Resonant Raman scattering studies of Cd$_{1-x}$Zn$_x$S nanocrystals

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Abstract. Optical phonons in Cd$_{1-x}$Zn$_x$S nanocrystals embedded in borosilicate glass are studied by resonant Raman scattering. A Raman-based assessment of the nanocrystal composition is performed. Compositional dispersion of the nanocrystals within the ensemble is revealed. The effect of confinement-related selection rules relaxation, scattering by surface phonons, and host matrix pressure on the Raman lineshape is analyzed.

1. Introduction
II-VI nanocrystals (NCs) have extensively been studied due to the size effects in their optical spectra resulting in a number of applications, especially in nonlinear optics, optoelectronics, and biology [1–3]. Ternary Cd$_{1-x}$Zn$_x$S NCs are obtained by colloidal synthesis in reverse micelles [4–7] or by solid-state precipitation in borosilicate glass [8–14]. An efficient non-destructive tool for the NC identification is Raman scattering. It is especially important, at least for Cd-rich compositions since for these compounds the Bohr radius is relatively small (2.8 nm for CdS [1]) and confinement-related maxima in the optical absorption spectrum can be observed only for smaller NC sizes.

Here we report on obtaining and Raman spectroscopic studies of Cd$_{1-x}$Zn$_x$S NCs in borosilicate glass and discuss the main factors affecting the Raman lineshape which should be taken into account for correct NC identification.

2. Experimental
Cd$_{1-x}$Zn$_x$S NCs were grown in borosilicate glass matrix by conventional solid-state precipitation technique, generally similar to that of [9, 11, 13]. Initial CdS-doped alkali zinc borosilicate glass samples were decoloured at about 950°C (the existing CdS NCs were dissolved). Then after a rapid quenching to room temperature the samples were annealed at 625 to 700°C during 2 to 12 h resulting in the formation of Cd$_{1-x}$Zn$_x$S NCs.

Resonant micro-Raman scattering measurements were performed at room temperature using a Dilor XY 800 triple monochromator equipped with a CCD camera. He-Cd ($\lambda_{\text{exc}} = 441.6$ nm) and Ar$^+$ ($\lambda_{\text{exc}} = 457.9$ and $476.5$ nm) lasers were employed for excitation. The instrumental resolution was $2.5–3$ cm$^{-1}$. In most cases the Raman signal was detected superimposed on a broad luminescence background which was afterwards subtracted for the analysis of the Raman spectra.
3. Results and discussion

Raman spectra of the borosilicate glass-embedded Cd$_{1-x}$Zn$_x$S NCs are shown in figure 1. The spectra contain a LO phonon band slightly above 300 cm$^{-1}$ and a two-phonon 2LO band at about double frequency. Contrary to CdS$_{1-x}$Se$_x$ where in the Raman spectra of the mixed NCs CdSe-like and CdS-like LO phonon bands are observed [15–20], Cd$_{1-x}$Zn$_x$S is a one-mode solid solution system where the LO phonon frequency smoothly varies with composition from 305 (for CdS) to 352 cm$^{-1}$ (for ZnS). This enabled us to use the LO phonon frequencies from the measured Raman spectra to determine, similarly to [9], the glass-embedded Cd$_{1-x}$Zn$_x$S NC composition, the corresponding $x$ values being indicated in figure 1.

![Figure 1](image1.png)

**Figure 1.** Raman spectra of Cd$_{1-x}$Zn$_x$S NCs, embedded in borosilicate glass, measured at room temperature with excitation by the 457.9 nm Ar$^+$/laser line.

![Figure 2](image2.png)

**Figure 2.** Compositional dispersion of the glass-embedded Cd$_{1-x}$Zn$_x$S NCs within the ensemble, clearly seen from the resonant Raman spectra of the same sample, measured at room temperature with excitation by two different Ar$^+$ laser lines.

The NCs comprise below 1% of the sample volume; hence resonant excitation conditions are required for the Raman signal enhancement. Cd$_{1-x}$Zn$_x$S NCs, diluted in a dielectric matrix, are characterized by a certain dispersion of composition and size within the ensemble. Since the main contribution into Raman scattering arises from the NCs whose size and composition favour resonance conditions, this may affect the LO phonon band position and halfwidth in the Raman spectra taken at different excitation wavelengths $\lambda_{\text{exc}}$ [21]. The effect of the compositional dispersion is clearly observed from Fig. 2 where the difference in the LO phonon frequency for the Raman spectra of the same sample, measured at $\lambda_{\text{exc}}$=457.9 and 476.5 nm, corresponds to the compositional difference of 0.08. It can be assumed that in each case a different part of the ensemble of the NCs embedded in the matrix gives the predominant contribution into the resonant scattering cross-section, depending on the matching of the HOMO–LUMO electronic transition energy with that of the exciting (incoming resonance) or scattered (outgoing resonance) photon. We observed a similar effect earlier for CdS$_{1-x}$Se$_x$ NCs [22], though in that case the difference in the NC composition was not so drastic. Hence, it is seen that in order to determine the average chemical composition of ternary NCs in the glass matrix, a single Raman measurement is not sufficient.
The known compositional dependence of Cd$_{1-x}$Zn$_x$S band gap $E_g(x)=2.45+0.705x+0.603x^2$ (eV) [23] gives the $E_g$ difference of 0.07 eV for the two compositions shown in figure 2. Meanwhile the energy difference between the laser exciting lines is higher (0.11 eV); hence, the observed resonant Raman selectivity of Cd$_{1-x}$Zn$_x$S NCs originates not only from compositional, but also from size dispersion of the NCs. However, correct separation of the two effects in this case can hardly be made.

Raman spectra of II-VI NCs in borosilicate glass are also affected by other factors. The host matrix pressure of about 0.5 GPa, arising due to the difference in the thermal expansion coefficients of the NCs and the borosilicate glass when the samples are rapidly cooled after the annealing from 600–650°C to room temperature [24, 25], leads to the lattice contraction and, consequently, to an LO phonon frequency increase by about 1%. On the contrary, phonon confinement in NCs result in a nonzero-wavevector phonons contribution into Raman scattering leading to a Raman line asymmetry with a more pronounced lower-frequency wing [17, 18, 21, 25]. Another factor, responsible for the apparent downward shift of LO phonon bands in NCs and their broadening at the low-frequency side, is scattering by surface phonons whose contribution increases with the size decrease.

According to the deformation-potential electron-phonon interaction model [16], the frequencies of surface modes, involved in Raman scattering in spherical quantum dots, are given by

$$\omega_{SO} = \omega_{TO} \left( \frac{\epsilon_0 L + \epsilon_M (L+1)}{\epsilon_\infty L + \epsilon_M (L+1)} \right)$$

(1)

where $\omega_{TO}$ is the TO phonon frequency, $\epsilon_0$ and $\epsilon_\infty$ are the static and high-frequency dielectric permeabilities of the NC material, respectively, $\epsilon_M$ is the static dielectric constant of the dielectric matrix, $L$ is a quantum number.

Figure 3. First-order Raman spectrum of Cd$_{0.87}$Zn$_{0.13}$S NCs in borosilicate glass-embedded (solid line) and the contribution of LO and surface optical phonon bands (dashed lines). The corresponding frequencies and halfwidths are indicated in the figure.

Figure 3 shows a typical first-order Raman spectrum of Cd$_{1-x}$Zn$_x$S NCs with the contributions from LO and surface optical phonons. For CdS the observed surface phonon frequency $\omega_{SO}$ is 287 cm$^{-1}$ which is somewhat lower than that obtained in [26]; however, one should take into account a pronounced dependence of the surface phonon frequency in NCs on the excitation wavelength. For 0.04 $< x < 0.13$ $\omega_{SO}$ slightly increases from 302 to 304 cm$^{-1}$, the surface phonon band halfwidth being practically independent of the NC composition.

4. Conclusions
Cd$_{1-x}$Zn$_x$S NCs embedded in borosilicate glass matrix were studied by resonant Raman spectroscopy which is an efficient non-destructive tool for identification of ternary semiconductor NCs in dielectric media. A strong dependence of the observed LO phonon frequency on the Raman excitation wavelength is the result of a considerable compositional dispersion of the NCs within the ensemble when the NCs of different composition correspond to the resonant conditions, contributing to the
Raman scattering at different excitation wavelength. The factors, affecting the Raman lineshape in the glass-embedded Cd$_{1-x}$Zn$_x$S NCs, are discussed. The measured surface phonon frequencies for the Cd$_{1-x}$Zn$_x$S NCs are compared with the results of calculations based on the deformation-potential electron-phonon interaction model.

**Acknowledgements**

Yu.M. Azhniuk is grateful to Deutsche Forschungsgemeinschaft for providing financial support for his research stay at Chemnitz University of Technology where the Raman studies were carried out.

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