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Elaboration and study of structural and optical properties of AuBr nanocrystals dispersed in KBr single crystals

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Abstract: The structural and optical properties of the AuBr nanocrystals embedded in the KBr single crystals grown by the Czochralski method were studied using several techniques. The X-ray diffraction reveals their formation and incorporation. The crystallite average radii calculated from XRD using the Scherrer's formula was found to vary between 19 and 39 nm. The photoluminescence spectra obtained on these same samples present an emission band located at 1.91 eV (650 nm), which can be attributed to the orange luminescence of AuBr nanocrystals. However, the photoluminescence excitation measurements of these nanocrystals exhibit an excitation band located at 3.44 eV (360 nm), slightly shifted towards higher energies in comparison with the massive crystal.

Key words: AuBr, nanocrystals, semiconductors, optical properties, structural properties

1. Introduction

Nanocrystals are the materials placed, according to their size between massive materials and molecular clusters. The interest in nanomaterials can be explained by their applications in technology such as nanoelectronics. On the other hand, dramatic changes of their properties as a function of size, very motivating for fundamental research, make them very promising for industrial applications.

Semiconductor based nanocrystals are among the most interesting nanocrystals because of their electronic properties and particularly their optical properties, which are strongly influenced by the transformation of their morphology on a nanometric scale. Indeed, increasing the energy band gap, as a result of quantum confinement effect, is attributed to a reduction in the nanocrystals size [1–4].

In the last years, much work has been devoted to nanocrystals incorporated in some dielectric matrices with a broad band gap like glass and alkali halides, which present stabilizing dots well adapted to the manufacturing devices [1–3,5,6].

Moreover, many researchers have works on copper halides (CuCl, CuBr, CuI) [5,6]. Nevertheless, gold halides were the subject of few studies $[7-11]$. AuBr is one of the interesting materials belonging to the family of gold halide semiconductors. The optical properties of this material were studied by Bobin et al. and others in the temperature range $293-140$ K [9]. They found that AuBr presents three absorption bands located at 4.87, 3.35, and 2.97 eV and three emission bands at 2.82, $1.65-1.55$, and 2.03-1.91 eV, respectively. These absorption and emission bands depend on the temperature. Crystallographic structures of AuBr were discovered

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by E.M.W. Janssen and G.A. Wiegers [12,13]. They show that AuBr crystallizes in four forms: I-AuBr (centered tetragonal), P-AuBr (simple tetragonal), BCC-AuBr (body centered cubic), and α-AuBr (the structure of α-AuBr is tetragonal and it is unknown). These forms illustrate two different structures: tetragonal and centered cubic during the AuBr phase transition.

In this paper, we shall focus on the elaboration, with the Czochralski method, of nanocrystals of gold bromide (AuBr) incorporated in single crystals of KBr. The nanocrystals were then characterized by X-ray diffraction and photoluminescence.

2. Materials and methods

The KBr single crystals doped with AuBr nanocrystals are obtained through to the following four steps:

1. Elaboration of pure KBr single crystals from the Czochralski method. The growth of the crystals follows the direction (100).

2. Cleavage of pure KBr single crystals: the obtained single crystals are cylindrical. They crystallize in the cubic system whose Bravais lattice is cubic with centered faces (NaCl structure). They cleave easily parallel to the plane (100). Thus, making it possible to obtain pastilles with faces perpendicular to the direction [100], with an approximate thickness of 2 mm.

3. Deposits of thin films of gold on pure cleaved pastilles of pure KBr (Au/KBr) using the vacuum thermal evaporation technique.

4. Elaboration of KBr single crystals doped with AuBr: The gold thin films aggregates separate when they are subjected to a heat treatment. This allows gold atoms to react with the bromide of KBr and form the AuBr (gold bromide) semiconductor material. Based on this phenomenon, our KBr single crystals doped with AuBr were prepared from the melting of the cleaved pastilles (Au/KBr) using the Czochralski method. The crystals obtained are then cleaved, for the second time, into several samples with a thickness of 1 mm.

X-ray diffraction (XRD) analyses were performed using a Bruker Advanced D8 diffractometer. The incident X-ray beam originates from a copper anticathode, it consists of a radiation with $\lambda k\alpha = 1.54056$ Å. It is supplied by a stabilized generator operating at a voltage of 40 kV with a current intensity of 40 mA in the range 2θ of 10-90°. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured at room temperature using a Jobin-Yvon spectrofluorometer Fluorolog-3. A Xenon lamp (450 W) was used as the excitation source.

3. Results and discussion

3.1. X-ray diffraction

The structural characterization of KBr single crystals doped with AuBr nanocrystals, was used to study the chemical nature, crystalline quality, size and orientation of nanocrystals dispersed in the crystalline matrix.

Figure 1 represents the X-ray diffractogram obtained starting from the reference pure single crystals of KBr. It clearly shows good crystallization of the elaborated single crystals, presenting only three peaks of diffraction located at 27.07, 55.83 and 89.03°. These three peaks correspond to the harmonic reflections of the planes (200), (400) and (600), respectively, identified using the file Number 36-1477 of Joint Committeed on Powder Diffraction Standards (JCPDS).

The X-ray diffractogram of KBr single crystal doped with AuBr nanocrystals is illustrated in Figure 2. The presence of three harmonic peaks of KBr and the appearance of six weak peaks comparing with those of KBr, located at 26.627°, 38.579°, 45.579°, 47.721°, 62.971°, and 69.834° were revealed. Respectively, these peaks are assigned to the lines (112), (004), (312), (204) and (413) of AuBr tetragonal structure with a symmetry group $I4_1/amd$; this agrees with the literature data of JCPDS card 01-083-2164. However, the last peak was attributed to the plane (224) of the simple tetragonal structure of AuBr characterized by the space group $P4_2/ncm$, in accordance with the JCPDS card 01-083-2165.

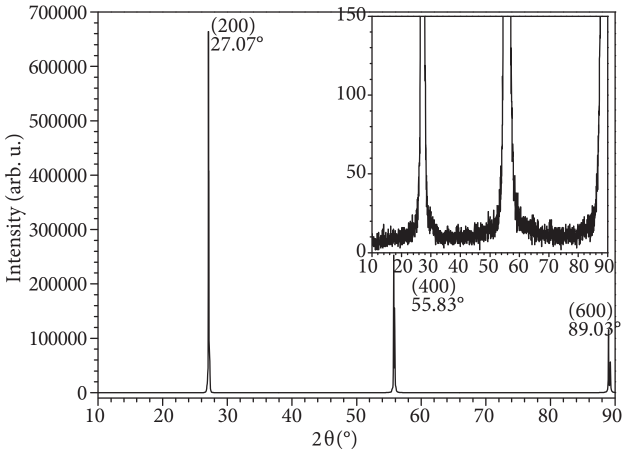

Figure 1. X-ray diffractogram of pure KBr single crystals.

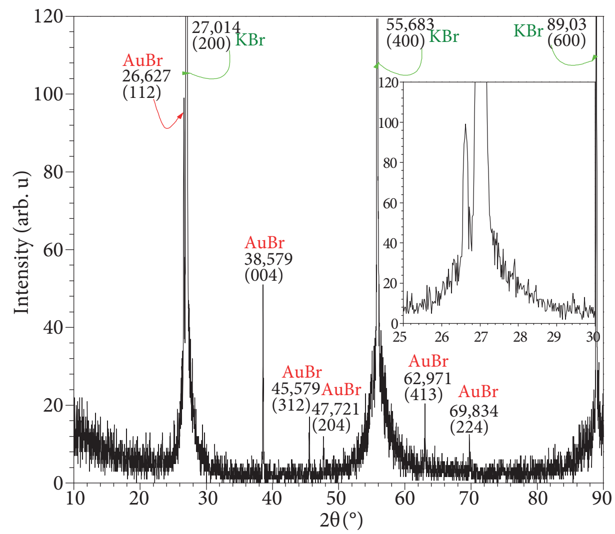

Figure 2. X-ray diffractogram of KBr single crystals doped AuBr nanocrystals.

This result suggests the formation and the incorporation of AuBr nanocrystals inside the KBr matrix. It was noted, also, a slight variation in the angular diffraction positions of AuBr nanocrystals compared to those reported in the card of JCPDS (Table 1). This shift is due to the effects of the stresses exerted by the KBr matrix on the AuBr crystallites. Moreover, it was observed that in spite of the introduction of the AuBr nanocrystals, the KBr crystal maintained its single crystal character. It was noticed, also, the total absence of impurity peaks of any secondary phase such as $AuBr_3$ (JCPDS card 00-027-0667).

Table 1. Average radii of AuBr inside KBr.

2θ (°)	(hkl)	Δ (°)	$2\theta_{th}$ (°)	$\Delta(2\theta)$ (°)	R (nm)
26.627	(112)	0.14526	26.437	0.19	28.09
38.579	(004)	0.10703	38.906	0.327	39.3
45.579	(312)	0.11305	45.721	0.142	38.36
47.721	(204)	0.11316	47.186	0.535	38
62.971	(413)	0.16154	62.848	0.123	28.82
69.834	(224)	0.24946	69.577	0.064	19.41

3.2. Calculation of the average radii of AuBr nanocrystals

The estimation of the average radii of AuBr included in the KBr matrix was made using Scherrer's formula [10,11]. The peaks of the X-ray diffractogram have been fitted by Gaussian functions. Considering that the nanocrystals have a spherical form, the average radius (R) of AuBr nanocrystals is given by the following relation:

$$D = 2R = \frac{0.9\lambda}{\Delta(rad)\cos\theta} = \frac{0.9\,\times\lambda\times 180}{\Delta(°)\times\pi\times\,\cos\theta}$$

where:

D is the average diameter of the nanocrystals,

λ is the wavelength of the X-ray radiation,

θ is the diffraction angle,

Δ is the full-width at half-maximum (FWHM) of the peak.

The computation results are given in Table1.

In conclusion, the nanocrystals of AuBr in KBr matrix have various sizes within the resolution limit of the used measurement technique.

3.3. Calculation of the parameters *a* and *c* of AuBr nanocrystals

A small displacement in the angular position of the AuBr diffraction peaks compared with those indicated in the card of JCPDS, was observed. In this section, the new parameters of AuBr will be determined, using the Bragg condition and the relation of the interreticular distance d of the tetragonal system [14]. The a and c values of AuBr are given in Table 2.

Table 2. Calculation of parameters a and c of AuBr inside KBr.

2θ (°)	(hkl)	a (Å)	c (Å)	a_{th} (Å)	c_{th} (Å)	Δa (Å)	Δc (Å)
38.579	(004)	6.6	9.327	6.94	9.252	0.34	0.075
47.721	(204)						

Comparing the theoretical values of the parameters a_{th} and c_{th} of AuBr given on JCPDS card, clearly, shows that there is a small variation. It is deduced that the constraints exerted by both lattices of KBr and AuBr cause a reduction in the parameter a and an increase in the parameter c.

4. Optical properties

To show the effect of size on the optical properties of AuBr nanocrystals, dispersed in KBr single crystals, optical measurements have been performed using photoluminescence (PL) and photoluminescence excitation (PLE) spectra at the ambient temperature.

The PL spectra obtained for pure KBr and KBr doped with AuBr excited in the wavelength range 330–370 nm, are shown in Figures 3 and 4, respectively. For pure KBr, we have a broad emission band between 400 and 500 nm, which is probably allotted to the color centers [15,16], while for KBr doped with AuBr, Figure 4 shows, in addition to the broad emission band attributed to color centers, a new broad emission band centered on 650 nm (1.91 eV). This band is assigned to the orange luminescence of the AuBr semiconductor [9]. The widening of this emission band is due to the great range in the nanocrystals sizes (Table 1) [1–4].

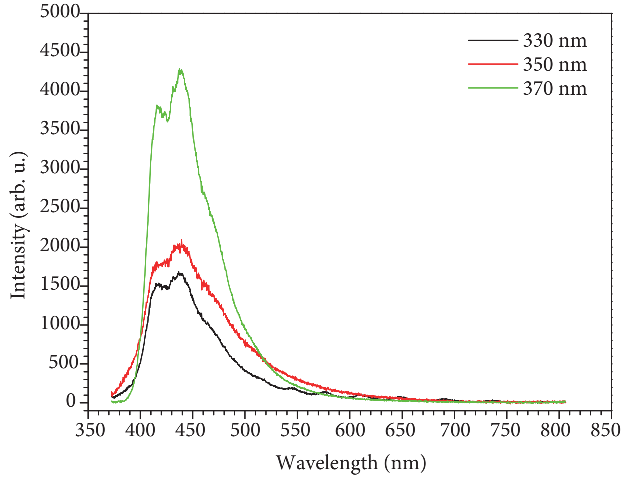

Figure 3. Emission spectra of pure KBr excited between 330-370 nm.

The measurement of the PLE at 650 nm gives the spectrum in Figure 5, which shows an excitation band at 360 nm (3.44 eV), attributed to the absorption band of AuBr nanocrystals. By comparison with the emission band of bulk AuBr (3.35 eV or 370 nm) [9], a small shift of excitation band towards short wavelengths or higher energies was noted. Indeed, a shift of 10 nm (0.09 eV) was measured. This shift is assigned to the effect of sizes of AuBr nanocrystals, which induces an effect of confinement, and thus an increase in the forbidden band of this semiconductor [1–4].

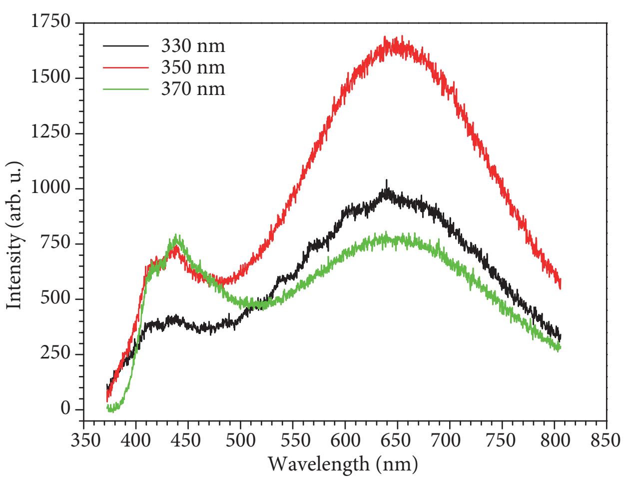

Figure 4. Emission spectra of KBr doped AuBr excited between 330-370 nm.

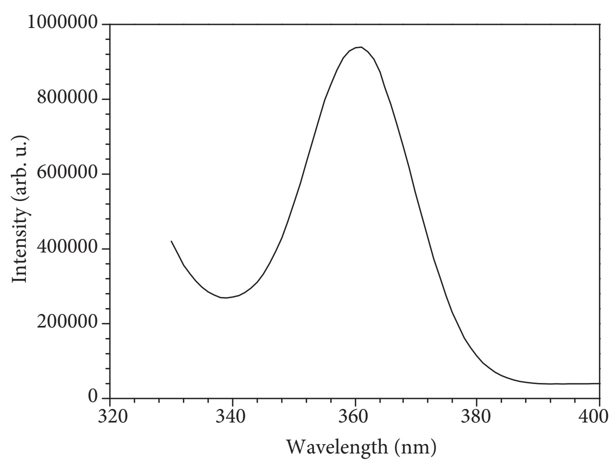

Figure 5. PLE spectrum of AuBr embedded in KBr single crystals measured at 650 nm.

5. Conclusion

In this paper, an experimental study, namely, the elaboration, structural, and optical characterization of KBr single crystals doped with AuBr nanocrystals is reported. The samples were prepared from the melting of thin films of gold that are deposited on pure samples of KBr single crystals using the Czochralski method. X-ray diffraction reveals the formation of AuBr nanocrystals inside the KBr matrix, through the appearance of peaks specific to the semiconductor AuBr and the KBr single crystals. Optical analysis by the photoluminescence spectra shows a characteristic emission band of AuBr nanocrystals around 1.91 eV. These results confirm a good formation and incorporation of the AuBr nanocrystallites inside the crystalline matrix.

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