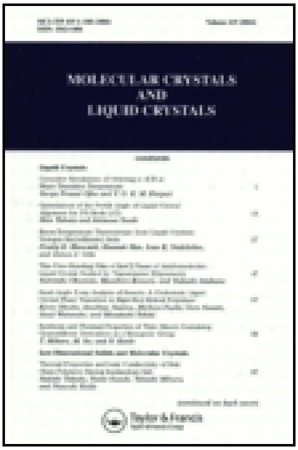

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FRENKEL EXCITONS IN ORDERED PbI_2 CLUSTERS INCORPORATED INTO ZEOLITE

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Abstract Diffuse reflection spectra are measured for $(PbI_2)_5$ clusters incorporated into supercages of zeolite LTA crystals, where the Frenkel exciton of cluster crystal is expected to be realized. The reflectivity at the exciton resonance energy drastically increases as the loading density nears the saturation level. This result can not be interpreted by the increase of the cluster density, but by the cluster ordering. We propose the order-induced decrease in the damping energy of the Frenkel exciton, because the motional narrowing of the exciton is expected in the ordered $(PbI_2)_5$ clusters. Electron diffraction pattern shows that clusters are arrayed in twice period of the zeolite cages.

INTRODUCTION

As the radius of a semiconductor cluster is much smaller than the Bohr radius of the bulk exciton, both electron and hole are confined three-dimensionally by the boundary of the cluster. The main phenomena of the quantum confinement are the blue shift in the exciton energy and the enhancement of the oscillator strength of the exciton.[1,2,3] To our knowledge, however, no one has reported the optical properties when such small clusters are periodically arranged in high density. In the previous papers,[3,4,5] we have developed a new method to prepare small clusters with the uniform size by using zeolite as the container, in which molecules are directly embedded in zeolite cages by the physical adsorption.

In the present paper, we use the zeolite LTA. The framework of LTA has supercages with the inner diameter of 11.4 Å. These supercages interconnect in a simple cubic structure by sharing the window with the inner diameter of 4 Å, as shown in Figure 1. Supercages are arrayed over the zeolite crystal with the lattice

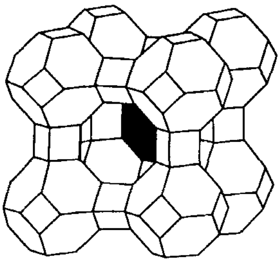

FIGURE 1 Schematic representation of the framework structure of zeolite LTA.

constant of 12.3 Å. In the present paper, it is found that the reflectivity of $(PbI_2)_5$ cluster incorporated into LTA increases drastically as the cluster density nears the saturation level. The order of cluster is proposed as the main origin of the reflectivity change.

EXPERIMENTAL PROCEDURES

Synthetic zeolite crystal of Na-type LTA (Linde type A) with the Si/Al ratio of unity was used. The particle size was $3 \sim 10$ μm. Hereafter, this zeolite is abbreviated to Na-LTA(1). Zeolite powders were dehydrated at 420 °C for 2 hours, and then sealed together with PbI_2 in a quartz ampule. PbI_2 clusters were incorporated into zeolite cages by vapour-phase transport at 420 °C for 24 hours, and successively annealed at 350 °C for 8 hours, then cooled gradually to room temperature. The loading density was controlled by the weight ratio of PbI_2 to zeolite powder. The diffuse reflection spectra were measured at 77 K, and converted into the spectra of the absorption coefficient K and the absorptive power A by using the functions $K \blacksquare (1 - r)^2/2r$ and $A = (1 - r)^2/(1 + r)^2$, respectively, where r is the diffuse reflectivity. At the strong absorption region, the reflectivity R is given by $1 - A$, because of the negligible transmission rate T, where $R + A + T = 1$. Raman spectra were obtained by using an argon ion laser and Jobin Yvon U-1000 double monochromator.

For the electron diffraction measurement, the specimens were crushed in an agate mortar under acetone and collected on micro-grids. The samples were examined in a 200 kV electron microscope (JEM-2000FX) with a large angle side entry goniometer.

RESULTS AND DISCUSSION

Figure 2 shows the absorptive power spectra of PbI_2 clusters in Na-LTA(1) at various loading densities. The average molecular number of PbI_2 in clusters is given by the molar ratio of PbI_2 to zeolite supercage. The molar ratio is indicated for each curve in the figure. In the specimen with the lowest loading density, the B_4 band appears at 3.5 eV. With increasing the loading density, the band B_5 appears at 3.25 eV and increases. In the saturated sample (the uppermost curve), the component of the band B_5 dominates the spectrum. The bands B_4 and B_5 are originated from the $(PbI_2)_4$ and $(PbI_2)_5$ clusters.[3,5] These clusters are located in the supercage,[6] and its size is expected to be restricted by the space of the supercage.

In Figure 2 the absorptive power of the B_5 band decreases rapidly, when the loading density approaches the saturation level, but this change is not obvious to eye in the figure. Closed circles in Figure 3(a) shows the reflectivity *R* at 3.25 eV as a function of the

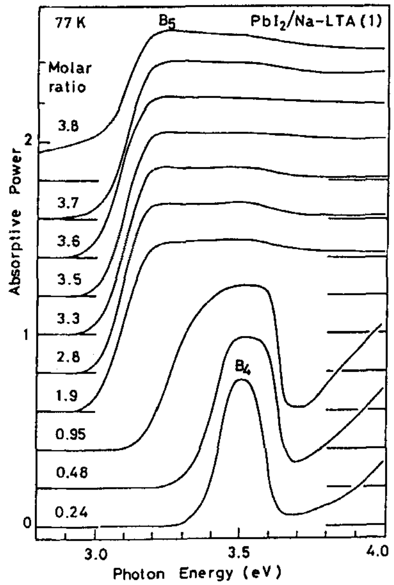

FIGURE 2 Absorptive power spectra of PbI_2 clusters in Na-LTA(1) at 77 K. The average number of PbI_2 molecules per supercage is indicated in each curve.

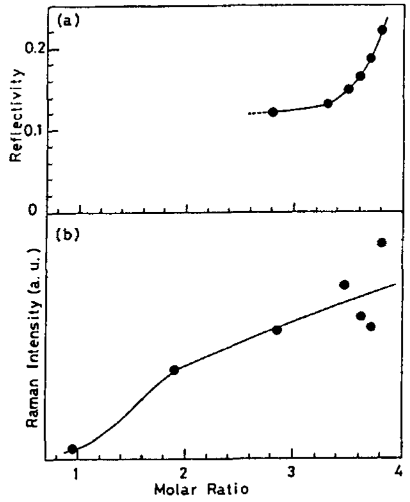

FIGURE 3 (a) Loading density dependence of the reflectivity of $(PbI_2)_5$ cluster at 3.25 eV. (b) Density of $(PbI_2)_5$ clusters estimated from the Raman scattering intensity.

loading density, where R is given by $1 - A$, because of the transmission at this energy can be neglected at high loading densities. The solid line is guide for eyes. It is clearly seen in Figure 3(a) that the reflectivity of $(PbI_2)_5$ clusters rapidly increases as the PbI_2 loading density nears the saturation level. In Figure 3(b), the density of $(PbI_2)_5$ clusters is indicated by closed circles, where the density is estimated from the $(PbI_2)_5$ component of the Raman scattering. The solid line is guide for eyes. Details of the Raman scattering of the PbI_2 clusters will be reported elsewhere. The density of $(PbI_2)_5$ clusters shows almost linear dependence on the PbI_2 loading density at the higher density region.

Usually, the reflectivity increases with the increase in the cluster density, because the electric susceptibility increases in proportion to the cluster density. The density of $(PbI_2)_5$ cluster, however, does not increase drastically in Figure 3(b), and hence, the drastic increase of the reflectivity in Figure 3(a) can not be interpreted by the density of $(PbI_2)_5$ cluster.

Generally, the damping energy of the Frenkel exciton decreases in perfect crystals compared with that of the isolated molecule or cluster, because of the motional narrowing effect of the exciton. Hence, if the high density $(PbI_2)_5$ clusters are ordered over the zeolite crystal, the excitation energy of the cluster will transfer from one cluster to another successively. This transfer will lead to the reduction of the damping energy due to the motional narrowing effect. Hence, the above experimental result can be interpreted qualitatively as follows. In low density sample, $(PbI_2)_5$ clusters are randomly dispersed in supercages of LTA. The clusters are distant from each other, and the energy transfer scarcely takes place. In the saturated sample, all of the possible supercages are occupied by the clusters, and the clusters are arrayed over the zeolite. If the orientations of $(PbI_2)_5$ clusters are also ordered, the energy transfer between clusters leads to the increase in the band width of the Frenkel exciton, namely, the decrease in the translational mass of the exciton. Therefore, the damping energy will decrease by the motional narrowing effect. Finally, the reflectivity will increase. This interpretation, however, is qualitative, and the theoretical calculation is needed for the estimation of the motional narrowing in the disordered molecular systems.

To examine the order of PbI_2 clusters, the electron diffraction pattern of the saturated sample is measured for the $[1\bar{1}0]$ incidence, as shown in Figure 4. The strong spots are due to the reflection from the framework structure of LTA. Except for the strong spots, some weak spots are seen between them. These weak reflections are forbidden to the symmetry $Fm\bar{3}c$ of LTA, but made to be allowed by the new symmetry of PbI_2 cluster crystal. One of the possible symmetry of the PbI_2 cluster crystal is Fm3m, where the internal symmetry of PbI_2 clusters are ignored. This symmetry means that $(PbI_2)_5$ clusters are arrayed in twice period of zeolite framework, i.e. 24.6 Å period. In the saturated samples, the average molecular number of the cluster is about 4, as shown in Figure 2. This means that supercages are partly occupied by $(PbI_2)_5$ clusters even in the saturation condition. The most possible interpretation which is commensurate with the electron diffraction pattern is the alternately arrayed clusters of $(PbI_2)_5$ and $(PbI_2)_3$.

The twice period may be originated from the deformation of the framework and/or the movement of cations induced by the incorporation

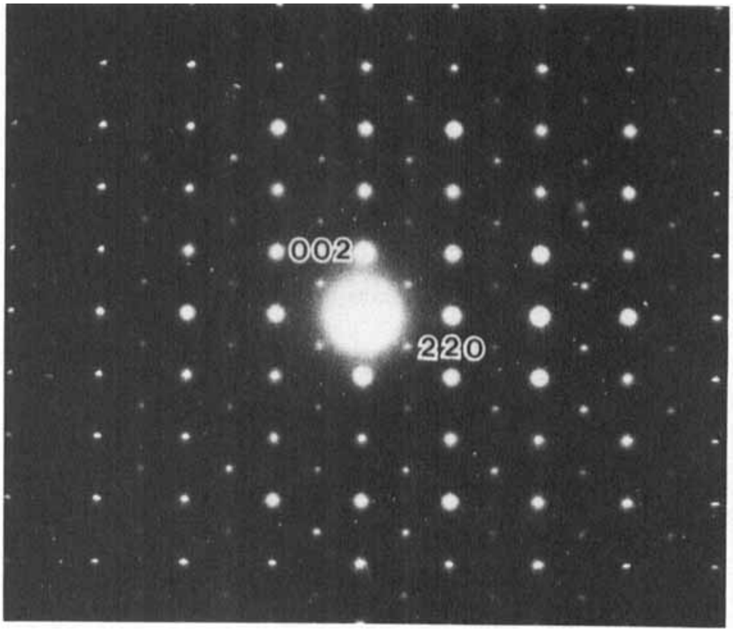

FIGURE 4 Electron diffraction pattern of PbI_2 in Na-LTA(1) with the saturated loading density at the $[1\bar{1}0]$ incidence.

of $(PbI_2)_5$ cluster. Hence, $(PbI_2)_3$ cluster can be incorporated in the nearest supercage, but $(PbI_2)_4$ and $(PbI_2)_5$ clusters can be no longer incorporated.

CONCLUSIONS

$(PbI_2)_5$ clusters are uniformly incorporated into supercages of LTA. The reflectivity at the exciton resonance energy increases as the loading density nears the saturation level. The reflectivity change is originated from the ordering of clusters, where the motional narrowing effect of the Frenkel exciton may play an important role in the increase in the reflectivity. The clusters are arrayed in the twice period of LTA framework in the saturated sample.

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REFERENCES

1. Al.L. Effros and A. L. Effros, Sov. Phys. Semicond. 16, 772 (1982).
2. Y. Kayanuma, Phys. Rev. B38, 9797 (1988).
3. Z.K. Tang, Y. Nozue and T. Goto, J. Phys. Soc. Jpn. 60, 2090 (1991).
4. Y. Nozue, Z.K. Tang and T. Goto, Solid State Commun. 3, 531 (1990).
5. O. Terasaki, Z.K. Tang, Y. Nozue and T. Goto, Proc. MRS 1991 Spring meeting.
6. O. Terasaki, Acta Chem. Scand. 45, 785 (1991).