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Journal of Raman Spectroscopy, Bognos Regis: John Wiley and Sons, v. 41, n. 10, p. 1302-1305, Oct. 2010

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Confirming the lattice contraction in CdSe nanocrystals grown in a glass matrix by Raman scattering

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This work gives the evidence of the lattice contraction in CdSe nanocrystals (NCs) grown in a glass matrix. The CdSe NCs were investigated by atomic force microscopy (AFM), optical absorption (OA), and Raman spectroscopy. The average size of CdSe NCs can be estimated by AFM images. Using the OA spectra and the effective-mass approximation, it was also possible to estimate the average sizes of CdSe NCs, which agree very well with the AFM data. These results showed that the CdSe NCs grow with increasing time of heat treatment. The blue shift of the longitudinal optical (LO) modes and surface optical (SO) phonon modes with an increase in the average radius of the NCs, shown in the Raman spectra, was explained by the lattice contraction in CdSe NCs caused by thermodynamic interactions at the interface with the host glass matrix. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: CdSe nanocrystals; lattice contraction; glass matrix; atomic force microscopy; optical absorption

Introduction

Quantum confinement effects in semiconductor CdSe nanocrystals (NCs) make them absorb or emit throughout the visible region of the electromagnetic spectrum depending on their size and shape. These interesting and unique properties imply that these NCs have a great potential for possible technological applications in optical devices as active elements for lasers,^[1] light-emitting devices,^[2] and solar cells^[3] among others. Several synthesis methods for CdSe NCs, such as reverse micelle method,^[4] colloidal solutions,^[5] and thin films^[6] among others, have been developed in an attempt to control their optical properties.

The interactions of NCs with the host matrix can greatly alter their optical properties, mainly due to the formation of surface states and the appearance of polarization in the NC–host material interface.^[7] These surface effects are heavily dependent on the NCs' size and become more important with increasing surface–volume ratio, which may cause changes in their vibrational modes.^[8,9]

In this paper, we study CdSe NCs grown in a glass matrix with the objective of investigating the interactions between quantum dots with different sizes and the surrounding materials. In this study, were employed the techniques of atomic force microscopy (AFM), optical absorption, and Raman spectroscopy.

Experimental

In this work, CdSe NCs were synthesized in the glass matrix SNAB with a nominal composition of 40SiO₂·30Na₂CO₃·1Al₂O₃·29B₂O₃ (mol%) adding (2CdO + 10Se) (wt%). The first step of sample preparation consisted of melting powder mixtures in an alumina crucible at 1200 °C for 30 min. Then, the crucible containing the melted mixture underwent quick cooling to room temperature. In the second step, thermal annealing of the previously melted

glass matrix was carried out at 560 °C for several hours in order to enhance the diffusion of Cd²⁺ and Se²⁻ species into the host matrix and to form CdSe NCs. The as-grown CdSe NCs were investigated by AFM, optical absorption (OA), and Raman scattering.

The AFM images were obtained with a Multimode Nanoscope IIIa (Digital Instruments – Veeco). Optical absorption measurements obtained at room temperature were performed with a Varian-500 spectrometer to obtain the absorption edge. The Raman spectra were obtained with JY-T64000 micro-Raman spectrometer in the backscattering geometry excited by the Ar⁺ laser 488 nm line.

Results and Discussions

The AFM images in three dimensions (3D), as well as the size distributions and morphologies of the CdSe NCs samples, are shown in Fig. 1(a) and (b). The average radii of the CdSe NCs samples estimated from these images were 3.36 and 3.78 nm

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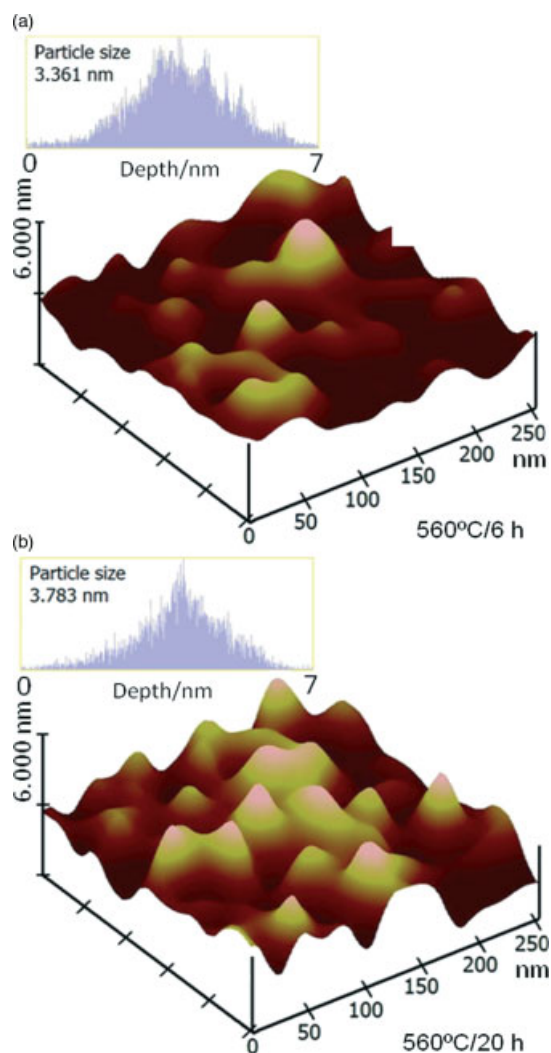


Figure 1. AFM 3D image of the CdSe NCs samples grown in the glass matrix SNAB, thermal treatment at 560 °C with annealing times of $t_a = 6$ and 20 h.

and the standard derivations were $\sigma = 0.33$ and 0.24 for the thermal treatments at 560 °C at annealing times of $t_a = 6$ and 20 h, respectively. It is also observed, in Fig. 1, that annealing for a longer time leads to an increase in the CdSe NCs' density.

Figure 2 shows the OA spectra of the samples subjected to thermal treatments at different annealing times of $t_a = 0, 6, 12, 14, 18,$ and 20 h, respectively. For comparison, an OA spectrum of the glass matrix SNAB is also shown. The formation and growth of the CdSe NCs in the glass matrix SNAB during the thermal treatment are also evidenced by the OA spectra. This fact is clearly observed by the shift of the OA band, which appeared at ~ 585 nm (2.12 eV), with an increase in the annealing time. This OA band is attributed to the $1S_h-1S_e$ excitonic transition. Using the OA spectra and a model of quantum confinement based on effective-mass approximation,^[10] it was possible to estimate the average radius of the CdSe NCs (Table 1), by the following expression:

$$E_{\text{conf}} = E_g + \frac{\hbar^2 \pi^2}{2\mu R^2} - 1.8 \frac{e^2}{\epsilon R} \quad (1)$$

where E_{conf} is the energy of the lowest exciton state, E_g is the energy gap of the material (bulk), μ is the reduced effective mass,

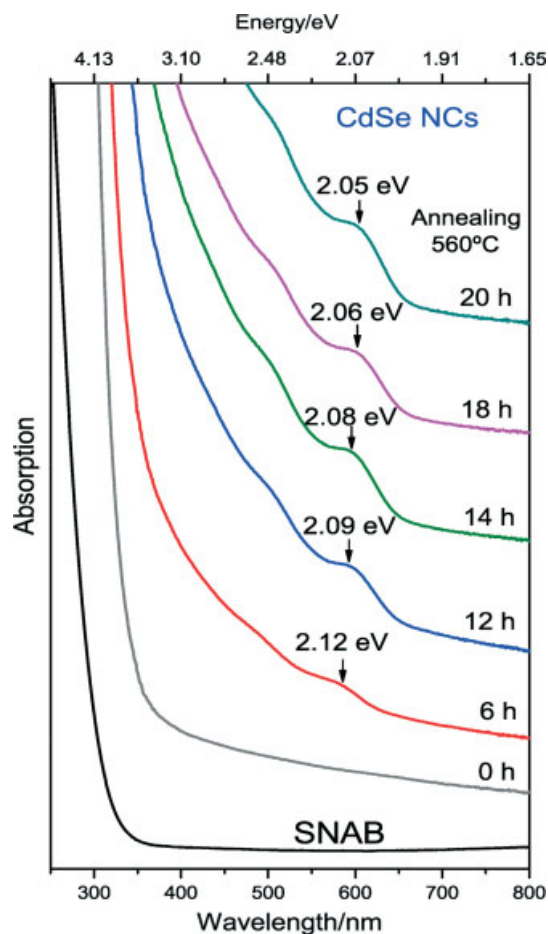


Figure 2. Absorption spectra at room temperature of the CdSe NCs samples, thermal treatment at 560 °C using different annealing times of $t_a = 0, 6, 12, 14, 18,$ and 20 h. The absorption spectrum of the glass matrix SNAB (bottom) is also shown. The arrows indicate the $1S_h-1S_e$ excitonic transitions energy in the CdSe NCs.

Table 1. Dependence of average radius of the CdSe NCs as a function annealing time

Annealing time (h)	Average radius (nm)	
	Cal.	AFM
6	3.39	3.36
12	3.54	–
14	3.59	–
18	3.70	–
20	3.76	3.78

e is the elementary charge, ϵ is the dielectric constant, and R is the average radius of the NCs. Note that these values agree very well with the values obtained from AFM images (Table 1).

Figure 3 shows the room-temperature (300 K) Raman spectra of the CdSe NCs samples subjected to thermal treatments at 560 °C at annealing times of 6, 12, 14, 18, and 20 h, respectively. The spectra-fitting procedure, using Lorentziana-like components, shows the presence of the two bands. The Raman feature presented in the region of lower wavenumbers is attributed to the surface optical phonon (SO),^[11–14] while the Raman peak at the higher

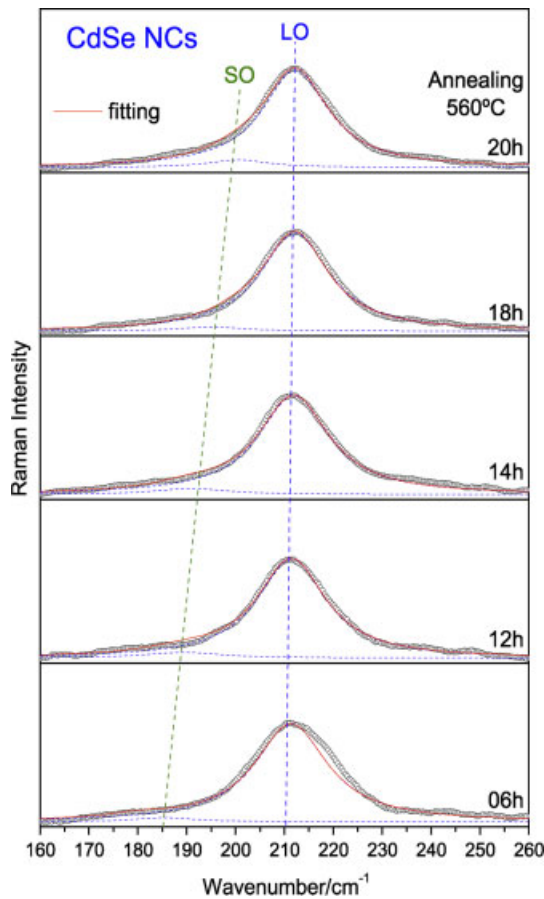


Figure 3. Raman spectra of the CdSe NCs subjected to thermal treatment at 560 °C at annealing times of 6, 14, 22, and 28 h, respectively.

wavenumber is CdSe-LO-phonon assigned. Note that, in Fig. 3, there is a blue shift of the LO phonon wavenumber with an increase in the NC radius. Similar behavior is observed in the case of SO phonons. The size dependence of the observed Raman shifts of CdSe NCs synthesized in the glass matrix SNAB is depicted in Fig. 4 (symbols).

Raman spectroscopy has been frequently used to investigate the interactions between the NCs grown in different media and their host matrix.^[15–18] The observation of a blue shift of LO phonon modes of CdSe NCs in borosilicate (B₂O₃–SiO₂) and silicate (SiO₂) glass matrices is attributed to the lattice contraction effect due to the compressive strain on the surface of the nanoparticles.^[19] This compressive strain is caused mainly by the mismatch of the linear thermal-expansion coefficients between microcrystals (α) and their host material (α'), as well as by an increase in the surface tension (σ), with a decrease in the microcrystal size.^[8] Considering the lattice contraction effect of the NCs and the effects of the phonon confinements with negative phonon dispersion, it is possible to show that LO phonon frequency, depending on the average NCs radius (R), is given by Ref [19]

$$\omega_{LO}(R) \cong \omega_L [1 - 3\gamma(\alpha' - \alpha)(T - T_g)] - \omega_L \left[\frac{1}{2} \left(\frac{\beta_L \mu_{np}}{\omega_L} \right)^2 - \gamma kb \right] \frac{1}{R^2} \quad (2)$$

where ω_L is the bulk's LO phonon frequency, γ is the Grüneisen parameter, and α' and α are linear thermal-expansion coefficients of the host glass and the NCs respectively. T and T_g are

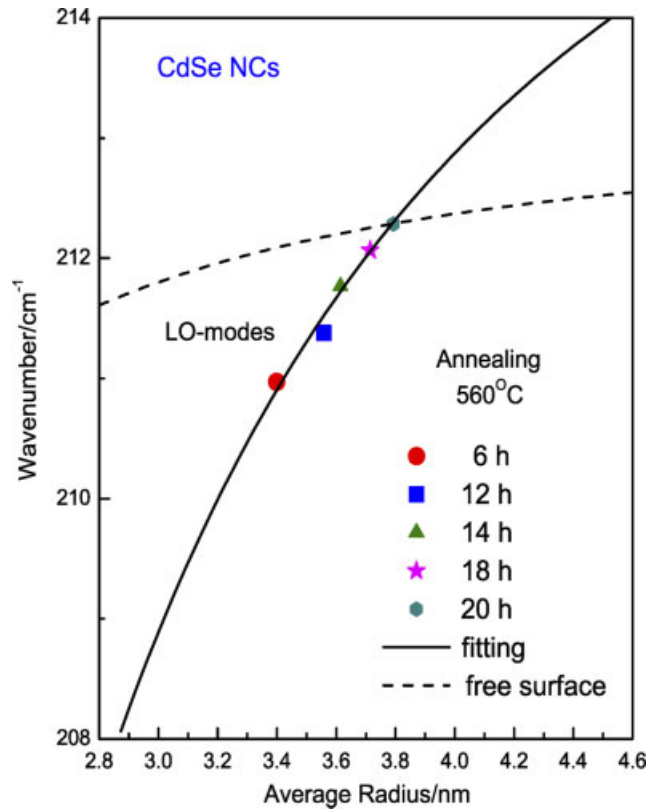


Figure 4. Raman wavenumber shifts of the CdSe NCs, thermal treatments at 560 °C at annealing times of 6 (circle), 12 (square), 14 (triangle), 18 (star), and 20 h (pentagon). The fitted curve (solid line) is described by the equation $\omega_{LO}(R) = 218 \text{ cm}^{-1} - 82 \text{ nm}^2 \text{ cm}^{-1}/R^2$, where R is the average radius. For comparison, the case where the CdSe NCs would be in the free surface condition (dashed line) is also shown.

the temperature under measurements and the heat-treatment temperature respectively, β_L describes the phonon dispersion (assumed to be parabolic), μ_{np} is the nonzero n_p -th root of the equation $\tan \mu = \mu$, and k is the compressibility of the bulk. The b -parameter describes the size-dependent surface tension of the nanocrystal that can be expressed by a function of the type $\sigma = \sigma_\infty + b/R$.^[8] When $R \rightarrow \infty$, the surface tension reduces to the bulk value σ_∞ and the term b/R clearly expresses the dependence on the surface-to-volume ratio. Studying the CdS_{1-x}Se_x microcrystal embedded in a borosilicate glass matrix, Scarmacio *et al.*^[8] found that $b = 0.85 \times 10^5 \text{ kbar } \text{Å}^2$ (expressing R in Å). This value is 10 times larger than the one we have found ($b = 0.84 \times 10^4 \text{ kbar } \text{Å}^2$). However, using the data of Ref. [19] for the CdSe NCs in borosilicate glass matrices and procedures of Ref. [8], we find that the final values are comparable to ($b = 0.9 \times 10^4 \text{ kbar } \text{Å}^2$).

It is interesting to verify the behavior of Eqn (2) when the NCs are in free surface condition, i.e. with $\alpha' = \alpha$ and $b = 0$.

$$\omega_{LO}(R) \cong \left[\omega_L^2 - \beta_L^2 \left(\frac{\mu_{np}}{R} \right)^2 \right]^{1/2} \quad (3)$$

Equation (3) corresponds to the result obtained by the theory of one-phonon Raman scattering in semiconductor microcrystallites and quantum dots,^[9] which includes a redshift in the LO phonon wavenumber with the decrease in the radius of the nanocrystals caused by the relaxation of the $q = 0$ selection rule, based on

the phonon confinement with negative phonon dispersion. This redshift has been observed in the powdered CdS and $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ NCs,^[11] as well as in CdSe NCs, grown in glass matrices.^[20] However, when NCs are grown into the host matrix, a competition between the compressive strain, which causes a blue shift, and the effects of the LO phonon confinement, which causes a redshift in Raman wavenumber, can arise. It is important to note that one of these effects may prevail over the other, depending on the NCs' size and the host material.

As shown in Figs 3 and 4, the Raman blue shift, with an increase in the average radius of CdSe NCs, evidenced which the glass matrix SNAB generates a compressive strain on the NCs. The experimental data were fitted with $\omega_{\text{LO}}(R) \cong A - B/R^2$, where $A = \omega_{\text{L}} [1 - 3\gamma(\alpha' - \alpha)(T - T_{\text{g}})]$ and $B = \omega_{\text{L}} \left[1/2 \left(\beta_{\text{L}} \mu_{n_p} / \omega_{\text{L}} \right)^2 - \gamma kb \right]$ in order to describe the behavior of the LO phonon frequency, depending on the NCs' radius. Figure 4 shows the fit obtained by the least square method. The numerical values of A and B are 218 cm^{-1} and $82 \text{ nm}^2 \text{ cm}^{-1}$, respectively. For comparison, the LO phonon wavenumber is also plotted in Fig. 4, depending on the average radius of the NCs in free surface condition according to Eqn (3). In this case, the bulk's LO CdSe phonon dispersion and wavenumber were described by the typical values $\beta_{\text{L}} = 2.969 \times 10^3 \text{ ms}^{-1}$ and $\omega_{\text{L}} = 213.1 \text{ cm}^{-1}$, respectively.^[21] The large detour between the experimental data fitted by Eqn (2) and the theory of one-phonon Raman scattering (Eqn (3)) clearly demonstrates the existence of the lattice contraction effect provoked by the compressive strain on the CdSe NCs' surface.

The similar behavior of SO modes suggests that these vibrations are also affected by compressive strain.

Conclusions

In conclusion, CdSe NCs were successfully synthesized in the glass matrix SNAB and investigated by AFM, OA, and Raman scattering. The blue shift of LO and SO Raman modes with the increase in the average radius of the NCs was explained by the lattice contraction effect in the CdSe NCs caused by thermodynamic interactions at the interface with the host glass matrix. Furthermore, the compressive strain on the CdSe NCs' surface undoubtedly affects the behavior of LO phonon modes and should be considered when they are embedded in host materials such as the glass matrices. We also found that the behavior of the size-dependent

surface tension (b -parameter) of the CdSe NCs in our samples is in excellent agreement with the results obtained from the data and procedures of the literature.

Acknowledgments

The authors acknowledge the financial support from the Brazilian agencies FAPEMIG and MCT/CNPq.

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