EFFECTS OF HEAT TREATMENT ON MORPHOLOGICAL AND OPTICAL PROPERTIES OF ZnS NANOCRYSTALS EMBEDDED IN KBr MATRIX.

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ABSTRACT

ZnS nanocrystals were embedded in KBr single crystal matrix using Czochralski growth technique. The X-ray diffraction and optical spectroscopy revealed the incorporation of ZnS nanocrystals.

A blue shift of the absorption edge of the obtained samples has been observed indicating the quantum confinement effect. Annealing led to a shift in the absorption edge towards longer wavelengths and an increasing of the emissions intensity. This results shows that KBr is a good matrix-host of ZnS nanocrystals and that the elaborated samples can be used for important technological applications.

Keywords: Annealing; X-ray diffraction; Structural properties; Single crystal, Czochralski method.

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1. INTRODUCTION

In the last years semiconductor nanocrystals (NCs) has attracted the attention of many researchers because of their new and unusual structural, electronic and optical properties[1,2], due to the quantum confinement effect and high surface-to-volume ratio; Because of this, their surface consist large number of atoms and lead to high surface reactivity. Different methods were used to produce NCs in a crystalline or amorphous matrix [3]. The nanocrystals can take a spherical shape [4], ellipsoid or a faceted appearance [5].

ZnS is a direct-transition semiconductor; with the widest energy band gap among the group II–VI compound semiconductor materials. It is an important material with an extensive range of applications, from blue/green light-emitting diodes (LED) and electroluminescent devices (ELD) to optoelectric modulators [6], it has a low exciton Bohr radius (2.5 nm) that makes its nanoparticles interesting as small biomolecular probes for fluorescence and laser scanning microscopy.

The properties of bulk and doped ZnS nanocrystals have been investigated in various laboratories [7, 8]. Nanostructures made of ZnS are attractive in applications of electronic and optoelectronic nanodevices.

The majority of these nanocrystals have been synthesized by a chemical route, in a non-structured medium [9, 10]. One of the main challenges of research activities is finding a simple synthetic method to produce NCs embedded into crystalline matrix.

In this work, we report the growth of ZnS NCs embedded in KBr single crystals by using Czochralski method. Obtained samples were characterized by X-ray diffraction and optical absorption before and after annealing.

2. RESULTS AND DISCUSSION

The diffraction pattern of KBr single crystal pastille containing ZnS nanocrystallites prove their incorporation in the matrix without deforming the KBr cell.

The UV/Vis absorbance spectrum of a pure KBr pastille (Fig.1) indicate clearly the transparency of KBr in the region 200 to 600 nm, so it presents a good host to study the optical properties of semiconductors in this region.

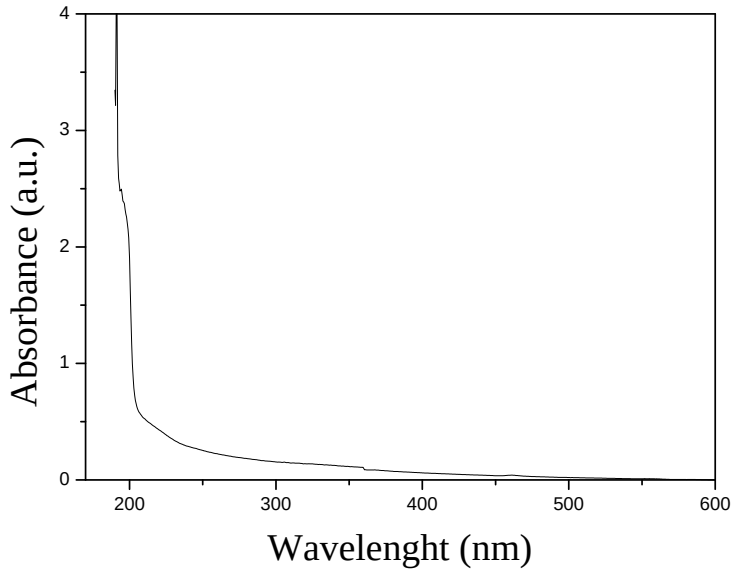

Fig 1. UV/Vis absorbance spectrum of pure KBr

To study the heat treatment effects on optical properties of ZnS NCs, doped pastilles were annealed at 600°C for 8, 16 and 24 hours.

Figure 2 shows the optical absorption of pastilles of ZnS NCs embedded in KBr monocrystals before and after annealing.

We observe a shift of the absorption edge towards higher energies in comparison with the pure KBr, due to the presence of ZnS nanocrystals.

The absorption coefficient α was analysed using the following expression for near-edge optical absorption of semiconductors: $\alpha h\nu = k(h\nu - E_g)^{n/2}$ where K is constant, E_g is the band gap and n is a constant that is equal to 1 for direct band gap semiconductors [11].

The edge gap value determined was determined by extrapolating the straight-line portion of the $(\alpha h\nu)^2$ against the hν graph on the hν-axis at $\alpha = 0$.

The shift of band gap might be used in determining the crystal radius (R) using the effective mass approximation relation [11]:

$$\Delta E = E_g(\text{nanocrystal}) - E_g(\text{bulk}) = h^2/8\mu R^2 - 1.8e^2/\varepsilon R$$

Where $1/\mu=1/m_e^* +1/m_h^*$ is the reduced mass of electron hole effective masse, and ε the bulk dielectric constant of ZnS (8.76). The particle average size obtained from this sample is 4.25nm.

The strong excitonic emissions suggest that the ZnS nanocrystals are of excellent optical quality.

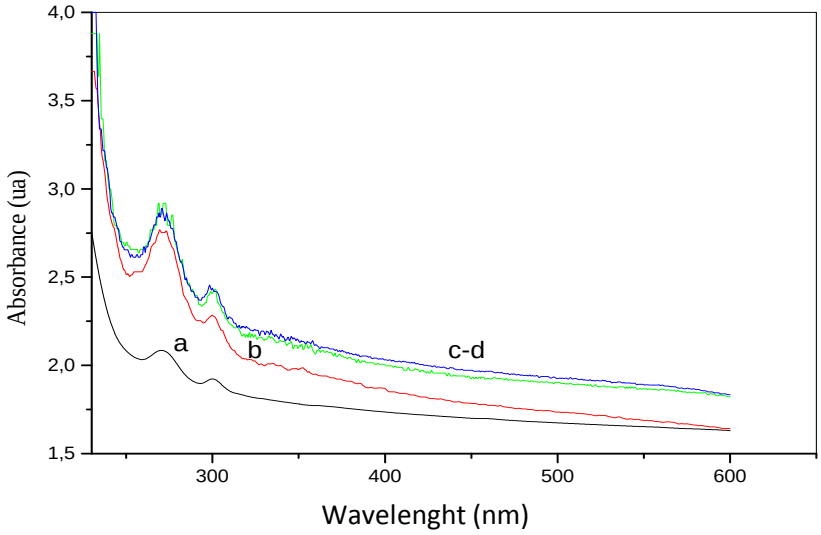

Fig2. Optical absorption spectra of ZnS nanocrystallites embedded in KBr single crystal.

a: non-annealed sample. **b**: sample annealed at 600°C for 8 hours.

c-d: samples annealed at 600°C for 16 and 24 hours.

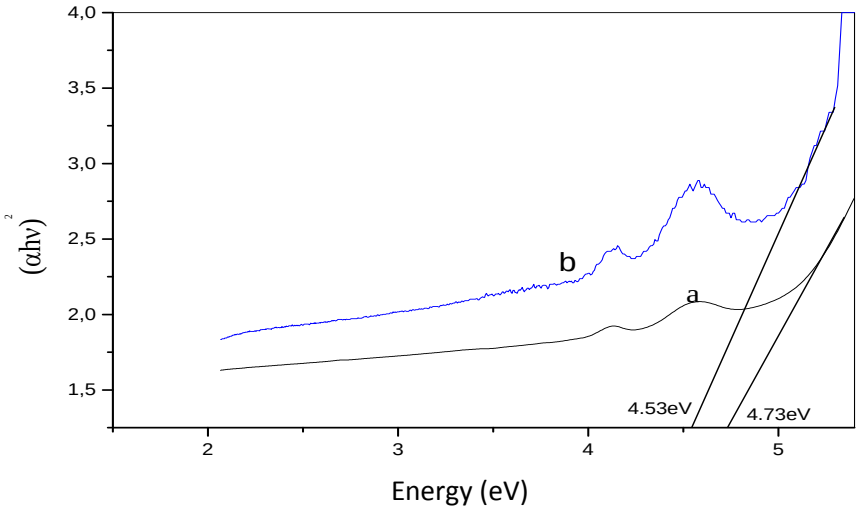

Fig.3. Optical gaps of ZnS nanocrystals measured by the extrapolation method.

a- before annealing. **b**- after annealing.

For the sample heat-treated at 600°C for 8 hours, we note, in the optical absorption spectrum (Fig.2), the increase in the intensity of excitonic absorption peaks and the decrease of the half-width at half maximum (HWHM) which may result from decrease of the width of nanocrystal size distribution (the size of the particles is increased due to the agglomeration of the nanoparticles).

Previous research demonstrated that HWHM could be used for qualitative evaluation of the nanocrystal size distribution (the wider size distribution results in larger value of HWHM) [12, 13].

We note also, that after annealing at 600 ° C for 8, 16 and 24 hours in a free atmosphere, the optical absorption spectrum (fig.3) shows a shift of the absorption edge towards the long wavelengths compared to that of the same pellet without annealing, which indicate that there is an increase in the size of the crystallites.

After the first 8 hours of annealing the displacement becomes very low which indicates that there is a limit to the maximum possible size, due to the constraints exerted by the KBr crystal lattice.

3. EXPERIMENTAL

The method used to elaborate the samples is based on the principle of Czochralski pulling, which allowed growth of large cylindrical ingots of KBr monocrystals doped by ZnS nanocrystals.

ZnS powder added to KBr has been prepared by a strong mechanical grinding to facilitate their incorporation.

After melting the KBr powder in a porcelain crucible, the seed oriented in such a way to have his [100] crystallographic direction parallel and coincident with the axis of draw, was dipped in the melt and pulled out with an appropriate rate (8 mm/h).

During the crystal pulling process, the melt was doped with adequate amounts of the ZnS micro-sized powder; overdose usually results in the formation of polycrystals. The growth is

carried out following the [100] direction.

X-ray diffraction (XRD) measurements were preformed using the Siemens D8 advanced diffractometer, and Cu K_α radiation (λK_α = 1.5402 Å) in the 2θ range (10–80°).

The transmittance of the films was measured by the UV-VIS Shimadzu 3101 PC spectrometer with a spectral range extending from ultraviolet to near infrared.

4. CONCLUSION

In summary, nanocrystals of 4.25nm have been successfully prepared by the Czochralski method. X-ray diffraction has confirmed the incorporation of the ZnS NCs (with a wurtzite structure) in the KBr matrix. Annealing process has significant influence on the optical properties of ZnS nanocrystals.

The strong UV emissions show possibility in the applications of high performance photonic nanodevices.

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