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Structural and optical properties of CdTe nanocrystals embedded in KH_2PO_4 (KDP) dielectric crystal

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In the present work, KH_2PO_4 (KDP) crystals doped with CdTe have been grown in aqueous solution supersaturated at 50°C using the lowering temperature method. X-ray diffraction spectra have shown that CdTe inclusions have been obtained with an average size of about 24nm. The optical gap (E_g=2.85eV) was deduced from the UV-vis absorption spectra. The gap widening compared with bulk CdTe crystals could be due to the nanometric size of CdTe particles (~2nm), revealing the intrinsic quantum confinement effect of these nanocrystals. Nevertheless, following experimental results from structural and optical characterisation the estimation of the CdTe particles size data shows a great dispersion, which must be taking into account. Furthermore, the possibility of embedding II-VI CdTe nanoparticles in KDP crystalline matrix has been proved.

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Keywords: KDP, CdTe nanocrystals, Optical absorption, Dielectric, XRD, UV-vis absorption spectra

1. Introduction

The synthesis and the properties of highly luminescent II-VI semiconductor nanoparticles have been extensively investigated from the basic research point of view to the application field. With the miniaturization of the particles the band gap expands and the energy levels of the core bands shift towards higher binding energy, and subsequently, some physical properties change. Generally the optical properties of crystals become extremely different with miniaturization of size [1]. Nanocrystals (NCs) are having an increasing importance due to their influence in the mechanical, electric, optic and magnetic different properties due to the quantum confinement stimulated by size decreasing [2]. Electron and phonon confinement is possible by II-VI NCs semiconductor when the size of particles tend to Bohr radius of the bulk crystal exciton showing new physical properties. These intriguing phenomena have been found new applications in telecommunication and transmission [3]. Potassium dihydrogenophosphate KH_2PO_4 (KDP) matrix has been recently used as a host of semiconductor CdTe NCs as it is a transparent crystal in the UV-vis region. KDP is a well known dielectric material[4] for its nonlinear optical and electro-optical properties [4, 5] and well suited for frequency conversion [6]. The study of E.Vlieg et al [7] on the interface atomic structure determination of KDP in contact with the growth mother solution using X-ray diffraction at a third generation synchrotron radiation source, determine the structure of both the (101) and (100) faces. They found that the (101) faces are terminated by a layer of K^+ and not by $H_2PO_4^-$ group resolving a longstanding issue that could not be predicted by theory concerning the favorable atomic absorption of cationic impurities on prismatic faces [8]. In the present paper, we describe the results obtained in our study of KDP crystals doped with CdTe by using X-ray diffraction and optical absorption as characterization techniques.

2. Experimental

Pure and doped KDP crystals were grown from aqueous solution by the lowering temperature technique. In doped KDP crystals the dopant was added in the form of CdTe powder. The mother solution was prepared at 50°C following the solubility condition in bidistilated water. KDP seeds grown from slow evaporation method were used. The growth run was carried out in the temperature range 50 to 25°C. KDP crystals present a simple morphology formed by a combination of pyramidal and prismatic faces, which follows the tetragonal structure, as it is shown in Figs. 1 and 2.

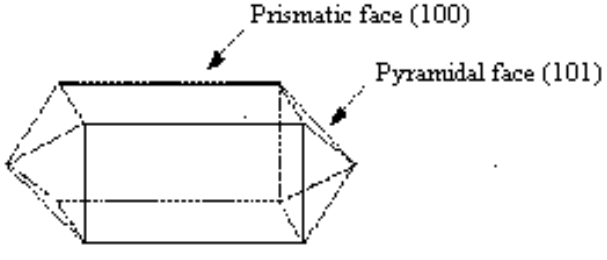

Fig. 1. KDP morphology.

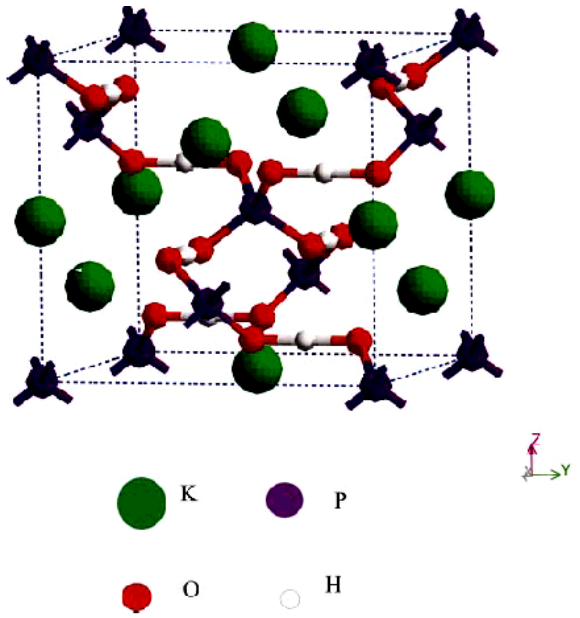

Fig. 2. The tetragonal structure of KDP [9].

X-ray diffraction data were collected using SIEMENS D8 advanced diffractometer ($\lambda_{K\alpha}$= 1.54 Å) and graphite monochromator. Optical absorption data were acquired at room temperature using Shimadzu UV-3101 PC spectrophotometer.

3. Results and discussion

3-1 Structural characterization

Figure 3 shows XRD patterns for KDP: CdTe-sample. The tetragonal KDP diffraction peaks clearly showed up in XRD pattern they coexist with XRD peaks corresponding to the (002), (110) and (201) lattice planes of hexagonal CdTe structure.

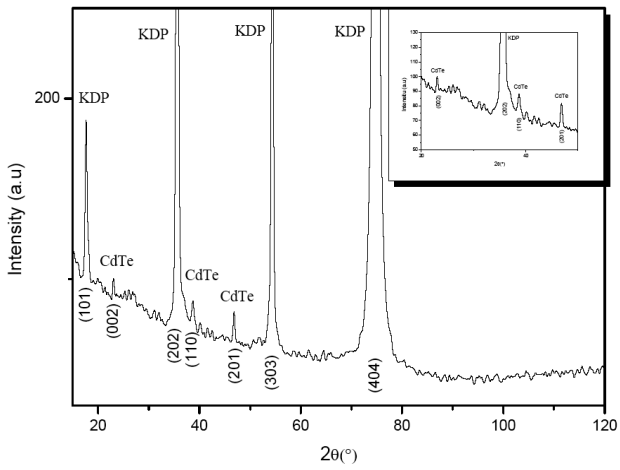

Fig. 3. XRD pattern of KDP doped with CdTe ((101) face).

We noted that CdTe nanocrystals incorporation in KDP matrix proceeds in different orientation. Based on Scherer's formula applied to X-ray diffraction patterns we assume that the shape of the nanocrystals embedded in KDP matrix were spherical. In order to determine the size of the CdTe-NCs we have calculated the FWHM (full width at half maximum) at different orientation of respectively 0.28, 0.45 and 0.36°. The corresponding diameters of these orientations are respectively 28.31, 18.37 and 24.37 nm, with an average size of about 24nm. We note that Scherrer formula is not a strict quantitative method to calculate particles size, however it help for choice of the better elaborated samples. In addition, we note a contraction along the $\vec{a}$ direction of CdTe unit cell (a=3.29Å compared with a $_{(bulk)}$ =4.58Å; and c=7.74Å compared with c $_{(bulk)}$ =7.5Å). The contraction of the unit cell could be the result of the nanometric size of CdTe particles which induce a surface relaxation.

3-2 Optical properties

Fig. 4 presents the optical absorption spectrum of pure KDP showing a transparence absorption in the UV-Visible region, with the band absorption gap near UV region due to KDP intrinsic structure defects.

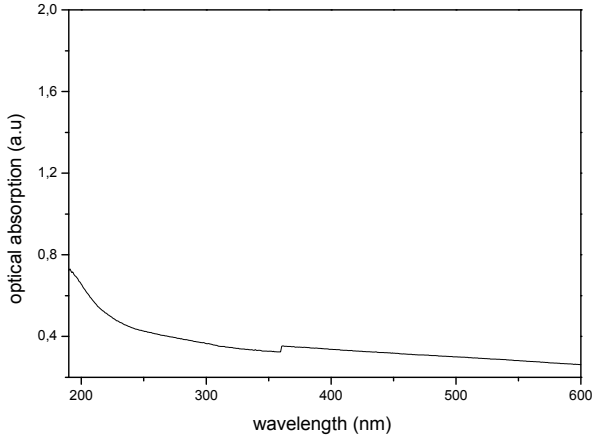

Fig. 4. UV-Visible absorption spectrum of pure KDP.

Nevertheless, for KDP: CdTe-NCs samples, the optical absorption spectrum is presented on Figure 5 which shows the presence of an intense 270-nm optical band typical of some impurity, plus other small band situated at 462 nm. The 270nm band was published by several authors to be due to Fe impurities in KDP crystals [10-13]. Ryabov et al [11] attributed this band to optical transitions in color centers based on a hydrogen vacancy. Furthermore, the 462nm band can be attributed to the optical response of CdTe nanocrystals incorporated in KDP crystalline matrix, showing a blue-shift of fundamental absorption edge to shorter wavelength due to quantum confinement effect.

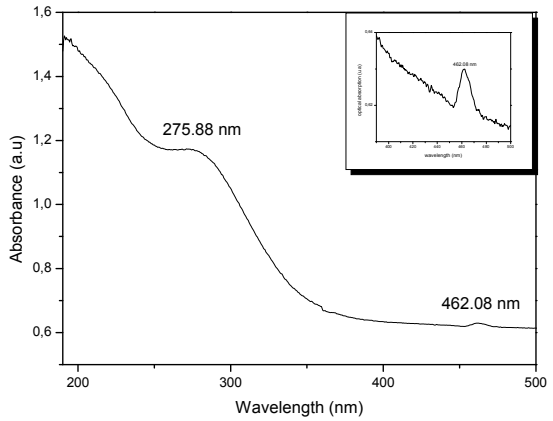

Fig. 5. UV-Visible absorption spectrum of KDP doped with CdTe.

We may calculate the size of CdTe NCs using Brus's formula [14]:

$$E(R) = E_g + \frac{\hbar^2 \pi^2}{2\mu R^2} - \frac{1.786 e^2}{\varepsilon R}$$

Where E(R) is the optical gap of CdTe NCs, R is the radius of particles, being E_g the bulk gap (E_g (CdTe) =1.56eV), μ the effective mass (m_e^*= $0.11\, m_e$, m_h^*=$0.48\, m_e$, μ= $0.085\, m_e$), ε_r the optical relative dielectric constant (ε_r (CdTe) =10.2).

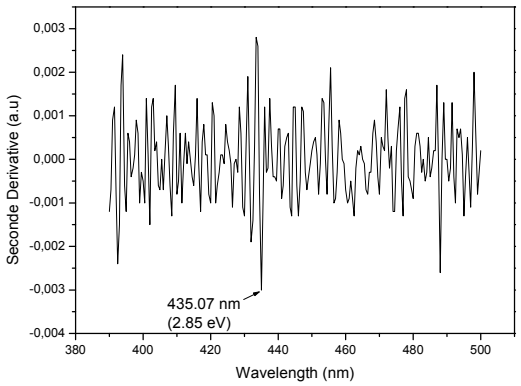

Fig. 6. Second derivative of optical absorption of KDP doped with CdTe.

In order to get a better accuracy of the optical gap of CdTe nanocrystals, it was determined from the second and not from the zero derivatives of optical absorption spectra E_o= 2.85 eV. We indicate a blue-shift of optical absorption band of CdTe nanocrystals due to reducing of size. Using Brus's formula the average radius was R (CdTe) ~ 2 nm.

4. Conclusion

Structural characterization by using X-ray diffraction indicates the incorporation of CdTe nanocrystals in the host matrix of KDP. UV-Vis absorption spectra reveal the band indicating impurity of KDP. It's proposed that the large blue shift of the band gap of CdTe NCs from 1.56 eV (bulk) to 2.85 eV (CdTe ~ 2 nm size) reveals the intrinsic quantum confinement effect of these nanocrystals. In this work we have proved the existence of CdTe nanoparticles embedded in KDP crystalline matrix. Nevertheless, in order the accurately determine the size of CdTe nanoparticles further TEM (transmission electronic microscopy) or SNOM (scanning near-field optical spectroscopy) have to be carried out.

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