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Optical Materials 25 (2004) 373–377
OPTICAL Materials
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# Characterization of CdS nanocrystals embedded in KCl single crystal matrix grown by Czochralski method

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Received 15 July 2003; accepted 17 September 2003

**Abstract**

The growth of CdS nanocrystals (NCs) embedded in bulk KCl single crystal matrix is performed using the Czochralski method. The X-ray diffraction reveals the incorporation of the CdS NCs with a cubic structure inside the KCl matrix. The optical density measurements of the CdS NCs embedded in KCl single crystal show a shift of the absorption edge towards higher energies. The optical band-gap is estimated to be about of 2.60 eV. The photoluminescence (PL) spectrum of the studied samples presents four emission bands in the range of 2.20–2.56 eV.


*Keywords:* CdS nanocrystals; X-ray; Photoluminescence; KCl; Bulk; Single crystal

## 1. Introduction

Several techniques have been developed to synthesize semiconductor nanocrystals (NCs) such as CdS, ZnO, GaN, CuCl, CuBr... [1]. The importance of the NCS is that when the dimensions of crystallites approach the atomic scale, significant changes can occur in the electronic and the optical properties compared to those of bulk materials [2]. In addition, the NCs are characterized by a large surface to volume ratio which makes the surface effects dominant [3].

More recently, a strong interest has been devoted to NCs of semiconductors embedded in wide gap matrix, such as glass [4–6] and alkali halide matrices [7–9]. One of the most versatile techniques for producing NCs at the surface of a host material is the utilization of ionic implantation at high doses followed by thermal annealing [10,11]. In this configuration, almost any ion can be implanted into any solid substrate.

The cadmium sulfide (CdS) is one of the interesting materials used in optoelectronic, electroluminescence, and in laser devices [12–14]. The energy band gap of CdS, at room temperature, is about of 2.5 eV [15] and the exciton Bohr radii is 3 nm [16]. A large blue-shift in the photoluminescence (PL) spectra from such CdS dots, in comparison with the CdS bulk emission, has been

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doi:10.1016/j.optmat.2003.09.005

observed [17]. In general, finding a simple synthetic method to produce CdS NCs embedded into crystalline matrices is one of the main challenges of recent research activities.

In this work, we report the growth of CdS NCs embedded in KCl single crystals by using Czochralski method. The KCl matrix is a dielectric medium and it has a wide gap energy (~8 eV) [18], which makes it a host matrix for growing CdS NCs. The characterization of the inclusion of CdS NCs in KCl is preformed utilizing the X-ray diffraction and the optical absorption. We also report the investigation of the PL of CdS NCs embedded in KCl.

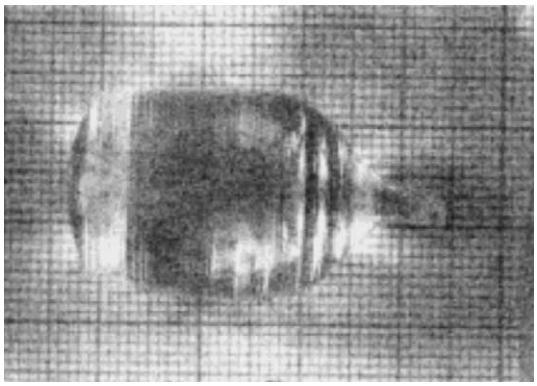

Fig. 1. Photograph of KCl single crystal containing CdS NCs.

## 2. Experimental

The fabrication of the samples is performed using the Czochralski method, which consists of melting the KCl matrix in a porcelain crucible. The starting material of KCl is provided by Panreac QUIMICA (Spain) company with a purity of 99.5%. the growth process is performed by using a seed oriented (1 0 0). During the crystal growth, the samples are doped by a submicronic powder of CdS. The latter has been prepared by a strong mechanical grinding in order to allow the CdS to diffuse inside the KCl matrix. The submicronic powder of the CdS dissociates and enters in KCl matrix. The growth is carried out following the crystallographic [1 0 0] axis. The running temperature is a round 900 °C (temperature of the melt) and the pulled rate is 7 mm/h at a rotation rate of 1 tr/mn. The pulled crystals generally have a cylindrical shape (see Fig. 1) with 6.2 and 4 cm for length and radius respectively and their density of dislocation is 100 dis/cm. Finally, the obtained crystals are cleaved parallel to the (100) plane in order to prepare 3 mm-thick pastilles.

X-ray diffraction (XRD) has been obtained using the copper radiation $k_\alpha$ ($\lambda_{k\alpha} = 1.5402$ Å) and Ni filter of Siemens Diffractometer (advanced D8) at 40 kV and 20 mA in the $2\theta$ range (10°–70°). In order to obtain the optical density we have used a UV–visible 3001 PC spectrophotometer (Shimadzu type) in the energy region of 2–6 eV. For PL investigation, the sample was mounted in a He-closed cycle refrigerator thermoregulated from 10 to 300 K and excited by an Argon laser ionized light ($E_{exc} = 2.62$ eV) with an output power of 20 mW at 10 K. The PL signals were detected by photon counting system with a photomultiplier.

## 3. Results and discussion

KCl crystal has a NaCl structure where the densest plan is the (1 0 0). Moreover, the crystal of CdS NCs embedded in KCl grows following [1 0 0] axis (oriented growth). Therefore, cleavage of the sample is easily carried out according to the plan (1 0 0). In that case, the use of the X-ray diffraction on the (1 0 0) face of KCl allows us to study the incorporation of CdS into the KCl crystal matrix.

Fig. 2 shows X-ray diffraction on the pastille of CdS NCs embedded in bulk KCl single crystal. We observe two peaks located at $2\theta = 28.346°$ and $2\theta = 58.642°$, which respectively correspond to the (2 0 0) reflection of KCl and its harmonic (4 0 0). Moreover, when we explore the 31–33° angular domain (inset of Fig. 1), we observe the presence of an other peak with a weak intensity, which is situated at $2\theta = 30.55°$. That peak is attributed to the (2 0 0) line of the CdS with cubic structure. Therefore, the plan (2 0 0) of KCl is parallel to the plan (2 0 0) of the cubic CdS. However, a slight shift ($\Delta(2\theta) = 0.25°$) of the CdS peak angular position towards lower angles can be noticed in comparison to the standard position indicated in the phase of CdS (JCPDS 10-454). This shift may

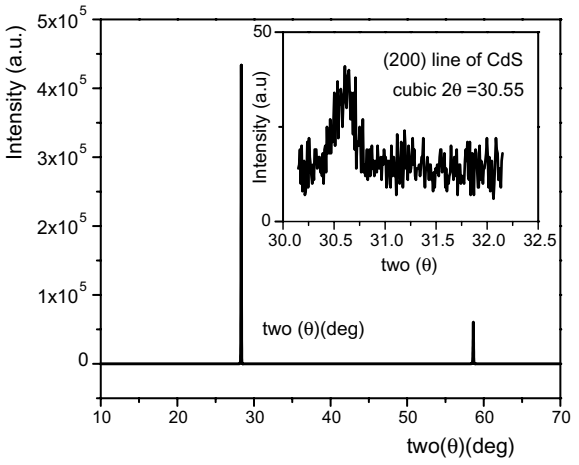


Fig. 2. X-ray diffraction on the pastille of CdS NCs embedded in KCl single crystal (10°–70° angular domain). The inset shows angular domain (31°–33°). The CdS cubic NCs line is located at 30.55°.

be attributed to the contraction of the CdS NCs cells in the KCl matrix [1].

We report on Fig. 3 the optical density of the CdS NCs embedded in KCl single crystal compared to that of pure KCl crystal prepared in the same conditions. We can notice that the optical density of a pure KCl crystal is virtually horizontal and no absorption band is, thus, observed. In fact, the matrix of KCl is transparent in the near UV and visible ranges. Concerning the CdS NCs

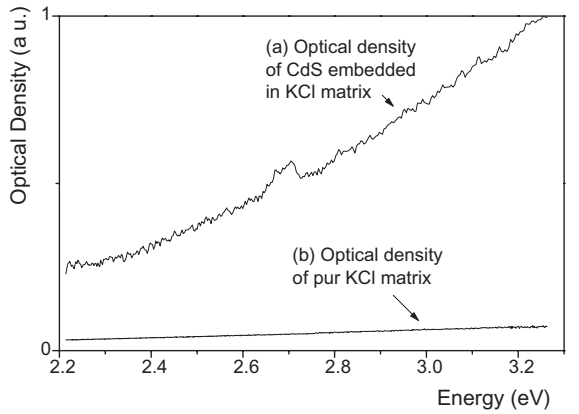


Fig. 3. Optical density of (a) CdS NCs embedded in KCl single crystal and (b) pure KCl matrix. We notice a small band around 2.67 eV.

embedded in the KCl crystal, we notice a shift of the absorption edge towards higher energies compared to the one of CdS bulk crystal. Moreover, we observe a small absorption band characterized by a large peak situated around 2.67 eV. That is quite surprising, since in the nanocrystals, the first transition (1s–1s) usually appears as a very narrow peak. However the existence of a size-dispersion of CdS NCs in the KCl would contribute to the broadening of the peak. Using the standard expression for the direct transition between two parabolic bands [21], the absorption edge was found to be 2.60 eV. The comparison of this value with that of the CdS bulk crystal ($E_g = 2.50$ eV) indicates a blue-shift of 0.1 eV. The average radius of the CdS NCs is estimated using the following equation [20]:

$$E_x = E_g + \frac{\hbar^2\pi^2}{2\mu R^2} - \frac{3.6e^2}{2\varepsilon R} \quad (1)$$

where $E_x$ is the absorption edge of CdS NCs, $R$ the average radius of the CdS NCs, $\hbar$ is the Planks constant, $E_g$ is the band gap energy of CdS bulk crystal, $\mu$ the CdS exciton reduced mass ($\sim$0.154 $m_e$—$m_e$ is the mass of the electron), $\varepsilon$ the bulk dielectric constant of CdS ($\sim$8.9) and $e$ is the charge of the electron.

The calculated average radius $R$ of the CdS NCs is 3.15 nm. This value is close to that of the Bohr radii of the exciton of CdS bulk crystals ($a_{ex} = 3$ nm). Therefore, we can deduce that we are in an intermediate confinement.

Finally, Fig. 4 displays the PL spectrum of CdS NCs embedded in KCl single crystal. A red shift of the PL compared to the optical density curve can be noticed. Beside, two bands at 2.52 and 2.56 eV which are related to near band edge emission can be also observed. These bands are assigned to the neutral-acceptor bound exciton band ($A^0$, X) and neutral-donor band ($D^0$, X). The energies of ($A^0$, X) and ($D^0$, X) bands obtained in this work are in close agreement with the values measured at 10.6 K by Chen et al. [19] from CdS crystals grown by physical vapor transport. The broad emission band with peak at 2.38 eV is due to donor–acceptor pair (DAP) band [19,22]. Our PL spectra is dominated by a DAP radiative recombination.

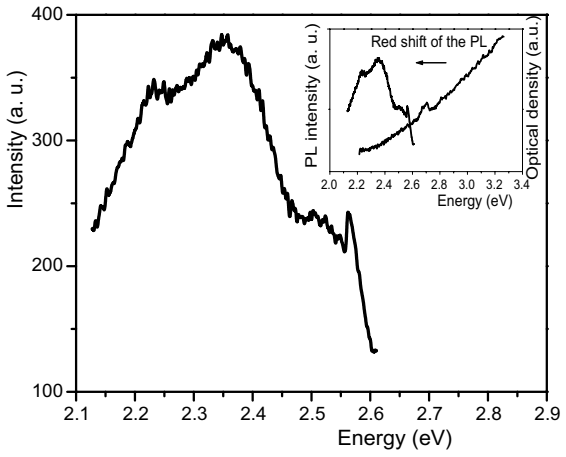


Fig. 4. Photoluminescence spectrum of CdS NCs embedded in KCl single crystal. The inset shows the red shift of the PL signal compared to optical density.

The large band at about 2.2 eV can be attributed to radiative recombinations from deep defect and impurity levels [23]. Chen et al. have mentioned 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 [19]. Agata et al. have also reported that this band can be present in CdS microcrystals and centred at around 2.2 eV [24]. These authors have associated this band to Cd interstitials. We have made the deconvolution process of the photoluminescence signal using four bands centered at 2.56, 2.52, 2.38 and 2.2 eV respectively. Fig. 5 outlines the followed fitting to separate the four bands utilizing Gaussian curves.

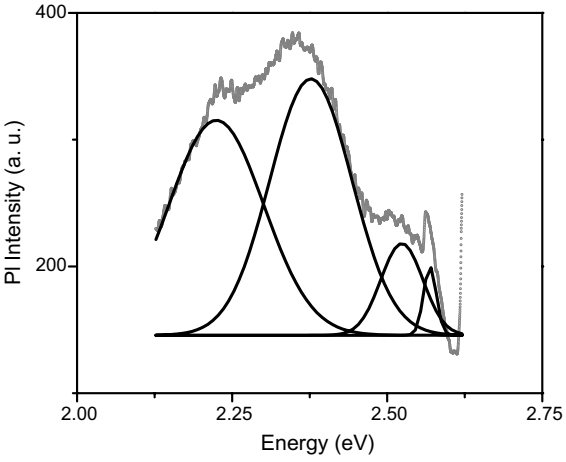


Fig. 5. Deconvolution of photoluminescence signal in foor Gaussian bands.

## 4. Conclusion

In conclusion, the X-ray diffraction has confirmed the incorporation of the CdS nanocrystals inside the KCl single crystal with a cubic structure by using Czochralski method. The optical density measurements have shown an intermediate confinement of CdS NCs, as well as a blue shift of the band gap as high as 0.1 eV. The PL spectrum presents four bands in the vicinity of the absorption edge (2.5–2.6). The spectrum is dominated by shallow-level excitons bound to neutral donors ($D^0$, X) or neutral acceptors ($A^0$, X). The band emission at 2.38 is dominated by the peak of the DAP, while the band at 2.2 eV is attributed to radiative recombinations from deep defect and impurity levels.

These results are the first step of the investigation of CdS NCs embedded in KCl matrix for nonlinear optic applications.

## Acknowledgements

The authors would like to thank Dr A. Benslama for his assistance. This work has been supported by the Crystallography Laboratory of Mentouri University-Constantine.

## References

[1] D. Nesheva, C. Raptis, Z. Levi, Z. Popovic, I. Hinic, J. lumin. 82 (1999) 233.
[2] A.G. Rolo, L.G. Vieira, M.J.M. Gomes, J.L. Ribeiro, M.S. Belsley, M.P. dos Santos, Thin Solid films 312 (1998) 348.
[3] S. Okamoto, Y. Kanemitsu, H. Hosokawa, K. Morakoshi, S. Yanagida, Solid state Commun. 105 (1) (1998) 7.
[4] T.M. Hayes, L.B. Lurio, J. Pant, P.D. Persans, Solid State Commun. 117 (2001) 627.
[5] P. Maly, T. Miyoshi, J. Lumin. 90 (2000) 129.

[6] A. Meldrum, C.W. White, L.A. Boatner, I.M. Anderson, R.A. Zuhr, E. Sonder, J.D. Budai, D.O. Anderson, Nucl. Ins. Meth. Phys. Res. B 148 (1999) 957.
[7] J. Zhao, M. Ikezawa, A.V. Federov, Y. Masumoto, J. Lumin. 87–89 (2000) 525.
[8] M. Haselhoff, K. Reimann, H.J. Weber, J. Cryst. Growth 196 (1999) 135.
[9] H. Harada, H. Kondo, N. Ichimura, S. Hashimoto, Jpn. J. Appl. Phys. 38 (1999) L1318.
[10] J.C. Budai, C.W. White, S.P. Withrow, M.F. Chisholm, J.G. Zhu, R.A. Zuhr, Nature 3902 (1997) 384.
[11] Y. Kanemitsu, M. Ando, D. Matsura, T. Kushida, C.W. White, J. Lumin. 94–95 (2001) 235.
[12] K.S. Ramaiah, R.D. Pilkington, A.E. Hill, R.D. Tomlinson, A.K. Bhatnagar, Mater. Chem. Phys. 68 (2001) 22.
[13] M.V. Artemyev, V. Sperling, U. Woggon, J. Cryst. Growth 184 (1998) 19.
[14] B. Ullrich, D.M. Bagnall, H. Sakai, Y. Segawa, J. Lumin. 87–89 (2000) 1162.
[15] M.V. Artemyev, V. Sperling, U. Woggon, J. Appl. Phys. 81 (10) (1997) 6975.
[16] V. Nair Selvakumar, T. Tagahara, Phys. rev. B 55 (8) (1997) 5156.
[17] A. Ejiri, A. Hatano, Inst. Phys. Conf. Ser. 193 (1992) 77.
[18] W. Jaskólski, J. Planelles, G. Peris, Physica E 4 (1999) 176.
[19] K.T. Chen, Y. Zhang, S.U. Egarievwe, M.A. George, A. Burger, C.H. Su, Y.G. Sha, S.L. Lehoczky, J. Cryst. Growth 166 (1996) 731.
[20] I. Mikulskas, E. Bernstein, J.C. Plenet, C. bovier, R. tomšiunas, V. Grivickas, J.V. Vaitkus, J. Mugnier, J. Dumas, Mater. Sci. Eng. B 69–70 (2000) 418.
[21] K.S. Ramaia, R.D. Pilkington, A.E. Hill, R.D. Tomllinson, A.K. Bhatnagar, Mater. Chem. Phys. 68 (2001) 22.
[22] S. Permogorov, A. Reznitsky, J. Lumin 52 (1992) 201.
[23] G. Perna, M. Ambrico, V. Capozzi, D. Smaldone, R. Martino, J. Lumin. 72–74 (1997) 90.
[24] M. Agata, H. Kurase, S. Hayashi, K. Yamamoto, Solid State Commun. 76 (1990) 1061.