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Nanoparticles of lead iodide (PbI_2) were prepared by exposure of Langmuir-Blodgett (LB) films of lead arachidate to hydrogen iodide. The photoluminescence (PL) spectrum of the nanoparticles consisted of three bands: an exciton band and two low-energy bands associated with stoichiometric and structural defects. The center of the exciton band was blue-shifted due to a quantum size effect. The PL spectra drastically changed when the temperature increased.

Keywords: nanoparticles; Langmuir-Blodgett (LB) method; lead iodide (PbI_2); quantum size effect; photoluminescence (PL)

INTRODUCTION

The synthesis and characterization of semiconductor nanoparticles have been extensively studied for their unusual physical and chemical properties and potential applications. However, there have been only a few reported studies of nanoparticles of lead iodide (PbI_2) with a layered structure [1-3]. In these cases, the nanoparticles were grown in colloidal solutions, zeolite cages, or

copolymer films. This paper reports the first fabrication of PbI_2 nanoparticles in Langmuir-Blodgett (LB) films. The LB technique is likely to be a powerful tool to arrange nanoparticles on accommodating sites in a well-controlled way [4]. The quantum size effect of the PbI_2 particles was also investigated based on photoluminescence (PL) measurements.

EXPERIMENTAL

The fabrication of PbI_2 fine particles involves the preparation of a multilayer by depositing successive monomolecular layers of lead arachidate $(C_{19}H_{39}COO)_2Pb$ on quartz followed by exposure to hydrogen iodide (HI) at room temperature. Each sample referred to in the present article has 51 monolayers of lead arachidate prior to the HI gas treatment. The PL spectra were recorded with sample excitation at 325 nm provided by a He-Cd laser in the temperature range between 23-65 K. This low temperature prevented sample photodecomposition, thus eliminating the possibility of a change in the particle size during the PL measurements.

RESULTS AND DISCUSSION

The inset of Figure 1 shows two representative PL spectra of PbI_2 particles at 23 and 65 K. Spectrum (a) at 23 K consisted of an exciton manifold and two broad bands (labeled L and G) below the exciton edge. The latter low-energy bands are associated with impurities or defects. Although the obtained PL pattern qualitatively resembled the bulk PbI_2 spectrum extensively investigated in the past [5], the exciton emission energy was blue-shifted with respect to the bulk. The observed shift in the nanoparticles being indicative of the quantum size effect was about 40 meV. This small blue-shift is a consequence of the unique properties of the PbI_2 exciton: a small Bohr radius with an exceptionally large Rydberg constant.

The amount of the exciton blue-shift depends on the relative dimensions

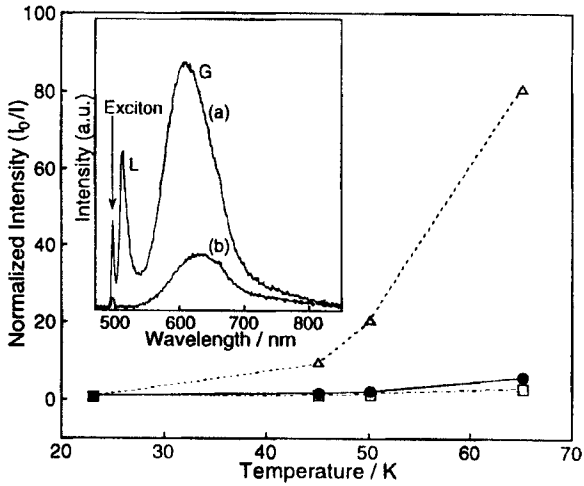

FIGURE 1 Temperature dependence of the reciprocal of the normalized PL intensity of the exciton (circles), the L band (triangles), and the G band (squares) of the PbI_2 nanocrystals. Inset: PL spectra of this sample at 23 (a) and 65 K (b).

of the mean particle radius (**a**) and the exciton Bohr radius (a_B). This study is associated with the so-called intermediate confinement regime in which $a_B < a < 3a_B$, and the exciton confinement mechanism is very complex. In addition, PbI_2 represents a case in which $m_e \gg m_h$. According to Ekimov *et al.* [6], the intermediate confinement regime in combination with a substantial difference in the effective masses results in a strong electron localization close to the particle center and free motion of the hole. They also demonstrated a theoretical curve describing the transition energy of such an e-h pair (named an acceptor-like exciton) as a function of mean particle radius. Based on this curve, the experimental blue-shift corresponds to the PbI_2 particles with about an 8-nm *diameter*.

Several changes occurred when the temperature increased: (i) the absolute intensity of all three bands decreased, accompanied by a change in their relative intensities, (ii) the band width increased, and (iii) the center of the G band shifted to lower energies, as can be seen in spectrum (b). Actually, the

center of L band also showed a similar shift, but this is hardly seen in the figure since the relative intensity of the L band at 65 K was too low. The intensity change of all three bands is plotted in Figure 1 as the ratio I_0/I. (I_0 is the band integrated at 23 K; I is the band integrated intensity at any other temperature T.) The exciton and G bands exhibited a similar qualitative temperature dependence; their intensities were almost constant in the measured temperature range. In contrast, the intensity of the L band sharply decreased as the temperature increased.

The temperature influence on the various bands, which Dag and Lifshitz [7] also observed for PbI_2 nanoparticles embedded in porous silica films, provides useful information concerning the nature of the defects. As in the previous case, the results obtained here might support the assumption that the L band is associated with bulk defects, localized in the internal volume of the particles while the G band is related to surface defects.

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