

# Optical properties of Cd<sub>1-x</sub>Mn<sub>x</sub>S nanoparticles: off-resonance Raman spectroscopy

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Cd<sub>1-x</sub>Mn<sub>x</sub>S nanoparticles (x=0.05-0.4) with average particle size of about 2.2nm were synthesized using the colloidal chemistry method and characterized by Raman scattering measurements. The dominant Raman line of Cd<sub>1-x</sub>Mn<sub>x</sub>S nanoparticles was at about 300cm<sup>-1</sup> showing asymmetric broadening for  $\omega < 300\text{cm}^{-1}$ . Significant change in the line intensity for different Mn content x and excitation wavelength  $\lambda$  was noticed.

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## 1. Introduction

Cd<sub>1-x</sub>Mn<sub>x</sub>S nanoparticles (NPs) with size quantum confinement belong to the diluted magnetic semiconductor quantum dot class of materials that has been widely studied in the last few years. The study of diluted magnetic semiconductors, such as Cd<sub>1-x</sub>Mn<sub>x</sub>S quantum dots, is strongly motivated due to the localization of magnetic ions in the same places as the free-like electron and hole carriers occurring in these nanomaterials [1,2]. This interesting phenomenon causes unique properties in diluted magnetic semiconductor dots that can be explored in different technological applications, such as wavelength tunable laser [3], solar cells [4,5], spintronic devices [6], etc. Cd<sub>1-x</sub>Mn<sub>x</sub>S is a typical example of diluted magnetic semiconductor. Mn<sup>2+</sup> ions can be incorporated in A<sup>II</sup>B<sup>VI</sup> semiconductor host in large proportions without substantially altering the crystallographic quality of the material. Finally, Mn<sup>2+</sup> ion is electrically neutral in an A<sup>II</sup>B<sup>VI</sup> host, thus avoiding the formation of any acceptor or donor impurities in the crystal.

Vibrational spectroscopy (Raman spectroscopy) is a powerful, non-destructive technique sensitive to local environment, ideal for *in site* probing during growth and device fabrication and operation [7]. Similar as for the bulk materials, Raman spectroscopy provides information about optical vibrational modes of semiconductor nanoparticles [8-10].

In this paper, we present a continuation of our effort to understand the properties of powders consisting of nanosized diluted magnetic semiconductors prepared using colloidal chemistry method. The influence of the composition and the excitation wavelength on the Raman active vibrations were studied in detail.

## 2. Synthesis and characterization

Colloidal dispersions consisting of Cd<sub>1-x</sub>Mn<sub>x</sub>S NPs were prepared by mixing a solution containing Cd(NO<sub>3</sub>)<sub>2</sub> and MnSO<sub>4</sub> with a solution containing Na<sub>2</sub>S in the presence of surface active agent hexametaphosphate (NaPO<sub>3</sub>)<sub>6</sub>. The concentration of cations ([Cd<sup>2+</sup>] + [Mn<sup>2+</sup>]) was constant (2×10<sup>-3</sup>M), while S<sup>2-</sup> ions were used in excess (2.4×10<sup>-3</sup>M). The concentration of (NaPO<sub>3</sub>)<sub>6</sub> was 2×10<sup>-2</sup>M. Light and air were excluded during the preparation of this colloid. After precipitation of colloidal particles, the solvent was removed by vacuum evaporation at room temperature. The obtained yellow powders could be redissolved in water to give a colloid with the same structured absorption spectrum as the solution before evaporation. The content of Mn<sup>2+</sup> ions was up to x=0.3 and was checked out by X-ray dispersive fluorescence analysis technique. This technique gives results with uncertainty of 10%.

The X-ray diffraction analysis of Cd<sub>1-x</sub>Mn<sub>x</sub>S NPs showed hexagonal wurtzite crystal structure. UV-Vis absorption spectra were recorded on Perkin-Elmer Lambda 5 instrument. A blue shift of the absorption onset of the Cd<sub>1-x</sub>Mn<sub>x</sub>S nanoparticles compared to the bulk Cd<sub>1-x</sub>Mn<sub>x</sub>S was about 0.3eV. The radius of the particles was calculated using an effective mass approximation model [11]. The calculated value for the particle size of Cd<sub>1-x</sub>Mn<sub>x</sub>S nanoparticles was found to be 2.2nm. The results of experimental and theoretical studies of the Raman active vibrations in nanosized CdS crystals we reported in Ref. [12].

## 3. Results and discussion

The unpolarized Raman spectra were excited by 488, 496.5, 501.7 and 514.5nm lines of an argon laser in the

back-scattering geometry. The Jobin Yvon U-1000 monochromator, with a conventional photo counting system was used. Measurements were performed in spectral region from 150 to 450 $\text{cm}^{-1}$  at room temperature. The main feature in measured Raman spectra was mode at  $\approx 300\text{cm}^{-1}$ . Raman mode at  $\approx 300\text{cm}^{-1}$  is slightly asymmetric and broadened toward lower frequencies and can be well identified as LO type phonon mode confined in a spherical nanocrystal.

All  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  NPs samples showed significant changes in experimental Raman line shape, mainly in intensity, as a function of excitation energy. For each Mn content ( $x$ ), the intensity of the line decreases with the increase of the excitation wavelength  $\lambda$ , where the rate of the decrease depends on the Mn content ( $x$ ). As an example, the Raman spectra of  $\text{Cd}_{0.9}\text{Mn}_{0.1}\text{S}$  sample for various excitation wavelengths ( $\lambda=488, 496.5, 501.7$  and  $514.5\text{nm}$ ) are presented in Fig.1. The ratio of Raman intensities ( $I_{488}/I_{514}$ ) of mode at about  $300\text{cm}^{-1}$  for various contents of  $\text{Mn}^{2+}$  is given in Fig. 2. This picture summarizes the change in the intensity for all contents ( $x=0; 0.05; 0.1; 0.15; 0.3$ ) and applied excitations. From Fig. 2 it is clear that the ratio of Raman intensities changes nonlinearly as a function of  $\text{Mn}^{2+}$  content and has a maximum at  $x=0.1$ . The observed effect can be explained by the fact that the band gap energy of  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  NPs is a function of particle size and content of  $\text{Mn}^{2+}$ .

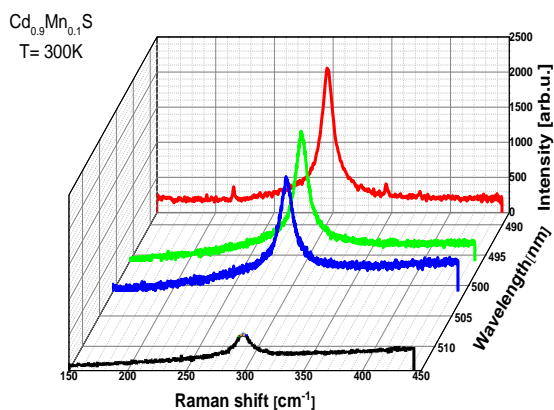


Fig. 1. Raman spectra of the  $\text{Cd}_{0.9}\text{Mn}_{0.1}\text{S}$  nanoparticles at different laser excitations (488, 496.5, 501.7 and 514.5nm).

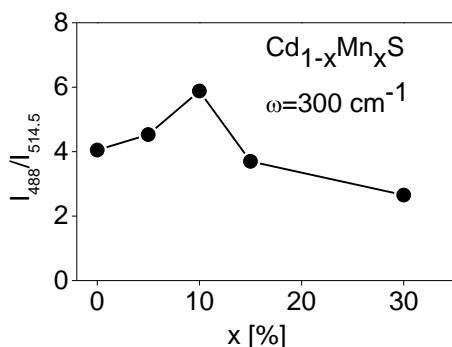


Fig. 2. Ratio of Raman intensities ( $I_{488}/I_{514}$ ) as a function of  $\text{Mn}^{2+}$  content.

Decrease of semiconductor nanocrystals size leads to an increase in band gap energy. For a fixed size of  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  nanoparticles the band gap energy is a function of  $\text{Mn}^{2+}$  content and has a minimum around  $x=0.1$  [13]. Because of that, among the  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  NPs with different  $\text{Mn}^{2+}$  content, the nanocrystals with  $x=0.1$  are the closest to the resonant regime, and potentially have the strongest intensity of Raman line. The experimental data confirmed that the strongest intensity of Raman line is for the  $x=0.1$  sample for all applied excitation energies.

The  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  NPs were not theoretically treated at this moment, because it is complicate to distinguish the influence of size and  $\text{Mn}^{2+}$  content on the phonon properties. In the  $\text{Mn}^{2+}$  doped bulk CdS samples new impurity modes appear between TO-LO frequencies of CdS [14,15]. The TO-LO modes originating from the impurities are not well resolved for the samples with low  $\text{Mn}^{2+}$  content.

#### 4. Conclusion

We investigated Raman spectra of  $\text{Cd}_{1-x}\text{Mn}_x\text{S}$  nanoparticles synthesized using colloidal chemistry method and small enough to show effects due to the phonon confinement. In the Raman spectra an asymmetric line was observed at about  $300\text{cm}^{-1}$ . Registered nonlinear change in intensity for different  $\text{Mn}^{2+}$  content  $x$  and excitation energies is connected to nonlinear changes of energy gap.

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