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Optical and structural characterization of KBr crystals doped cadmium bromide (CdBr₂)

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ABSTRACT

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Keywords: KBr Czochralski technique CdBr₂ aggregates Optical absorption Photoluminescence In this paper we demonstrate the presence of CdBr₂ and cadmium aggregates in KBr matrix during Czochralski growth of KBr crystals. The chemical decomposition of CdBr₂ due to high temperature of crystallisation and reformation of cadmium bromide seems to be responsible for this effect. © 2009 Elsevier B.V. All rights reserved.

1. Introduction

Cadmium bromide is known as a photochromic crystal and is widely used as window for Infrared applications [1–4]. It crystallises in the CdCl₂ type structure with the space group D_{3d}^5 belonging to the divalent metal halide crystals with layer structure [5,6]. The alkali halides are characterized by an extended transparency domain that extends from the far ultraviolet to the far infrared [7] in which the optical absorption and emission of defects of the lattice are easily detected and studied. Formation of extrinsic punctual defects is stimulated by doping, and their easy studying in UV-visible region is due to KBr transparency. KBr:CdBr₂ crystals were grown by the Czochralski technique, under N₂ flow in order to avoid the presence of oxygen-containing ion emission bands. The aim of this work is to study the in-situ formation of CdBr₂ aggregates during the crystal growth after chemical decomposition of cadmium bromide induced by the crystallisation process at high temperature. The optical properties of KBr:CdBr₂ samples have been studied by using optical absorption and photoluminescence. Structural analysis has been studied using X-ray diffraction.

2. Experimental

The samples were prepared in Crystal Growth Laboratory at the University of Autonoma de Madrid by using Czochralski (Cz) under nitrogen flux. High purity (4 N) CdBr₂ powder was added to 4 N KBr starting material. Two different CdBr₂ concentrations have been tried (0.1 and 0.5 mol%). The final mixtures were obtained by standard mechanical grinding. 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 a BRUKER-AXS D8 diffractometer ($\lambda_{K\alpha}$ =1.54 Å) and a graphite monochromator.

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3. Results and discussion

In order to start KBr samples characterisation optical absorption measurements were carried out in the three crystals (pure,

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Fig. 1. Optical absorption spectra of pure KBr.



Fig. 2. Optical absorption spectra of $KBr:CdBr_2$ wafers (named b, d, f, h, j and k) 0.1 mol%.

0.1% and 0.5 mol%). The collected spectra from different crystals are shown in Figs. 1–3. An absorption band peaking at 250 nm can be clearly observed in the sample with the highest initial $CdBr_2$ content (0.5 mol%). We attribute this band to the incorporation of the dopant Cd to the KBr matrix.

According to Jain et al. [8], such band in Cd-doped KBr crystals is due to cadmium incorporation. Nevertheless, the figure shows the transparency of pure KBr in the region [240–800 nm]. We note optical absorption of KBr in the region [190–240 nm]; the absorption band peaking at 215 nm is due to U centers (H^- ions) [9].

We have also performed PL measurements at room temperature. The corresponding PL spectra corresponding to both crystals are shown in Figs. 4–6.

PL spectrum of pure KBr at room temperature (λ_{excit} =264 nm) shows emission bands in the UV–visible located at 308, 322, 350, 372, 409 and 472 nm. According to Günter Gummer [10] and Zehani and Sebais [11], emission bands of KBr grown under oxygen atmosphere in UV–visible region except for the band located at 372 nm are due to the (O^{2–} – F⁺) centers in the region < 400 nm and attributed to O₂⁻ centers above 400 nm [12,13]. Correlation with intrinsic luminescence properties of alkali halides leads to the assignment of the 375 nm band to emission



Fig. 3. Optical absorption spectra of KBr:CdBr $_2$ wafers (named b, d, f, i, k, m, o, q, u and w) 0.5 mol%.



Fig. 4. Room temperature PL spectrum of pure KBr.



Fig. 5. Room temperature PL spectrum of KBr:CdBr₂ 0.1 mol%.



Fig. 6. Room temperature PL spectrum of KBr:CdBr₂ 0.5 mol%.

from Br_2^{2-} centers [14]. In order to confirm this hypothesis EPR measurements are necessary.

The PL spectrum of KBr:CdBr₂ 0.1 mol% shows that doping by CdBr₂ influences the emission intensity (decreasing), a few other band emissions disappear. The most intense band, located at 409 nm, indicates that the mechanism of creation of O_2^- centers is dominant. The PL spectrum of KBr:CdBr₂ 0.5 mol% shows that the intensity of the bands situated at 375 and 308 nm has dramatically been increased in the more concentrated crystal compared to the intensity of the band located at 409 nm. This result is due, respectively, to increasing concentration of Br_2^{2-} centers stimulated by high concentration of CdBr₂ dopage and ($O^{2-}-F^+$) centers formed by transformation at high temperature of O_2^- centers in the presence of F centers to ($O^{2-}-F^+$):

$$0_{2}^{-}+2F \rightarrow 2(0^{2-}-F^{+})$$

The most intense band located at 375 nm indicates that the mechanism of creation of Br_2^{2-} centers is dominant.

Our crystals are fabricated by the Cz technique proceeding by vacuum and N₂ flow; nevertheless we note the existence of U and O_2^- centers. Intrinsic H₂O in starting materials seems to be the origin of these centers. In addition, according to Mehendru and Radhakrishna [15] the presence of Cd impurity in KBr suppresses the formation of $(O^{2-} - F^+)$ centers. After comparison of our spectra with Zehani and Sebais [11] results we note the very low intensity of our emission bands information on the low concentration of color centers in our samples.

In order to get further information about these results, XRD measurements were performed on these samples. The spectrum obtained from a sample from pure KBr, 0.1 and 0.5 mol% crystal is shown, respectively, in Figs. 7–9.

KBr diffraction peaks are clearly shown in the XRD pattern. They coexist with XRD peaks of hexagonal cadmium and rhombohedral cadmium bromide structures. We note that incorporation of these aggregates in KBr matrix proceeds in different orientations. Based on Scherer's formula applied to X-ray diffraction patterns we assume that the shape of the nanocrystals embedded in KDP matrix was spherical. In order to determine the size of the CdTe-NCs we calculated the FWHM (full-width at halfmaximum) at different orientations. The average size of CdBr₂ in 0.1% and 0.5% crystals was, respectively, 36 and 44 nm. The results of Jain and Radhakrishna [8] on KBr:Cd showed that colloids of Cd metal are formed when additively colored Cd-doped



Fig. 7. XRD spectrum of pure KBr.









crystals of KBr are heated at around 600 °C. In our work we have confirmed chemical decomposition of $CdBr_2$ due to the high-temperature effect and reformation of $CdBr_2$ aggregates, and formation of cadmium crystallites. The average size of Cd in 0.1 and 0.5 mol% crystals was, respectively, 38 and 54 nm.

4. Conclusions

We have analysed the optical and structural properties of CdBr₂-doped KBr crystals grown by the Czochralski technique. The optical absorption measurements show the 250 nm absorption band due to cadmium incorporation in KBr, which confirms the chemical decomposition of CdBr₂. Preliminary PL measurements demonstrate that the mechanism of creation of Br²₂⁻ centers is dominant in a higher concentration of doping. These results must be verified by EPR measurements and PL analysis at low temperature. Regarding the X-ray diffraction spectra, the appearance of new diffraction peaks different from KBr, CdBr₂ has been demonstrated. This feature confirms the formation of crystallites of cadmium.

Acknowledgments

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