

Determination of Composition of CdS_xSe_{1-x} Microcrystals in Semiconductor-Doped Glasses Using Raman Scattering

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Raman spectra of CdS_xSe_{1-x}-doped glasses are reported. The composition x is determined from the difference between CdS- and CdSe-like longitudinal optical (LO) phonon frequencies. Glass samples from different manufacturers show different compositions x of CdS_xSe_{1-x} microcrystals, even if these glasses exhibit almost the same optical transmission spectra.

KEYWORDS: semiconductor, microcrystal, quantum dot, Raman spectrum

The optical properties of glasses doped with semiconductor microcrystals have been studied extensively, since these glasses have large optical nonlinearity. Photoinduced changes in the optical properties are observed and are called photodarkening effects. Differences in the optical nonlinearity and the photodarkening effects between samples from different manufacturers have been observed in CdS_xSe_{1-x}-doped glasses.^{1,2)} Yanagawa et al.¹⁾ ascribed the differences to the difference in glass composition. However, composition x of CdS_xSe_{1-x} microcrystals also differs between samples from different manufacturers. Here, we report the measurements of Raman spectra of CdS_xSe_{1-x}-doped glasses from different manufacturers to determine the composition x .

The samples investigated were commercial CdS_xSe_{1-x}-doped filter glasses from different manufacturers: Toshiba, Hoya, Schott and Corning. These glasses are listed in Table I.

For the Raman-scattering measurement, we used 514.5 nm light from an Ar-ion laser (Lexel 88-P). The measurements were performed in the backscattering geometry using a microscope. The incident laser light was focused on the sample at 300 K to a spot of 2 μm in diameter. Laser power at the sample was about 3 mW. Scattered light from the sample was led to a triple monochromator (Jasco NR-1800) and the spectrum was measured using a charge coupled device (CCD) camera (Princeton Instruments LN/CCD).

Figure 1 shows the Raman spectra of four filter glasses: Toshiba 0-56, Hoya 0-56, Schott OG570 and Corning 3-66. These glasses show almost the same optical transmission spectra. Peaks near 300 cm^{-1} are from CdS-like longitudinal optical (LO) modes and peaks near 200 cm^{-1} are from CdSe-like LO modes. The composition x of CdS_xSe_{1-x} microcrystals is determined from the Raman shift y following the procedure in ref. 3. The relation between x and y is

$$x = 0.020y - 1.29 , \quad (1)$$

where y is the difference between the frequencies of CdS-like and CdSe-like modes. The accuracy of the measurement of y is about $\pm 1 \text{ cm}^{-1}$, so that the error of x is about ± 0.02 . Moreover, large systematic error exists when using only one mode to determine the composition, since strain and phonon confinement effects cause both CdS-like and CdSe-like modes to shift in the same direction. In contrast, compositional change causes

them to shift in opposite directions.⁴⁾ Thus we determined the composition using the two modes to reduce the systematic error. However, the LO-phonon peak of CdSe shifts faster than that of CdS with decrease of the microcrystallite size. The peak shifts are about 3 cm^{-1} for CdSe microcrystals and about 2 cm^{-1} for CdS microcrystals with radius of 5 nm.^{5,6)} Thus the systematic error of x is about 0.02. Tu and Persans⁴⁾ reported that the maximum systematic error in x due to the strain effect is about ± 0.03 for any single mode. However, the actual error is estimated to be about 1/10 of the maximum value for Schott filter glass.⁴⁾ The error is further reduced by taking the difference between the frequencies of the two modes.

The values of x of most glasses investigated are listed in Table I. It is difficult to determine x for glasses near $x = 0$ and 1, since the peak of the CdS-like mode is very weak for glasses near $x=0$ and that of the CdSe-like mode is very weak for glasses near $x = 1$. Values in parentheses for Schott filter glasses are values reported by Bersani and Lottici.³⁾ These values were obtained from Raman spectra and are in agreement with the present results, except for OG530. The difference in x for OG530 may be attributable to the difference in samples. The sample measured by Bersani and Lottici may be older than that measured by us. We consider that these samples were fabricated under different conditions. Values in parentheses for Corning filter glasses, reported by Borrelli et al.⁷⁾ are larger than the present results. These values were calculated from crystallite lattice parameters determined from X-ray diffraction data. The strain effect should provide a change in lattice parameters and an apparent change in compositions. Since the lattice constant of CdS is less than that of CdSe, a smaller lattice constant seems to cause x to be somewhat high. While the strain effect for Schott glass is negligibly small,⁴⁾ the strain effect for Corning glass may be larger than that for Schott glass, since the composition of the host glass of Corning filter glass is different from that of Schott glass.¹⁾

The optical properties of glasses, shown in Fig. 1, were investigated by Horiuchi and Uesu.²⁾ These glasses show different optical nonlinearity and photodarkening effects. These differences are considered to be attributable to the difference in the glass composition and the composition of semiconductor microcrystals. Further experiments will be carried out to investigate the main cause of the differences in the

optical properties.

In summary, Raman spectra of various $\text{CdS}_x\text{Se}_{1-x}$ -doped glasses were measured at 300 K. The composition x is determined from the Raman shift. The results are compared with the reported results. Glass samples from different manufacturers show different compositions, even if these glasses show almost the same optical transmission spectra.

References

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Figure caption

Fig. 1. Raman spectra of four filter glasses: (a) Toshiba 0-56, (b) Hoya 0-56, (c) Schott OG570 and (d) Corning 3-66. Composition x is determined from the difference between the frequencies of CdS-like mode (near 300 cm^{-1}) and CdSe-like mode (near 200 cm^{-1}).

Table I. Composition x of $\text{CdS}_x\text{Se}_{1-x}$ microcrystals in glasses. Values in parentheses are from ref. 3 for Schott filter glasses and from ref. 7 for Corning filter glasses.

Toshiba filter	Composition (x)	Hoya filter	Composition (x)	Schott filter	Composition (x)	Corning filter	Composition (x)
Y-51	0.70						
Y-52	0.58	Y-52	0.58	OG515	0.82(0.89)	3-69	0.82
0-53	0.58			OG530	0.67(0.83)		
0-54	0.22	0-54	0.42			3-68	0.79
0-55	0.21			OG550	0.67(0.67)		
0-56	0.23	0-56	0.26			3-67	0.68
0-57	0.16			OG570	0.60(0.62)	3-60	0.64(0.72)
0-58	0.09	0-58	0.25				
0-59	0.12			OG590	0.55(0.51)	2-73	0.56
R-60	0.12	R-60	0.16			2-63	0.54
R-61	0.12			RG610	0.32(0.40)	2-62	0.48
R-62	0.09	R-62	0.06			2-61	0.36(0.52)
R-63	0.03			RG630	0.36(0.34)	2-60	0.34(0.46)
R-64	0.06	R-64	0.04			2-59	0.20(0.36)
				RG645	0.23(0.21)	2-58	0.29
						2-64	0.11(0.26)

Fig. 1

