CdTe aggregates in KBr crystalline matrix

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ABSTRACT

In this work, we report the experimental results on the fabrication and optical characterization of Czochralski (Cz) grown KBr single crystals doped with CdTe crystallites. The results of the optical absorption have shown two bands, the first one located at 250 nm demonstrates the incorporation of cadmium atoms in the KBr host followed by a partial chemical decomposition of CdTe, the second band located at 585 nm shows an optical response of CdTe aggregates. Photoluminescence spectra at room temperature before annealing showed a band located at 520 nm (2.38 eV), with a blue shift from the bulk gap of 0.82 eV (E_g (CdTe) = 1.56 eV). While the photoluminescence spectra after annealing at 600 °C showed a band situated at 640 nm (1.93 eV), these bands are due to band-to-band transitions of CdTe nanocrystals with a blue shift from the bulk gap at 0.38 eV. Blue shift in optical absorption and photoluminescence spectra confirm nanometric size of dopant. X-ray diffraction (XRD) spectra have shown the incorporation of CdTe aggregates in KBr.

1. Introduction

The nanocrystals are supermolecules with nanometric size, arranged periodically in three directions of space. From the technological point of view, the main motivations for studying nanomaterials is to search new applications by controlling their physical properties as a function of size. This is the subject of some specific fields such as electronics and integrated optics. One of the most important parameter in nanomaterials is their size and not the exact number of atoms. This is due to the fact that it is from a critical size where the physical and chemical properties of these particles dramatically change, as the effect of surface atoms dominates. This justifies the efforts of many theoreticians to develop models (the effective mass, the jellium model, the drop-liquid and surface relaxation model..., studying electronic structure of nanoparticles) based on two approaches (bottom-up and top-down) [1,2]. There is a little research on nanocrystals embedded in crystalline lattices. In the case of alkali halides, we have been successful in embedding ZnO nanocrystals in KBr crystals [3]. Samah et al. [4–9] have analysed alkali halides (KBr, NaCl) doped with II–VI and I–VIII semiconductors like ZnO, CuBr and CuCl.

CdTe is an interesting material with technologically important physical properties, used to produce various high-performance electro-optical and infrared detectors. It is also used in medical imaging [10,11]. It is a direct-gap semiconductor being 1.56 eV at room temperature, allowing vertical transitions between the valence and conduction bands and therefore presenting radiative transitions. Its exciton Bohr radius a_B is 65 Å. CdTe has the largest exciton Bohr radius amongst all the II–VI semiconductors which are already grown as micro-crystallites. Therefore, quantum confinement effects can occur even in the case of large size micro-crystallites [12]. These properties make CdTe a very interesting material for application in optoelectronics [13,14].

The aim of this work is to isolate CdTe nanocrystals in a KBr crystalline lattice, which is a dielectric material, and transparent in the visible and near-ultraviolet range, which is the range of optical response of CdTe nanocrystals. The optical properties of KBr samples have been studied by using optical absorption and photoluminescence. Structural analysis has been studied using X-ray diffraction.

2. Experimental

KBr is optically transparent in the spectral range covering the visible and near-ultraviolet, so it can be used for studying the optical properties of CdTe nanocrystals in the visible region of the electromagnetic spectrum. The samples were prepared in Crystal Growth Laboratory at the University of Autonoma de Madrid by using Czochralski (Cz) technique. CdTe powder added to KBr (0.5% mol) has been obtained by mechanical grinding. The Cz technique in this work is carried out by a standard Czochralski

chamber under N_2 flow (inert atmosphere), a combination of translation and rotation motion of the seed holder are controlled by changing their speeds according to our crystal growth conditions. The crystal obtained is shown in Fig. 1 (wafers studied in this work are named b, d, f and h). Several wafers were cut perpendicular to the growth axis. After polishing the obtained samples were characterized by optical absorption, photoluminescence and X-ray diffraction.

The optical absorption measurements were carried out by using a spectrophotometer type Shimadzu UV-3101 PC. Room temperature emission spectra were recorded by using a Perkin-Elmer LS 50B luminescence spectrometer. The crystal holder was located at a suitable angle with respect to the excitation beam in order to optimize the fluorescence signal and minimize the scattered incident light. The spectra were corrected considering the wavelength-dependent detection efficiency using the correction curve delivered by the spectrometer supplier. X-ray diffraction data were collected using BRUKER-AXS D8 diffractometer ($\lambda_{K\alpha} = 1.54$ Å) and graphite monochromator.
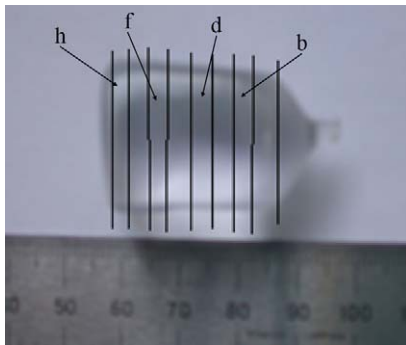

Fig. 1. Photograph of KBr:CdTe: 0.5% mol, (wafers b, d, f and h).

3. Results and discussion

Fig. 2 shows optical absorption spectra before and after annealing of samples named b, d, f and h (Fig. 1). Most of the samples reveal the existence of the 250 nm band due to incorporation of cadmium atoms in KBr matrix revealing the chemical decomposition of CdTe. According to Jain and Radhakrishna [15], Cd-doped KBr introduces several optical absorption bands in UV region. We have also observed a optical absorption band peaking at 250 nm. We associate this band to cadmium incorporation in KBr matrix. This result reveals CdTe chemical decomposition.

Sample b has no significant annealing effect, sample d shows the appearance of a new band located at 270 nm. We also attribute this band to the incorporation of cadmium atoms in KBr lattice. Two bands located at 255 and 585 nm, respectively, appear in sample f. The first band is due to cadmium incorporation in KBr, but the second band reveals the existence of CdTe nanoparticles. Sample f presents macroscopic defects (fissures) with some dark clusters around this defect. These results confirm the existence of CdTe nanoparticles in the KBr host. This defect is due to an annealing effect. During the thermal treatment, the existing aggregates undergo a re-crystallisation resulting in increasing size due to stress effects on the KBr matrix. In our case, the formation of macroscopic defects in KBr allow the diffusion of CdTe aggregates around this region, resulting in a significant absorption band situated at 585 nm. Sample h shows only one band located at 255 nm. The coexistence of Cd and CdTe optical responses in the KBr host confirms the partial chemical decomposition of CdTe during the growth process. However, their concentration is so low in samples named (b, d and h) that their optical response lies below the detection limit of our UV–visible spectrophotometer. In Fig. 4, a well-resolved absorption shoulder is observed associated to the first electronic transition in CdTe aggregates, thus we can calculate the optical gap from the zero derivative and not from first or second derivative. The widening of
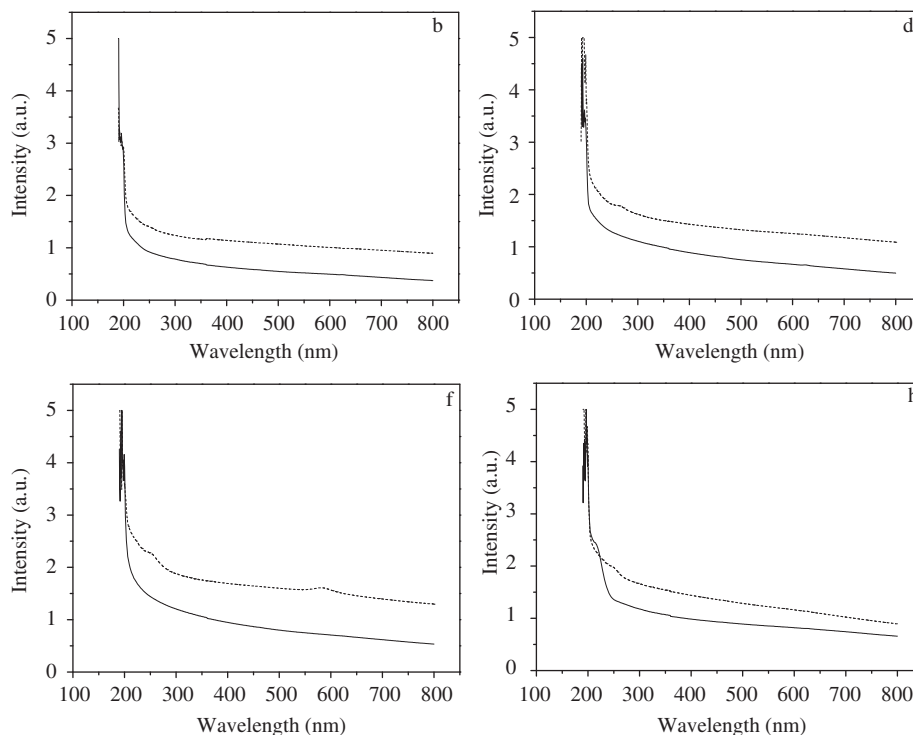

Fig. 2. Optical absorption spectra of KBr:CdTe wafers (named b, d, f and h) 0.5% mol before (solid line) and after annealing (dashed line) at 600 °C (12 h).
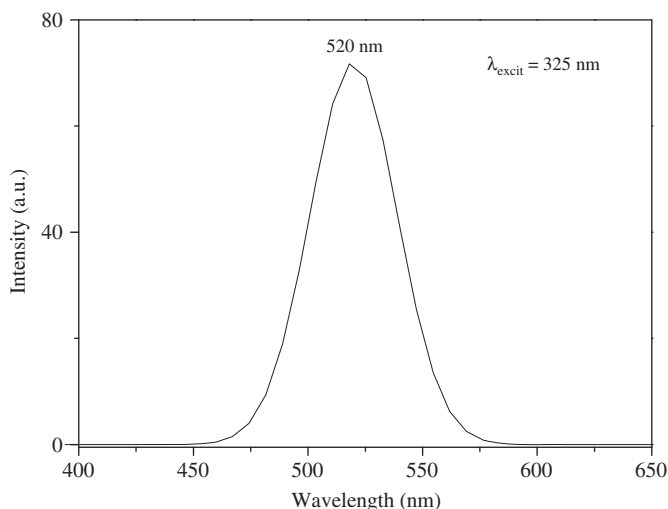
Fig. 3. Room-temperature photoluminescence spectrum of KBr:CdTe (sample f) before annealing.
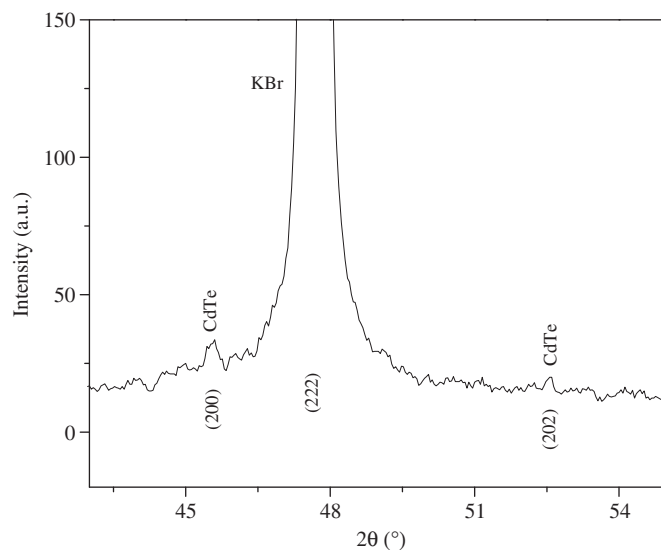

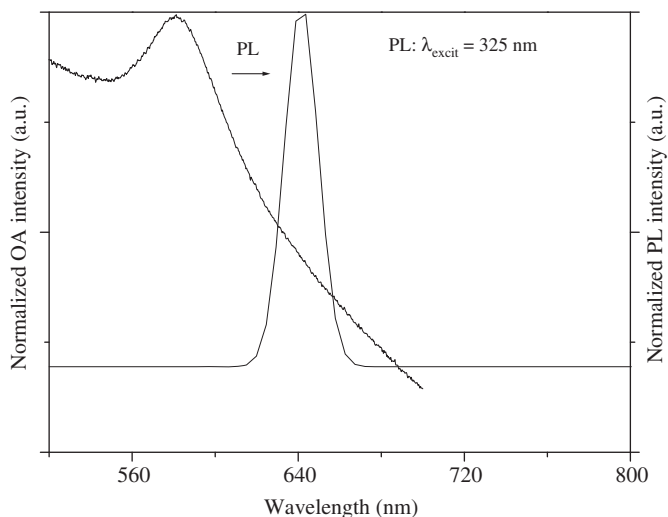**Fig. 5.** X-ray diffraction pattern of KBr:CdTe.

Fig. 4. Room-temperature emission and absorption normalized spectra of KBr:CdTe (sample f) after annealing at 600 °C (12 h).

this band reveals the existence of a strong size dispersion of CdTe crystallites in KBr matrix. We may calculate the size of CdTe nanocrystals using Brus's formula [16]

$$E(R) = E_g + \frac{\hbar^2 \pi^2}{2\mu R^2} - \frac{1.786 e^2}{\varepsilon R} \qquad (1)$$

where $E(R)$ is the optical gap of CdTe nanocrystals, R the radius of particles, being E_g the bulk gap (E_g (CdTe) = 1.56 eV), μ the effective mass ($m^*_e = 0.11 m_e$, $m^*_h = 0.48 m_e$, $\mu = 0.085 m_e$) and ε_r the optical relative dielectric constant (ε_r (CdTe) = 10.2). The optical gap of CdTe nanocrystals is 2.12 eV (585 nm). We observe a blue shift of optical absorption band around 0.56 eV due to nanometric size of particles. Using Brus's formula, the average radius was R (CdTe) ~4 nm.

Fig. 3 shows the emission spectrum of sample named f before annealing at room temperature, showing a luminescence band located at 520 nm (2.38 eV, $\Delta E = 0.82$ eV: blue shift from E_g (bulk) of CdTe). We assign this band to band to band transitions. These results prove the existence of CdTe nanoparticles in KBr matrix. Fig. 4 shows the normalized emission spectrum from sample f after annealing at 600 °C during 12 h, showing a luminescence

band located at 640 nm (1.94 eV, $\Delta E = 0.38$ eV: blue shift from E_g (bulk) of CdTe). Due to the size increasing of the CdTe aggregates during temperature treatment, this band is shifted to the red compared to PL spectrum before annealing.

These results show optical emission of our samples, nevertheless we have proved an undesirable chemical decomposition of CdTe due to high-temperature effect; which inform us that KBr is not the most appropriate for isolating CdTe nanoparticles and redirecting us to ADT measurements in order to study chemical decomposition of CdTe and simultaneously; using other semiconductors doping, which cannot be influenced by temperature effect, to control the optical properties of the synthesized composite after aggregates embedding in KBr crystalline matrix.

Fig. 5 presents X-ray diffraction patterns for KBr: CdTe sample. The cubic KBr diffraction peak clearly showed up in XRD patterns. They coexist with XRD peaks corresponding to the (2 0 0) and (2 0 2) lattice planes of hexagonal CdTe structure. Therefore, X-ray diffraction results also confirm the embedding of CdTe nanocrystals in KBr matrix.

4. Conclusion

In this work, we have grown KBr:CdTe crystals by using Czochralski technique. Optical absorption results confirm a partial chemical decomposition of CdTe showing two absorption bands at 250 and 585 nm, revealing, respectively, Cd and CdTe incorporation in the KBr lattice. Photoluminescence spectra at room temperature after annealing show a luminescence band located at 640 nm (1.94 eV, $\Delta E = 0.38$ eV: blue shift from E_g (bulk) of CdTe), due to size increasing of CdTe aggregates during temperature treatment. This band is shifted to the red compared to PL spectrum before annealing. KBr is not the most appropriate for isolating CdTe nanoparticles due to CdTe chemical decomposition. ADT measurements are being currently developed in order to study the partial chemical decomposition of CdTe. X-ray diffraction patterns also confirm CdTe incorporation in the KBr lattice.

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