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Structural and optical properties of CdS nanocrystals embedded in NaCl single crystals

B. Boudine[a,*], M. Sebais[a], O. Halimi[a], H. Alliouche[b], A. Boudrioua[c], R. Mouras[c]

[a] *Laboratoire de Cristallographie, Faculté des Sciences, Université Mentouri, Route Ain el bey, Constantine 25000, Algeria*
[b] *Département de Chimie, Faculté des Sciences, Université Mentouri, Route Ain el bey, Constantine 25000, Algeria*
[c] *MOPS-CLOES, Supelec 2, rue E. Belin, 57078 Metz Cedex 3, France*

Abstract

The elaboration of the CdS nanocrystals embedded in a NaCl single crystal has been performed using the Czochralski method. The optical density spectrum shows a blue shift of the absorption edge towards the high energies. The energy gap has been found to be 2.70 eV. The photoluminescence has been assigned to the neutral-donor band (D^0, X) and radiative recombinations from deep defect and impurity levels.

Keywords: CdS; NaCl; Czochralski method; Balls milled; Photoluminescence; Energy band gap

1. Introduction

The synthesis and characterization of small particles of materials is currently an area of intense theoretical and experimental research. Semiconductor nanocrystals (NCs) are small crystallites of semiconductor material between 10 and 100 Å. The confinement of electrons and holes is possible in II–VI semiconductor NCs, when the particle size approaches the Bohr radius scale of massive exciton [1], leading to new optical properties. These materials have very interesting nonlinear optical properties, which make them suitable materials for use in elctroluminescent and laser devices.

Several techniques have been developed to synthesize semiconductor NCs such as CdS, ZnO, GaN, CuCl, CuBr, etc. [2]. Ball-milling is one of the techniques used for nanocrystalline powders fabrication. The mechanism of ball-milling is thought to involve the repeated fracture of powder particles during ball–powder–ball and ball–powder–container collisions. The embeddeing of CdS NCs in dielectric media have been performed using several techniques such as sol–gel [3], ion implantation [4], colloidal solution [5] and cell methods [6].

The size-dependent spectral characteristics of photoluminescence (PL) due to the size quantization effect allows the control of the color of emitted light simply by adjusting the size of NCs during synthesis [7]. The NCs are characterized by a large surface to volume ratio which makes the surface effects dominant [8].

In the present work, the authors have elaborated CdS NCs embedded in a NaCl single crystal matrix and studied their structural and optical properties. The NaCl single crystal has a wide energy band gap ($E_g > 7$ eV) [9] which makes it a transparent matrix in the UV-Vis region.

2. Experimental procedure

The nanocrystalline powder of the CdS was elaborated by ball-milling. The micro-sized powder of CdS was sealed in a cylindrical vial under an argon atmosphere with stainless steel balls. The nanocrystalline phase elaboration was performed in a planetary ball mill at room temperature. The milling time was 48 h.

The elaboration of the CdS NCs embedded in a NaCl single crystal matrix is performed using the Czochralski method, which consists in melting the NaCl matrix in a porcelain crucible [10]. Then, the seed is dipped in the melt and pulled out with an appropriate rate (10 mm/h). During the crystal pulling process, we dope the melt with the CdS nanocrystalline powder. The growth is carried out following the crystallographic [1 0 0] axis. The obtained crystals are cleaved parallel to the (1 0 0) plane in order to prepare 3–5 mm thick pastilles.

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[*] Corresponding author. Tel.: +213-31-61-4342; fax: +213-31-61-4747.
E-mail address: b.boud@caramail.com (B. Boudine).

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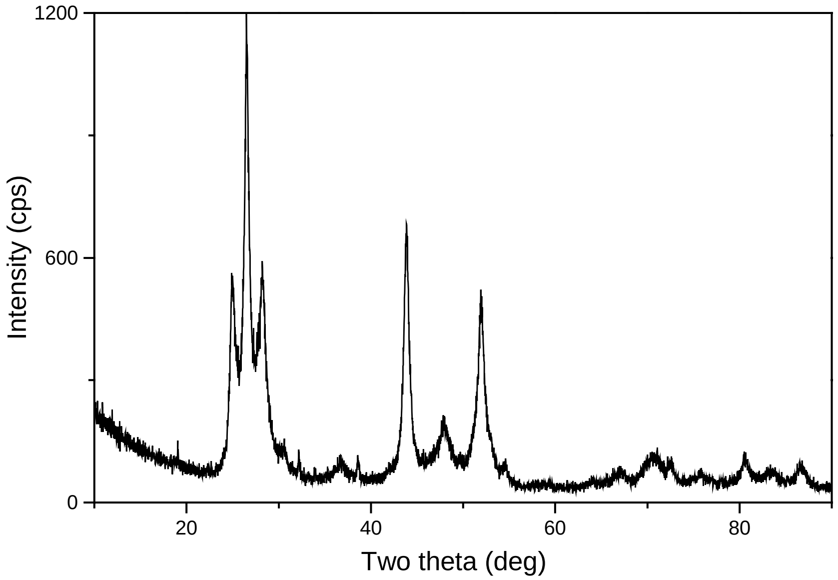

Fig. 1. XRD diffractogram of CdS nanocrystalline powder. The powder has an hexagonal structure and presents a (0 0 2) texture.

X-ray diffractograms (XRD) have been obtained using the Cu Kα radiation ($\lambda_{K\alpha} = 1.5402$ Å) and a Ni filter with Siemens diffractometer (advanced D8) at 40 kV and 20 mA in the 2θ range (10–80°). In order to obtain the optical density, we have used an UV-Vis Shimadzu 3001 PC spectrophotometer in the energy region of 2–6 eV. The PL was measured at pumped helium temperature (1.2 °K). The pastille was excited by an argon laser (ionized light $E_{\rm exc} = 3.47$ eV) with an output power of 20 mW. The PL signals were detected with a photon counting system with a photomultiplier.

3. Results and discussion

We report in Fig. 1 the XRD diffractogram of the CdS nanocrystalline powder prepared by balls milled (process). We observe a weak broadening of the diffraction peaks which is due to submicronic grain sizes of CdS powder. The peaks of the XRD spectrum have been fitted by Gaussian functions. Using the Scherrer formula, the size of grains was found to be in the range 7.3–14.2 nm.

Fig. 2 displays X-ray diffraction on the pastille of CdS NCs embedded in a NaCl single crystal. We observe two

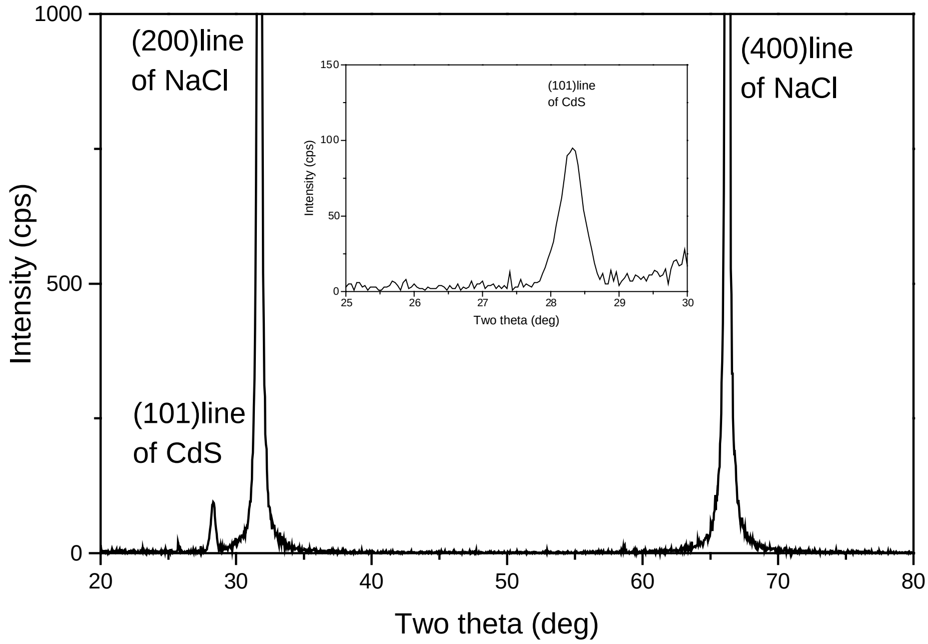

Fig. 2. XRD diffractogram of CdS NCs embedded in a NaCl single crystal pastille. The inset presents the 25–29° angular domain. We note a peak, with a weak intensity situated at $2\theta = 28.305°$ which corresponds to the most intense line (1 0 1) of CdS wurtzite.

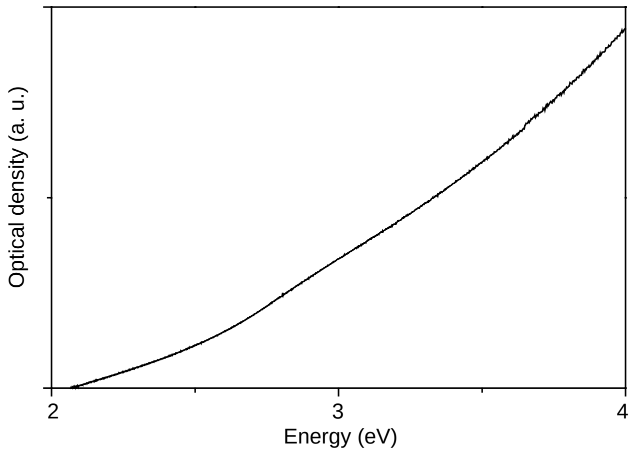

Fig. 3. Optical density of CdS NCs embedded in a NaCl single crystal.

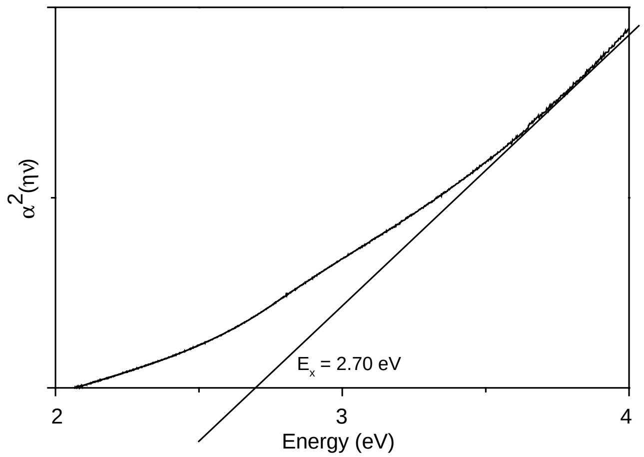

Fig. 4. A plot of the square of the absorption α^2 vs. $\overline{h}\omega$ for the CdS NCs embedded in a NaCl single crystal. The linear portion is extrapolated to deduce the optical band gap of the CdS.

peaks located at $2\theta = 31.733^\circ$ and $2\theta = 66.245^\circ$, which respectively, correspond to the (2 0 0) reflection of NaCl and its harmonic (4 0 0). Moreover, we note the presence of another peak with a weak intensity, which is situated at $2\theta = 28.306^\circ$. This peak is attributed to the (1 0 1) line of the CdS with the hexagonal structure. A slight shift ($\Delta(2\theta) = 0.123^\circ$) of the CdS peak angular position towards higher angles can be noticed in comparison to the standard position indicated in the ASTM file for CdS (JCPDS 43-0985). This shift may be attributed to the contraction of the CdS NCs cells in the NaCl matrix [2].

Fig. 3 presents the optical density of the CdS NCs embedded in a NaCl matrix. We observe a shift of the absorption edge towards higher energies in comparison with the CdS bulk crystal. The absorption edge was determined using the extrapolation of the $\alpha^2(\overline{h}\omega)$ curve (α is the absorption edge) (Fig. 4) [11]. The band gap is then found as the intercept of the linear portion of the plot. For a direct band gap semiconductor, the absorption near the band edge is given by Eq. (1):

$$(\alpha\overline{h}\omega) = C(\overline{h}\omega - E_{\mathrm{x}})^{1/2} \tag{1}$$

where C is a constant, E_{x} the optical band gap and $\overline{h}$ the Plank's constant.

We found $E_x = 2.70\,\mathrm{eV}$. The comparison of this value with that of the CdS bulk crystal ($E_{\mathrm{g}} = 2.50\,\mathrm{eV}$) indicates a significant blue shift of the absorption edge ($\Delta E = 0.2\,\mathrm{eV}$). The average radius of the CdS NCs is estimated using the following equation [12]:

$$E_{\mathrm{x}} = E_{\mathrm{g}} + \frac{\overline{h}^2\pi^2}{2\mu R^2} - \frac{3.6e^2}{2\varepsilon R} \tag{2}$$

where R is the average radius of the CdS NCs, E_{g} the band gap energy of CdS bulk crystal, μ the CdS exciton reduced

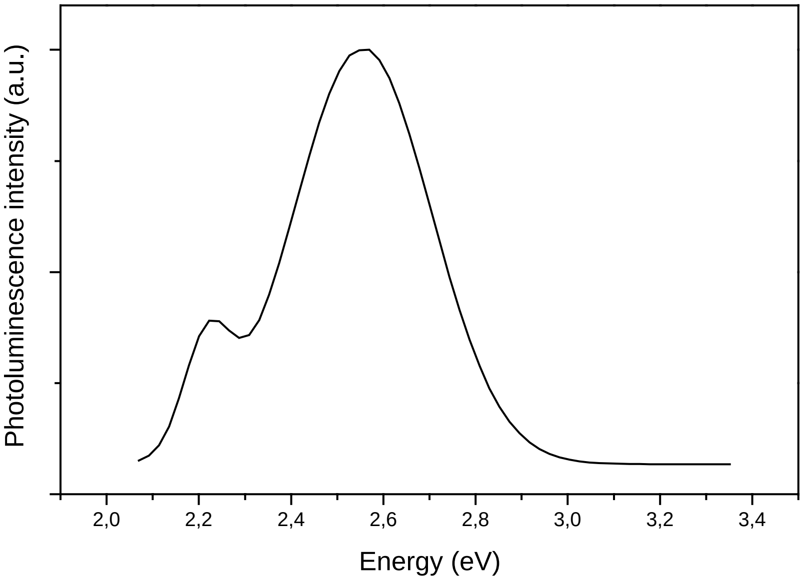

Fig. 5. Photoluminescence spectrum of CdS NCs embedded in a NaCl single crystal.

mass (~0.154 m_e, where m_e is the mass of the electron), ε the bulk dielectric constant of CdS (~8.9) and e is the charge of the electron. The calculated average radius R of the CdS NCs is 2.12 nm. In our case, the size of the NCs was well below the Bohr radius of the exciton in bulk CdS (3 nm).

Finally, Fig. 5 displays the PL spectrum of CdS NCs embedded in a NaCl single crystal. A red shift of the PL compared to the optical density curve can be noticed. Besides, two bands at 2.56 and 2.22 eV, which are related to near band edge emission, can also be observed. The first band is assigned to the neutral-donor band (D^0, X). The energy of (D^0, X) bands obtained in this work is in close agreement with the values measured at 10.6 K by Chen et al. [13] from CdS crystals grown by physical vapor transport. The second band emission at 2.2 eV is due to radiative recombinations from deep defect and impurity levels [14]. Our PL spectrum is dominated by a (D^0, X). Chen et al. have reported that the deep-level defects in CdS, such as the ones usually created by impurities and vacancy complexes, lie in the 1.4–2.2 eV range [13]. Agata et al. has also reported that this band can be present in CdS microcrystals and centered at around 2.2 eV [15]. These authors have associated this band with Cd interstitials.

4. Conclusion

X-ray diffraction has confirmed the incorporation of the CdS in the NaCl matrix using the Czochralski method. The incorporated CdS is in nanocrystalline form, as indicated by the optical density spectrum, which exhibits a significant blue shift of the energy band gap of the CdS NCs. It is then possible to obtain semiconductor NCs (CdS) embedded in alkali-halide matrix (NaCl) using the Czochralski method. The PL of the CdS NCs presents two emission bands. The PL is dominated by a (D^0, X).

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