Incorporation of zinc into CdS$_{1-x}$Se$_x$ nanocrystals in glass matrix studied by optical spectroscopies

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The formation of quaternary Cd$_{1-y}$Zn$_y$S$_{1-x}$Se$_x$ nanocrystals in a borosilicate glass matrix due to incorporation of zinc into CdS$_{1-x}$Se$_x$ quantum dots under heat treatment is investigated by Raman scattering and optical absorption spectroscopy. Average size and composition of the nanocrystals are determined. Factors affecting the accuracy of Raman scattering-based determination of the mixed nanocrystal composition are analyzed.

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1 Introduction

Among the semiconductor nanocrystals (quantum dots) being the object of intense scientific interest glass-embedded CdS$_{1-x}$Se$_x$ nanocrystals belong to the most extensively studied and well-known objects. They are interesting not only due to the size-dependent effects related to charge carrier spatial confinement (see e.g. [1, 2]) and their traditional use as optical cutoff filters, but also due to applications as nonlinear optical devices [3 and references therein], and, in particular, as active optical emitters in three-dimensional optical cavities called photonic dots and consisting of micrometer-sized glass spheres [4]. The main parameters, determining the properties of the nanocrystals, are their chemical composition, shape, average size and size dispersion. Near-spherical shape of CdS$_{1-x}$Se$_x$ quantum dots in borosilicate glass is observed by transmission electron microscopy (TEM) [5–7]. Raman scattering spectroscopy is generally considered to be a powerful and fast non-destructive technique, enabling the determination of the composition of glass-embedded nanocrystals [8, 9] and their size [10–13] (the latter can be also evaluated from transmission electron microscopy, small-angle X-ray scattering and optical absorption). A number of detailed studies were devoted to specific broadening and asymmetry of phonon bands in the Raman spectra of CdS$_{1-x}$Se$_x$ quantum dots explained by confinement-induced scattering from phonons with non-zero wave vectors [14–19] as well as by the increasing role of surface phonons [14, 15, 19–21]. Two additional factors to be taken into account when analyzing Raman spectra of nanocrystals are frequency shifts due to compressive strain arising from the glass matrix pressure [22, 23] and disorder effects induced by nanocrystal size fluctuations [24].

However, among these studies only few works [8, 9] covered the wide range of the quantum dot compositions, while the others were performed for rather narrow compositional intervals using the depend-

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ence obtained in the pioneer paper by Tu and Persans [8] to determine the nanocrystal composition. Meanwhile, in some cases the deviations of the observed phonon frequencies from the general trend did not fit into the generally considered (2–3)-% accuracy interval for determination of CdS$_{1-x}$Se$_x$ quantum dots composition by the Raman technique [25 and references therein].

One could suspect these deviations to be in some cases related to the initial presence of zinc in the matrix and its thermally induced diffusion from the matrix into the nanocrystals, resulting in the change of their chemical composition (earlier a similar way of formation of Cd$_{1-y}$Zn$_y$S [26–28] and Cd$_{1-y}$Zn$_y$S$_{0.95}$Se$_{0.05}$ [29] quantum dots has been reported). In order to check this assumption, we have performed a study of a rather extensive set of samples with CdS$_{1-x}$Se$_x$ quantum dots embedded in borosilicate glass matrix, some of which contained zinc. Here, we present explicit evidence for the annealing-induced formation of quaternary Cd$_{1-y}$Zn$_y$S$_{1-x}$Se$_x$ quantum dots in borosilicate glass based on the results of Raman scattering and optical absorption studies which enabled us to estimate the nanocrystal size and composition.

2 Experimental

The investigated samples were CdS$_{1-x}$Se$_x$ nanocrystals, grown in borosilicate glass matrix by a conventional technique of solid-state precipitation similar to the method described in [5, 7, 30]. Part of the samples were subjected to high-temperature (1000 °C, 2 h) annealing resulting in sample melting and complete dissolving of nanoparticles in the borosilicate glass (decolouring). After rapid quenching these samples were annealed at different temperatures within 625 to 700 °C, the annealing duration being varied from 2 to 9 h resulting in the precipitation of semiconductor nanocrystals from the supersaturated solution. The temperature during annealing was kept constant with an accuracy of ±5 °C. The formation of the quantum dots was evidenced by the sample colouring (from pale yellow to intense red, depending on the annealing temperature and duration).

Optical absorption spectra were measured using a LOMO MDR-23 monochromator and a FEU-100 phototube with a resolution better than 2 nm.

Conventional Raman measurements were carried out on a LOMO DFS-24 double grating monochromator with a FEU-136 phototube and an Ar$^+$ laser operating at 514.5 nm as the excitation source. Micro-Raman spectra were measured using a Dilor XY 800 triple monochromator equipped with a CCD camera and a Kr$^+$ laser at 482.5 and 647.1 nm. The micro-Raman setup enabled the exciting laser light to be focused to a 1 µm spot. In all cases the experimental resolution did not exceed 3 cm$^{-1}$.

All measurements were performed at room temperature.

3 Results and discussion

Since the effective scattering volume of CdS$_{1-x}$Se$_x$ nanocrystals comprises below 1% of the glass sample volume [13], resonant excitation conditions are required to register Raman scattering from the quantum dots. This system of solid solutions is known to possess a two-mode behaviour, with the spectrum containing both CdS-like and CdSe-like phonons [31]. Figure 1 presents micro-Raman spectra of CdS$_{1-x}$Se$_x$ nanocrystals for which the divergence of the band frequencies is accompanied by the weakening of the CdSe-like LO$_1$ phonon band and the increase of the CdS-like LO$_2$ phonon intensity when the sulphur content increases. Knowing the compositional dependence of the LO$_1$ and LO$_2$ phonon frequencies for the mixed crystals, one can estimate the average composition of the quantum dots in the sample. The applicability of such a method for the determination of CdS$_{1-x}$Se$_x$ nanocrystal composition in a broad compositional range was shown in [8] and its accuracy is estimated to be 2–3%, being somewhat lower for the compositions close to CdSe and CdS due to the weakness of one of the phonon bands [8, 9].

The observed LO phonon bands in the Raman spectra of the glass-embedded quantum dots have a typically asymmetric shape with a more pronounced low-frequency side (Fig. 1). Such a phonon line-shape observed is related to several factors. Nanocrystal size decrease results in the increasing contribution of scattering by surface phonon modes below the corresponding LO phonon frequencies [14, 15, 20,
Raman scattering by nonzero-wavevector phonons arising from the relaxation of selection rules due to phonon confinement leads to the downward shift of the phonon bands accompanied by asymmetric broadening \[33, 34\]. On the other hand, the effect of compressive strain in the nanocrystals due to the host matrix pressure, estimated as about 0.5 GPa \[35–37\], can result in the LO phonon frequency increase by about 1% \[25\] what correlates with the experimentally observed values of the pressure-induced LO phonon frequency shift in borosilicate glass-embedded CdS\(_{1-x}\)Se\(_x\) quantum dots of 5 cm\(^{-1}\)/GPa \[38, 39\].

It should be noted that the Raman spectrum of one of the samples under investigation, labeled KS-11N, shows a remarkable deviation from the typical behaviour. While the ratio of LO phonon band intensities follows the generally assumed compositional trend, the frequency of the CdSe-like LO\(_1\) phonon peak appears unusually high (220 cm\(^{-1}\)) even being much higher than that for CdSe (210 cm\(^{-1}\)). Besides, the shape of the observed LO\(_1\) phonon band is especially asymmetric with a pronounced shoulder near 210 cm\(^{-1}\) where the CdSe-like LO phonon peak would have been expected. Note that the Raman spectra of this sample measured at different excitation wavelengths (482.5 and 514.5 nm), are identical.

In order to determine the selenium content \(x\) in the quantum dots we plotted the difference of the CdS-like and CdSe-like LO phonon frequencies \(\nu_2-\nu_1\) for the measured samples spectra along the known reference data plot based on the results of \[8\] complemented with those of other authors \[25\] (Fig. 2a). Note that plotting the LO phonon frequency difference significantly reduces the errors of \(x\) determination resulting from the glass matrix pressure as well as possible systematic instrumental errors. As seen from Fig. 2 (b and c), the experimental values of the CdS-like and CdSe-like LO phonon frequencies in most cases are in agreement with the reference data, though they not always fall into the generally considered \(\Delta x = 0.03\) tolerance interval, e.g. the observed frequencies are slightly higher than the expected values near \(x = 0.5\) and somewhat lower for CdSe-rich samples. However, the data for the above discussed sample labeled KS-11N are drastically out of the general trend and appear at much higher frequencies (marked by open triangles in Fig. 2) than it could have been expected for the corresponding \(x\) value for CdS\(_{1-x}\)Se\(_x\) quantum dots.

An additional, though less accurate measure of the quantum dot composition is the ratio of the CdS-like and CdSe-like LO phonon band intensities. Such approach is reasonable in the case of small concentrations of one of the components with a considerably increasing error of determination of the weak band
The values of CdSe-like phonon intensity contribution to the first-order Raman spectrum of the sample $x_{\text{CdSe}} = I_{\text{CdSe}}/(I_{\text{CdSe}} + I_{\text{CdS}})$, plotted against the $x$ value, evaluated from the phonon frequency difference (Fig. 3) show good qualitative, but not quantitative correlation. The discrepancy of the compositions determined by the two methods is especially noticeable for CdSe-rich samples. Meanwhile, the value for the above mentioned KS-11N sample shown here as an open triangle differs greatly from those for other high-$x$ samples. It should be noted that here in all cases integrated Raman band intensities are considered, since the surface phonons and confinement-related nonzero-wavevector phonons which form the asymmetric low-frequency wing of the observed spectral bands, contribute to the scattering cross-section from the same sublattice as the relevant LO phonons.

From such behaviour one could suspect the presence of lighter cation, most likely zinc, in the nanocrystals of KS-11N sample. Since CdS$_{1-x}$Se$_x$ quantum dots are often grown in zinc-containing borosilicate matrices, thermal diffusion of zinc into the nanocrystals in the course of their growth is quite probable. Note that annealing at 600–725 °C was used to obtain ternary Cd$_{1-x}$Zn$_x$S quantum dots in glass matrices [26–28] and Raman studies have shown zinc to incorporate in the nanocrystals in the amount of up to 20% [28]. Zinc is also known to substitute cadmium in epitaxially grown CdS nanocrystals capped with ZnS, penetrating into the quantum dot from the cap layer [40].

Therefore, we have performed annealing studies which enabled us to monitor the growth of nanocrystals in the glass matrix depending on the heat treatment temperature and duration which could affect zinc incorporation into CdS$_{1-x}$Se$_x$ quantum dots. For this purpose we have chosen the samples labeled KS-10N and KS-11N with nearly similar optical absorption spectra, but quite different Raman behaviour. The samples, subjected to the annealing treatment, as described in Section 2, were studied by optical absorption and Raman scattering spectroscopy, the corresponding spectra being presented in Figs. 4 and 5 for KS-10N and KS-11N, respectively.

The increase of the annealing duration and temperature results in features gradually appearing in the absorption spectra as an edge, at first rather smooth, then more pronounced with distinct maxima in the near-edge spectral range (See Figs. 4b and 5b) which are revealed in the spectra of nanocrystals whose
radius is smaller than the Bohr radius of the exciton in the bulk semiconductor [2, 41]. The maxima in the absorption spectra slightly above the edge correspond to the lowest confined electron–hole pair transitions, and the application of a rather simple effective mass model [41] enabled us to determine similarly to [26, 42, 43], the average nanocrystal radii which for the samples with distinct confinement-related maxima ranged from 2.5 to 4 nm. The values for the initial, non-decoloured samples in both cases were estimated from the absorption spectra as 3.0 nm.

Note that the absolute values of absorption coefficient in Figs. 4b and 5b characterize not the quantum dot themselves, but the whole composite sample, of which the nanocrystals comprise only a small part (below 1%), the rest being the transparent host matrix, hence the effective thickness of the nanocrystals is by about two orders of magnitude smaller than that of the sample.

Along with the absorption data, observation of CdS-like and CdSe-like LO phonon bands in the Raman spectra of the annealed samples confirms the nanocrystal formation. However, the behaviour of KS-10N and KS-11N samples with increasing heat treatment is quite different. In the former the phonon bands become more intense due to the increase of the number and the volume of the quantum dots while their frequencies remain practically unchanged, corresponding to the value of $x = 0.23$ (See Fig. 2), and only the most intense heat treatment (700 °C, 4 h) results in a very slight upward shift of both phonon frequencies by 2 cm$^{-1}$ (Fig. 4a).

Contrary, for KS-11N sample the variation of the annealing conditions dramatically changes the Raman spectra. In the sample, subjected to the least intense heat treatment among those, for which Raman scattering could be observed (675 °C, 2 h), two distinct $LO_1$ and $LO_2$ peaks are observed at 202.5 and 278 cm$^{-1}$, respectively (See Fig. 5a). With the increase of the annealing temperature to 700 °C $LO_1$ peak narrows down by almost twice (from 20 to 11.5 cm$^{-1}$) and shifts up to 206 cm$^{-1}$. The increase of the annealing duration not only results in further $LO_1$ phonon band maximum shift, but also substantially changes its lineshape where a pronounced shoulder appears at 206 cm$^{-1}$. This spectrum is already rather close to the one initially observed for KS-11N, and even higher frequency position of the $LO_1$ phonon for the latter (221 cm$^{-1}$) makes one suppose that it had been subjected to more intense or durable heat treatment. It is worth noticing that the $LO_2$ phonon band shift towards higher frequencies with heat treatment is much slower, and for the initial (actually, most heavily annealed) KS-11N sample it is noticeably broader and somewhat higher in frequency (280 cm$^{-1}$). Fitting of the observed first-order Raman spectrum of this sample by multiple Lorentzian peaks enabled us to estimate the contribution of LO and surface phonons for both selenide and sulphide sublattices (Fig. 5). Surface phonon frequencies (202 cm$^{-1}$ for the CdSe-like and 279 cm$^{-1}$ for the CdS-like bands) are noticeably below those of LO phonons ($\nu_1 = 221$ cm$^{-1}$ and $\nu_2 = 293$ cm$^{-1}$, respectively). Simultaneously, the surface phonon bands are much broader (27 cm$^{-1}$ for the CdSe-like and 24 cm$^{-1}$ for the CdS-like) than the corresponding LO phonon peaks (11 cm$^{-1}$ and 8 cm$^{-1}$, respectively). The frequencies and linewidths of the surface and LO phonon maxima are in good agreement with the earlier results for CdS$_{1-x}$Se$_x$ quantum dots [20, 25].
Fig. 4  Micro-Raman (a) and optical absorption (b) spectra of the sample KS-10N with glass-embedded CdS$_{1-x}$Se$_x$ nanocrystals, measured after decolouring at 1000 °C and subsequent annealing (the heat treatment parameters are indicated in the figure). Raman spectra were measured using the 482.5 nm Kr$^+$ laser line for excitation. Dashed and dotted curves denote absorption spectra for the samples annealed at 650 °C during 2 h and 4.5 h, respectively, for which no Raman signal could be detected.

Note that the second-order Raman spectra for the heat-treated samples are quite consistent with the behaviour of the first-order Raman scattering spectra. In KS-11N sample the frequencies of 2 LO$_1$ and LO$_1$ + LO$_2$ phonon bands gradually shift from 407 and 485 to 435 and 494 cm$^{-1}$, respectively, with increasing heat treatment (Fig. 6b) while for KS-10N they remain practically independent of the annealing parameters (Fig. 6a).

Such behaviour of the Raman spectra of the KS-11N sample can be explained by thermally-induced involvement of zinc being contained in the glass matrix into the nanocrystal growth and formation of quaternary Cd$_{1-y}$Zn$_y$S$_{1-x}$Se$_x$ quantum dots. This process appears to be temperature-dependent and occurs at somewhat higher temperatures than reported for Cd$_{1-y}$Zn$_y$S nanocrystals [28] what is probably related to the differences in the glass matrix composition. Namely, in our case at the least intense annealing (675 °C, 2 h) of the KS-11N sample Cd$_{1-y}$Zn$_y$S$_{1-x}$Se$_x$ quantum dots are formed, the composition of which can be estimated from Fig. 2 as $x = 0.68$ (dark triangles). Heat treatment at higher temperatures and of higher duration results in gradual incorporation of zinc into the quantum dots.

To the best of our knowledge, no studies of phonon spectra of Cd$_{1-y}$Zn$_y$S$_{1-x}$Se$_x$ quaternary system have been reported so far, and their compositional transformation can be analyzed, based on the data available.
Fig. 5 Micro-Raman (a) and optical absorption (b) spectra of the sample KS-11N with glass-embedded Cd$_{1-y}$Zn$_y$S$_{1-x}$Se$_x$ nanocrystals, measured after decolouring at 1000 °C and subsequent annealing (the heat treatment parameters are indicated in the figure). Raman spectra were measured using the 482.5 nm Kr$^+$ laser line for excitation. Fitting of the non-decoloured sample Raman spectrum in Fig. 5 (a) shows the contribution of LO phonons (dashed lines) and surface phonons (dotted lines). In Fig. 5 (b) dashed and dotted curves denote absorption spectra for the samples annealed at 650 °C during 2 h and 4.5 h, respectively, for which no Raman signal could be detected.

for ternary Cd$_{1-x}$Se$_x$, ZnS$_{1-x}$Se$_x$, Cd$_{1-x}$Zn$_x$S and Cd$_{1-x}$Zn$_x$Se systems. Since the former two rows of anion-substituted solid solutions are known to exhibit two-mode behaviour [31, 44, 45], and the latter two (cation-substituted) – one-mode behaviour [46, 47], it is reasonable to assume that the quaternary Cd$_{1-y}$Zn$_y$S$_{1-x}$Se$_x$ system will possess two-mode compositional behaviour with selenide-like (LO$_1$) and sulphide-like (LO$_2$) phonons. Since the compositional dependence for LO phonons in the one-mode Cd$_{1-x}$Zn$_x$S and Cd$_{1-x}$Zn$_x$Se solid solutions is known [28, 46, 47] it is possible to estimate the Zn content $y$ in the quantum dots from Zn-induced increment of the experimentally observed LO$_1$ and LO$_2$ phonon frequencies over the corresponding values for CdS$_{1-x}$Se$_x$ with the same $x$. This can be done assuming that the chalcogen content in the quantum dots is independent of the heat treatment parameters and depends only on the content of the relevant components in the initial mixture. We suppose such assumption to be reasonable, at least for the annealing temperature and duration range under investigation, since the spectra of KS-10N sample show rather good reproducibility. A slight variation of the CdS$_{1-x}$Se$_x$ nanocrystal composition depending on the annealing process is reported only for much longer duration of heat treatment than in our case ($\Delta x = 0.05$ for 70 h) [28]. Therefore we assume the selenium content $x = 0.68$, $y = 0.32$. 

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Fig. 6 Second-order micro-Raman scattering spectra of the samples with glass-embedded (a): CdS$_{1-x}$Se$_x$ (KS-10N) and (b): Cd$_{1-y}$Zn$_y$S$_{1-x}$Se$_x$ (KS-11N) nanocrystals, measured after decolouring at 1000 °C and subsequent annealing (the heat treatment parameters are indicated in the figure). Dashed vertical lines correspond to 2 LO and LO$_1$ + LO$_2$ phonon frequencies in the least annealed samples.

determined from the LO phonon peak frequency difference for the sample subjected to the least intense heat treatment, to be the same for all KS-11N samples with quantum dots. Note that in the investigated samples with Cd$_{1-y}$Zn$_y$S$_{1-x}$Se$_x$ quantum dots the sulphide-like LO$_2$ phonon band due to small content of sulphur is much weaker in intensity and broader, and its annealing induced-shift is noticeably smaller. Therefore it is more convenient and reliable to determine the zinc content in Cd$_{1-y}$Zn$_y$S$_{1-x}$Se$_x$ quantum dots based on the annealing-induced shift of the selenide-like LO$_1$ phonon frequency. Thus, knowing the empirical compositional dependences derived for LO phonons for the one-mode solid solution systems of Cd$_{1-y}$Zn,S [28].

\[ \nu(y) = 303 + 91.4y - 44.2y^2 \text{ (cm}^{-1}\text{)} \]  

(1)

and Cd$_{1-y}$Zn,Se [46, 47]

\[ \nu(y) = 210 + 51y - 9y^2 \text{ (cm}^{-1}\text{),} \]  

(2)

we have weighted the contributions of Eqs. (1) and (2) by factors of $(1-x) = 0.32$ and $x = 0.68$, respectively, and calculated the values of $y$, corresponding to the annealing-induced increment of LO$_1$ phonon frequency of 11 cm$^{-1}$ (for the KS-11N sample, annealed at 700 °C during 4 h, $y = 0.18$) and 18.5 cm$^{-1}$ (for the initial KS-11N sample, $y = 0.32$). Meanwhile, the presence of zinc in the CdS$_{0.23}$Se$_{0.77}$ nanocrystals of the most intensely annealed KS-10 sample does not exceed 3% which is comparable to or even below the accuracy of its determination.

Therefore, the values obtained for the zinc content in Cd$_{1-y}$Zn,S$_{1-x}$Se$_x$ quantum dots show that the thermal treatment can result in even higher percentage of incorporated zinc than observed earlier for ternary Cd$_{1-y}$Zn,S nanocrystals [26–28]. Moreover, extraordinarily high frequencies of selenide-like (229 cm$^{-1}$) and sulphide-like (298 cm$^{-1}$) phonons reported in [48] for CdS$_{0.23}$Se$_{0.77}$ nanocrystals, can be explained only by zinc incorporation and show its content to be even higher, though the authors of [48] do not comment on it. It is also worth noticing that earlier studies of annealing-induced changes in CdS$_{0.88}$Se$_{0.12}$ [10] and CdS$_{0.65}$Se$_{0.35}$ [19] quantum dots revealed an increase of phonon frequencies up to 7
and 5 cm$^{-1}$, respectively. In both cases the authors attributed the phonon frequencies in the non-annealed samples (with smaller quantum dots) to be shifted down by phonon confinement the effect of which decreases with the annealing-induced nanocrystal size increase, resulting in the observed upward shift of the phonon frequencies. However, as our calculations performed on the base of the well-known Campbell and Fauchet model [33, 34] have shown [25], for the range of the CdS$_{1-x}$Se$_x$ nanocrystal mean radii quoted in [10] (2.6–10.4 nm) and [19] (2.8–4.0 nm), phonon confinement cannot lead to noticeable phonon frequency shifts. Moreover, such an explanation contradicts other Raman studies on annealing-induced CdS$_{1-x}$Se$_x$ nanocrystal growth as well as the present results for CdS$_{0.23}$Se$_{0.77}$ (sample KS-10N) where the annealing-induced frequency shift is by several times smaller though the average radii range (at least, in its lower limit, where the confinement-related effects can be revealed) is generally similar. In view of the present data, it seems more reasonable to attribute the annealing-induced phonon frequency shift in CdS$_{0.88}$Se$_{0.12}$ [10] and CdS$_{0.65}$Se$_{0.35}$ [19] quantum dots to the change of the nanocrystal composition due to zinc incorporation, similarly to the data presented here.

Formation of Cd$_{1-y}$Zn$_y$S$_{1-x}$Se$_x$ quantum dots in a borosilicate glass matrix is also interesting from the point of view of its mechanism which for II–VI semiconductor-doped glasses is generally known to comprise three stages – nucleation, diffusion-limited growth and coalescence (competitive growth, or Ostwald ripening) [2, 5, 7]. The mechanisms of nucleation and growth for Cd$_{1-y}$Zn$_y$S and CdS$_{1-x}$Se$_x$ quantum dots in glass matrices are stated to be quite different. Namely, in Cd$_{1-y}$Zn$_y$S a stage of homogeneous nucleation is followed by a rapid transition to ripening while CdS$_{1-x}$Se$_x$ particles undergo nucleation and growth simultaneously with a gradual transition into the ripening stage [28]. It can be expected that the growth pattern for quaternary Cd$_{1-y}$Zn$_y$S$_{1-x}$Se$_x$ quantum dots formation is somewhat intermediate, possessing the features of both types. Some indications for this can be seen from optical absorption spectra. It is clearly seen that for CdS$_{0.88}$Se$_{0.12}$ the absorption coefficients of the samples annealed within the whole studied range of temperatures and durations, are far below the values of the non-decoloured KS-10N sample (Fig. 4b). Meanwhile, for zinc-containing nanocrystals the absorption values of the samples annealed at 675–700 °C are of the same order as those for the initial KS-11N sample (Fig. 5b). This indicates more rapid quantum dot formation when zinc atoms are involved. The dependence of the Zn-related shift of the phonon frequencies on the heat treatment parameters (temperature and duration) shows that thermally induced substitution of cadmium by zinc in the nanocrystals goes on independently of the growth stage. This is quite consistent with the results of [29] where incorporation of zinc from the matrix to CdS$_{0.99}$Se$_{0.01}$ nanocrystals is reported to occur at the annealing of non-decoloured samples. However, in our opinion, the discussion of competing mechanisms of Cd$_{1-y}$Zn$_y$S$_{1-x}$Se$_x$ nanocrystals growth requires more detailed studies in an extended range of annealing temperatures and durations as well as different $x/y$ ratios.

4 Conclusions

The performed studies have shown that in semiconductor-doped glass matrices not only ternary CdS$_{1-x}$Se$_x$, but also quaternary Cd$_{1-y}$Zn$_y$S$_{1-x}$Se$_x$ quantum dots can be formed under heat treatment at the temperature 675–700 °C. Optical absorption and Raman scattering spectroscopic investigation has enabled their average radii and chemical composition to be evaluated. As follows from the phonon frequency shift, the content of zinc can reach at least 30%. Zinc incorporation into CdS$_{1-x}$Se$_x$ nanocrystals is shown to be taken into account for correct determination of their composition and explanation of the observed behaviour of Raman spectra.

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