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Structural and optical properties of CdSe doped KCl single crystal

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Abstract

Undoped and doped KCl single crystals by CdSe nanocrystals (NCs) have been grown by Czochralski (CZ) method with pulling rates in the 8-10 mm/h range. The crystals thus obtained were cleaved into samples of required size. The structural investigation of these samples has been deduced from $\Theta 2\Theta$*(XRD) and Raman spectroscopy. The nano-size of CdSe aggregates in KCl host determined from XRD measurements by using the Sheerer formula. The Raman spectroscopy presented the LO mode vibration relative of (Cd-Se) chemical liaison. Moreover, the results of the optical absorption and photoluminescence spectra confirmed the nano-size of CdSe aggregates were observed band absorption located at 622,5nm relative of electronic transition 1se-1s3/2 of CdSe, with a blue shift from the bulk gap of* $\Delta E_g=0{,}26\,eV$ *(Eg (CdSe) bulk=1,73eV), while the photoluminescence showed a band situated at 643, 55 nm, with displacement Eg towards the short wavelength (blue shift), this bleu shift due to the nanometric size of CdSe aggregates.*

Key words *nanocrystals, KCl single crystal, Cz method, XRD, Raman spectrometer, UV-Vis absorption, photoluminescence.*

1. Introduction

The II–VI semiconductors and in particular CdSe, with a suitable band gap of 1,74 eV, has attracted considerable attention due to the optical tenability over the entire visible range of the solar spectrum [1,2]. Hence there is a great technological interest in CdSe quantum dots for applications such as light emitting diodes [3], lasers [4], optoelectronic devices [5,6] and biological labels [7]. For their use, CdSe nanocrystals (NCs) can be dispersed into organic or inorganic matrix. The size, distribution and structural properties of nanocrystals strongly affect the performance and reliability of the constructed devices.

In the present paper, we report results of structural and optical study of KCl single crystals doped with CdSe nanocrystals (KCl:CdSe). Samples have been successfully grown using Czochralski method (Cz). The KCl host matrix has a wide band gap (Eg ≈ 6, 43 eV) which makes it transparent in the UV-Visible spectral range and allows to study the optical properties of CdSe nanocrystals in this range, it has been reported earlier for ZnO and CdS nanocrystals embedded respectively in single crystals of KBr and NaCl [8,9].

The charge carriers (excitons), in the semiconductor nanocrystals, are confined and the effect of confinement leads to fundamental changes in the electronic structure. When the particle size approaches the Bohr radius scale of exciton in bulk semiconductor, new optical properties appear [10]. These properties are highlighted in the present work.

2. Experimental details

KCl and KCl:CdSe single crystals were prepared using Cz method. Chemical reagents are KCl powder procured from "LABOSI/Chemicals products and reaction laboratory" with 99,9% purity, and CdSe nanopowder procured from "Aldrich chemicals" with 99,99% purity. The KCl:CdSe single crystals were prepared with starting materials 1 mol% of CdSe nanopowder (50nm) and 99 mol% of KCl. This mixture was heated to melting. The oven temperature has been controlled by the control system: Controller [REX-C100 SEPIES] and the platinum/platinum-Radium (10%) thermocouple. During the crystal growth, the pulling rates of 8 -10 mm/h and the rotation speed is about 1 round/mn are used along the operation.

The growth is carried out following the crystallographic axis [100]. The obtained crystals, with diameter of 2,5 cm and length of 7,5 to 10 cm, are cleaved parallel to the (100) plane in pellets with required size.

XRD data have been obtained using the Cu K_α radiation ($\lambda_{K\alpha}$ =1,5402 Å) and graphite filter of BRUKER-AXS D8 diffractometer. The structural composition of pellets was carried out by using a (Jobin-Yvon) µ-Raman spectrometer at room temperature (RT). Optical properties were analyzed using UV–Visible spectrophotometer (Shimadzu, UV-3101). Furthermore, the photoluminescence (PL) was measured at RT and the samples were excited by an argon laser (ionized light E_{exc}=514,5 nm) with an output power of 10 mW.

3. Results and discussion

XRD studies have been also performed on pure KCl single crystal in order to determine its structural state. Fig.1 shows the XRD diagram of a pure KCl single crystal. It exhibits three intense peaks at 2θ=28,48°; 2θ=58,78° and 2θ= 95° corresponding to plan (200) and its harmonics (400) and (600) respectively. This result shows that KCl crystal has cubic structure with the symmetry of Fm3m space group by referring to data of JCPDS 41-1476 file, discloses that the sample has single crystal character and confirms that the crystal was cleaved parallely to the (100) plan.

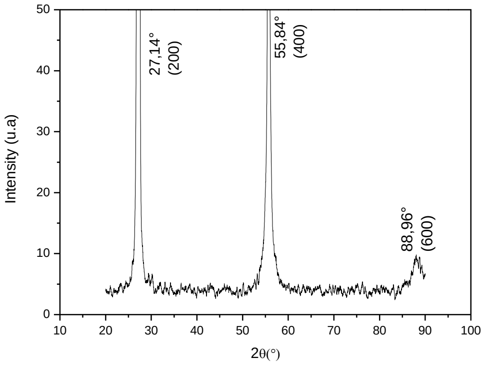

Fig. 1 XRD pattern of pure KCl single crystal

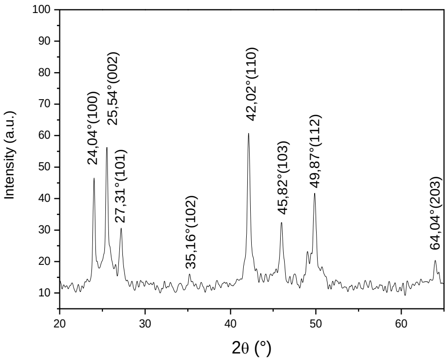

Fig. 2 XRD pattern of CdSe NCs.

The XRD spectrum of CdSe NCs, used for doping, is presented in figure 2. The good resolution and the high intensity of peaks indicate that CdSe NCs are of good crystalline quality. By comparing the positions of peaks with that of JCPDS 08-0459 file, we can deduce that CdSe NCs have hexagonal (wurtzite) structure with symmetry of space group $P6_3mc$.

Figure 3 displays the XRD spectrum of KCl:CdSe sample. It presents two peaks at 2θ=28,7° and 2θ=59° corresponding respectively to (200) and its harmonic (400) plans of KCl cubic structure. Moreover, it also reveals additional peaks with a weak intensity at 2θ=23,35° , 2θ=25,52° and 2θ=40,80°. They are attributed respectively to the reflections (100), (002) and (110) of CdSe NCs. This result means the incorporation of CdSe NCs in the KCl single crystal.

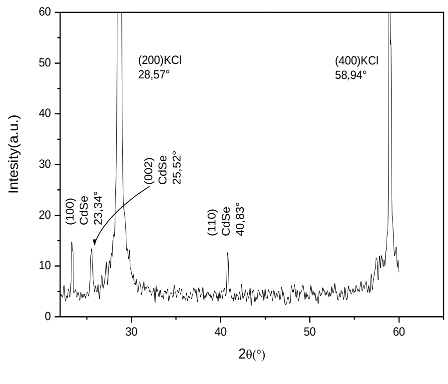

Fig.3 XRD pattern of KCl:CdSe single crystal.

For the size estimation of CdSe NCs, we have used the formula of Scherer (1) and the peaks have been fitted by Gaussian function.

$$D(nm)=\frac{0,9\lambda(nm)}{B(\theta)\cos(\theta)} \quad (1)$$

Where D is the crystallite diameter, λ the wavelength, θ the Bragg angle, B(θ) the full-width at half-maximum (FWHM) of the peak.

Table 1 presents the average sizes of CdSe crystallites embedded in KCl single crystal. The average radius found is about 45,34 nm.

(hkl)	(100)	(002)	(110)
2 θ (deg.)	23,35	25,52	40,80
FWHM (deg.)	00,17	00,23	00,16
D (nm)	47,66	35,41	52,96

Tabl.1: Average sizes of CdSe nanocrystals embedded in KCl single crystal

Fig.4 exposes Raman spectra of pure KCl and KCl:CdSe recorded at RT. They shows three peaks at 93,31 ; 141,12 and 183,87 cm^{-1} relative respectively to $T_{2g,2}$, $T_{2g,1}$ and A_{1g} Raman modes of KCl [11] these peaks are in the two spectra of KCl and KCl:CdSe. Furthermore there is an additional peak at 202,44 cm^{-1} in Raman spectrum of KCl:CdSe which is characteristic of phonon mode LO of CdSe [12-15]. It is known that the phonon mode LO of CdSe bulk crystal has a number wave of 213 cm^{-1}. But this peak shifts to the low energy side (up to 202,44 cm^{-1}) with decreasing CdSe NCs sizes due to phonon confinement and strain induced effects [16,17].

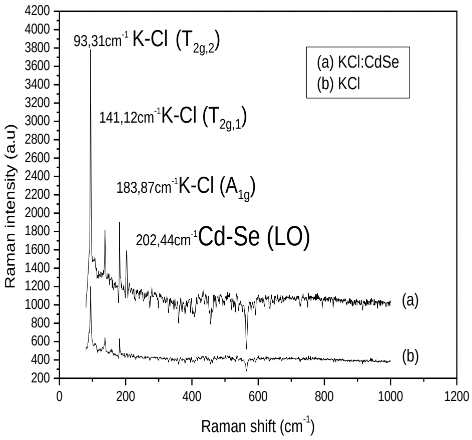

Fig 4: μ-Raman spectra: (a) pure KCl
(b) KCl:CdSe.

Optical absorption spectrum of pure KCl single crystal (Fig. 5(a)) shows that it is transparent in the visible region and has a strong absorption in the near ultraviolet. The absorption edge E_g ≈ 6,20 eV is determined by the second derivative method [18] represented in Fig 5(b).

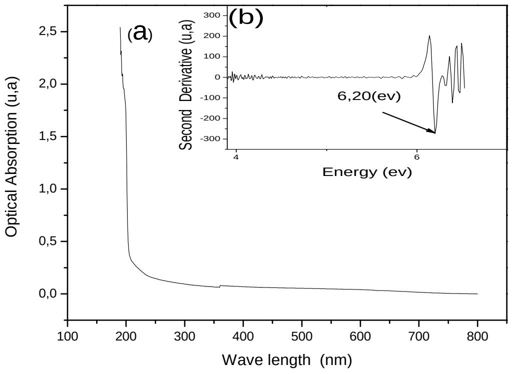

Fig. 5: Optical absorption spectra of KCl single crystal (a) and E_g of pure KCl (b).

Fig. 6(a) exhibits optical absorption spectrum of KCl:CdSe, which presents a band around 1,99eV (Fig. 6(b)) relative to the first absorption maximum ^1S_e-$^1S_{3/2}$ of CdSe according to work of S.V. Gaponenko [19]. It has been concluded from XRD patterns that the used CdSe powder has a wurtzite structure, whose bulk band gap energy is located at E_g = 1,73eV [20]. It appears a blue shift of band gap in value of ΔEg=0,26eV for CdSe NCs in comparison to that of bulk CdSe in wurtzite structure. This shift of band gap energy was caused by the well known quantum confinement effect.

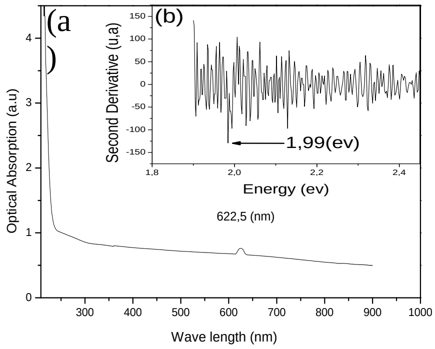

Fig. 6: Optical absorption spectra of KCl:CdSe single crystal (a) and the edge of CdSe NCs(b).

The photoluminescence (PL) spectrum of CdSe NCs embedded in KCl single crystal at RT is presented in Fig.7. It shows a broad emission band centered at 643, 55 nm which is consistent with optical absorption measurement. In comparison to the PL peak from wurtzite bulk CdSe, there is a blue shift ΔE_g= 0,19 eV due to quantum confinement effect. Moreover, the strong PL intensity from the KCl:CdSe can be attributed to the high crystalline quality of CdSe nanocrystals, which is in good agreement with the XRD patterns of CdSe powder discussed earlier. Therefore we can deduce that KCl single crystal is a suitable matrix to study the optical properties of CdSe NCs in UV-Visible range.

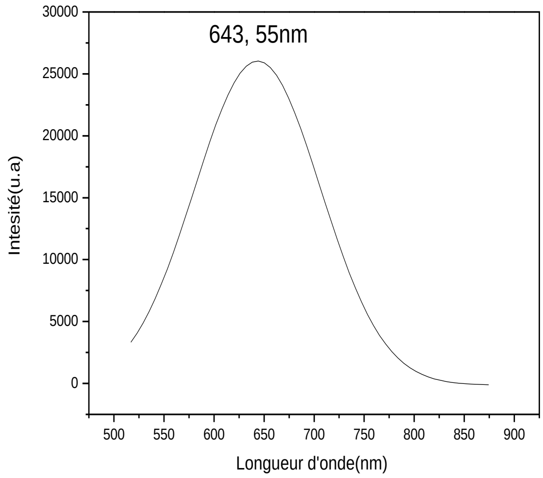

Fig. 7 Room temperature PL of KCl:CdSe single crystal.

4. Conclusion

KCl single crystals, pure and doped with CdSe NCs, were prepared by Cz method. Structural characterization by XRD reveals the inclusion of CdSe NCs in KCl single crystal (host matrix) and shows that CdSe NCs have wurtzite structure. Furthermore KCl preserves its single crystal character. In addition, optical absorption spectra show a band located at 622,50 nm confirming CdSe NCs incorporation in KCl and demonstrates a blue shift of absorption edge (ΔEg=0,26eV) in comparison with CdSe bulk crystal. Photoluminescence of KCl:CdSe at RT shows a red luminescence band located at 643,55nm, with displacement to the short wavelengths (blue shift) which is due to the nanometric size of CdSe nanocrystals.

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