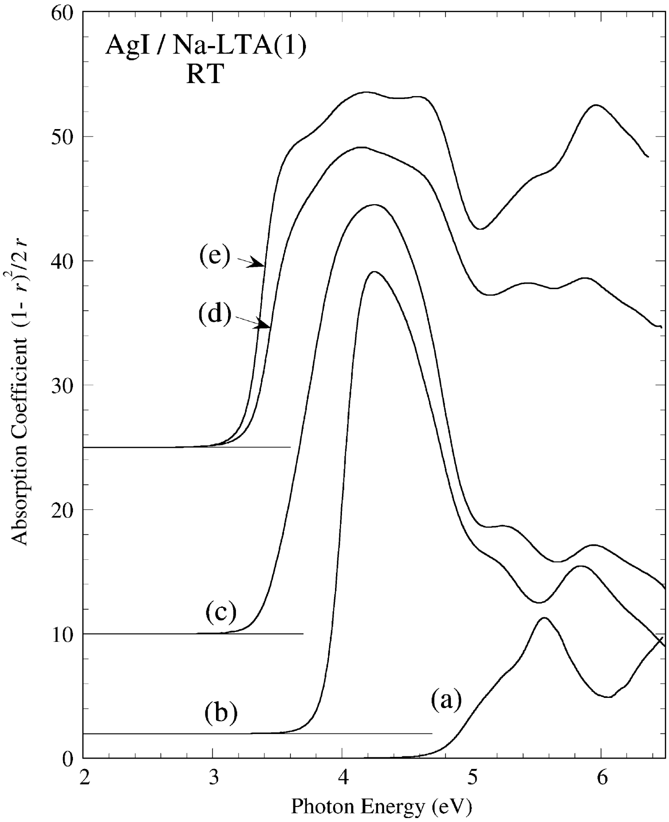

**Fig. 2.** Absorption spectra of AgI/Na-LTA at room temperature. Loading densities of AgI are 0.2, 1.0, 2.0, 3.0, and 4.0 molecules per $\alpha$-cage in curves (a)–(e), respectively.

## 3 Results and discussion

### 3.1 Optical absorption spectra

Absorption spectra of the AgI-loaded Na-LTA (AgI/Na-LTA) are shown in Fig. 2. The densities of AgI are 0.2, 1.0, 2.0, 3.0, and 4.0 molecules per $\alpha$-cage for curves (a)–(e), respectively. For the curve (e) sample, the loading density was nearly saturated. In curve (a), an intense peak appears at 5.6 eV with a shoulder peak at 5.2 eV. In curves (b) and (c), a notable absorption band appears at 4.2 eV. In curve (d), the shape of the spectrum has a large difference compared with that of curves (b) and (c). There are three bands at 3.6, 4.1, and 4.7 eV in curve (d). The three bands observed are also seen in curve (e), accompanying the band at 3.6 eV more obviously. In curves (b)–(e), there are common bands at 5.4 and 5.9 eV.

The AgI molecule is stable in the vapor phase. In curve (a) of Fig. 2, the band at 5.6 eV is assigned to the isolated AgI molecules, because the density of the AgI molecules is sufficiently lower than unity per $\alpha$-cage. These molecules will be in the $\alpha$-cage, because an eight-membered ring window is large enough for the molecules to pass through, but a six-membered ring (6MR), shared with $\alpha$- and $\beta$-cages and capped by an $Na^+$ ion [3], is too small for them to pass through. In the vapor phase, the excitation energy of the $(0,0)$ transition of the AgI molecule is 31 152.24 $cm^{-1}$ (3.9 eV) [5]. The observed energy of the molecule in Na-LTA is quite high. The interaction between the molecule and the LTA framework or the $Na^+$ ions is not negligible. The iodine atom seems to be close to the $Na^+$ ion, because the negative charge of the iodine atom, due to not only a covalent bond but a weak ionic bond between Ag and iodine atoms, has an attractive force with the $Na^+$ ion. It is confirmed that the magnitude of the interaction between the alkali-metal cations and the AgI depends on the type of alkali cations, because the absorption bands assigned to the AgI molecules shift to the lower energy by exchange of the $Na^+$ ions with the $K^+$ or the $Cs^+$ ions in the initial zeolite [6].

It is well known that with increasing size of semiconductor clusters or small particles, their photoexcitation energy becomes small, because the kinetic energy of the photoexcited electron and hole (exciton) is reduced [7,8]. The redshift of the absorption bands in curves (b)–(e) of Fig. 2, as compared with curve (a), can be interpreted by a model of new bands originating from the $(AgI)_n$ $(n > 2)$ clusters. The saturated loading density is about 4 molecules per $\alpha$-cage. If the formed AgI clusters have a uniform size in each $\alpha$-cage, the cluster is $(AgI)_4$ at this loading density. Therefore, the observed lowest absorption band at 3.6 eV originates from this cluster. The three bands at 4.1, 4.2, and 4.7 eV originate from $(AgI)_2$ or $(AgI)_3$ clusters, because the formed clusters have to be larger than the AgI molecule and smaller than the $(AgI)_4$ cluster. The bands at 4.1 and 4.7 eV have the same origin, because their relative intensities do not change in curves (d) and (e). These bands can be assigned to the $(AgI)_3$ clusters, because the density of AgI in this sample is higher than that of the samples of curves (b) and (c). The remaining band at 4.2 eV originates from the $(AgI)_2$ clusters. Although the AgI is loaded under a saturated condition in curve (e), the bands assigned to the $(AgI)_4$ and $(AgI)_3$ clusters coexist. This means that in some $\alpha$-cages, one $(AgI)_3$ cluster and one AgI molecule coexist. In curve (e), the shape of the spectrum in the energy region of 5–6 eV is very similar to that of curve (a) with a small energy shift. This manifests the existence of the AgI molecules under the saturated conditions.

## 3.2 XRD patterns

Figure 3 shows the XRD patterns of samples (a), only dehydrated Na-LTA, and (b)–(e), AgI/Na-LTA. The densities of AgI are 1.0, 2.0, 3.0, and 4.0 molecules per $\alpha$-cage in patterns (b)–(e), respectively. In pattern (a), all the reflection peaks can be assigned using the space group of $Fm\bar{3}c$. With increasing density of AgI, the relative intensity of these reflections gradually changes. The reflections of (200), (220), and (222) indicated in pattern (a) with lattice plane spacings of $d = 1.23$, 0.868, and 0.709 nm, respectively, are the typical ones. With increasing loading density, the (222) reflection becomes strong. In contrast, the (200) and (220) reflections become relatively weak. This change in relative intensity and the lack of observation of reflections, attributable to the crystal structure of the bulk AgI, are direct evidence for the adsorption of AgI in the cages of Na-LTA in all the AgI/Na-LTA. Furthermore, there is no splitting in equivalent reflections by loading the AgI. This means that cubic symmetry is conserved in AgI/Na-LTA.

The most interesting result in the XRD patterns is the appearance of forbidden reflections, i.e., superlattice reflections, in the space group of the original Na-LTA. In patterns (b) and (c), there are broad backgrounds or reflections whose peak positions are $2\theta = 5.3°$. In patterns (d) and (e), reflections labeled A and B appear at $2\theta = 6.2°$ and 7.8°, respectively. The $d$-spacing values of these reflections are A: $d = 1.42$ nm and B: $d = 1.00$ nm. In the case in which the lattice constant is not changed from the original LTA, 2.46 nm, corresponding reflection indices of reflections A and B are (111) and (211), respectively. These two reflections appear suddenly at pattern (d) with increasing loading density. Superlattice reflections were also observed at $PbI_2$ clusters incorporated into the $\alpha$-cages of Na-LTA in the case of a saturated loading density [9, 10]. In the present case, there should be a large change in the arrangement of the guest AgI at the loading density between 2 and 3 molecules per $\alpha$-cage. Based on the comparison with the optical spectra, it can be seen that the formation of the $(AgI)_3$ clusters may play an important role in the appearance of the superlattice reflections.

The XRD patterns give us information about the average structure of AgI/Na-LTA, whereas optical absorption spectra reflect the local electronic states of the loaded AgI. Therefore, the discussion of the structure of the AgI clusters in the $\alpha$-cages is based on both results, with the following speculations. The average structure of the clusters has a cubic structure, as has already been mentioned. The eight $Na^+$ ions at the center of the eight 6MR have $O_h$ symmetry. When four molecules of AgI are loaded into one $\alpha$-cage, four iodine atoms can have tetrahedral symmetry, if they are near the $Na^+$ ions at 6MR. Ag atoms can also have the same symmetry, if they are near the remaining four $Na^+$ ions at 6MR. The space group of Na-LTA, including four Ag atoms and four I atoms with this symmetry in $\alpha$-cage, is $F\bar{4}3c$. Reflections of (111) and (211), however,

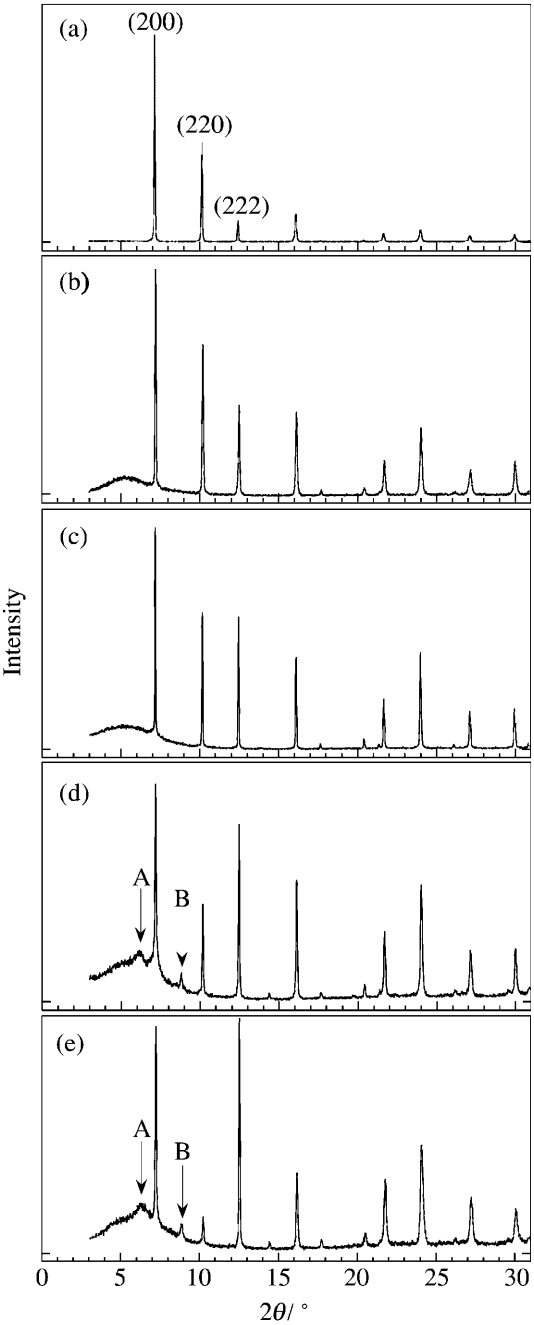

**Fig. 3.** XRD patterns of dehydrated Na-LTA and AgI/Na-LTA at room temperature. Pattern (a) is only dehydrated. In patterns (b)–(e), loading densities are 1.0, 2.0, 3.0, and 4.0 molecules per $\alpha$-cage, respectively.

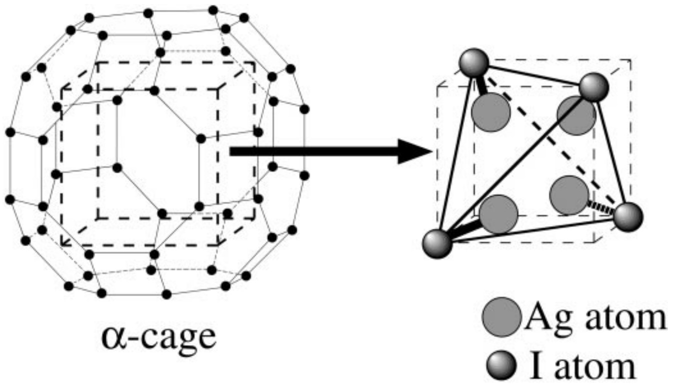

**Fig. 4.** Schematic representation of an average structure of Ag and I atoms in the $\alpha$-cage under the saturated loading condition of AgI.

are not allowed in this space group. Therefore, this model should be partly modified. The Ag atoms are more or less shifted from this high-symmetry site to reduce the repulsive force of the $Na^+$ ions and make the (111) and (211) reflections allowed. The plausible average structures of the guest Ag and iodine atoms in the $\alpha$-cages are illustrated in Fig. 4. The solid lines between the Ag and iodine atoms represent their bond. The Ag atoms are on the regular triangle plane of the tetrahedron of the four Ag atoms.

From a simple calculation using the lattice constant of bulk AgI [11], it can be seen that the inner volume of the $\alpha$-cage has a capacity to incorporate ten AgI molecules. The actual saturated loading density, however, is four per $\alpha$-cage. This difference between the calculation and the actual result seems to have occurred by the simultaneous meeting of the following two conditions upon formation of the actual cluster; AgI molecules are adsorbed in the $\alpha$-cage by only the bound to the $Na^+$ ions, and the AgI molecules in the $\alpha$-cage are close enough to have chemical bonding. Therefore, bonds between the molecules, i.e., Ag−I−Ag, should be realized. The distance between the Ag and the iodine atoms is 0.244 and 0.28 nm in a gas phase molecule [5] and in a solid phase with a zinc-blend structure [11], respectively. The shortest distance between the $Na^+$ ions at 6MR is about 0.7 nm. If the iodine atoms are tightly bound to the $Na^+$ ions, it is quite difficult for the bonds, Ag−I−Ag, to be realized for the average structure illustrated in Fig. 4. The local structure must be slightly different from this if the distance between the Ag and iodine atoms of the different molecules is to be reduced. The broad half-widths of reflections A and B may reflect this; the Ag and iodine atoms have a large thermal fluctuation, or their superlattice periodicity is short-range due to the disorder of the sites of the Ag and I atoms. It is concluded from the optical spectra that, at the saturated condition, $(AgI)_4$ and $(AgI)_3$ clusters coexist in different $\alpha$-cages. The $(AgI)_3$ clusters may have a lower total energy than $(AgI)_4$. For the $(AgI)_4$ cluster to be formed, all the guest atoms have to participate. Therefore, it seems that they should be displaced from their average positions toward the center of the $\alpha$-cage. In the case of the formation of $(AgI)_3$, the displacement of the three AgI molecules may be small, and the remaining AgI molecule in the same $\alpha$-cage is too far to have a bond with it.

## 4 Summary

When the loading densities of AgI molecules per $\alpha$-cage are controlled, absorption bands originating from $(AgI)_n$ ($n = 1 - 4$) clusters in the $\alpha$-cage of the zeolite Na-LTA were observed. In the case where AgI was loaded under saturated conditions, not only the $(AgI)_4$ clusters but also the $(AgI)_3$ clusters and the AgI molecules coexist. In the XRD patterns, by the incorporation of the AgI clusters, not only the variation in the relative intensity of the original reflections but also the appearance of superlattice reflections was also observed for the high loading sample. The structure of the AgI clusters, which are the origin of the superlattice reflections, seems to be based on the tetrahedral symmetry.

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## References

1. V.I. Srdanov, N.P. Blake, D. Markgraber, G.D. Stuky: Stud. Surf. Sci. Catal. **85**, 115 (1994)
2. G.A. Ozin, A. Kuperman, A. Stein: Angew. Chem. Int. Ed. Engl. **28**, 359 (1989)
3. J.M. Adams, D.A. Haselden: J. Solid State Chem. **47**, 123 (1983)
4. T. Kodaira, T. Ikeda, H. Takeo: Chem. Phys. Lett. **300**, 493 (1999)
5. B.A. Brice: Phys. Rev. **38**, 658 (1931)
6. T. Kodaira: (to be submitted)
7. Z.K. Tang, Y. Nozue, T. Goto: J. Phys. Soc. Jpn. **60**, 2090 (1991)
8. L.E. Brus: J. Chem. Phys. **80**, 4403 (1984)
9. O. Terasaki, Z.K. Tang, Y. Nozue, T. Goto: Mater. Res. Soc. Symp. Proc. **233**, 139 (1991)
10. N. Togashi, T. Monji, H. Sakuma, J. Sakanoue, Z.K. Tang, Y. Nozue, O. Terasaki: in *Abstracts of NAIR Workshop '95 on Cluster Science,* 1995, p. O7
11. Landolt-Börnstein: New Series **III/22a**, 299 (1982)