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Incorporation of CdSe quantum dots (QDs) in KH_2PO_4 (KDP) crystalline host: Processes of elaboration and characterization

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ABSTRACT

The aim of this work is to survey experimentally the effect of doping CdSe quantum dots (QDs) on structural and optical properties of Di-hydrogen phosphate KH_2PO_4 (KDP) single crystal, where we expose a simple and reproduced technic to obtain KDP:CdSe single crystal starting from aqueous solution phase. In order to characterize the samples comfortably, the obtained crystals were cleaved into pellets with suitable size each surface being parallel to the faces (100). The XRD results denote that the CdSe QDs inside KDP single crystal have only one preferred direction (110) and the estimated size as derived from Sheere's formula proved the nano-regime of guest material. On the other side, UV–vis absorption spectrums appear that a pure KDP crystal has transparence property in the visible range with a large window where E_g (KDP) ≈ 7.17 eV. However, KDP:CdSe sample exhibits two bands located at 425 nm and 625 nm attributed to the transition band to band and excitonic, respectively. As an accordance result, photoluminescence (PL) measurements indicate that the band gap of CdSe QDs inside KDP single crystal appears a significant amount of blue-shift (ΔEg = 0.284 eV) due to well recognized quantum confinement effect exerted by the CdSe QDs.
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1. Introduction

To date, QDs of semiconductors have received much attention because of an exceptional property where they appear the size-dependants on their properties such as structural, optical and optoelectronics properties which change dramatically compared to the bulk semiconductors. Commonly, these new behaviors of nanosemiconductors can be interpreted through the quantum confinement effect and a large surface-volume ratio [1]. The II—VI semiconductors occupy an important position; they have been widely used for different applications such as lasers, biomedical tags, and solar cells [2–4]. Among the II—VI semiconductors, CdSe is extensively used in different application devices [5]. As a bulk crystal, CdSe exhibits direct band gap energy ($E_g \approx$ 1.75 eV) with exciton Bohr radius 3.67 nm [6,7]. Moreover, The CdSe QDs have amazing size-dependants emissions, due to this feature they have greatly interested in the pharmaceutical and biological science [8].

In order to use QDs in the optical experiments, their nano-size makes a big challenge. Therefor QDs need, in general, to support or matrix host. Recently, many investigations have been interested in the optical properties of nanosemiconductors dispersed in crystalline matrix, for example: KBr:CuO, NaCl:CdTe, KBr:AgBr, KCl:AgCl KCl:Sb_2O_3, NaCl:ZnO, and KDP:CdTe

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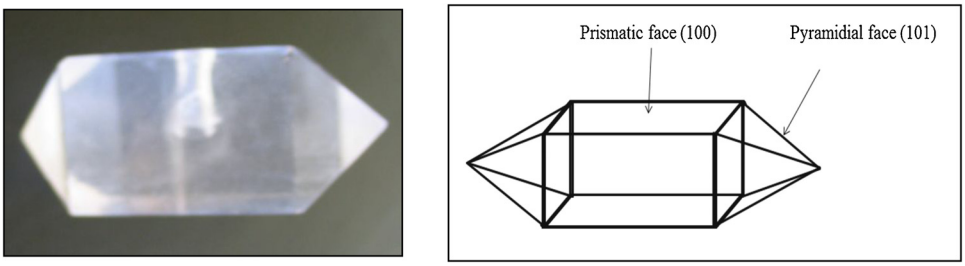

Fig. 1. Photograph of a KDP:CdSe single crystal.

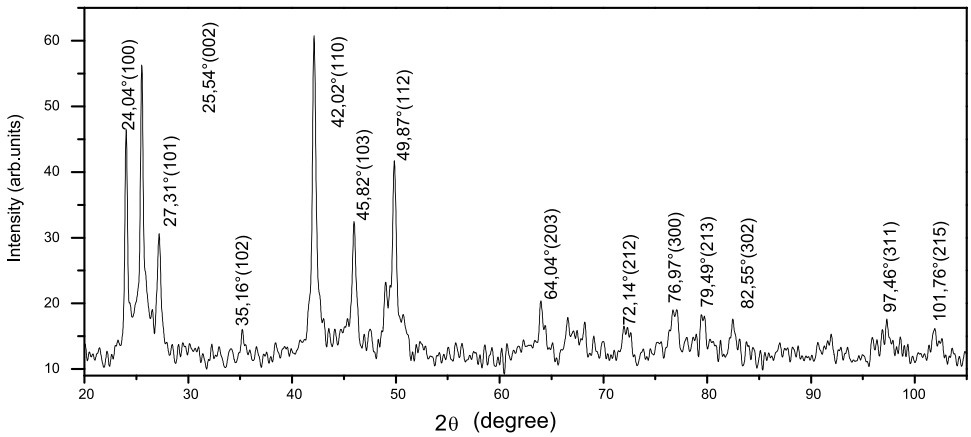

Fig. 2. XRD pattern of the CdSe nanopowder.

[9–15]. On the other hand, KDP crystal is one of the first inorganic materials with nonlinear optical properties [16–18]. It was already used in various laser systems for the generation of the second harmonic, the manufacture of the guide waves, optoelectronic commutations [19,20] In addition, KDP is a dielectric material, where it offers a large window in the UV–vis region with E_g = 7.8 eV and it has a wide range of possible doping impurities [21–25], these properties encourage us to investigate the structural and optical properties of CdSe QDs as bulk defects inside the KDP crystalline matrix.

2. Experimental details

The pure and 1.0 mol % CdSe doped KDP single crystals were grown from aqueous solution by the lowering temperature technique. The homogenous saturated solutions were prepared by mixing the KDP with pure water obtained from bidistillation. The KDP seeds were obtained from the slow evaporation method. To make the solution supersaturated, the temperature of the solutions was raised to 50 °C. At this temperature, the solutions were stirred for 4–5 h to get the homogenous mixture of supersaturated solution. After getting the homogeneous solution, the temperature was slowly decreased to ambient conditions. The obtained KDP single crystals have sizes around 15 × 15 × 60 mm and they display a simple morphology formed by a combination of the prismatic (100) and pyramidal (101) faces (Fig.1). The samples are cut parallel to the faces (100) as pellets with a 3 mm thickness. The faces of these pellets are polished for optical measurements. In order to obtain KDP:CdSe single crystal, the same experimental protocol was used. However, in this time the CdSe QDs were added to the homogenous saturated solutions during the growth process of KDP single crystal.

XRD data were obtained using BRUKER-AXSD8 diffractometer withe Cu radiation (35 kV, 30 mA) and a graphite filter. All the samples were analyzed under the same experimental conditions at room temperature (RT) in the angular range of 20–110° of 2θ, with the scan rate of 0.001°/s. The optical properties were studied using a UV–vis spectrophotometer (Shimadzu, UV-3101). Furthermore, the PL was measured at RT and the samples were excited by an argon laser (ionized light λ_{exc} = 313 nm).

3. Results and discussion

The XRD spectrum of CdSe QDs was presented in Fig. 2. It offers a remarkable broadening of the diffraction peaks due to nano-size of CdSe powder. Furthermore, it is easy to conclude that the CdSe QDs crystallize in hexagonal (wurtzite) with lattice parameters a = 0.4299 nm and c = 0.701 nm, and they have a symmetry of space group ($P6_3mc$) as reported in the JCPDS (08-0459) card. The significant intensities of these peaks indicate the high crystalline quality surface of these crystallites.

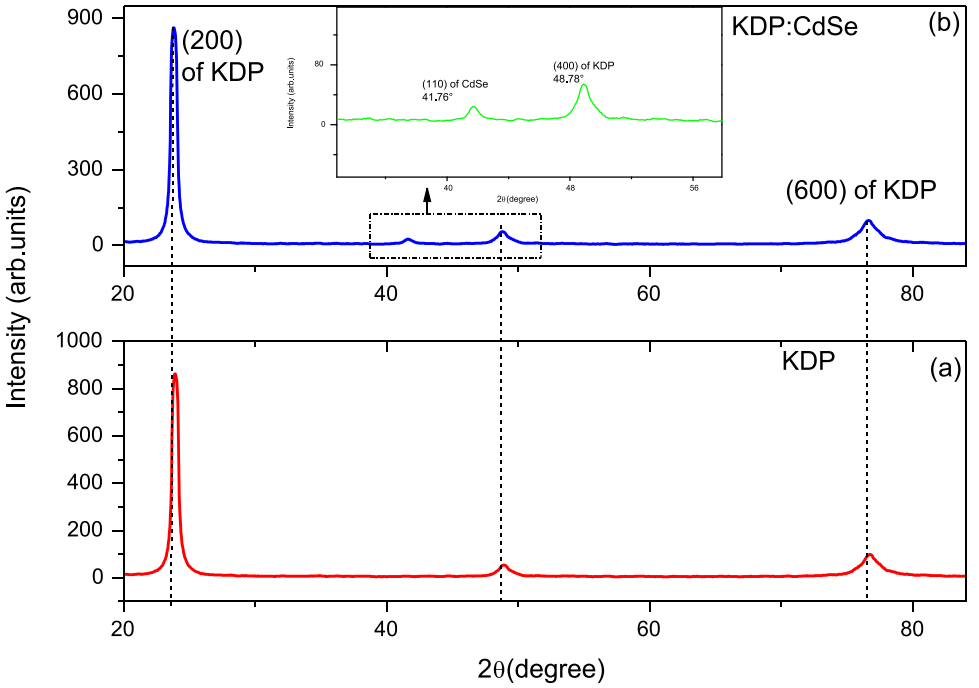

Fig. 3. The XRD pattern of : (a) A KDP single crystal (faces are parallel to the (100) plane) and (b) A KDP:CdSe single crystal (faces are parallel to the (100) plane).

In order to estimate the size of crystallites using Scherer formula, the peaks of the XRD spectrum were fitted by Gaussian function. The size was found to be in 38-72 nm range.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

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.

XRD studies have been performed on samples of pure KDP and KDP:CdSe crystals to determine their crystallographic structure. Fig. 3 (a) displays the XRD spectrum of a pure KDP single crystal, which exhibits three peaks located at $2\theta = 23.92^\circ$, $2\theta = 48.88^\circ$ and $2\theta = 76.72^\circ$. These peaks correspond respectively to the (200) plane and its harmonic (400) and (600). This result indicates that pure KDP crystallize in the tetragonal system with the $I\bar{4}2d$ symmetry space group as reported in the JCPDS (35-0807) card. In addition, it denotes that the sample has a single crystal character with high purity, and confirms that the crystal is cleaved in the direction parallel to the (100) plane.

In Fig. 3 (b), the typical XRD pattern of the KDP:CdSe sample is displayed. Besides the peaks related to the host (KDP), there is a weak peak located at $2\theta = 41.76^\circ$, attributed to the CdSe phase. The other peaks of CdSe are not visible, and this observation indicates that the crystallites of CdSe display preferred direction. On the other hand, this result demonstrates the incorporation of CdSe QDs inside the KDP host and the absence of peaks corresponding to other phases, indicating that there is no chemical reaction between CdSe and KDP. Furthermore, the size of CdSe QDs embedded in KDP is 13.20 nm as derived from Scherer formula. The size of CdSe QDs in KDP host is smaller than the CdSe nanopowder. Due to this feature, we speculate that available conditions in environment of crystal growth contribute to the decomposition process of aggregates of CdSe during the crystal growth of KDP:CdSe single crystal. According to the position of the peaks of host it is interesting to note that the XRD spectra of the KDP:CdSe reveals a shift towards lower angle for the main peaks compared to the main peaks of the pure KDP (see Fig. 3(a) and (b)). This reality indicates a systematic lattice expansion.

The Fig. 4(a) offers the optical absorption of KDP. The spectrum of pure KDP shows a strong absorption near ultraviolet region ($E_g \approx 7.17$ eV). Also, it appears a slight absorption in the visible spectrum due to defects in the KDP single crystal. These defects can be attributed to the hydrogen vacant sites. The same result has been observed by N. Garces et al [26]

On the other hand, on the spectrum of the KDP:CdSe (Fig. 4(b)), we observe two band situated at 625 nm and 460 nm. Suganthi and al [9] have assigned the band located at 625 nm due to the transition band to band. The band which is located at 461.42 nm also found by Frederic [10], this band is attributed to the excitonic transition. The optical band gap E_g of KDP:CdSe sample is determined by the minimum of second derivative method (see Fig. 5 (b)) [27]. We found that E_g equal to 1.98 eV [11]. Cdse exhibits a displacement of the band gap towards high energies. The shift of the band gap ($\Delta E_g = 0.25$ eV) is a result of the quantum confinement of the carriers (electrons and holes) that appears due to reducing of the crystallites size to nano-metric regime.

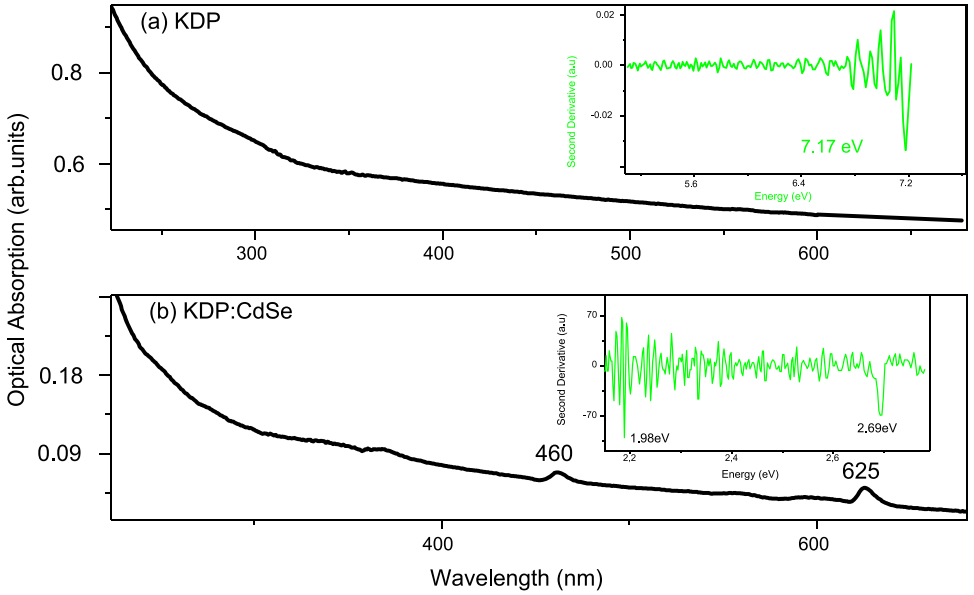

Fig. 4. (a) Optical absorption spectrum of a pure KDP crystal and (b) Optical absorption spectrum of a KDP: CdSe crystal.

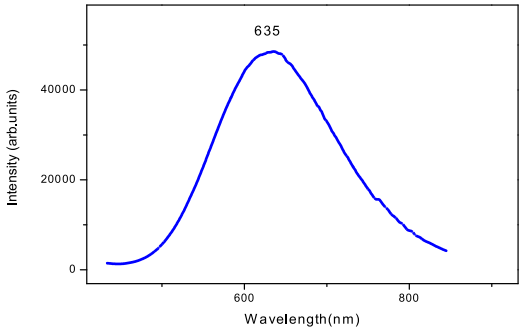

Fig. 5. Photoluminescence spectrum of a KDP:CdSe crystal at RT.

Fig.5 represents the spectrum of photoluminescence of KDP:CdSe at RT excited by wavelength λ_{ext} = 313 nm. The spectrum shows an intense band of emission at 635 nm. X. Zhou et al [28] have obtained this band using λ_{ext} = 631 nm. We also note a shift of the luminescence signal toward lower energies compared to the absorption spectrum. Furthermore, the strong PL intensity from the CdSe QDs embedded in KDP can be attributed to their high crystallization and to their good surface, which is in agreement with the XRD patterns of KDP:CdSe discussed earlier. In addition, the optical characterizations of KDP:CdSe single crystal confirm that the KDP is a suitable host for studying the optical properties of CdSe QDs in the UV–vis range.

4. Conclusion

To reveal clearly the doping effect on the growth and properties of KDP single crystals, the structural characterization by X-ray diffraction confirms the incorporation of CdSe QDs in the KDP single crystals. In other side, optical absorption spectrum of KDP:CdSe single crystal proves that the guest material (CdSe) style has a nano-regime where the band gap shifts toward to the high energy (ΔEg = 0.25 eV). Furthermore, the measurement of PL at RT is so coherent with the presiding results those obtained from XRD and UV–vis absorption, where the PL spectrum appears an intensity band located in 635 nm with a red-shift of the emission band of CdSe QDs in comparison with the absorption spectrum. All these results prove that the CdSe QDs still have nano-regime inside the KDP crystalline host and the elaboration of KDP:CdSe QDs has been achieved.

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