

Sol–gel preparation of $\text{CdS}_x\text{Se}_{1-x}$ solid solution microcrystal-doped glasses

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$\text{CdS}_x\text{Se}_{1-x}$ solid solution microcrystal-doped glasses with a significant quantum-sized effect were prepared by the sol–gel process. Gels synthesized by the hydrolysis of complex solution of $\text{Si}(\text{OC}_2\text{H}_5)_4$, $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and selenium were treated in H_2S and hydrogen gas atmospheres to form $\text{CdS}_x\text{Se}_{1-x}$ solid solution crystals, whose compositions were determined from the X-ray diffraction and Raman scattering spectra. Sulphur in CdS crystals is substituted for selenium by heating in hydrogen gas, and its content decreases with increasing temperature. On the other hand, the sulphur content increases on reacting the CdSe crystal-precipitated glasses with H_2S gas. The optical absorption spectra are shifted towards the red as the crystal size increases, and the gap energy is reciprocally proportional to the square of the crystal size.

1. Introduction

Since Jain and Lind measured the high third-order optical non-linearity using the $\text{CdS}_x\text{Se}_{1-x}$ -doped glasses [1], small-sized semiconductors have received much attention in glass science and technology. In these glasses, the photoexcited electron-hole carriers and excitons are three-dimensionally defined by the deep confinement potential of the dielectric-glass matrices. Such a quantum-sized effect is expected to give rise to large third order nonlinearity. To date, $\text{CdS}_x\text{Se}_{1-x}$ microcrystal-doped glasses which are commercially available as sharp-cut-off colour filters, have been used for the measurements of nonlinearities [2–6]. In these glasses, however, $\text{CdS}_x\text{Se}_{1-x}$ semiconductor particles, in general, deviate from the desired chemical compositions and their sizes are too large to display a significant quantum-sized effect. Therefore, it is desired to develop glasses doped with well-controlled amounts, size and size distribution of microcrystals, which would expand the application of the glasses to non-linear photonics materials.

Various methods have been used to obtain the small-sized semiconductor-doped glasses in addition to the melting method. We have proposed a novel method for the preparation of these glasses, which is based on the sol–gel process, and have reported results for glasses doped with small-sized CdS and CdSe crystals [7–10]. Glasses containing CdO were prepared from an alkoxy-derived solution, then allowed to react with H_2S gas to precipitate fine CdS crystals in the glass matrices [7–9]. CdSe-doped glasses could also be produced by heating silica glasses containing cadmium and selenium compounds in an atmosphere of mixed $\text{H}_2\text{--N}_2$ gas [10]. Thus, the sol–gel method

can produce glasses doped with semiconducting crystals without melting the raw materials, which is of greater advantage than a glass-melting method.

In this study, the sol–gel method was used in the preparation of $\text{CdS}_x\text{Se}_{1-x}$ solid solution crystal-doped glasses. Gels synthesized by the sol–gel process were treated in order to precipitate $\text{CdS}_x\text{Se}_{1-x}$ microcrystals in atmospheres of H_2S and $\text{H}_2\text{--N}_2$ gas. The chemical composition and the size of the microcrystals were determined. The quantum size effect of the $\text{CdS}_x\text{Se}_{1-x}$ microcrystals is discussed from optical absorption data.

2. Experimental procedure

2.1. Glass preparation

The materials were commercially available and were used as-received: $\text{Si}(\text{OC}_2\text{H}_5)_4$ (Colcoat Co.), $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and Se (Nacalai Tesque, Inc). 35.44 g $\text{Si}(\text{OC}_2\text{H}_5)_4$ was at first hydrolysed by dropping it into a mixed solution of 3.08 g 0.15 M HCl solution and 7.84 g $\text{C}_2\text{H}_5\text{OH}$. After this solution was stirred for 1 h, 0.28 g $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 0.08 g Se, dissolved in 5 g CH_3OH and 2 g HNO_3 , respectively, were added, followed by stirring for 1 h at room temperature. The resultant homogeneous solution was poured into polystyrene containers, covered and left for about 1 week to form a stiff gel, followed by drying without a cover for a further week at room temperature. This gel was heated in an atmosphere of H_2S gas and/or under flowing ($\sim 50 \text{ ml min}^{-1}$) mixed gas of 3% H_2 and 97% N_2 in a fused silica tube previously under a vacuum.

2.2. Characterization: XRD pattern, Raman spectra and optical absorption spectra

The X-ray diffraction (XRD) measurements were carried out using a monochromated $\text{CuK}\alpha$ radiation from a rotary anode X-ray generator (Rigaku, Rad-C System, 12 kW) at 40 kV to 100 mA in the range $2\theta = 35^\circ\text{--}60^\circ$ in 0.04° steps and counting for 100 s. The diffractometer was calibrated for systematic errors by using CdO reagent crystal powders as a standard substance. The lattice constants of $\text{CdS}_x\text{Se}_{1-x}$ crystals were determined on the basis of the obtained Debye-Scherrer pattern. In order to deconvolute the overlapping peaks, the profile fitting method, which was developed by Toraya [11], was used.

The Raman scattering spectra of glasses ~ 0.2 mm thick were measured with a laser Raman spectrometer (Jasco, NR-1100) in the range $100\text{--}400\text{ cm}^{-1}$. The optical absorption spectra of glasses 0.1–0.5 mm thick were measured with a spectrometer (Jasco, U-best 50) in the range 300–800 nm.

3. Results and discussion

3.1. Formation of $\text{CdS}_x\text{Se}_{1-x}$ solid-solution crystals

In a previous paper, we reported that the gels were heated above 300°C in a $\text{H}_2\text{--N}_2$ gas atmosphere to precipitate hexagonal CdSe microcrystals with particles ranging from 3–7 nm in diameter [10]. The dried gels were transparent and porous. This porous structure remains unchanged in glasses heated below 800°C , at which temperature the glasses transform into non-porous glasses. On reacting the porous glasses with H_2S gas, hexagonal wurtzite CdS crystals were precipitated [7–9].

CdS and CdSe crystals are completely miscible throughout the entire range of composition. Therefore, $\text{CdS}_x\text{Se}_{1-x}$ solid-solution crystals are expected to form on heating in H_2S gas and/or $\text{H}_2\text{--N}_2$ gas atmospheres. The gels were exposed to H_2S gas, followed by heating in $\text{H}_2\text{--N}_2$ gas or vice versa. The XRD patterns are shown in Fig. 1 over a range of 2θ from $35^\circ\text{--}60^\circ$, which show relatively diffuse peaks on the amorphous halo background, although the pattern of the sample heated in $\text{H}_2\text{--N}_2$ gas at 800°C (Fig. 1d) is sharpened. The position of these peaks closely resembles that of hexagonal CdS and CdSe crystals, as shown in Fig. 1, in which the position and relative intensity are taken from the JCPDS Powder Diffraction Files 60314 for CdS and 80459 for CdSe.

In order to determine the crystal structure, the diffuse spectra were deconvoluted by the profile fitting method using a pseudo-Voigt function, details of which were reported in previous papers [8, 10]. The data profiles of Fig. 1 could be all fitted well to those of the hexagonal crystal. The positions of the (110) and (103) peaks were used to calculate the lattice constants. The lattice constants of Fig. 1a and d are $a = 0.414$ nm and $c = 0.672$ nm, and $a = 0.430$ nm and $c = 0.700$ nm, respectively, which are nearly equal to values from bulk crystals of CdS and CdSe, confirming that CdS and CdSe crystals are formed.

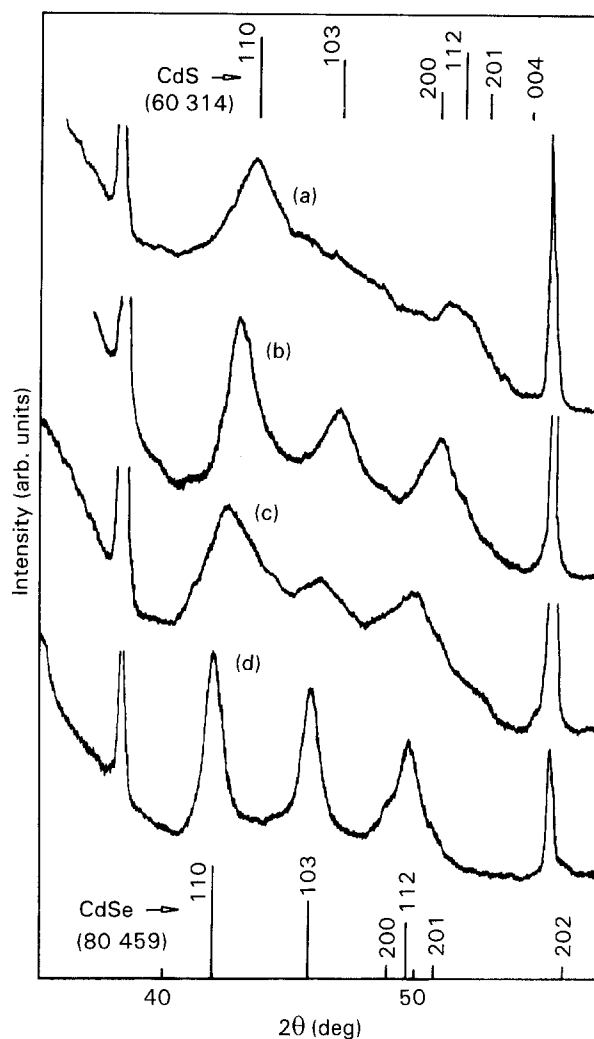


Figure 1 X-ray diffraction patterns of glasses treated at various conditions: (a) 200°C in H_2S , (b) 300°C in H_2S and then 700°C in $\text{H}_2\text{--N}_2$, (c) 800°C in $\text{H}_2\text{--N}_2$ and then 300°C in H_2S and (d) 800°C in $\text{H}_2\text{--N}_2$. Data for CdS and CdSe crystals were taken from Powder Diffraction File Cards 60314 and 80459, respectively. Diffraction peaks near $2\theta = 38^\circ$ and 56° are from CdO crystals added as a standard substance.

When CdS-precipitated glasses were heated in $\text{H}_2\text{--N}_2$ gas, the lattice constants increased to $a = 0.422$ nm and $c = 0.686$ nm (Fig. 1b). On the contrary, on reacting the CdSe-precipitated glasses with H_2S gas, the lattice constants decreased to $a = 0.425$ nm and $c = 0.697$ nm (Fig. 1c). These changes in lattice constants suggest the formation of solid solutions between CdS and CdSe crystals.

If a complete series of solid solution occurs between CdS and CdSe crystals, the mole fraction of anions can be determined from Vegard's law using the lattice constants for CdS and CdSe as end members. For samples shown in Fig. 1b and c, the compositions are calculated as $\text{CdS}_{0.5}\text{Se}_{0.5}$ and $\text{CdS}_{0.3}\text{Se}_{0.7}$, respectively, which are the average of mole fractions calculated using the lattice constants of a and c .

As previously mentioned, however, the diffuse XRD patterns make the precise determination of the peak position difficult and the lattice constants of CdS and CdSe crystals are very close to each other. Owing to this the formation of $\text{CdS}_x\text{Se}_{1-x}$ solid solution is still open to question.

To investigate whether or not the precipitated crystals are solid solution, the Raman scattering spectra of samples were measured, and are shown in Fig. 2. The spectra show two Raman peaks near 300 and 200 cm^{-1} , although the spectra of CdS- or CdSe-precipitated glasses show one peak at 300 or 200 cm^{-1} . From a comparison of the spectra with those given in the literature for bulk CdS and CdSe crystals, we attribute the peaks near 300 and 200 cm^{-1} to the longitudinal optical phonons of CdS and CdSe crystals, respectively, in $\text{CdS}_x\text{Se}_{1-x}$ crystals. It is apparent that the peak positions of samples treated with both H_2S and $\text{H}_2\text{-N}_2$ gases are shifted to lower wave number sides compared with those for CdS and CdSe crystals.

Tu and Persans [12] conducted Raman experiments on the commercially available $\text{CdS}_x\text{Se}_{1-x}$ microcrystal-doped glasses and showed that peak positions of CdS and CdSe modes of $\text{CdS}_x\text{Se}_{1-x}$ crystals depend in a straightforward way on the mole fraction of anions in $\text{CdS}_x\text{Se}_{1-x}$ crystals. Following their technique, we determined the compositions of $\text{CdS}_x\text{Se}_{1-x}$ crystals from the Raman shifts of glasses treated under various conditions. The composition of the crystal shown in Fig. 2b was found to be to $\text{CdS}_{0.7}\text{Se}_{0.3}$. Fig. 3 shows a comparison of crystal compositions determined by Raman shifts with those determined from XRD profiles. A linear relationship is held with small errors, indicating the formation of solid solution of $\text{CdS}_x\text{Se}_{1-x}$.

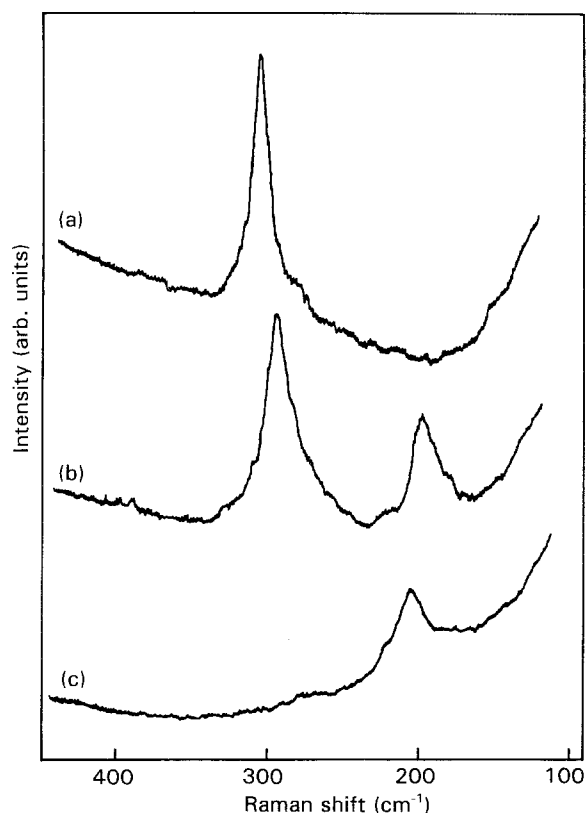


Figure 2 Raman spectra of glasses heated (a) at 200°C in H_2S , (b) at 200°C in H_2S and then 600°C in $\text{H}_2\text{-N}_2$, and (c) at 600°C in $\text{H}_2\text{-N}_2$.

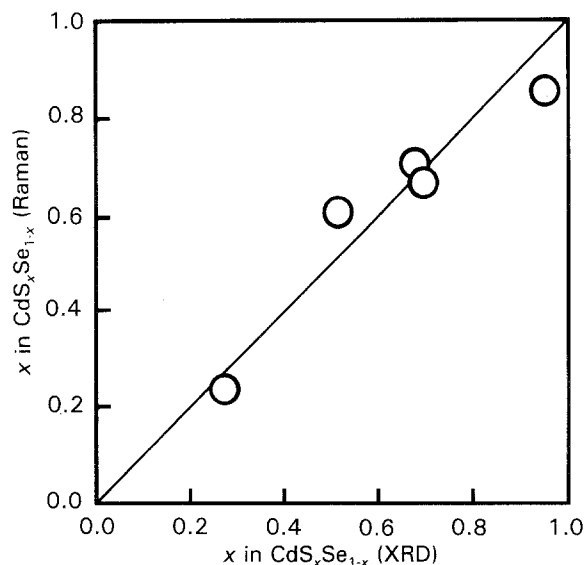


Figure 3 Comparison of crystal compositions determined by Raman spectra and XRD patterns.

3.2. Crystal composition of $\text{CdS}_x\text{Se}_{1-x}$ precipitated in glasses

The gels and glasses were treated under various conditions, and the composition of the crystals was determined from Vegard's law using the lattice parameter of the XRD experiments and the peak shift from the Raman spectra. Representative results are presented in Figs 4 and 5. When the glasses previously reacted with H_2S at 200°C for 5 h are heated in $\text{H}_2\text{-N}_2$ gas, the mole fraction of sulphur in $\text{CdS}_x\text{Se}_{1-x}$ crystals decreases with increasing temperature of heat treatment (Fig. 4). On the other hand, the sulphur content increases on reacting the CdSe-precipitated glasses with H_2S (Fig. 5). These experimental results imply the composition of $\text{CdS}_x\text{Se}_{1-x}$ crystals can be controlled by changing the conditions of heat treatment.

3.3. Quantum size effect of optical absorption edge energy

In the $\text{CdS}_x\text{Se}_{1-x}$ solid-solution crystals, the band gap energies vary with the composition from 2.4 eV of CdS

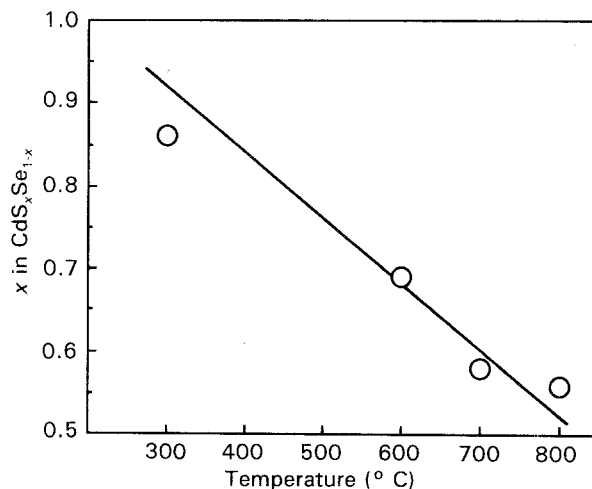


Figure 4 Change in sulphur content in $\text{CdS}_x\text{Se}_{1-x}$ crystals precipitated in glasses which were reacted with H_2S at 200°C for 5 h, followed by heating in $\text{H}_2\text{-N}_2$ gas at various temperatures.

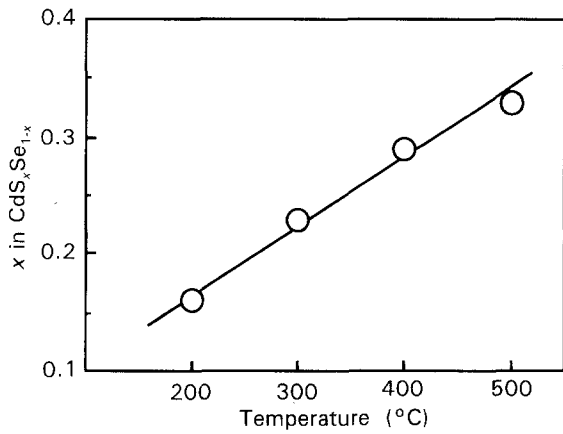


Figure 5 Change in sulphur content in $\text{CdS}_x\text{Se}_{1-x}$ crystals precipitated in glasses which were heated in $\text{H}_2\text{-N}_2$ at 600°C for 2 h, followed by reacting in H_2S at various temperatures.

to 1.7 eV of CdSe. This phenomenon is used to control the cut-wavelength of colour filter glasses. It is known that the band-gap energies also are dependent on the size of small particles. According to theory, when the particle size becomes less than a critical value, the gap energy becomes discrete, increasing with decreasing particle size. This phenomenon is interpreted in terms of a quantum confinement effect of small crystal size.

To investigate the quantum size effect of band-gap energies of $\text{CdS}_x\text{Se}_{1-x}$ solid-solution crystals, the glasses were heat treated to precipitate crystals of the same composition and their optical absorption spectra were measured. Fig. 6 shows the absorption spectra of glasses precipitating $\text{CdS}_{0.5}\text{Se}_{0.5}$ crystals, in which the spectra of CdS- and CdSe-microcrystal-doped glasses are also shown for comparison. The absorption is attributed to a transition from the highest hole sub-band level to the lowest electron sub-band level of the crystals. However, the absorption spectra showed no well-resolved band structure, but with a shoulder at a wavelength less than the absorption edge. It appears that the reason for the shoulder is

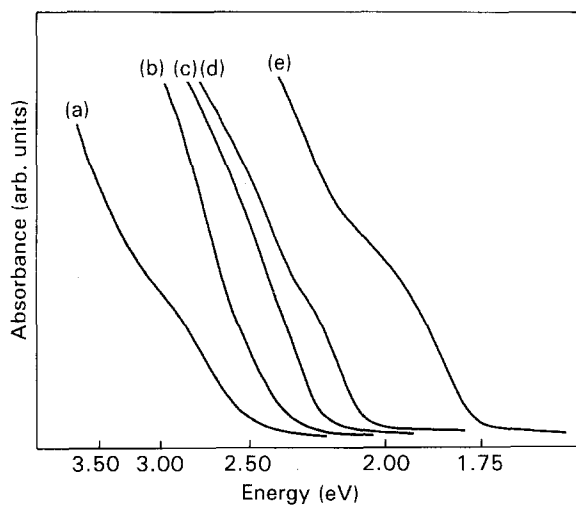


Figure 6 Optical absorption spectra of glasses treated under various conditions: (a) 200°C in H_2S , (b) 700°C in $\text{H}_2\text{-N}_2$ and then 400°C in H_2S , (c) 300°C in H_2S and then 700°C in $\text{H}_2\text{-N}_2$, (d) 200°C in H_2S and then 800°C in $\text{H}_2\text{-N}_2$, and (e) 800°C in $\text{H}_2\text{-N}_2$. The crystal composition of (b), (c) and (d) is the same $\text{CdS}_{0.5}\text{Se}_{0.5}$.

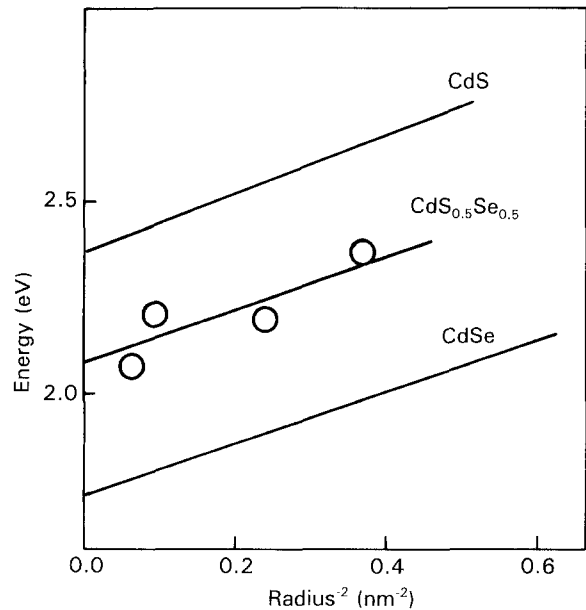


Figure 7 Relationship between absorption edge energy and the inverse square of the radius of $\text{CdS}_{0.5}\text{Se}_{0.5}$, CdS [9] and CdSe [10] microcrystals precipitated in glasses.

due to a wide distribution of crystal sizes. We assumed the edge position of the absorption spectrum to be band-gap energy and it was obtained by interpolating the absorbance to zero. The energies for Fig. 6b, c and d are 2.37, 2.21, and 2.07 eV, respectively. These energy shifts appear to be caused by the small-sized $\text{CdS}_{0.5}\text{Se}_{0.5}$ crystals. The crystal size was calculated for broadening of the deconvoluted XRD peaks using Scherer's equation.

Fig. 7 shows the relationships between absorption edge energy and the inverse square of the crystal radius, in which the relationships for CdS and CdSe microcrystal-doped glasses are shown for comparison. The data are well fitted by a linear function, indicative of a quantum size effect occurring in $\text{CdS}_{0.5}\text{Se}_{0.5}$ crystals prepared in this study. According to the theoretical treatment for these small crystals [13], the electron and hole wave functions are individually confined by the deep potential well, and the band-gap energy, E , is inversely proportional to the square of the crystal radius, R , as follows

$$E = E_g + \hbar^2\pi^2/2\mu R^2 \quad (1)$$

where E_g is the band gap for bulk crystal, \hbar is Planck's constant divided by 2π , and μ is the reduced mass of the electron and hole.

The corresponding gap energy of bulk crystal, obtained by extrapolating $1/R^2$ at 0, was 2.10 eV. The reduced mass, determined from the slope of the straight lines, is $0.38 m_0$, which is comparable with those obtained for CdS and CdSe microcrystal-doped in silica glasses prepared by the sol-gel process.

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