Effect of Heat and Gases on the Photoluminescence of CdS Quantum Dots Confined in Silicate Glasses Prepared by the Sol–Gel Method

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The effects of heat (130, 200, and 600 °C) and added gases (NH_3 and SO_2) on the photoluminescence of CdS particles prepared by the sol–gel method were examined in order to elucidate the influence of the chemical environment on photoluminescence. Green and red photoluminescence (PL) were observed in non-heated samples. Exposure of the added gasses to the samples caused characteristic decreases of the green and red PLs. The intensity ratio of the green PL to that of the red PL for a 600-R sample (heated at 600 °C in H_2S) showed a reversible behavior against exposure to SO_2. These results indicate that there is adduct formation between CdS and SO_2. The PL changes were fitted to the Langmuir adsorption isotherm model, and yielded the adduct formation constants. There are three emitting and three final states in the specimen.

The use of band-gap photoluminescence (PL) enables one to carry out the in situ characterization of the optical properties of crystalline semiconductor materials (such as CdS, CdSe, and CdS(e)). It has been established that the PL intensity of single-crystal II—VI semiconductors, such as CdS and CdSe, can be reversibly perturbed by surface adduct formation. Lewis bases, such as amines, enhance the PL intensity relative to a reference ambient, while Lewis acids, such as SO_2, quench the PL intensity relative to the ambient.[1—10] The increase and decrease have been analyzed using a dead-layer model.[1,11] These effects are based on the interaction of intraband gap surface electronic states with the molecular orbitals of the adsorbing species.

The PL of small- or quantum-sized semiconductor particles is a characteristic of their particle size and circumstance.[12—24] For example, the band-gap emission and interstitial sulfur or sulfur and cadmium vacancies in a CdS crystal yield green fluorescence having maxima at around 515 and 525 nm.[18,19] The PL of CdS colloids prepared in acetonitrile exhibit bright red fluorescence with a particle size that is dependent on the emission maximum, owing to a sulfur vacancy at the CdS surface.[20] PL enhancement by surface-modification procedures, such as exchanging the aqueous solvent by alcohol, has been observed.[25—27]

Recently, CdS quantum dots confined in silicate glass[28—34] have been prepared by the sol–gel method[35—37] from silicon alkoxide. The spectral feature of the PL of CdS quantum dots prepared by the sol–gel method depends on their chemical environment. Coffer et al. investigated the effect of the titration of quantum-confined CdS clusters in an inverse micell solution with dilute lanthanide β-diketonates and ferrocene derivatives.[38,39] They observed changes in the PL for a Langmuir adsorption isotherm,[4,5,7—10] from which the average adduct formation constants were determined. It is of interest to examine the influence of added gasses on the PL of CdS quantum dots confined in silicate glasses prepared by the sol–gel method. In this paper we report on the influence of a heat treatment and the presence of NH_3, a Lewis base, or SO_2, a Lewis acid, on the PL properties of CdS dots confined in silicate glasses prepared by the sol–gel method. The results will serve as a tool for clarifying the nature of the emitting states and the photoluminescence mechanism for quantum-size particles.

Experimental

Materials. CdCl (Baker and Wako), $Cd(NO_3)_2$ (Wako), TEOS (tetraethyl orthosilicate, Aldrich and Wako), ethanol (Aldrich and Wako), H_2S (Matheson, 99.9% and Nihon Sanso, 49.1% in N_2), NH_3 (Matheson, 99.99%), and SO_2 (Matheson, 99.9%) were used without further purification. Water was deionized.

Sample Preparation. The starting solution of the reaction system contained 0.1 mL of $CdCl_2$ or $Cd(NO_3)_2$ aqueous solution (4×10^{-1} mol dm^{-3}), 4.9 mL of ethanol, 0.8 mL of H_2O, and 4.2 mL of TEOS. The mixture used for PL observations was thoroughly stirred for 30 min, and then poured into a crystal growing disk. The disk was covered by a thin polymer film having several holes, and then allowed to undergo a sol-to-gel reaction at 30 °C. Gelation occurred

at 2 d. After 11 d, the gel sample was exposed to H_2S gas for 15 min. The gel sample changed to pale yellow. The disk was then placed in a 40 °C oven for 15 h to complete the reaction. The prepared xerogel was heated at 130, 200, and 600 °C under air (oxidizing atmosphere) or under H_2S (reducing atmosphere) for 5 h, abbreviated as systems 130-O, 200-O, 600-O, 130-R, 200-R, and 600-R, respectively. The untreated sample is referred to as system N. The specimens used for the visible and IR absorption spectra (system A) were prepared using a similar procedure to that described above. For system A, gelation occurred at 3 d, and an aging process was carried out for 53 d at under 303 K. The reaction of a prepared gel sample including Cd with H_2S was performed for 16 h at 53 d.

Optical Measurements. The sample cell used for emission measurements was a glass tube with a gas inlet tube. The gel sample was held between two pieces of Teflon®. The PL measurements were carried out under various pressures of NH_3 or SO_2. A Coherent Innova 90-5 Ar^+ laser (457.9 nm) was provided for band-gap excitation, as previously described;[4—10] the resulting green and/or red PL of CdS was monitored. The UV-vis and IR absorption spectra of CdS samples were observed using a Hitachi 3210 recording spectrophotometer and a Shimadzu FT-IR 8200A spectrophotometer.

Results and Discussion

Visible Absorption Spectrum. Nosaka et al. showed a relation between the absorption edge of CdS particles and the particle diameter.[40,41] Nogami et al.[31] found that the shift of the absorption-edge energy of CdS particles of reciprocally is proportional to the square of the crystal size, obtained by an analysis of the X-ray diffraction pattern; the relation reproduced the results by Nosaka et al. The absorption spectra of CdS particles in the gel state is shown in Fig. 1. The spectral feature is similar to those obtained by a similar sol–gel method.[27—31] The spectrum obtained by treating the short reaction time with H_2S and the at the first reaction stage was located on the higher energy side compared to that of a sample by treating a long reaction time with H_2S, though the spectrum by treating a long reaction time with H_2S shows a slight spectral shift upon heating.[42] This red shift indicates that the particle size increased with the reaction time. The absorption intensity decreases rapidly at around 480 nm. The band gap of this system can then be estimated at ca. 2.6 eV, corresponding to the particle size having an average diameter of ca. 37 Å.[30,31,33,40,41] According to the relation obtained by Nogami et al, the 50 Å particle size for a CdS particle corresponds to the absorption edge at 498 nm. Since the spectrum was observed at 53 d by preparing the starting solution for the sol–gel reaction and adding H_2S gas, the diameter of CdS presented in the specimen is not larger than ca. 50 Å.

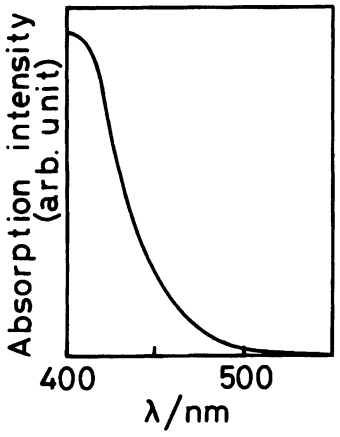

Fig. 1. The visible absorption spectrum of the prepared CdS particles in the xerogel state. After reaction with H_2S for 16 h.

Fluorescence Spectra. Figure 2 shows the fluorescence spectra of various pretreated samples. System N shows peaks at around 535, 700, and 740 nm, abbreviated as G2, R1, and R2, respectively. It is noted that the intensity of the red emissions (R1+R2) is much stronger than that of the green emission. The peaks or shoulder wavelengths are peaked at ca. 510, 700, and 735 nm for system 130-O, at ca. 510, 535 (shoulder), 690, and 770 nm for system 130-R, at ca. 510, 705, and 745 nm for system 200-O, at ca. 555, 695, and 740 nm for system 200-R, at ca. 490 (shoulder), 535, 690, and

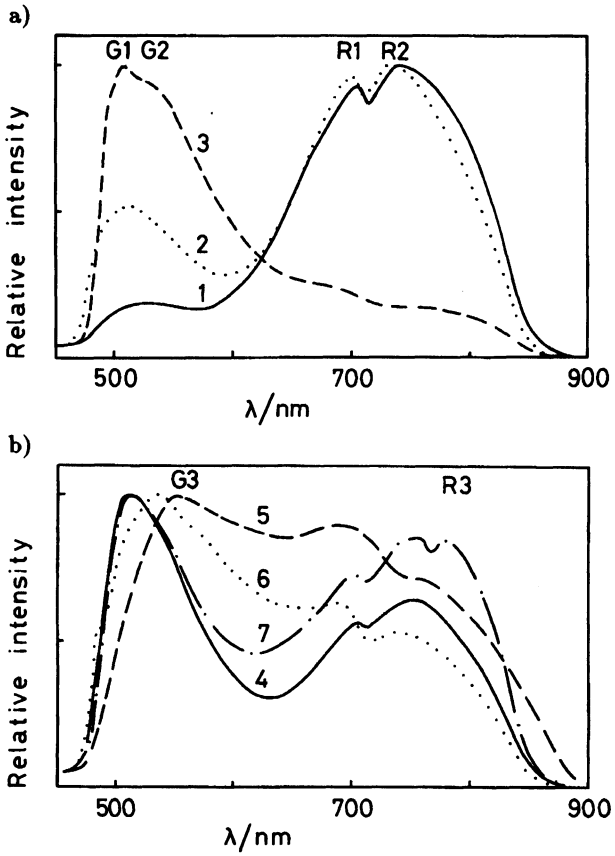

Fig. 2. The Fluorescence spectra of the prepared CdS particles prepared by the sol–gel method. System (1)N, (2) 130-O, (3) 130-R, (4) 200-O, (5) 200-R, (6) 600-O, and (7) 600-R.

735 nm for system 600-O, and at ca. 510, 700, 740, and 780 nm for system 600-R, respectively. The peaks at around 510, 555, and 780 nm are abbreviated as G1, G3, and R3, respectively. Therefore, there are six characteristic peaks, which are located at around 510 (G1, ca. 19600 cm^{-1}), 530—540 (G2, ca. 18700 cm^{-1}), 555 (G3, ca. 18000 cm^{-1}), 690—705 (R1, ca. 14300 cm^{-1}), 730—745 (R2, ca. 13600 cm^{-1}), and 770—780 (R3, ca. 12900 cm^{-1}). The transition observed at 490 nm (ca. 2.5 eV) corresponds to the band gap for the CdS particles of the sample. It is noted that the intensity of green emissions for the systems, except for system N and 130-O, are stronger than those of red emissions. These classifications suggest that there are more than two emitting states for the prepared CdS quantum dots. The energy difference between G1 and G2, G2 and G3, R1 and R2, and R2 and R3 are estimated at ca. 800±100 cm^{-1}, respectively. This equally spaced energy difference among them indicates that there are at least three final states.

The IR bands for the prepared gel are characterized at 799, 957, 1084, and 1185 cm^{-1} in this region (Fig. 3a).[43,44] The FT-IR spectrum observed in a CdS crystal exhibited the characteristic IR bands at 619, 1011, and 1113 cm^{-1} (Fig. 3b). There is no 800±100 cm^{-1} IR band for the CdS crystal. Therefore, the possibility of transitions to the equally 800 cm^{-1} spaced vibronic state in the ground state of the CdS particle can be excluded for the final states.

In the case of crystalline CdS, the total emission spectra have various emitting bands. They have been assigned to the emissive transition of electron-hole recombinations from the conduction band to the valence band (515 nm), from a trapped level by interlattice S to the valence band (ca. 525 nm), from the conduction band to Cd vacancies (535 nm), from S vacancies to the valence band (ca. 700 nm), from S vacancies to Cd vacancies (750 nm), etc.[18,19] On the other hand, the peak wavelength of emission from the CdS colloidal particles in solutions depends on their particle size.[18—20,24] The fluorescence spectra of the specimen in the present study can be classified into six. Further, the peak positions of the luminescences are substantially constant, indicating that the emitting properties of the CdS particles encapsulated in the silicate glass did not vary much during the heating process.

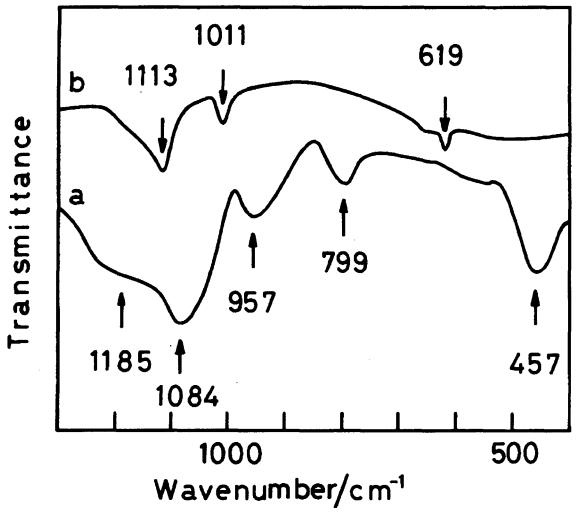

Fig. 3. FT-IR spectra of the prepared gel(a) and CdS crystal(b) in KBr.

Figure 2 also shows the relative intensity change between the red emissions by a heat treatment with H_2S. The addition of H_2S results in a relative decrease in the red PL, especially if there is a large difference between lines 1 and 3. Since the trap level of S vacancies in the specimen shown in line 3 would be partially fulfilled of S by added H_2S, this decrease indicates that S vacancies, which similarly occur in crystalline CdS, are responsible for the origin of the red PL. The increase in the relative intensity of the green PL to the red PL upon a heat treatment can be explained by a partial fulfillment of S vacancies and a decrease in the nonradiative rate occurring at the surfaces of CdS particles.

Influence of Added Gases. Upon excitation with 457.9 nm light, CdS particles encapsulated into a transparent gel emit green and red PL. Figure 4 shows the PL responses of a CdS particle monitored at 735 nm upon adsorption of NH_3 and SO_2 for system N. Exposure of gaseous NH_3 and SO_2 causes a decrease in

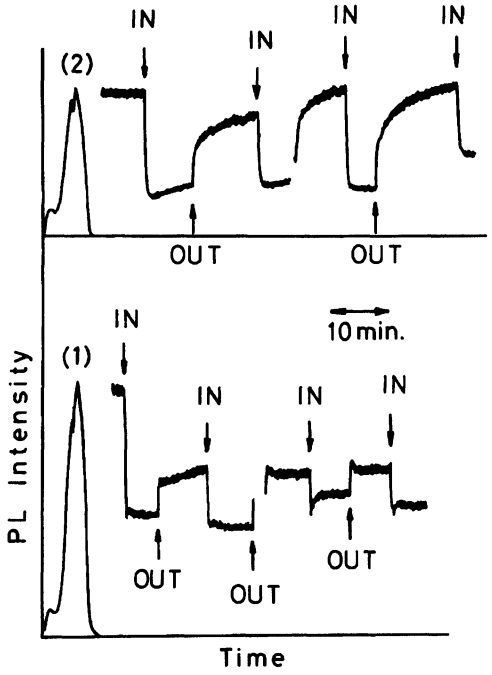

Fig. 4. Influence of added NH_3 and SO_2 on the fluorescence spectra of (1) system N and added NH_3, (2) system N and added SO_2. Monitored wavelength was 735 nm. IN and OUT indicate inject and outgas of NH_3 or SO_2. In cases of NH_3 adsorption, the PL intensities were momentarily small increased and next showed steep decrease.

the PL intensities relative to the original intensity under a vacuum. The PL intensities for systems 130-O, 130-R, 200-O, and 200-R also showed a decrease upon exposing additional gasses, regardless of their property of the Lewis acid or Lewis base. The change in the PL intensity for 600-O, and 600-R was either small or negligible, except for 600-R by H_2S. It is noted that the decrease in the PL intensity occurred for both the Lewis base (NH_3) and Lewis acid (SO_2) in contrast with the result for crystalline CdS and CdSe.[1—10] This decrease, which was observed for all systems, indicates that CdS particles prepared by the sol–gel method increase the nonradiative rate constant by the formation of an adduct, regardless the electronic character of the adsorbed gasses.

It is also noted that after an outgassing procedure of NH_3 on system N, the PL intensity recovered by ca. 65%. This result indicates that a portion of additional NH_3 formed chemical species on the surface, the desorption at which would not be easy, or the addition of NH_3 deformed a part of the surface structure, and this deformed area obtained a nonradiative nature. On the other hand, the recovery after SO_2 outgassing was 100%. The speeds of the increase and decrease upon NH_3 addition were faster than those by SO_2 addition. This indicates that the potential barrier for the adsorption and desorption (binding energies of adduct formation) for SO_2 is higher than that for NH_3.

Equilibrium Constants by Adduct Formation. The equilibrium constants for adduct formation between adsorbates and surfaces of CdS quantum dots can be estimated from the concentration dependence of PL changes by using the Langmuir adsorption isotherm model.[4,5,7—10,38,39] The quantitative form of the model is given by

$$\theta = KP/(1+KP) \quad (1)$$

and

$$\theta^{-1} = 1+(KP)^{-1}, \quad (2)$$

where θ is the fractional surface coverage, K the equilibrium constant, and P the partial pressure of the adsorbing gases.

Using a static system, we constructed adsorption isotherms at 295 K by plotting the fractional decrease in the PL intensity as a function of the NH_3 or SO_2 partial pressure. Figure 5 presents the raw data of NH_3 or SO_2 adsorptions for system N. Figure 5 shows that our data yield a good fit to Eqs. 1 and 2. The thus-obtained K values are given in Table 1. The K values for NH_3 adsorption are comparable for the adduct formation constant between the NH_3 and CdSe surface.[3] It is noted that the K for a 130 °C treatment under oxidizing conditions has a larger value than that under an H_2S atmosphere. The K values for SO_2 adsorptions are somewhat larger than those for NH_3 adsorption. The K values for high-temperature treatments become small. The reaction route from CdS to CdO, elimination of

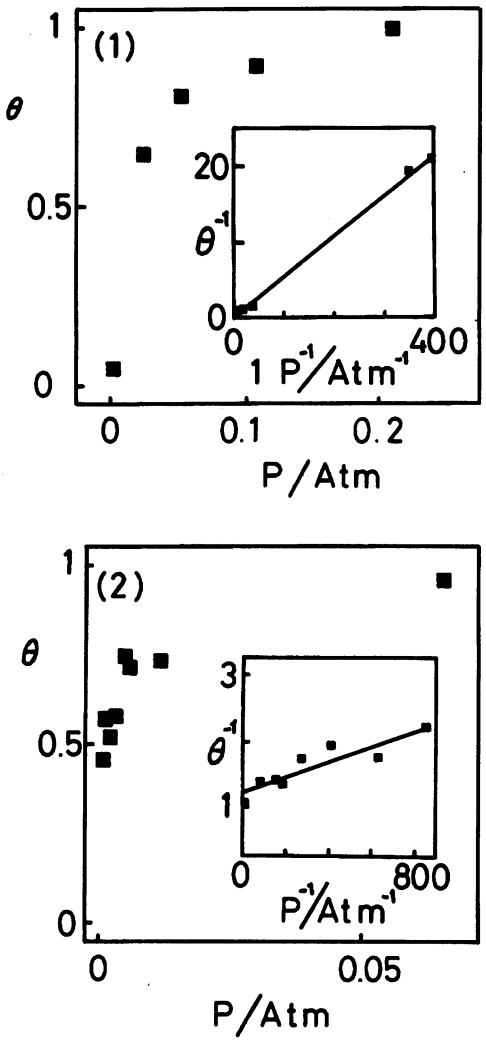

Fig. 5. Plots of the fractional surface coverage, θ, obtained from adduct-induced PL changes by use of Eq. 1 in the text as a function of the partial pressure of NH_3(1) and SO_2(2) for system N. The inset presents these same data as a double-reciprocal plots for NH_3(1) and SO_2(2): the lines shown are least-squares best fits to the data and lead to adduct formation constants of 19+1 atm^{-1} for NH_3 and 840+160 atm^{-1} for SO_2.

Table 1. Adduct Formation Constants ($K atm^{-1}$) of CdS Quantum Dots by NH_3 and SO_2 Adsorption

Temperature	Treatment	NH_3	SO_2
Untreated		19+1	840+160
130 °C	Air	33+3	42+5
	H_2S	*	1
200 °C	Air	2	92+4
	H_2S	36+3	79+5
600 °C	Air	*	*
	H_2S	*	3

*indicates that the added gases have very small or negligible effect on the PL intensities.

adsorbed H_2O and ethyl alcohol, and sintering between gel particles may be responsible for the changes.

Influence of SO_2 Adsorption on the PL Intensity for System 600-R. The influence of SO_2 adsorption on the total PL intensity for System 600-R is shown in Fig. 6 as a function of the partial pressure of SO_2. It can be seen that the peak intensity monitored at the red PL is constant through measurements by considering the intensity fluctuation with time from laser light. On the other hand, the peak intensity at 510 nm varies with the partial pressure of SO_2! This distinct behavior indicates that the emitting mechanism of the two bands is difference, and that the radiative and nonradiative rate constants from excited electronic state of CdS particles do not influence the red PL or the green PL by the formation of an adduct at the surface of CdS particles. Figure 7 shows the relative intensity of PL (510 nm) to that of PL (760 nm) as a function of the partial pressure of SO_2. Except for the original ratio (point 1), the ratios were lower than 1 and the reproducibility good (it may become a good sensor for SO_2 concentration).

The temperature dependence of the excitonic fluorescence and trapped fluorescence intensities of surface-modified quantum-sized CdS colloids has been well interpreted as being the difference in the trap population between shallow and deeper traps.[23] The excitonic and trapped fluorescences correspond to the green and red PLs in the present study. In our case, the photogenerated electrons would be trapped both in deeper and shallow traps.

The S vacancies in CdS crystal are responsible for the origin of the red PL. The insensitive behavior of the red PL for SO_2 adsorption indicates that the emitting origin from a deeper trap is not affected by adduct formation at the surface on CdS particles. The sensitive green PL for the adduct formation indicates that the radiative and nonradiative rates for the green PL, which originated from shallow traps, are influenced by adduct formation between SO_2 and CdS dots. In the present case it is also noted that the spectral features of the green and red PLs were unchanged by the formation of a surface adduct. Especially, it is noted that the relative intensities among G1, G2, and G3 and among R1, R2, and R3 remained constant. These bahaviors indicate that substantial electronic properties of the upper states were maintained by adduct formation, and that there are three lower final states. These three final states correspond to the levels of the valence band (or HOMO), Cd vacancies, interstitial S, etc., in agreement with previous reports.[12—14] It is therefore concluded that there are three emitting states (one showed a 490 nm peak, one G1, G2, and G3 peaks, and the other R1, R2, and R3 peaks) in nature in this specimen.

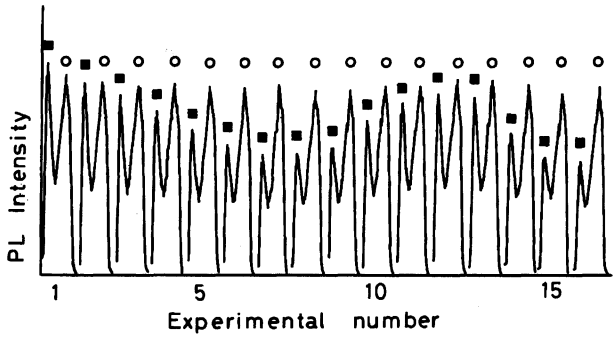

Fig. 6. Influence of SO_2 concentration on the total fluorescence intensity of system 600-R. ■ and ○ indicate the wavelengths of at 510 and at 760 nm, respectively. Partial pressures of SO_2 were 1: $< 10^{-3}$, 2: 0.049, 3: 0.11, 4: 0.21, 5: 0.41, 6: 0.68, 7: 1.01, 8: 0.77, 9: 0.53, 10: 0.13, 11: 0.029, 12: $<10^{-3}$, 13: $<10^{-3}$, 14: 0.28, 15: 0.59, and 16: 0.94, respectively. Time interval between each observations were 10 to 20 min. The variation of the PL intensities monitored at 760 nm would be influence of output fluctuation from laser intensity.

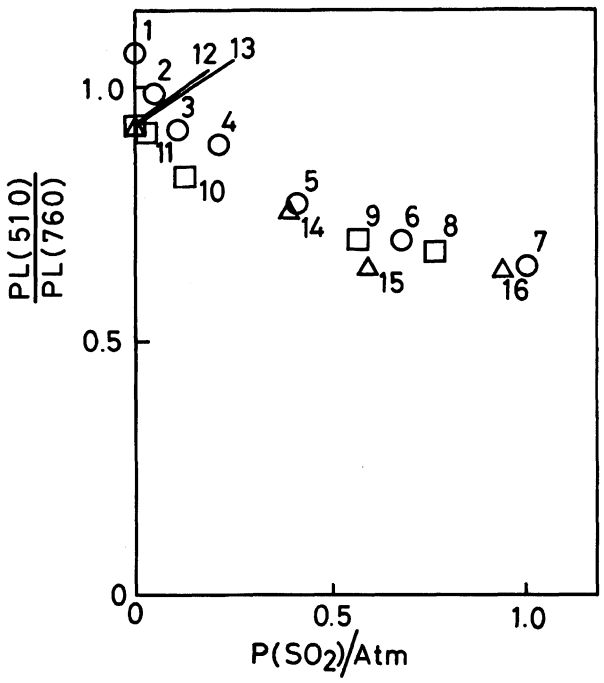

Fig. 7. Relation between intensity ratio of PL at 510 nm to that of 760 nm and pressure of SO_2. ○, □, and △ indicate different experiment. Numbers correspond to the experimental number given in Fig. 6.

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