Structural phase transition of CdS microcrystals embedded in GeO_2 glassy matrix under high pressure

Structural phase transition of CdS microcrystals embedded in GeO$_2$ glassy matrix under high pressure

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Abstract. CdS microcrystals of various sizes embedded in a germanium dioxide glass matrix have been studied by Raman scattering and optical absorption under high pressure up to about 9 GPa. Structural phase transition of the CdS microcrystals from wurtzite to rock salt phase was observed at a pressure higher than 6 GPa, which is far above the bulk CdS transition pressure of 2.7 GPa. Under a pressure higher than 6 GPa, the 1-LO Raman intensity of the wurtzite phase of CdS microcrystals decreases gradually with time. After the pressure is released from about 9 GPa to atmospheric pressure, the high pressure rock salt phase is preserved at room temperature. We found that CdS microcrystals of the rock salt phase recovered to the wurtzite phase by temperature annealing at atmospheric pressure. Our observations suggest that the GeO$_2$ matrix plays an important role.

1. Introduction

The physical properties of semiconductor microcrystals of dimensions ranging from a few nanometres to several tens of nanometres differ widely from those of corresponding bulk crystals. Over the past decades, optical and vibrational properties as well as structural phase transitions of bulk semiconductors, for example CdS and CdSe [1–5], have been studied extensively under applied pressure. The effects of finite size on the structural phase of semiconductor microcrystals are of great interest in comparison with the structural phase transition of the bulk semiconductors [6–16]. Recently, it was found that the melting point of CdS microcrystals decreases with decreasing particle size [8], and that CdS microcrystals with diameter of 2 nm synthesized by yeast have a rock salt structure without applying external pressure [9]. Furthermore, temporal fluctuation of structural phase in metal nanocrystals has been directly observed by transmission electron microscopy [10]. Hence, the phase stability is strongly influenced by the finite volume.

There are many factors which control the pressure induced structural phase transition in a finite system. Alivisatos and co-workers have investigated the pressure induced structural phase transition from a tetrahedral to a rock-salt phase in colloidal CdS and CdSe nanocrystals [11–15]. Quantum confinement effects on direct and indirect transitions in CdSe nanocrystals were discussed in [11]. [12] and [13] report that the increased surface tension in the rock-salt phase is responsible for the elevation of the transition pressure in

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nanocrystals. They have explained the result by fundamental thermodynamic theory which predicts the $1/d$ dependence of ΔP. Recently, they reported that the limited extent of the crystallites affects the kinetics as well as the thermodynamics of the transition [14, 15], and they gained insight into the kinetics of transformations in nanocrystal systems.

We also investigated the pressure induced structural phase transition of CdS microcrystals embedded in various matrices [6, 16]. In our previous work on the phase-transition behaviour of CdS microcrystals of various sizes d in an SiO film as a matrix [16], it was found that the elevation of the phase-transition pressure ΔP of those CdS microcrystals did not seem to be explained simply by the thermodynamic theory. In addition, it was found that the transition pressure depends strongly on the kind of matrix. Thus, there should be some other factors that explain all the high pressure data on finite systems.

We have already discussed how the crystallinity of microcrystals affects the phase transition [16]. Besson *et al* have also discussed the effects of crystalline defects on the structural phase transition of GaAs [17]. The effects of strain and dislocation at the surface or the interface on the phase stability has been reported by Weinstein *et al* [18, 19].

The matrix surrounding the microcrystals is also an important factor which affects the phase stability. The behaviour of a-GeO$_2$, which was used as the matrix of the CdS microcrystals in this study, has been studied under pressure as an interesting amorphous solid. Itie *et al* have reported that the coordination of Ge in GeO$_2$ glasses changes gradually from fourfold to sixfold at pressures between about 6.6 and 10 GPa with increasing pressure, using x-ray absorption measurements [20]. This coordination change involves an irreversible densification of about 20%, that is, the amorphous GeO$_2$ has a higher sound velocity after releasing the pressure from beyond 10 GPa than before applying pressure [21]. For a-SiO$_2$, which has a similar structure, the same coordination change and the irreversible densification also occur. Moreover, when the coordination of Si changes under constant high pressure, the Brillouin frequency of a-SiO$_2$ shifts gradually to a higher value with time [22]. The Brillouin frequency of densified a-SiO$_2$, which is obtained by releasing the pressure from 18 GPa, shifts to a lower value at atmospheric pressure with increasing annealing temperature [22]. The same phenomena (the coordination change with time and the structural relaxation with annealing temperature) are also considered to occur in GeO$_2$ glasses. Therefore, it is very interesting to investigate the phase stability of the CdS microcrystals in densified GeO$_2$ glasses under high pressure, and after releasing from high pressure to the atmospheric one.

In this paper, we report results on Raman scattering and optical absorption for CdS microcrystals embedded in a GeO$_2$ glass matrix under high pressure. Comparing the current results with our earlier work on CdS microcrystals embedded in an SiO matrix [16], we discuss a matrix effect on the structural phase transition. The phase stability of CdS microcrystals used in this study is considered to be affected by the pressure dependence of the GeO$_2$ glass matrix.

2. Experiments

CdS microcrystals embedded in GeO$_2$ were prepared in two stages. The first stage was the synthesis of base glasses doped with Cd and S atoms/ions as a supersaturated solid solution by using a melt-quench method. The host glasses were GeO$_2$ which contained Na$_2$O soda in the form of Na$_2$GeO$_3$. The molar ratios of Cd, S, GeO$_2$ and Na$_2$GeO$_3$ powder, which were mixed as the base glasses, were 0.9:2.59:87.7:8.81, respectively. The second stage was the thermal annealing of the base glasses for the growth of CdS microcrystals in the glassy matrix. The detail have been described in [23]. For the sample of largest microcrystal size, the average size of CdS microcrystals was estimated by transmission electron microscopy.

For the other samples, it was estimated by applying the Brus quantum confinement theory [24] to the observed lowest excited state energy. For our samples, the Brus theory [24] is a good approximation at sizes larger than about 7 nm [25]. In this way, we obtained samples with average sizes of 6.9 nm, 8.1 nm and 50 nm. (Hereafter the size is referred to as diameter.) The volume ratio of CdS microcrystals to GeO₂ glasses was about 1.6%.

The samples were polished down to about 50 μm thickness, and loaded into a Bassett-type gasketed diamond-anvil cell (DAC). A 4:1 methanol–ethanol mixture was used as pressure medium. The pressure was determined with a standard ruby-fluorescence technique. As the CdS microcrystals are surrounded in the GeO₂ glass matrix, the pressure applied to the microcrystals through the matrix and its nonhydrostaticity must be examined. As described below, the pressure coefficient of the 1-LO Raman frequency of CdS microcrystals for all samples showed a good agreement with that of bulk CdS up to 6 GPa. Therefore, we consider that CdS microcrystals feel on average the pressure determined by the ruby fluorescence.
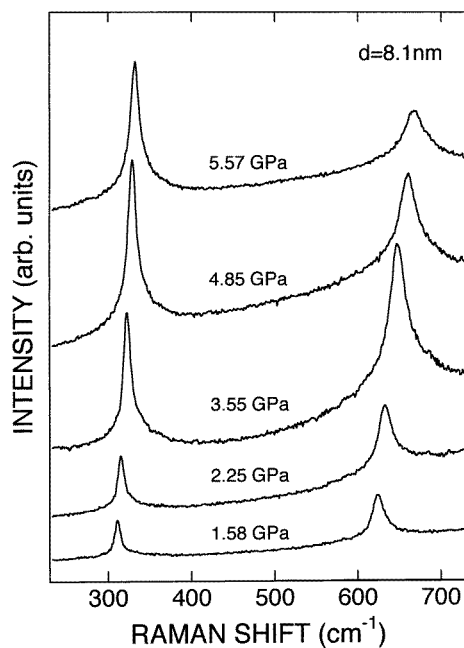

Figure 1. Resonance Raman spectra of 1-LO and 2-LO modes of CdS microcrystals embedded in GeO₂ glasses with $d = 8.1$ nm at several pressures.

In order to estimate the quality of the pressure, we observed the full width at half maximum FWHM of the 1-LO Raman spectrum under applied pressure. The FWHM of the samples with $d = 50$ nm and 8.1 nm increases by almost the same rate as that of bulk CdS. In addition the GeO₂ matrix used in this study is a glassy material, i.e. an isotropic material. Therefore the nonhydrostaticity of the CdS microcrystals is considered to be small. The FWHM of the 6.9 nm sample, however, increases by a slightly larger rate than that of bulk CdS for increasing pressure higher than 4 GPa. This could be due to the nonhydrostaticity which increases gradually with increasing pressure.

For Raman scattering measurements, the 488.0 nm line of an Ar-ion laser was used at atmospheric pressure, and the 457.9 nm line under applied pressure. Raman scattering
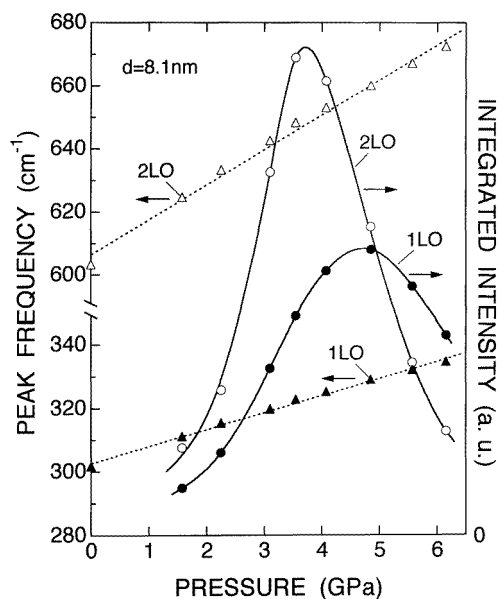
Figure 2. Peak frequencies (▲, △) and integrated intensities (●, ○) of 1-LO and 2-LO Raman spectra of CdS microcrystals embedded in GeO$_2$ glasses with $d = 8.1$ nm as a function of pressure. The dotted lines connecting the solid and open triangles, respectively, are least-squares fits. The solid curves connecting the solid and open circles, respectively, are to guide the reader's eye.

spectra were measured with a triple spectrometer system (Jasco TRS-600) equipped with a CCD (Photometrics TK512CB) detector. The backscattering geometry was used with a laser intensity of about 1 kW cm^{-2}.

Optical absorption spectra were obtained by a conventional method. The light of a tungsten lamp was monochromatized, and focused to the gasket hole of the DAC. The light passing through the gasket hole was focused by a camera lens onto a small pin hole in a screen in front of the photomultiplier. Only the light transmitted through the sample passed the small pin hole and reached the detector.

All Raman and absorption measurements were carried out at room temperature.

3. Results

Figure 1 shows the resonance Raman spectra of the 1-LO and 2-LO modes of CdS microcrystals embedded in GeO$_2$ with $d = 8.1$ nm at several pressures up to 6 GPa. At atmospheric pressure, the Raman frequencies of 1-LO and 2-LO phonons are 301.8 and 603.3 cm^{-1}, respectively. The 1-LO frequency of 301.8 cm^{-1} is lower by about 1.5 cm^{-1} than that of bulk CdS. Figure 2 shows the pressure dependences of both peak frequencies and integrated intensities of the 1-LO and 2-LO Raman modes. As shown in figure 2, the peak frequencies of 1-LO and 2-LO phonons were found to shift linearly to higher frequencies with pressure at the rate of 5.0 cm^{-1} GPa^{-1} and 10.3 cm^{-1} GPa^{-1}, respectively. These values show a good agreement with those of bulk CdS, 4.9 and 10.0 cm^{-1} GPa^{-1}. This indicates that CdS microcrystals feel the pressure measured by ruby fluorescence through the GeO$_2$ glass matrix. With regard to the integrated intensities, 1-LO and 2-LO modes increase

gradually and reach a maximum by resonance at about 4.7 GPa and 3.7 GPa, respectively. Then they decrease with increasing pressure. No diminution of Raman intensity, which would indicate the occurrence of a structural phase transition from a wurtzite to a rock-salt phase, was observed up to 6 GPa for samples of all sizes. In other words, CdS microcrystals preserve the wurtzite phase up to much higher pressure, compared with the phase transition pressure, 2.7 GPa, of bulk CdS. This is consistent with the results of high pressure absorption measurement as described below.
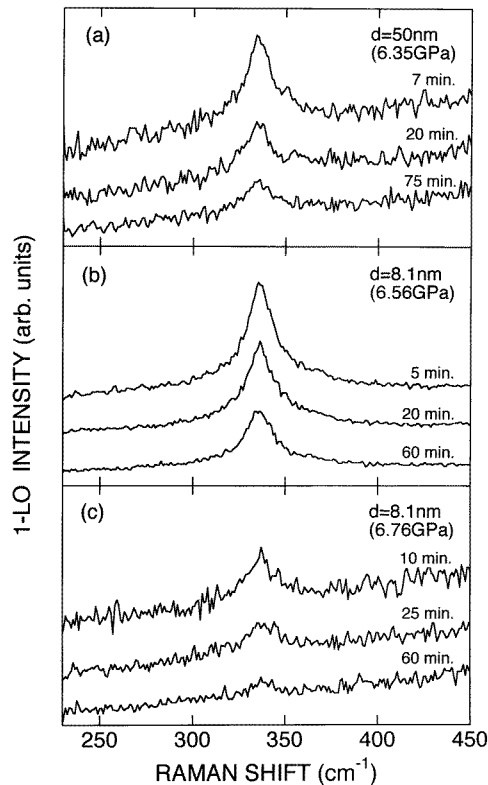

Figure 3. Temporal change in the Raman spectra of the 1-LO mode of CdS microcrystals embedded in GeO$_2$ glasses under a constant pressure higher than 6 GPa.

A gradual decrease in the intensity of the 1-LO Raman mode with time, however, was observed under the pressures 6.56 GPa and 6.76 GPa for the sample with $d = 8.1$ nm as shown in figure 3. A similar behaviour was observed at 6.35 GPa for the sample with $d = 50$ nm. The temporal change in the spectra of the sample with $d = 6.9$ nm, unfortunately, could not be observed because of the very weak intensity due to the off-resonance condition under pressures higher than 6 GPa. Figure 4 shows the time dependence of the 1-LO Raman intensity at various pressures. As shown in figure 4, the 1-LO Raman intensity of the sample with $d = 50$ nm does not change under pressure up to 6.04 GPa, while it decreases gradually with time under pressures higher than 6.35 GPa. The decrease in intensity for the sample with $d = 8.1$ nm accelerates as the sample is kept under higher pressure.

In order to clarify the origin of the temporal change in the Raman spectra under high
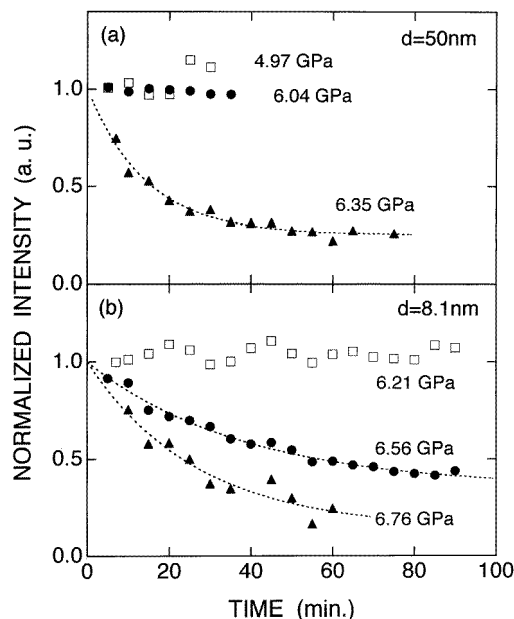
Figure 4. Time dependence of 1-LO Raman intensity of CdS microcrystals embedded in GeO_2 glasses at various pressures.

pressure as seen in figure 4, high pressure optical absorption was measured. In figure 5, the optical absorption spectra of CdS microcrystals at several pressures up to 7 GPa are shown. Whereas the optical absorption spectrum of the sample with $d = 50$ nm smoothly shifts to higher energies with increasing pressure up to 5.51 GPa, an abrupt change in the spectral shape is seen between 5.51 and 6.25 GPa. Changes in the spectral shape are seen between 6.20 and 6.79 GPa for the sample with $d = 8.1$ nm. It occurs between 6.60 and 6.98 GPa for the sample with $d = 6.9$ nm. These changes correspond to the transformation from a wurtzite (direct optical transition) to a rock-salt (indirect optical transition) phase. Figure 6 shows the size dependence of the phase-transition pressure obtained by the optical absorption measurement (solid circles). Open circles show the pressure at which the 1-LO Raman intensity starts to decrease as shown in figure 4. The result suggests that the phase transition from a wurtzite to a rock-salt phase would be responsible for the temporal decrease in the intensity of the 1-LO Raman mode under high pressure.

　　Figure 7 shows the original absorption spectra at atmospheric pressure and the absorption spectra after releasing the pressure from about 9 GPa to atmospheric pressure. The pressure, 9 GPa, is higher than the phase transition pressure. It is found that the spectra after releasing the pressure from about 9 GPa do not recover to the original ones. They exhibit wide absorption in the region of the low energy side of the absorption edge. This indicates indirect absorption. It implies that the high pressure rock-salt phase is preserved even at atmospheric pressure.

　　We investigated a recovery process from the rock-salt to the wurtzite phase with annealing at atmospheric pressure. Figure 8 shows the integrated intensity of the 1-LO Raman mode of CdS microcrystals as a function of annealing temperature at atmospheric pressure. Here, the annealing time was 1 hour and the Raman measurement was made at room temperature. The integrated intensity is normalized by the intensity observed before applying pressure. As shown in figure 8, the integrated intensities are almost zero at
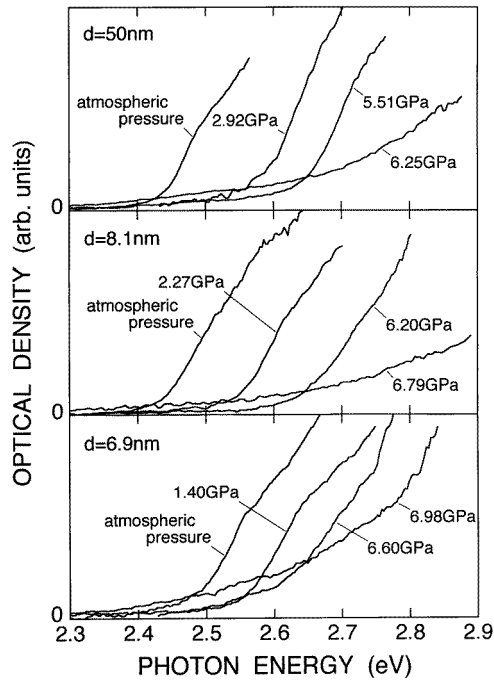
Figure 5. Optical absorption spectra of CdS microcrystals embedded in GeO_2 glasses at various pressures. These absorption spectra of wurtzite phase shift to the high energy side, and they change to those of the rock-salt phase with increasing pressure.
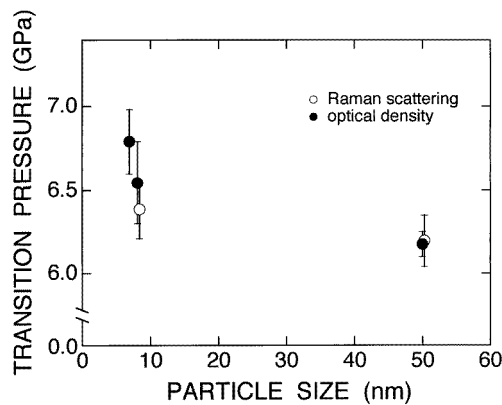

Figure 6. Size dependence of the phase-transition pressure for CdS microcrystals embedded in GeO_2 glasses. Solid circles represent the transition pressure estimated from the change in the spectral shape in figure 5. The pressures at which the 1-LO Raman intensity starts to decrease are also shown by open circles.

room temperature after releasing the pressure from about 9 GPa to the atmospheric one, but recover gradually with an increase of the annealing temperature for all samples. This indicates the recovery from the rock-salt phase to the wurtzite phase. It looks as if the
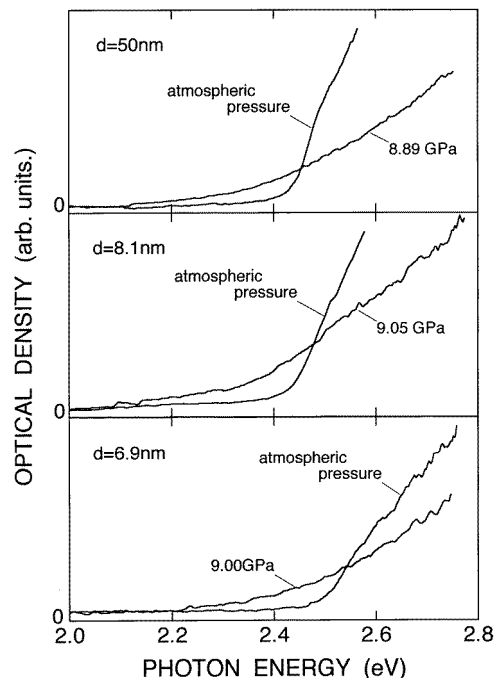
Figure 7. Original absorption spectrum of CdS microcrystals embedded in GeO_2 glasses at atmospheric pressure and the absorption spectrum after releasing from the pressure indicated in the figure to atmospheric pressure.
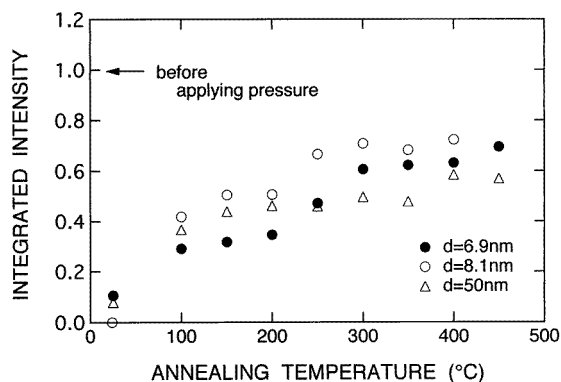

Figure 8. Annealing temperature dependence of integrated intensity of 1-LO Raman mode of CdS microcrystals embedded in GeO_2 glasses at atmospheric pressure.

normalized intensity does not recover to 1.0, even at the highest annealing temperature in figure 8. One explanation for this point is a change in the optical transmission of the GeO_2 glass matrix. The GeO_2 glasses could become inhomogeneous or fogged by small cracks created after releasing from about 9 GPa to atmospheric pressure. This can make the optical transmission of this sample decrease. In this case, the Raman intensity of CdS microcrystals embedded in the GeO_2 glass matrix after releasing pressure becomes lower

than that before applying pressure even if the reverse transformation of CdS microcrystals is complete. However, we cannot exclude the possibility that the reverse transition is not completed even after the annealing at 450 °C so that a small amount of wurtzite phase still remains in the samples. Further careful study will be needed to clarify this point.

4. Discussion

It was found in our previous work on CdS microcrystals embedded in an SiO film as a matrix that the phase transition pressure is 4.51 GPa for the sample with $d = 6.9$ nm, 4.67 GPa for $d = 4.4$ nm and 4.92 GPa for $d = 3.4$ nm [16]. Thus the phase transition pressure increased with decreasing microcrystal sizes. As shown in figure 6, even at the large size of 50 nm, the phase transition pressure is higher than 6 GPa in the present study. This is much higher than for CdS microcrystals embedded in a SiO matrix. Whereas the CdS microcrystal size decreases greatly from 50 to 6.9 nm, the phase transition pressure changes little, 6.35–6.98 GPa. That is, the phase transition pressure of CdS microcrystals embedded in GeO$_2$ glasses does not depend strongly on the microcrystal size. It is reasonable to assume that the structure of SiO is more flexible than that of GeO$_2$ glasses because of the polymeric nature of SiO. This may be one of the reasons why CdS microcrystals embedded in SiO even at small particle size have a lower phase-transition pressure than CdS microcrystals embedded in GeO$_2$. This suggests that the matrix surrounding the microcrystals plays an important role in the structural phase transition.

Jorgensen [26] and Houser *et al* [27] have reported that the predominant effect of the volume contraction on crystalline GeO$_2$ of α-quartz structure at pressures up to about 6 GPa is the tilting of the corner-sharing GeO$_4$ tetrahedra arising from changes in O–Ge–O angles. On the other hand, GeO$_2$ glass shows a local structure similar to that of crystalline GeO$_2$, i.e. corner sharing tetrahedra, but the absence of a long range order due to a distribution of Ge–O–Ge angles [28]. There is no large change of Ge–O distance up to 6.6 GPa revealed by x-ray absorption measurements [20]. So, it is considered that the tilting of the corner-sharing tetrahedra is a predominant effect of the volume contraction up to about 6 GPa even in the case of GeO$_2$ glasses, and this tilting is not so large as to compensate for the volume contraction of the phase transition of CdS microcrystals, which is about 20% [1]. This is one of the reasons that the phase transition of CdS microcrystals embedded in a GeO$_2$ glass matrix below 6 GPa does not occur. As mentioned in the introduction, the coordination of Ge in GeO$_2$ glasses changes gradually from fourfold to sixfold at pressures between about 6.6 and 10 GPa, which results in the densification [20]. CdS microcrystals with various sizes transform from the wurtzite to the rock-salt structure near 6.6 GPa, and this size insensitive pressure corresponds to the pressure at which the coordination of Ge in GeO$_2$ glasses begins to change from fourfold to sixfold. The densification due to the coordination change of Ge can compensate the volume contraction of CdS microcrystals at the phase transition. This is the reason why the transition pressure of CdS microcrystals does not depend strongly on the microcrystal size.

As shown in figure 4, the 1-LO Raman intensity of CdS microcrystals decreases gradually with time under high pressure. Their decay times are rather long. From high pressure optical absorption measurements, the decrease in the intensity is found to correspond to the occurrence of a phase transition from wurtzite to first order Raman inactive rock-salt phase. No temporal change was observed for CdS microcrystals embedded in SiO. So, this gradual decrease of the 1-LO Raman intensity of CdS microcrystals can be considered to be derived from the matrix effect.

As the densification of a-SiO$_2$ occurs gradually with time under a constant high pressure

[22], the same phenomenon could be considered to occur for GeO_2 glasses. Therefore, when the GeO_2 glass matrix densifies with long time scale at a pressure higher than 6.35 GPa, CdS microcrystals transform from the wurtzite phase to the rock-salt phase depending on the densification time of the GeO_2 glass matrix. Thus, the gradual densification of the GeO_2 glass matrix is responsible for the slow decrease in the Raman intensity. On the other hand, the densification does not occur in SiO under pressures up to 6 GPa. This explains why the temporal decrease in the 1-LO Raman intensity of CdS microcrystals embedded in an SiO matrix was not observed.

As shown in figure 7, the spectra after releasing the pressure from about 9 GPa differed largely from the original one. The high pressure rock-salt phase of CdS microcrystals is preserved fairly well at room temperature even after releasing to atmospheric pressure. So there must be a kinetic barrier to suppress the reverse transition (transition from rock-salt to wurtzite phase). Tolbert and Alivisatos studied the reverse transition and the kinetic barrier for colloidal CdSe microcrystals, and have reported that the low pressure wurtzite phase of colloidal CdSe microcrystals with $d = 2$ nm recovered up to about 80% at the reverse transition [14,15].

It has been reported that the a-GeO_2 densifies irreversibly by applying pressures beyond 10 GPa [21]. Thus, irreversible densification would be considered for the GeO_2 glass matrix after releasing the pressure from 9.05 GPa. Therefore, the structurally densified GeO_2 matrix suppresses the volume expansion of CdS microcrystals at the reverse transition. This matrix effect is responsible for the suppression of the reverse transition. This may be the reason why CdS microcrystals embedded in a GeO_2 glass matrix have a larger hysteresis than colloidal CdSe microcrystals.

A large hysteresis was also observed in the integrated intensities of the 1-LO Raman spectra as shown in figure 8. However, the rock-salt type CdS microcrystals recovered gradually to the wurtzite phase with increasing annealing temperature. In order to clarify the origin of the recovery, we prepared densified GeO_2 glasses by releasing the pressure from about 9 GPa to the atmospheric one, and measured the Raman spectra at room temperature after annealing at various temperatures for 1 hour. The result is shown in figure 9. The Raman spectrum of the densified GeO_2 glass at room temperature recovered gradually with increasing annealing temperatures to the spectrum of the undensified GeO_2 glass which was obtained before applying pressure. The spectra of the annealed samples can be decomposed well into two components. One is from the spectrum of the densified GeO_2 glass indicated by the dotted line, and the other from that of the undensified GeO_2 glass shown with the broken line in figure 9. The ratio of the integrated Raman intensity of the densified GeO_2 glass to that of the undensified one is plotted as a function of the annealing temperature in figure 10. We found that the fraction of the densified GeO_2 glass component decreases gradually with increasing annealing temperature. A similar behaviour has also been reported for densified a-SiO_2 [22].

The decrease of the densified GeO_2 component coincides with the increase in the 1-LO Raman intensity shown in figure 8. Therefore, the structural relaxation of the matrix is responsible for the volume expansion by about 20% through the recovery of CdS microcrystals from the rock-salt phase to the wurtzite one. Hence, it can be considered that the kinetic barrier which preserves the rock-salt phase of CdS microcrystals at atmospheric pressure is formed by the matrix surrounding the microcrystals.
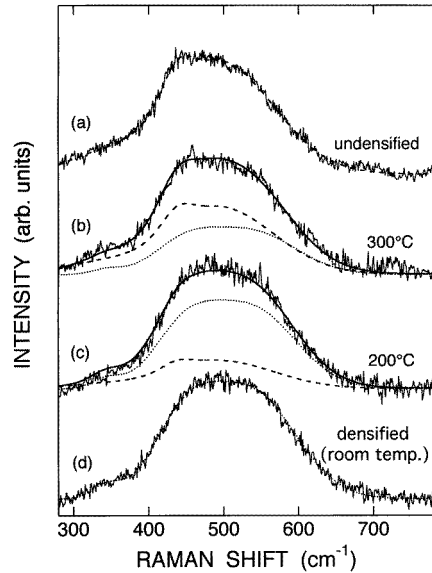
Figure 9. Raman spectra of (a) the undensified GeO$_2$ glass, (b) the densified GeO$_2$ glass annealed at 300 °C for 1 hour, (c) the densified GeO$_2$ glass annealed at 200 °C for 1 hour and (d) the densified GeO$_2$ glass at room temperature. The spectra of (b) and (c) can be decomposed well into the spectra of (a), broken line, and (d), dotted line.
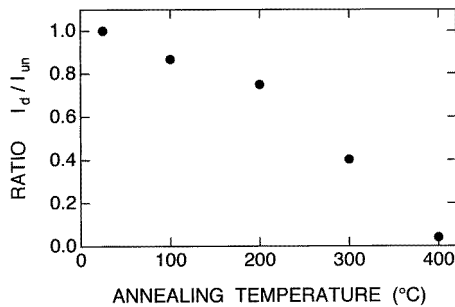

Figure 10. Ratio of the integrated Raman intensity of the densified GeO$_2$ glass (I_d) to that of the undensified one (I_{un}) as a function of annealing temperature.

5. Conclusion

We measured Raman scattering and optical absorption of CdS microcrystals embedded in germanium dioxide glass matrix under high pressure. We studied the phase transition behaviour by examining CdS microcrystals of various sizes, and discussed the matrix effects on the phase transition.

Structural phase transition from wurtzite to rock-salt phase is observed at pressures between 6 and 7 GPa, which is far above the bulk CdS transition pressure of 2.7 GPa. We attribute this result to the difference in volume contraction under pressure between CdS microcrystals and the GeO$_2$ matrix.

Under pressures higher than 6.35 GPa, the 1-LO Raman intensities of the wurtzite phase of CdS microcrystals decrease gradually with time. This result can be explained by the time

evolution of the densification of the GeO$_2$ glass matrix under pressure.

   We obtained a fairly stable rock-salt phase of CdS microcrystals after releasing the pressure from about 9 GPa to the atmospheric one, and investigated the recovery process of CdS microcrystals from the rock-salt to the wurtzite phase with annealing. Our results suggest that the irreversible densification of the GeO$_2$ glass under high pressure and its relaxation by annealing play an important role in the phase transition of CdS microcrystals.

Acknowledgments

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