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Optical Properties in PbI_2 , HgI_2 and BiI_3 Clusters Incorporated into Zeolite Cages

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Abstract

As a semiconductor particle becomes smaller and smaller, some quantum size effects will occur due to the confinement of excitons or electron-hole pairs. A translational motion of an exciton is confined when the particle radius is much larger than the Bohr radius of the exciton. As the particle radius is in the order of the Bohr radius, the electron (hole) is confined by the boundary of the particle and the hole (electron) is trapped indirectly by the potential induced by the electron (hole) wave function. In recent years, the electronic properties in these semiconductor particles have been actively investigated both in theoretical and in experimental. On the other hand, properties of a molecule, which is the limit of the smallest particle, had been well known in early time. But, little is known about the electronic properties in a small cluster whose size is between the particle and the molecule. It is difficult to investigate this problem, since there is no suitable method to prepare such small clusters. By usual methods, such as solid matrix method, colloid method and smoke-evaporation method, one failed in preparing such small clusters. In this thesis, we have developed a new method to prepare small semiconductor clusters by using zeolite as a container. One to five molecular clusters of PbI_2 and HgI_2 , and one to two molecular clusters of BiI_3 were incorporated into zeolite cages by vapor adsorption method. Quantum size effects on the electronic states in these clusters have been investigated. In addition, the cluster crystal is realized in $\text{PbI}_2/\text{Na-LTA}(1)$, where clusters are arranged periodically, just like a molecular crystal.

The framework of FAU, one kind of zeolites, has supercages with inside diameter of 13Å. The supercages are interconnected each other in a diamond structure by sharing windows of 7Å in diameter. In the framework of zeolite LTA, supercages with diameter of 11Å are interconnected in a simple cubic structure by sharing windows of 4.5Å in diameter.

Excitation energies in clusters largely shifted to higher energies compared to that of excitons in bulk crystal. For example, the blue shift of the excitation energy is as large as 0.6 eV in five-molecular PbI₂ cluster. The excitation energies shift to higher energies for smaller clusters, or for the material with larger Bohr radius of exciton. This phenomenon can be qualitatively interpreted by the quantum size effect on the electron hole pair based on the effective mass approximation. Quantitatively, however, the experimental results are quite smaller than that calculated in effective mass approximation, which means that the effective mass approximation no longer leads to the correct estimation in such small clusters.

The oscillator strength is found to be hardly change in PbI₂ clusters even the molecular numbers of clusters change from one to five. This phenomenon is very different from that appeared in the exciton confinement region, where the oscillator strength is proportional to the volume of the particle. The oscillator strength in unity volume of cluster (or per molecule) is remarkably enhanced for smaller clusters, especially for the mono-molecule, where the oscillator strength is estimated from the absorption spectrum to be in the order of unity. This oscillator strength is much stronger than the bulk exciton value, 0.036. The enhancement in oscillator strength is also found in HgI₂ and BiI₃ clusters. The experimental results are qualitatively in agreement with theoretical calculation based on the quantum size effect on the exciton oscillator strength.

Raman spectra in PbI₂ clusters are very different from that in bulk crystal. Some new Raman signals are found in the acoustic phonon region. The signal intensity in the optical phonon region, on the other hand, becomes relatively weaker in clusters than in bulk crystal. These results show that, the Frolich interaction between the electron (hole) and the optical phonon is greatly reduced, and the deformation-potential interaction between the electron (hole) and the acoustic phonon is enhanced due to the quantum size effect of electron (hole) in small clusters.

The electron diffraction pattern in a saturated sample of PbI₂/Na-LTA(1) shows that (PbI₂)₅ clusters are arrayed in twice period of zeolite framework. This means that a cluster crystal is formed in the zeolite framework. The reflectivity at the exciton resonance energy in the cluster crystal remarkably increases as the number density of the clusters approaches saturation level. The remarkable increase in the reflectivity can not be explained by usual Lorentz model with a constant damping energy, but by the following two models. One is the motional narrowing effect, where the transfer of excitation energy from one cluster to another leads to the decrease in damping energy. The other reason is that the reflectivity increase as the arrangement of clusters changes from disorder to order since the scattering probability of exciton polaritons decreases as suggested by Kayanuma.