

Structural and optical characterisation of ZnO nanocrystals embedded in bulk KBr single crystal

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Abstract

The ZnO nanocrystals (NCs) embedded in KBr single crystal matrix has been fabricated using the Czochralski (Cz) method. X-ray diffraction has confirmed the embedding of ZnO nanocrystals inside the bulk KBr matrix. A blue shift of the absorption edge of the obtained samples has been observed. Moreover, ZnO nanocrystals embedded in bulk KBr single crystals, present photoluminescence (PL) bands, at 1.6 K, associated with free and bound excitons. These results confirm that bulk KBr single crystal is a suitable matrix-host for ZnO nanocrystals.

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1. Introduction

In the last decade, a great interest has been devoted to semiconductors nanocrystals (NCs) embedded in wide gap matrices, such as glass matrix [1–3] and alkali halide matrices [4–6], in order to develop new optoelectronics devices [7]. The NCs are characterized by a dominant surface effects and they have a considerable surface–volume ratio. In that respect, the optical properties of semiconductors considerably change when their sizes become comparable to the Bohr radii of bulk crystal [8]. This change is due to the quantum confinement of the electronic excitations. The confinement in three dimensions of the electron–hole pair, exciton and biexciton could be at the origin of strong nonlinear properties which make it possible to develop efficient light sources.

The ZnO NCs are very promising materials for fabricating electroluminescence devices [8]. The photoluminescence (PL) band of ZnO NCs is observed in the UV region which is due to excitons bound to surface [9–12]. Several techniques have been developed to fabricate ZnO NCs. For instance, van Dijken et al. [11] studied ZnO NCs suspended in non-aqueous solvent. The measured PL spec-

trum showed two bands emission: the first one was related to the exciton emission in the UV region (3.6 eV), and the second one, in the visible region (about of 2 eV), was caused by the transition from the conduction band to the deep trap. On the other hand, Harada et al. [13] fabricated ZnO NCs embedded in thin alkali halide crystals from their melts. In their PL measurement, the bound exciton (BE) and free exciton (FE) appeared clearly. The BE was located at 3.363 eV, the FE appeared at 3.373 eV and the 1 phonon and 2 phonon replica were observed at 3.32 and 3.25 eV, respectively. However, the authors indicated that the PL signals have never been detected for the ZnO NCs embedded in bulk alkali halide matrices grown by usual Bridgeman technique.

In this work, we report the investigation of ZnO NCs embedded in KBr bulk single crystal fabricated by using Czochralski (Cz) method. The KBr single crystal present a wide gap energy ($E_g \sim 7$ eV) [14]. We, particularly, studied the PL of the obtained samples.

2. Experimental procedure

The ZnO powders are prepared by a long mechanical grinding. The particle size and the morphology are examined by scanning electron microscopy (SEM). The samples of ZnO NCs embedded in KBr single crystal are fabricated

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by using the Czochralski (Cz) method, which consists of pulling the bulk single crystal of KBr doped by ZnO NCs from the melt. The growth is carried out by using a seed oriented following the crystallographic axis [100].

The X-ray diffraction (XRD) of ZnO embedded in KBr single crystal and the ZnO powders are performed by using the K_{α} line of copper $\lambda=1.5402 \text{ \AA}$ of a D8 Advanced Siemens Diffractometer. The optical density is measured at room temperature by a double beam UV–visible 3001 Shimadzu spectrophotometer. Finally, PL signals at pumped helium temperature (1.6 K), excited by an Argon laser ionized light (3.53 eV) with an output power of 10 mW, are detected by a photon counting system with a photomultiplier.

3. Results and discussion

Firstly, as an example, Fig. 1 shows the SEM image of the ZnO powders. We observe different ZnO aggregates formed by a coalescence of the ZnO NCs. The grain size is in the range of 100–900 nm.

We report in Fig. 2 the XRD of the ZnO powder. We observe a weak broadening of the diffraction peaks which is due to submicronic grains size of ZnO powder. The peaks of the XRD spectrum have been fitted by Gaussian functions. Using the Scherrer formula, the size of grains was found to be in the same range of that obtained by using the SEM, i.e. 100–900 nm.

Secondly, for this work, we prepared 3-mm pastilles of ZnO NCs embedded in KBr matrix by cleaving the single crystal parallel to the (100) plane.

Fig. 3 displays the XRD spectrum of the obtained pastilles. We note that the peaks are located at $2\theta=27.09^{\circ}$ and $2\theta=55.73^{\circ}$ which, respectively, correspond to the (200) reflection of KBr and its harmonic (400). The peak positions

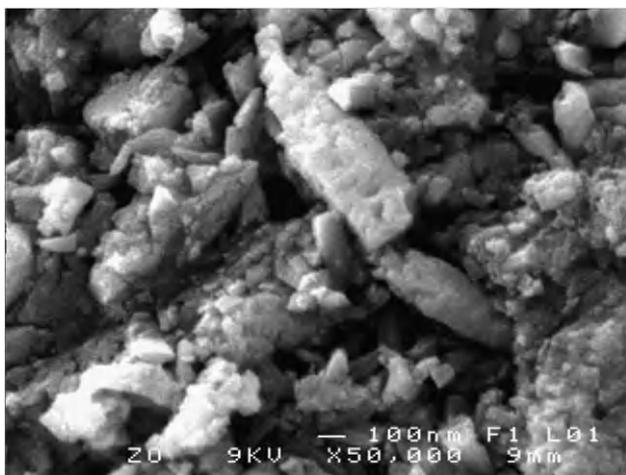


Fig. 1. SEM image of the ZnO powder. Agglomeration of ZnO nanocrystals in different grains is observed.

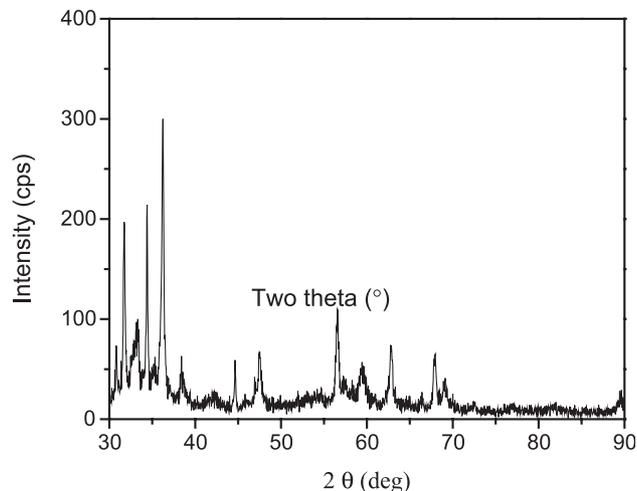


Fig. 2. XRD spectrum of the ZnO powder.

are very close to the standard positions reported on the JCPDS file of the KBr phase. Moreover, we observe the presence of a peak with a weak intensity located at $2\theta=36.30^{\circ}$, which is attributed to the most intense line (101) of ZnO wurtzite. We notice a slight shift of the ZnO peak ($\Delta(2\theta)=0.15^{\circ}$) which is very likely related to the contraction of the ZnO NCs cells in the KBr matrix.

These results indicate that ZnO has been embedded in the KBr single crystal without deforming the KBr cell. Indeed, the melting point of the ZnO (1750°C) is higher than that of the crystal pulling temperature (around 1100°C). Thus, during the crystal growth process, ZnO does not melt, and its incorporation was carried out in solid phases. Consequently, the aggregates of the ZnO dissociate into nanocrystalline size in the melt and enter in the KBr matrix with no structure modification.

Fig. 4 reports the optical density of ZnO NCs embedded in KBr matrix. We observe a shift of the absorption edge towards the strong energies compared to that of bulk ZnO

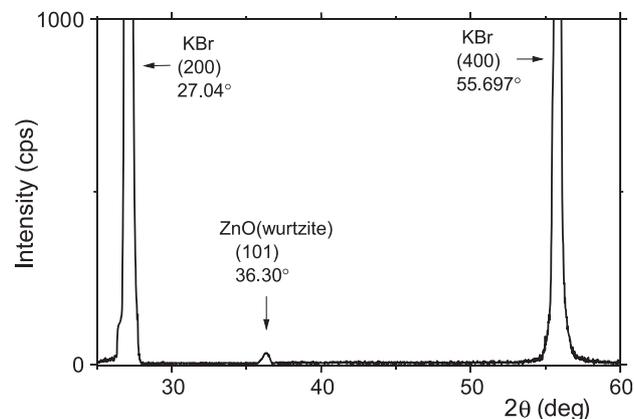


Fig. 3. XRD spectrum of the ZnO nanocrystals embedded in KBr single crystals.

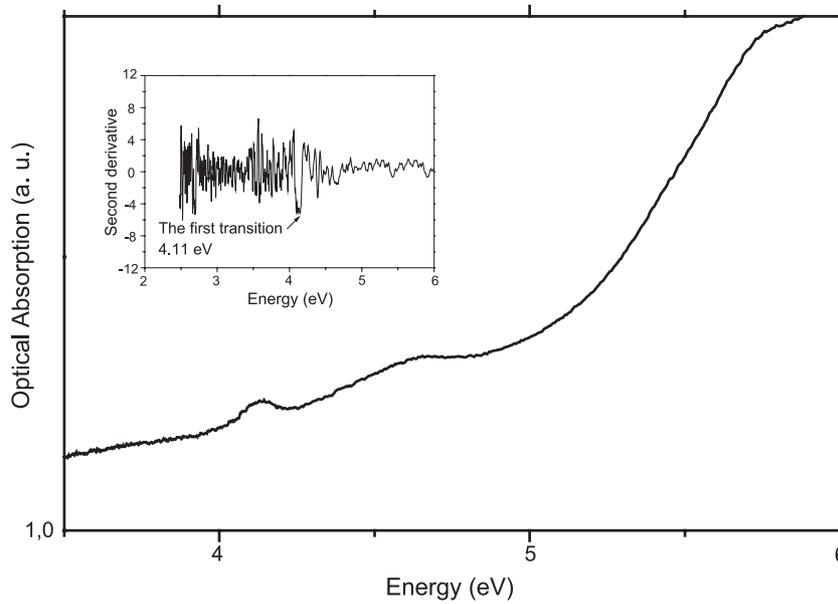


Fig. 4. Optical absorption of ZnO NCs embedded in KBr single crystal.

crystals. The absorption edge determined by the second derivative method [15] is equal to 4.11 eV (see the inset Fig. 4). By comparing this value with that of the ZnO bulk crystal ($E_g = 3.40$ eV), we find a shift of 0.71 eV. The size of ZnO NCs is estimated by using the following equation [11]:

$$E_x = 3.40 + \frac{2.10}{R^2} - \frac{0.297}{R}$$

where E_x is the absorption edge of ZnO NCs and R the average radius of the ZnO NCs.

We find that the average radius R of the ZnO NCs is 1.5 nm. This value is close to that of the Bohr radii ($a_B = 1.3$ nm) of ZnO bulk crystal. Therefore, we can deduce that ZnO NCs present an intermediate confinement situation.

The PL spectrum of ZnO NCs embedded in the bulk KBr at 1.6 K is presented in Fig. 5. One can note that the emission lines are very sharp compared to those of the powder [13]. A strong bound exciton (BE) emission lines is observed at 3.367 eV, which corresponds to the surface bound exciton transition (BE) in ZnO NCs [13]. The very small shoulder (3.373 eV) situated after the BE line is caused by the decay of free excitons (FE) [13].

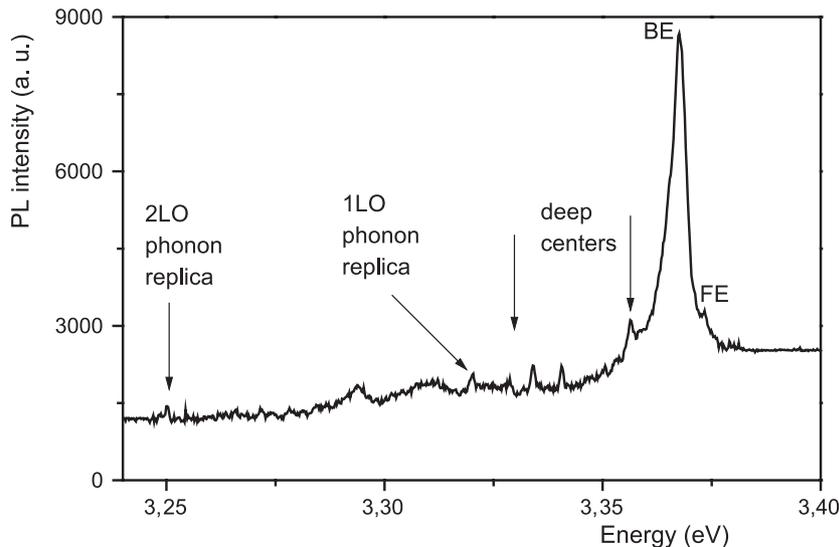


Fig. 5. PL spectrum measured at 1.6 °K for ZnO NCs embedded in KBr Single crystal.

The peaks situated at 3.32 and 3.25 are, respectively, due to one and two LO phonon replicas associated with the FE [13]. The peaks located in [3.33 eV, 3.55 eV] domain correspond to the deep centers as reported by Studenikin et al. [12].

Finally, regarding the obtained shape of BE and FE lines, we can deduce that the ZnO NCs have a high crystalline quality. On a whole, this study indicates that KBr single crystal is a suitable matrix to grow ZnO NCs.

4. Conclusion

In this study, we investigated ZnO NCs embedded in KBr single crystal fabricated by using Czochralski method. The X-ray diffraction demonstrated that the KBr cell has not been deformed after the incorporation of ZnO NCs. The optical density measurements indicated a shift of the absorption edge about of 0.71 eV. Moreover, they showed that ZnO NCs present an intermediate confinement. The study of PL at 1.6 K of ZnO NCs embedded in KBr single crystal showed that the signals are dominated by the BE exciton lines.

This work indicates that Czochralski method allows the fabrication of semiconductor NCs embedded in Alkali halide matrices with a high crystalline quality. The investigation of nonlinear optical properties of a such variety of NCs makes it possible to develop optoelectronics devices.

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