

Research Article

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

Yuriy M. Azhniuk,¹ Yuriy I. Hutych,¹ Vasyl V. Lopushansky,¹ Mykola V. Prymak,¹ Alexander V. Gomonnai,¹ and Dietrich R. T. Zahn²

¹ Institute of Electron Physics, National Academy of Sciences of Ukraine, 21 Universytetska Street, Uzhhorod 88017, Ukraine

² Semiconductor Physics, Chemnitz University of Technology, 09107 Chemnitz, Germany

Correspondence should be addressed to Yuriy M. Azhniuk, yu.azhniuk@gmail.com

Received 31 May 2011; Accepted 18 July 2011

Academic Editor: Sandip Dhara

Copyright © 2012 Yuriy M. Azhniuk et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

A series of samples with quaternary $\text{CdS}_{1-x-y}\text{Se}_x\text{Te}_y$ 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 $\text{CdS}_{1-x-y}\text{Se}_x\text{Te}_y$ 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 ($\text{CdS}_{1-x}\text{Se}_x$, $\text{CdSe}_{1-x}\text{Te}_x$), 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 ($\text{Cd}_{1-x}\text{Zn}_x\text{S}$), 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 $\text{CdS}_{1-x}\text{Se}_x$ [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 $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ [9, 11, 17] and $\text{CdSe}_{1-x}\text{Te}_x$ [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 $\text{Cd}_{1-y}\text{Zn}_y\text{S}_{1-x}\text{Se}_x$ 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 $\text{CdS}_{1-x-y}\text{Se}_x\text{Te}_y$ semiconductor nanocrystals by diffusion-limited growth in borosilicate glass and their characterization by Raman spectroscopy. To our knowledge, no data regarding $\text{CdS}_{1-x-y}\text{Se}_x\text{Te}_y$ 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 $\text{CdS}_{1-x-y}\text{Se}_x\text{Te}_y$ nanocrystals was prepared from commercially available Schott and LZOS optical cutoff filters made of borosilicate glass doped with $\text{CdS}_{1-x}\text{Se}_x$ and $\text{CdSe}_{1-x}\text{Te}_x$ nanocrystals. After melting 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 $5 \times 5 \text{ mm}^2$ 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 $150\text{--}160 \text{ cm}^{-1}$), CdSe-like LO₂ ($190\text{--}200 \text{ cm}^{-1}$), and CdS-like LO₃ ($260\text{--}290 \text{ cm}^{-1}$) phonons. Even though studies of CdS_{1-x-y}Se_xTe_y nanocrystals have never been reported before, scarce Raman spectroscopic data for individual samples of CdS_{1-x-y}Se_xTe_y 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 CdS_{1-x-y}Se_xTe_y system, CdTe possesses cubic (sphalerite or zinc-blende) structure, and CdSe at normal conditions is hexagonal (wurtzite) while CdS can exist in both zinc-blende and wurtzite structures [28]. Moreover, the structure of CdS_{1-x}Se_x nanocrystals is reported to be size dependent, and zinc-blende and wurtzite nanocrystals can coexist in the same sample [1, 24]. However, since the local environment of an atom in the two structures is very similar (tetrahedral coordination), the LO phonon frequencies for zinc-blende and wurtzite CdS are almost the same [29].

The series of spectra shown in Figure 1 illustrates the compositional behaviour of the Raman spectra of quaternary CdS_{1-x-y}Se_xTe_y nanocrystals with a strong variation of sulphur content in the nanocrystals and roughly equal content of selenium and tellurium ($x \approx y$). The LO phonon frequency in CdS (305 cm^{-1}) is known to be much higher than the frequency of local vibration of the sulphur impurity in CdSe or CdTe [30]. With the decrease of the sulphur content

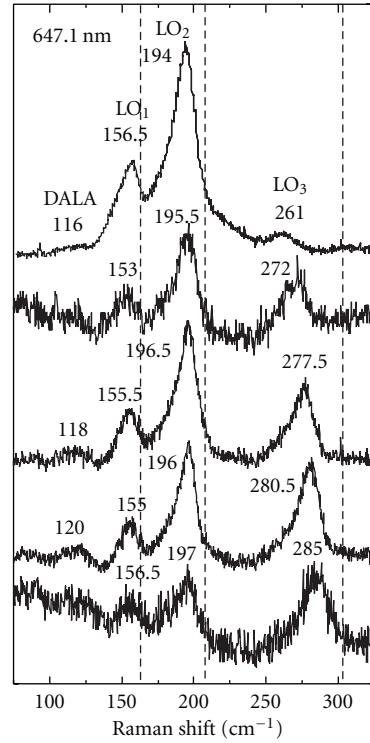


FIGURE 1: First-order Raman spectra of borosilicate glass-embedded CdS_{1-x-y}Se_xTe_y nanocrystals synthesized with roughly equal content of Se and Te ($x \approx y$) and a broad variation of S content (increasing from top to bottom). The spectra were measured at 295 K with excitation at $\lambda_{\text{exc}} = 647.1 \text{ nm}$. Vertical short-dashed lines correspond to the LO phonon frequencies of pure CdTe (162 cm^{-1}), CdSe (208 cm^{-1}), and CdS (305 cm^{-1}) crystals.

in the nanocrystals, the CdS-like LO₃ phonon frequency decreases, tending towards the frequency of local vibration of sulphur in CdSe_{1-y}Te_y ($255\text{--}260 \text{ cm}^{-1}$ for the given content of Se and Te). The decrease of the CdS-like LO₃ phonon frequency in the spectra in Figure 1 clearly correlates with the decrease of the corresponding band intensity revealed at lower content of S in the nanocrystals. Note that there is a spread in both the nanocrystal composition and size over the ensemble of nanocrystals in the sample; so the resonant conditions are exactly met only for those nanocrystals, 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 CdS_{1-x-y}Se_xTe_y 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

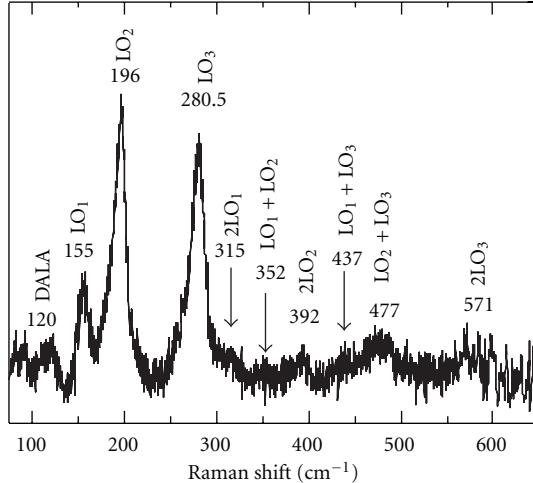


FIGURE 2: First- and second-order Raman spectra of borosilicate glass-embedded $\text{CdS}_{1-x-y}\text{Se}_x\text{Te}_y$ nanocrystals measured at 295 K with excitation at $\lambda_{\text{exc}} = 647.1$ nm.

the efficiency and sensitivity of the Raman spectroscopic technique at the correct choice of the resonance conditions. 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 $\text{CdS}_{1-x-y}\text{Se}_x\text{Te}_y$ 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 $117\text{--}120\text{ cm}^{-1}$. This feature can most likely be related to Raman scattering from acoustic phonons with nonzero 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 $117\text{--}120\text{ cm}^{-1}$, it can be assigned to DALA phonons.

Raman spectra of $\text{CdS}_{1-x-y}\text{Se}_x\text{Te}_y$ 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

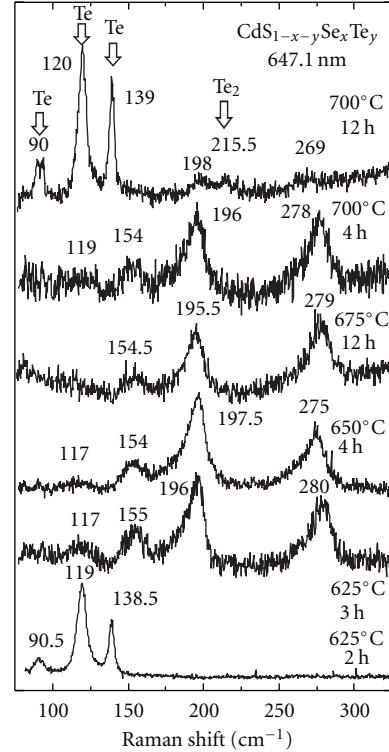


FIGURE 3: First-order Raman spectra of $\text{CdS}_{1-x-y}\text{Se}_x\text{Te}_y$ nanocrystals grown in borosilicate glass from the same initial mixture at different thermal treatment temperature and duration. The spectra were measured at 295 K at excitation with $\lambda_{\text{exc}} = 647.1$ nm laser line.

differ much, and the intensity ratio for these bands is about the same for all the samples. Hence, the composition of the $\text{CdS}_{1-x-y}\text{Se}_x\text{Te}_y$ nanocrystals formed of the same initial mixture is relatively stable with the variation of thermal treatment duration τ 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 $\text{CdS}_{1-x}\text{Se}_x$ nanocrystals grown in the borosilicate glass we observed earlier a clear trend of increase of the predominant chalcogen content with τ 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 (τ 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 ($T_a = 625^\circ\text{C}$, $\tau = 2\text{ h}$) and the most intensely ($T_a = 700^\circ\text{C}$, $\tau = 12\text{ h}$) 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 τ 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 $\text{CdS}_{1-x-y}\text{Se}_x\text{Te}_y$ 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 $\text{CdS}_{1-x-y}\text{Se}_x\text{Te}_y$ 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 $\text{CdS}_{1-x-y}\text{Se}_x\text{Te}_y$ nanocrystal composition.

References

- [1] U. Woggon, *Optical Properties of Semiconductor Quantum Dots*, Springer, Berlin, Germany, 1997.
- [2] H. S. Nalwa, *Nanostructured Materials and Nanotechnology*, Academic Press, New York, NY, USA, 2002.
- [3] M. J. Bowers, J. R. McBride, and S. J. Rosenthal, “White-light emission from magic-sized cadmium selenide nanocrystals,” *Journal of the American Chemical Society*, vol. 127, no. 44, pp. 15378–15379, 2005.
- [4] S. Rühle, M. Shalom, and A. Zaban, “Quantum-dot-sensitized solar cells,” *ChemPhysChem*, vol. 11, no. 11, pp. 2290–2304, 2010.
- [5] A. Tu and P. D. Persans, “Raman scattering as a compositional probe of II–VI ternary semiconductor nanocrystals,” *Applied Physics Letters*, vol. 58, no. 14, pp. 1506–1508, 1991.
- [6] A. Mlayah, A. M. Brugman, R. Carles, J. B. Renucci, M. Y. Valakh, and A. V. Pogorelov, “Surface phonons and alloying effects in $(\text{CdS})_x(\text{CdSe})_{1-x}$ nanospheres,” *Solid State Communications*, vol. 90, no. 9, pp. 567–570, 1994.
- [7] W. S. O. Rodden, C. N. Ironside, and C. M. S. Torres, “A study of the growth of $\text{CdSe}_x\text{S}_{1-x}$ crystallites within a glass matrix,” *Semiconductor Science and Technology*, vol. 9, no. 10, article 015, pp. 1839–1842, 1994.
- [8] V. Spagnolo, G. Scamarcio, M. Lugarà, and G. C. Righini, “Raman scattering in $\text{CdTe}_{1-x}\text{Se}_x$ and $\text{CdS}_{1-x}\text{Se}_x$ nanocrystals embedded in glass,” *Superlattices and Microstructures*, vol. 16, no. 1, pp. 51–54, 1994.
- [9] H. Yükselici, P. D. Persans, and T. M. Hayes, “Optical studies of the growth of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanocrystals in borosilicate glass,” *Physical Review B*, vol. 52, no. 16, pp. 11763–11772, 1995.
- [10] A. Roy and A. K. Sood, “Surface and confined optical phonons in $\text{CdS}_x\text{Se}_{1-x}$ nanoparticles in a glass matrix,” *Physical Review B*, vol. 53, no. 18, pp. 12127–12132, 1996.
- [11] M. Rajalakshmi, T. Sakuntala, and A. K. Arora, “The effect of annealing on the properties of $\text{CdS}_{0.95}\text{Se}_{0.05}$ nanoparticles dispersed in oxide glass containing Zn,” *Journal of Physics Condensed Matter*, vol. 9, no. 45, pp. 9745–9757, 1997.
- [12] A. Ingale and K. C. Rustagi, “Raman spectra of semiconductor nanoparticles: disorder-activated phonons,” *Physical Review B*, vol. 58, no. 11, pp. 7197–7204, 1998.
- [13] A. V. Gomonnai, Y. M. Azhniuk, V. O. Yukhymchuk, M. Kranjčec, and V. V. Lopushansky, “Confinement-, Surface- and disorder-related effects in the resonant Raman spectra of nanometric $\text{CdS}_{1-x}\text{Se}_x$ crystals,” *Physica Status Solidi B*, vol. 239, no. 2, pp. 490–499, 2003.
- [14] M. Y. Azhniuk, A. G. Milekhin, A. V. Gomonnai et al., “Resonant Raman studies of compositional and size dispersion of $\text{CdS}_{1-x}\text{Se}_x$ nanocrystals in a glass matrix,” *Journal of Physics Condensed Matter*, vol. 16, no. 49, pp. 9069–9082, 2004.
- [15] A. V. Bragas, C. Aku-Leh, S. Costantino, A. Ingale, J. Zhao, and R. Merlin, “Ultrafast optical generation of coherent phonons in $\text{CdTe}_{1-x}\text{Se}_x$ quantum dots,” *Physical Review B*, vol. 69, no. 20, Article ID 205306, 11 pages, 2004.
- [16] V. Bellani, A. Migliori, S. Petrosyan, L. Grigorian, and P. Petrosyan, “HRTEM, Raman and optical study of $\text{CdS}_{1-x}\text{Se}_x$ nanocrystals embedded in silicate glass,” *Physica Status Solidi A*, vol. 201, no. 13, pp. 3023–3030, 2004.
- [17] Yu. M. Azhniuk, A. V. Gomonnai, V. V. Lopushansky, Yu. I. Hutych, I. I. Turok, and D. R.T. Zahn, “Resonant Raman scattering studies of $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ nanocrystals,” *Journal of Physics: Conference Series*, vol. 92, no. 1, article 012044, 4 pages, 2007.
- [18] Y. M. Azhniuk, Y. I. Hutych, V. V. Lopushansky, L. A. Prots, A. V. Gomonnai, and D. R. T. Zahn, “Phonon spectroscopy of $\text{CdSe}_{1-x}\text{Te}_x$ nanocrystals grown in a borosilicate glass,” *Physica Status Solidi C*, vol. 6, no. 9, pp. 2064–2067, 2009.
- [19] Y. M. Azhniuk, A. V. Gomonnai, Y. I. Hutych et al., “Thermal treatment-dependent chemical composition of ternary $\text{CdS}_{1-x}\text{Se}_x$ nanocrystals grown in borosilicate glass,” *Journal of Crystal Growth*, vol. 312, no. 10, pp. 1709–1716, 2010.
- [20] Y. M. Azhniuk, A. G. Milekhin, A. V. Gomonnai et al., “Incorporation of zinc into $\text{CdS}_{1-x}\text{Se}_x$ nanocrystals in glass matrix studied by optical spectroscopies,” *Physica Status Solidi A*, vol. 201, no. 7, pp. 1578–1587, 2004.
- [21] Y. M. Azhniuk, A. G. Milekhin, A. V. Gomonnai, Y. I. Hutych, V. V. Lopushansky, and D. R. T. Zahn, “Phonon spectra of quaternary $\text{Cd}_{1-y}\text{Zn}_y\text{S}_{1-x}\text{Se}_x$ semiconductor nanocrystals grown in a glass matrix,” *Physica Status Solidi C*, vol. 6, no. 9, pp. 2068–2071, 2009.
- [22] N. F. Borrelli, D. W. Hall, H. J. Holland, and D. W. Smith, “Quantum confinement effects of semiconducting microcrystallites in glass,” *Journal of Applied Physics*, vol. 61, no. 12, pp. 5399–5409, 1987.
- [23] L.-C. Liu and S. H. Risbud, “Quantum-dot size-distribution analysis and precipitation stages in semiconductor doped glasses,” *Journal of Applied Physics*, vol. 68, no. 1, pp. 28–32, 1990.
- [24] A. Ekimov, “Growth and optical properties of semiconductor nanocrystals in a glass matrix,” *Journal of Luminescence*, vol. 70, no. 1–6, pp. 1–20, 1996.

- [25] V. M. Burlakov, A. P. Litvinchuk, V. N. Pyrkov, G. G. Tarasov, and N. I. Vitrikhovskii, "Optical properties of the quaternary II–IV mixed crystals in the far infrared region," *Physica Status Solidi B*, vol. 128, no. 2, pp. 389–400, 1985.
- [26] M.Y. Valakh, A. P. Litvinchuk, and G. G. Tarasov, "Laser raman scattering in II-VI semiconductor-based multicomponent solid solutions," *Kvantovaya Elektronika*, vol. 28, pp. 68–79, 1985 (Russian).
- [27] H. C. Gupta, G. Sood, J. Malhotra, and B. B. Tripathi, "Optical phonon frequencies in the quaternary $\text{CdTe}_{1-x-y}\text{Se}_x\text{S}_y$ mixed system," *Physical Review B*, vol. 34, no. 4, pp. 2903–2905, 1986.
- [28] O. Madelung, *Semiconductors: Data Handbook*, Springer, Berlin, Germany, 2004.
- [29] M. L. Nusimovici and J. L. Birman, "Lattice dynamics of wurtzite: CdS," *Physical Review*, vol. 156, no. 3, pp. 925–938, 1967.
- [30] A. S. Barker and A. J. Sievers, "Optical studies of the vibrational properties of disordered solids," *Reviews of Modern Physics*, vol. 47, supplement 2, pp. S1–S179, 1975.
- [31] L. Saviot, B. Champagnon, E. Duval, I. A. Kudriavtsev, and A. I. Ekimov, "Size dependence of acoustic and optical vibrational modes of CdSe nanocrystals in glasses," *Journal of Non-Crystalline Solids*, vol. 197, no. 2-3, pp. 238–246, 1996.
- [32] P. Verma, W. Cordts, G. Irmer, and J. Monecke, "Acoustic vibrations of semiconductor nanocrystals in doped glasses," *Physical Review B*, vol. 60, no. 8, pp. 5778–5785, 1999.
- [33] M. Ivanda, K. Baboci, C. Dem, M. Schmitt, M. Montagna, and W. Kiefer, "Low-wave-number Raman scattering from $\text{Cd}_x\text{Se}_{1-x}$ quantum dots embedded in a glass matrix," *Physical Review B*, vol. 67, no. 23, article 235329, 8 pages, 2003.
- [34] S. K. Gupta, P. K. Jha, S. Sahoo, A. K. Arora, and Y. M. Azhniuk, "Confined acoustic phonon in $\text{CdS}_{1-x}\text{Se}_x$ nanoparticles in borosilicate glass," *Journal of Nanoscience and Nanotechnology*, vol. 9, no. 9, pp. 5541–5544, 2009.
- [35] H. Kawamura, R. Tsu, and L. Esaki, "Disorder-activated acoustic mode in raman spectrum of $\text{Ga}_x\text{Al}_{1-x}\text{As}$," *Physical Review Letters*, vol. 29, no. 20, pp. 1397–1400, 1972.
- [36] Y. M. Azhniuk, V. V. Lopushansky, Y. I. Hutych, M. V. Prymak, A. V. Gomonnai, and D. R.T. Zahn, "Precipitates of selenium and tellurium in II-VI nanocrystal-doped glass probed by Raman scattering," *Physica Status Solidi B*, vol. 248, no. 3, pp. 674–679, 2011.

