

# Control on arrangement of AgI clusters incorporated into zeolite LTA

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**Abstract.** AgI clusters were incorporated into Li, Na, and K-form LTA zeolites with a loading number of four AgI molecules per  $\alpha$ -cage. The X-ray powder diffraction (XRD) patterns and optical absorption spectra of the samples were obtained. The XRD patterns indicate that the sizes of the clusters and their arrangements depend on the type of alkali-cations. AgI clusters with different sizes, *i.e.*,  $(\text{AgI})_n$  and  $(\text{AgI})_{8-n}$  ( $5 \leq n \leq 7$ ), are arrayed alternatively in Na-form LTA conforming to the space group of  $P2_13$ . AgI-loaded Li-form LTA also conformed to the space group of  $P2_13$ , although  $(\text{AgI})_n$  clusters seem to be distributed disorderly. On the contrary,  $(\text{AgI})_4$  cluster is in each cage in K-form LTA conforming to the space group of  $Fm\bar{3}c$  or  $F\bar{4}3c$ . The optical spectra showed that Li and Na-form LTAs include  $(\text{AgI})_n$  ( $5 \leq n$ ), and that K-form LTA includes  $(\text{AgI})_4$  cluster in each cage.

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## 1 Introduction

Nano-sized clusters can be arrayed three dimensionally at a density of  $\sim 10^{20}/\text{cm}^3$  by using zeolite cages. In zeolite LTA,  $\alpha$ -cages, whose inner size is *ca.* 11 Å, take the arrangement of a simple cubic (SC) structure. Previously, we reported the observation of super-lattice reflections in an X-ray powder diffraction (XRD) pattern of Na-form LTA (Na-LTA) by incorporating AgI clusters [1]. The appearance of these reflections depends on the loading density of the AgI [2]. This suggests to us that the space group is lower than the original Na-LTA and that the AgI clusters are not simply arrayed in the SC structure conforming to the arrangement of the cages of LTA.

Zeolites are well-known to act as a molecular sieve. In LTA, lots of cations are distributed in the space of the framework. By changing the type of the cations, the cage free volume and effective size of the windows, which connect the adjacent  $\alpha$ -cages, can be controlled. As a result, the type and number of molecules adsorbed on to LTA can be selected [3]. Therefore, if the cation species are varied, the size of the clusters will be influenced by the change on the effective inner size of the cages.

Based on the above backgrounds, AgI was loaded into LTA zeolites, whose alkali cations in the cages are exchanged from  $\text{Na}^+$  to  $\text{Li}^+$  and  $\text{K}^+$  to control the size and

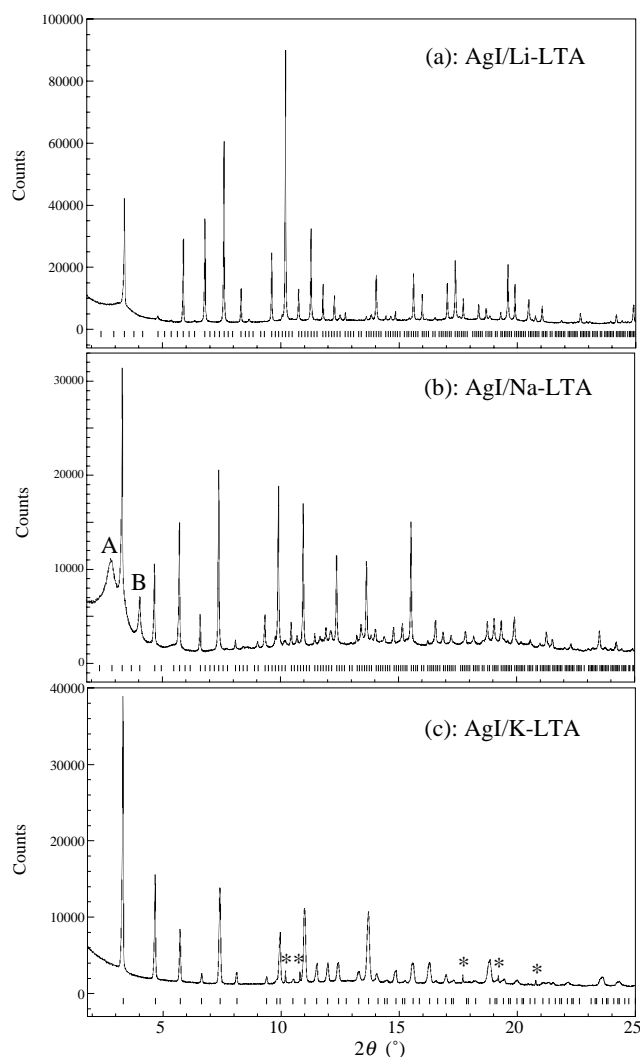
the arrangement of the AgI clusters. In order to obtain accurate information regarding the cluster arrangement, XRD patterns of these samples were measured using synchrotron radiation.

## 2 Experimental

Li-form (Li-LTA) and K-form LTA (K-LTA) were obtained from Na-LTA by soaking it in aqueous solutions of LiCl and KCl, respectively. The ideal chemical formulae of these LTAs were  $M_{96}\text{Al}_{96}\text{Si}_{96}\text{O}_{384}$  ( $M = \text{Li}, \text{Na}, \text{and K}$ ), which hereafter are abbreviated as  $M$ -LTA. The lattice constant is the twice size of the  $\alpha$ -cage. We confirmed by the ICP emission spectroscopy that more than 95% of the  $\text{Na}^+$  ions are exchanged to the  $\text{Li}^+$  and  $\text{K}^+$  ions in the actual samples. AgI was adsorbed onto these LTAs after dehydration [1, 2, 4]. The loading density can be controlled by the weight ratios of the bulk AgI and the  $M$ -LTA zeolites before the adsorption. We fixed the density of adsorbed AgI molecules at four per  $\alpha$ -cage in common. This condition of AgI loading is a saturated one for Na-LTA.

To measure the XRD patterns, AgI-loaded  $M$ -LTA ( $\text{AgI}/M$ -LTA) samples were sealed in glass capillary tubes with diameters of 0.5 mm without exposure to air. Synchrotron radiation XRD patterns were obtained at the

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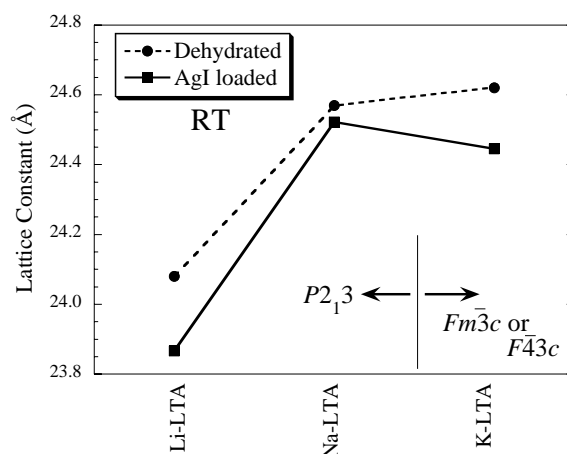
**Fig. 1.** XRD patterns of AgI/*M*-LTA samples. Asterisk marks (\*) indicate reflections from AgI in bulk. Short vertical marks below the observed patterns indicate the positions of the allowed Bragg reflections in the proposed space groups. Reflections A and B in pattern (b) are indexed as 111 and 211, respectively [1,2].

beam line BL4B2 (Photon Factory in KEK). The wavelength of monochromatized X-ray was fixed at 0.7070 Å. The optical absorption spectra of the samples were also obtained by transforming the diffuse reflection spectra in order to discuss their local electronic states. The optical data were obtained at room temperature without exposing the samples to air. Namely, the samples were sealed in vacuumed quartz glass tubes.

## 3 Results and discussion

### 3.1 XRD patterns

The XRD patterns of the AgI/*M*-LTA samples are shown in Figure 1. The indexed reflections in AgI/Li-LTA and AgI/Na-LTA satisfy a reflection condition that  $h = 2n + 1$

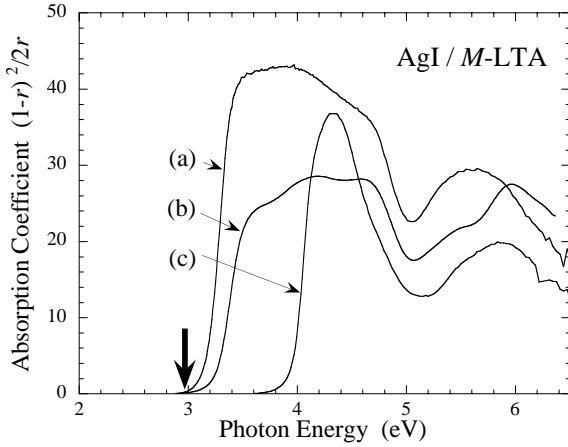


**Fig. 2.** Lattice constants of AgI-loaded and dehydrated *M*-LTAs. Space groups shown in the figures are for the AgI/*M*-LTA samples. Space group of dehydrated *M*-LTAs is  $Fm\bar{3}c$ .

do not appear in  $h00$  reflections. Only the space group of  $P2_13$  fulfils this condition. At AgI/K-LTA, the reflection condition shows no difference from that of the original K-LTA. This means that the space group of AgI/K-LTA is  $Fm\bar{3}c$  or  $F\bar{4}3c$ , because both space groups have same extinction rules for the Bragg reflections. Very weak reflections which originate from AgI in bulk is observed in AgI/K-LTA. It seems that this sample was slightly damaged during the transfer of the sample powder to the capillary tube, because no photo-absorption which originates from bulk AgI was observed in the spectrum measured before the XRD experiment.

At space groups of  $Fm\bar{3}c$  and  $F\bar{4}3c$ , atomic arrangements in adjacent  $\alpha$ -cages are symmetrically equivalent. Therefore, the clusters stabilized in each K-LTA cage should be  $(AgI)_4$ , because the average loading density of AgI molecules per  $\alpha$ -cage is four. In contrast, in the space group of  $P2_13$ , atomic arrangements in adjacent  $\alpha$ -cages are symmetrically non-equivalent. Therefore, AgI clusters of two sizes or AgI clusters with same size which are alternatively oriented can exist in the adjacent cages. As discussed later, the possibility of the latter seems to be excluded.

The lattice constants of AgI/*M*-LTA samples were also refined as plotted in Figure 2 which includes those of merely dehydrated *M*-LTA for references [5–7]. The lattice constants of dehydrated *M*-LTAs increase monotonically in the order of  $Li^+$ ,  $Na^+$ , and  $K^+$ . All these dehydrated *M*-LTAs belong to space group  $Fm\bar{3}c$ . The cation sizes, which increase in the order of  $Li^+$ ,  $Na^+$ , and  $K^+$ , seem to correlate with this change of lattice constants. In AgI/*M*-LTA as well as dehydrated *M*-LTA, it is reasonable to assume the variation on the lattice constants of  $M = Li$  and  $Na$ . By changing the cation from  $Na^+$  to  $K^+$ , however, the lattice constant decreases with a structural phase transition. Furthermore, the lattice constants of all *M*-LTAs decreases with the incorporation of the AgI compared to those of dehydrated ones. This is discussed later.



**Fig. 3.** Optical absorption spectra of (a): AgI/Li-LTA, (b): AgI/Na-LTA, and (c): AgI/K-LTA at room temperature. The lowest absorption energy of AgI in bulk is displayed by a downward arrow [9].

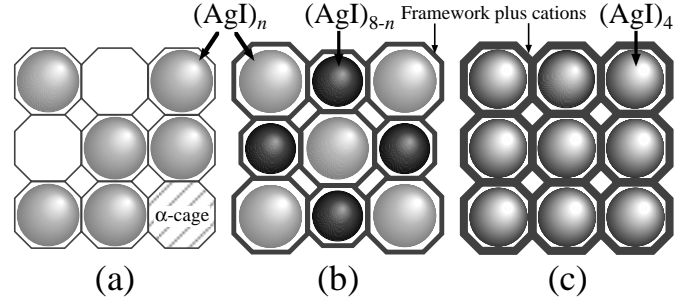
### 3.2 Absorption spectra

Figure 3 shows the absorption spectra of AgI/*M*-LTA samples. In the spectra of AgI/Li-LTA and AgI/Na-LTA, the lowest absorption band appears at 3.4 eV. In the spectra of AgI/K-LTA, it appears at 4.3 eV. According to a theory regarding the quantum confinement effect on the photo-excited state of a semiconductor nano-particle, with increases in the size of the particle, the lowest photo-excitation energy decreases monotonously and finally approaches that in bulk. The lowest absorption band of bulk AgI in a zinc-blende structure is observed at 3.0 eV [9]. Actually, with an increase in the loading number of AgI molecules per  $\alpha$ -cage, the lowest absorption band decreases its energy. Previously, we assumed that the band at 3.4 eV in the AgI/Na-LTA sample originated from (AgI)<sub>4</sub> clusters [2]. In AgI/K-LTA, however, the absorption band at 4.3 eV should be assigned to (AgI)<sub>4</sub> clusters referring the XRD data. Thus, the bands at 3.4 eV in AgI/*M*-LTA (*M* = Li and Na) should be interpreted as larger clusters than (AgI)<sub>4</sub>, *i.e.*, (AgI)<sub>*n*</sub> ( $5 \leq n$ ).

### 3.3 Arrangements and sizes of AgI clusters

Both AgI/Li-LTA and AgI/Na-LTA samples show similar optical spectra and belong to same space group. There is, however, a large difference in the appearance of reflections 111 and 211, labeled as A and B, respectively, in pattern (b) of Figure 1. The existence of these reflections suggests that large modulation of electron density occurs at large *d*-spacing in an average structure. (AgI)<sub>*n*</sub> ( $5 \leq n \leq 7$ ) clusters which may be quite stable, *i.e.*, a magic number cluster, are selectively formed and are not completely ordered in Li-LTA as illustrated in Figure 4a.

On the contrary, in the AgI/Na-LTA sample, (AgI)<sub>*n*</sub> and (AgI)<sub>8-*n*</sub> ( $5 \leq n \leq 7$ ) clusters, whose average number becomes (AgI)<sub>4</sub> per  $\alpha$ -cage, are arrayed alternatively. In other words, two kinds of AgI clusters of differing sizes



**Fig. 4.** Schematic representation of arrangements of AgI clusters in (a): Li-LTA, (b): Na-LTA, and (c): K-LTA. The average effective inner size of the cage decreases from (a) to (c).

are arrayed in a manner to the atomic arrangement of the NaCl structure. It seems that the inner size of the cage at Na-LTA is slightly smaller than the size of the magic number (AgI)<sub>*n*</sub> cluster. The cluster slightly deforms the framework or displaces the Na<sup>+</sup> ions from their initial sites. As a result, the inner size of the neighboring cages becomes smaller for the stabilizing magic number cluster, and small clusters, (AgI)<sub>8-*n*</sub>, are formed as displayed in Figure 4b.

In *M*-LTA, the effective inner size of the cage decreases in the order of *M* = Li, Na, and K, because the sizes of M<sup>+</sup> ions increase with increases in the atomic numbers of them. From this reason, the (AgI)<sub>4</sub> cluster, not magic number cluster (AgI)<sub>*n*</sub>, is formed in each cage of K-LTA, and (AgI)<sub>4</sub> clusters array in the SC structure as illustrated in Figure 4c. Therefore, the reduction of the lattice constant of AgI/K-LTA in comparison with that of AgI/Na-LTA seems to occur in relation with the phase transition which does not occur in the original dehydrated *M*-LTAs.

The lattice constants of all AgI-loaded *M*-LTAs decrease in comparison to those of dehydrated *M*-LTAs as plotted in Figure 2. Strong attractive interaction between host zeolite and guest AgI clusters seems to lead to this result. In AgI/Li-LTA, the magic number cluster, (AgI)<sub>*n*</sub>, is slightly smaller than the effective size of the cage. The attractive interaction, which reduces the inner size of the cage in order to fit the cluster, may induce the reduction of the lattice constant.

Both AgI/Na-LTA and AgI/K-LTA have same AgI loading number. Therefore, in AgI/Na-LTA, if the AgI clusters in adjacent cages have same size, the absorption bands from these clusters should appear in the same energy of the AgI/K-LTA sample and the lattice constant should be monotonously increased with the increase of the cation M<sup>+</sup> size as well as dehydrated *M*-LTAs. Therefore, it seems that not the AgI clusters with same size, *i.e.*, (AgI)<sub>4</sub>, are alternatively oriented but the clusters with different sizes are in the adjacent cages. The magic number *n* is quite difficult to determine in present. For simple consideration, let us start from the bulk AgI structure with a zinc-blende structure. In this condition, it is possible to stabilize (AgI)<sub>8</sub> cluster in maximum size at AgI/Na-LTA. The maximum loading density, however, of AgI in Na-LTA is about half from this value. Although we

illustrated in Figure 4 that the AgI clusters have a spherical shape, the structure of the actual AgI cluster seems to be quite different from the fragment of the bulk AgI crystal.

Martin and Schaber reported IR spectra of AgX and CuX ( $X = \text{Br}$  and  $\text{Cl}$ ) monomers, dimers and trimers in solid argon matrix [10]. According to their calculation to explain the vibrational spectra, a ring-like structure of the trimers is proposed. They also commented that  $(\text{CuCl})_4$  may have an eight-ring structure. These results also support our forecast that AgI clusters in the cages do not have a bulk-like atomic configuration, but may have a ring-like structure. These results also supports that AgI clusters in the zeolite cages do not have a bulk-like atomic configuration, but may have a ring-like structure. The ring-like shape will decrease the numbers of dangling bonds to reduce the total energy of the covalent bond materials.

## 4 Summary

Exchanging the cation, which is distributed in the space of the LTA framework, can control the arrangement of AgI cluster. In Na-LTA, large and small size AgI clusters are alternatively arrayed. In K-LTA, AgI clusters with homogeneous sizes, *i.e.*,  $(\text{AgI})_4$ , are arrayed in a simple cubic structure. In Li-LTA, AgI clusters with

a particular size are disorderly distributed. With the change of space groups, lattice constants of AgI/K-LTA decrease compared to that of AgI/Na-LTA. It seems that the existence of magic number AgI clusters and following deformation of the framework and/or the  $\text{Na}^+$  displacement will have a relation to the alternative ordering of the AgI clusters with different sizes.

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