Research Article
Raman Spectra of Quaternary CdS$_{1-x-y}$Se$_x$Te$_y$ Nanocrystals Embedded in Borosilicate Glass

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Received 31 May 2011; Accepted 18 July 2011

Abstract
A series of samples with quaternary CdS$_{1-x-y}$Se$_x$Te$_y$ nanocrystals with cations of three types distributed over nanocrystal lattice sites were grown in a borosilicate glass matrix by the diffusion-limited growth technique. Their Raman spectra confirm the three-mode compositional behaviour of CdS$_{1-x-y}$Se$_x$Te$_y$ phonon spectra. The compositional dependence of the LO phonon frequencies is analysed experimentally for a series of samples containing nanocrystals with $x \approx y$.

1. Introduction
Within recent decades, II–VI semiconductor nanocrystals, obtained by various techniques, have attracted continuous interest due to the size tunability of their optical properties, resulting in numerous applications [1–4]. Raman spectroscopy has proved to be a reliable tool for fast and non-destructive characterization of ternary II–VI nanocrystals, namely, the determination of their chemical composition for both one-mode and two-mode systems [5–19]. In two-mode ternary systems (CdS$_{1-x}$Se$_x$, CdSe$_{1-x}$Te$_x$), the nanocrystal composition is usually determined from the difference of frequencies of LO phonons corresponding to the two sublattices of the nanocrystal [5, 10, 12–14, 19] or from their intensity ratio [5, 6]. In one-mode systems (Cd$_{1-x}$Zn$_x$S), a good measure of composition is the LO phonon frequency which varies continuously with the component ratio. Among the ternary nanocrystal systems, the most widely studied is CdS$_{1-x}$Se$_x$ [5–8, 10, 12–14, 16, 19] where much attention has been paid to nanometer-size-related effects on the Raman spectra (phonon confinement, marked contribution of surface phonons due to the high surface-to-volume ratio, glass matrix pressure, size dispersion of NCs within the ensemble). Fewer studies have been devoted to Cd$_{1-x}$Zn$_x$S [9, 11, 17] and CdSe$_{1-x}$Te$_x$ [8, 15, 18] nanocrystals.

Even less investigated are quaternary II–VI nanocrystals, for which extremely few studies were reported, namely, our earlier work devoted to fabrication and optical identification of Cd$_{1-x}$Zn$_x$S$_{1-x}$Se$_x$ nanocrystals in borosilicate glass [20, 21]. This system of nanocrystals was shown to exhibit a two-mode type of compositional behaviour of the phonon spectrum. Our present work is aimed at obtaining quaternary CdS$_{1-x-y}$Se$_x$Te$_y$ semiconductor nanocrystals by diffusion-limited growth in borosilicate glass and their characterization by Raman spectroscopy. To our knowledge, no data regarding CdS$_{1-x-y}$Se$_x$Te$_y$ nanocrystals have been reported so far.

2. Experimental
Quaternary II–VI semiconductor nanocrystals were obtained in borosilicate glass by the diffusion-limited growth (solid-state precipitation) technique, the basic details of which can be found in [1, 22–24]. The initial mixture for the fabrication of CdS$_{1-x-y}$Se$_x$Te$_y$ nanocrystals was prepared from commercially available Schott and LZOS optical cutoff filters made of borosilicate glass doped with CdS$_{1-x}$Se$_x$ and CdSe$_{1-x}$Te$_x$ nanocrystals. After comelting of the mixture and annealing at 1000°C for 1–1.5 h, colourless transparent glass
platelets were obtained, in which Cd, S, Se, and Te atoms were more or less randomly distributed over the borosilicate glass network. The nanocrystal growth was carried out at thermal treatment for 2 to 12 h, the temperature ranging from 625 to 700 °C.

The obtained samples of brownish orange to red colour with about 5 × 5 mm² lateral size were polished down to 0.2–0.3 mm thick plates for optical measurements. Raman spectra were measured using a Dilor XY 800 spectrometer with a CCD camera, the excitation was provided by an Ar⁺ (514.5 nm) or Kr⁺ (647.1 and 676.4 nm) laser. The instrumental resolution was better than 2.5 cm⁻¹. All measurements were performed at room temperature.

3. Results and Discussion

Raman spectra of the semiconductor-doped borosilicate glass samples obtained are shown in Figure 1. They clearly show the presence of three maxima which could be quite reasonably assigned to CdTe-like LO₁ (in the frequency range 150–160 cm⁻¹), CdSe-like LO₂ (190–200 cm⁻¹), and CdS-like LO₃ (260–290 cm⁻¹) phonons. Even though studies of CdS₁₋ₓ₋ₓ₋ₓ Teₙ nanocrystals have never been reported before, scarce Raman spectroscopic data for individual samples of CdS₁₋ₓ₋ₓ₋ₓ Teₙ single crystals report this quaternary system to show a three-mode behaviour [25–27]. For mixed nanocrystals, all the observed LO phonon frequencies are lower than those for the corresponding binary crystals (the latter are shown by vertical short-dashed lines in Figure 1). This is in agreement with the three-mode behaviour of this mixed crystal system.

In our case, similar to the earlier studies of other II–VI nanocrystals embedded in dielectric media [5–14, 16–21], only LO phonons are revealed in the first-order Raman spectra. This is related to the fact that the nanocrystals comprise only a tiny part (as a rule, below 1%) of the sample scattering volume. Hence, in order to obtain a detectable Raman signal, one should apply resonant Raman conditions which provide better LO phonon scattering enhancement.

It is worth mentioning that among the binary compounds formed by the elements comprising the quaternary CdS₁₋ₓ₋ₓ₋ₓ Teₙ system, CdTe possesses cubic (sphalerite or zinc-blende) structure, and CdS at normal conditions is hexagonal (wurtzite) while CdS can exist in both zinc-blende and wurtzite structures [28]. Moreover, the structure of CdS₁₋ₓ₋ₓ₋ₓ Seₙ nanocrystals is reported to be size dependent, and zinc-blende and wurtzite nanocrystals can coexist in the ensemble of nanocrystals in the sample; so the resonant condition for which the energy of the incident or scattered light matches the energy gap. Since the gap varies with both composition and size, the variation of these two parameters clearly affects the signal-to-noise ratio in the spectra, clearly seen from Figure 1.

The rich second-order Raman spectrum obtained under resonant conditions confirms the composition of CdS₁₋ₓ₋ₓ₋ₓ Seₙ Teₙ nanocrystals obtained by diffusion-limited growth in borosilicate glass (see Figure 2). One can clearly see all the maxima corresponding to the processes with simultaneous generation of two LO phonons. The frequencies of the observed two-phonon bands enable their clear identification. Such a rich and distinct two-phonon spectrum is evidence for both the good quality of the samples obtained (relatively low dispersion of the nanocrystal composition and size) and
Similarly to ternary II–VI nanocrystals [5, 6, 10, 18–21], the
intensity of the second-order Raman features in the spectrum is considerably lower than the first-order Raman peaks due to the lower probability of two-phonon processes at room temperature.

It should be noted that for many of the experimental Raman spectra of the CdS$_{1-x-y}$Se$_x$Te$_y$ nanocrystals in borosilicate glass, besides the above discussed peaks due to first- and second-order LO phonon scattering, one more less intense band was observed at 117–120 cm$^{-1}$. This feature can most likely be related to Raman scattering from acoustic phonons with non-zero wavevectors revealed in the Raman spectra due to the breakdown of selection rules. The latter can be caused by the phonon confinement in nanocrystals. The frequencies of acoustic phonons observed in the Raman spectra of II–VI semiconductor nanocrystals due to phonon confinement depend on the nanocrystal size [31–34]. Additionally, a noticeable disorder in the anion sublattice due to the random occupation of its sites by three types of anions (S, Se, and Te) results in the feature of acoustic phonon density of states revealed in the Raman spectra. A similar effect of disorder-activated longitudinal and transverse (DALA and DATA) acoustic phonons in first-order Raman scattering is known for semiconductor solid solutions [35]. From the frequency of the band observed at 117–120 cm$^{-1}$, it can be assigned to DALA phonons.

Raman spectra of CdS$_{1-x-y}$Se$_x$Te$_y$ nanocrystals in borosilicate glass at different thermal treatment conditions are shown in Figure 3. This series of samples was obtained from the same initial mixture at different thermal treatment durations and temperatures. It can be seen from the figure that in most of the spectra (with the exception of those subjected to the least intense and the most intense thermal treatments) the frequencies of CdTe-like ($LO_1$), CdSe-like ($LO_2$), and CdS-like ($LO_3$) phonons in the spectra do not differ much, and the intensity ratio for these bands is about the same for all the samples. Hence, the composition of the CdS$_{1-x-y}$Se$_x$Te$_y$ nanocrystals formed of the same initial mixture is relatively stable with the variation of thermal treatment duration $\tau$ and temperature $T_a$ within a certain interval which is optimal for the II–VI nanocrystal formation. The observed slight spread of the LO phonon frequencies is, in our opinion, an evidence for fluctuations of the nanocrystal composition rather than for a systematic trend with the thermal treatment characteristics. Meanwhile, for CdS$_{1-x}$Se$_x$ nanocrystals grown in the borosilicate glass we observed earlier a clear trend of increase of the predominant chalcogen content with $\tau$ and $T_a$ and pushing the minority chalcogen atoms out of the nanocrystals across the nanocrystal/glass interface [19]. However, one should keep in mind that, as follows from the frequencies and intensities of the LO phonon bands in the Raman spectra, for the batch of samples studied, the initial mixture contains three chalcogens (S, Se, and Te) in roughly equal quantities. This very probably ensures better stability of the nanocrystal composition under variation of the thermal treatment conditions.

It is also known that in case the thermal treatment parameters ($\tau$ and $T_a$) are beyond the optimal interval for the Se- and Te-containing II–VI nanocrystal formation, one can expect precipitation of elemental selenium or tellurium in the form of molecular Se$_2$ or Te$_2$ clusters or even larger...
aggregations which can be clearly evidenced by Raman spectroscopy [36]. Here, as seen from Figure 3, we clearly observe Raman bands corresponding to crystalline tellurium phonons (90, 120, and 139 cm$^{-1}$) as well as Te$_2$ molecular dimer vibrations (215.5 cm$^{-1}$) for the least intensely ($T_a = 625^\circ$C, $\tau = 2$ h) and the most intensely ($T_a = 700^\circ$C, $\tau = 12$ h) heat-treated samples. This agrees well with our earlier data showing Raman evidence for tellurium precipitation as an alternative to the formation of II–VI nanocrystals with high Te content [36]. Still, within the range of $\tau$ and $T_a$ optimal for the II–VI nanocrystal formation their composition appears to be quite stable with respect to the thermal treatment characteristics.

4. Conclusions

A series of samples with quaternary CdS$_{1-x}$Se$_x$Te$_y$ nanocrystals were grown in a borosilicate glass matrix by diffusion-limited growth technique. Their Raman spectra confirm the presence of cations of three types distributed over nanocrystal lattice sites. The CdS$_{1-x-y}$Se$_x$Te$_y$ system is shown to possess three-mode compositional behaviour of the phonon spectrum. The compositional dependence of the LO phonon frequencies is shown experimentally for a series of samples containing nanocrystals with $x \approx y$. In the second-order Raman spectrum, the presence of distinct bands, corresponding to different two-phonon processes, confirms both the quality of the nanocrystals obtained and the Raman technique sensitivity for the identification of matrix-embedded CdS$_{1-x-y}$Se$_x$Te$_y$ nanocrystal composition.

References


