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Electronic processes in doped ZnO nanopowders

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Abstract. ZnO nanocrystals, undoped and doped with Iridium or Indium were prepared by solar irradiation in Heliotron reactor in PROMES CNRS facilities, France. The comparative analysis of the excitonic spectra of ZnO single crystal and ZnO nanocrystals (NCs) doped with In and Ir was performed. It is shown that the excitonic processes in Ir doped nanocrystals coincide well with electronic processes in undoped NC and single crystal; however, the electronic processes in In-doped nanocrystals are significantly different from those in single crystal. The radioluminescence spectra of ZnO:In was analysed and additional luminescence band at ~ 3.18 eV was detected due to In-doping. The luminescence decay time depends on In concentration in nanocrystals and is significantly less in ZnO:In compared with undoped nanocrystals. The fast scintillation of ZnO:In makes this material promising for application

1. Introduction

ZnO has excellent luminescence characteristics - especially fast intrinsic luminescence [1] and application for fast scintillators [2]. The electronic processes in ZnO crystal, nanocrystals (NCs), coatings and ceramics are vastly different and depend on various factors: doping concentration, intrinsic defects, electron/hole traps distribution and others. Donor-acceptor pair (DAP) luminescence can also serve as a direct probe of the acceptors in ZnO [3]. The luminescence spectroscopy is classically used as an informative method for the electronic processes and doping effect studies in ZnO.

Another advantage of this material is that there are various already established methods of synthesis of nanostructured ZnO with many more under development. In the present study, the relatively new synthesis method is used: solar physical vapour deposition (SPVD) [4]. Apart from NCs, for the practical applications, the ZnO ceramics are also promising. It was proven that semi-transparent ZnO ceramics can be obtained from undoped and In, Ga doped powders [5,6] and the excitonic luminescence of such materials is in the sub-nanosecond time region and therefore is perspective for use in fast scintillators. In the present study, we evaluate the possibilities of low temperature excitonic luminescence in ZnO, ZnO:In and ZnO:Ir NCs. The study is based on measurements of spectra and decay kinetics at 300K of ZnO and ZnO:In NCs with the idea of using of such NCs as raw material for the production of fast scintillators.

2. Experimental

2.1. Samples preparation

ZnO NCs undoped and doped with Ir, In were prepared by evaporation using condensed solar light in Heliotron reactor in Font Romeu, PROMES CNRS, France [2]. The concentration of dopants was changed by introducing of various concentrations (wt.%) of oxides of the corresponding dopants in the



target. In concentration was 0.5 wt.%, 1.0 wt.%, 3.0 wt.%. Ir concentration used in this study was 3.0 wt.%.

2.2. Experiment

Radioluminescence was measured under x-ray excitation (30 kV; 10 mA, W-anode). Photoluminescence was excited with 266 nm; 1 ns laser pulses. The luminescence spectra and decay kinetics were measured with Streak-scope C4334 (HAMAMATSU) under 30 ps pulses with 330 nm excitation. The spectra registration time gates were 1 ns and 5 ns. The pellets with powders were attached to a metallic surface placed inside a closed cycle helium gas cryostat (Advanced Research Systems, Model CSW-202). The temperature of measurements was in the region of 10 K-300 K. The radioluminescence spectra were recorded using the Andor Shamrock B-303i spectrograph with a CCD camera (Andor DU-401A-BV).

3. Results

3.1. Low temperature radioluminescence

The low-temperature luminescence spectra of ZnO are studied in detail and the interpretation of the main bands is fairly well known [3]. The low-temperature exciton spectra already can be used to get information about the quality of the material. However, the search for hole centers in ZnO is still undergoing and the presence of DAP luminescence shows the formation of hole centers. In the present paper we compare the excitonic spectra of the ZnO single crystal and ZnO NCs doped with In and Ir (Fig.1). The main band in the single crystal and ZnO:Ir is located at 3.358 eV is ExD^0 , a band at 3.33 eV is due to 1LOFEx and these bands are well resolved. In addition, the band at ~ 3.22 eV in ZnO:Ir may be caused by donor-acceptor pairs (DAP). Thermal quenching of DAP luminescence is in $T < 100$ K [2]. In the case of ZnO:In, the radioluminescence spectrum has a distinctive nature. Excitonic bands of ExD^0 and 1LOFEx in ZnO:In are hidden under the edge of fundamental absorption and/or under a wide band associated with the In - doping.

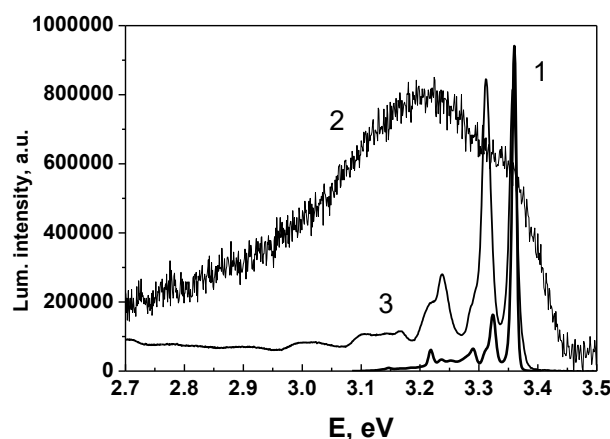


Figure 1. Radioluminescence spectra at 9 K of ZnO single crystal (1), In doped (3 wt.%) (2) and Ir (3 wt.%) (3) doped NC.

3.2. Fast luminescence of ZnO and ZnO:In NC at 300K

The fast luminescence spectra and decay kinetics at 300 K were measured under 266 nm excitation in 1 ns time gate. The spectra are shown in Fig.2. Analysis of spectrum gives the basis to conclude that the spectra of ZnO and ZnO:In differs significantly and therefore the decomposition of the spectra into Gaussian components has been carried out. The results are presented in Fig.3, a,b,c. One band peaking at 3.2 eV with FWHM ≈ 0.12 eV is observed in undoped NCs. The high-energy edge of the luminescence band may be slightly distorted due to the reabsorption associated with the edge of fundamental absorption.

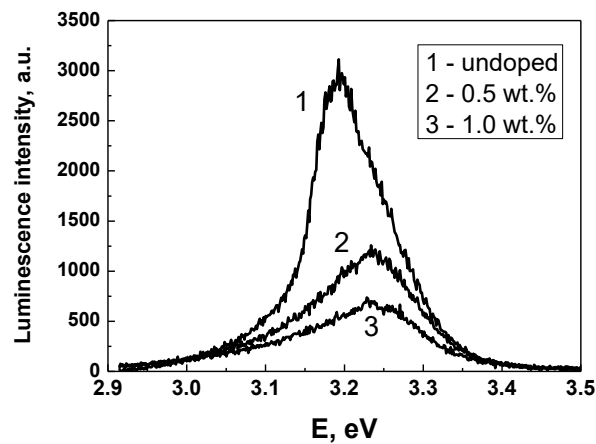


Figure 2. Luminescence spectra of ZnO and ZnO:In at 300 K in 1 ns time range and 266 nm excitation

On the other hand, in ZnO:In doped NCs the spectra consists of two Gaussian components. The additional component position is shifted to low-energy region and the FWHM is increased when compared to undoped NCs. The additional peak is located at 3.18 eV and FWHM is 0.24 eV. The obtained results show that the additional fast luminescence peak in In - doped NCs can be used to explain the effect of scintillation peak broadening in doped samples.

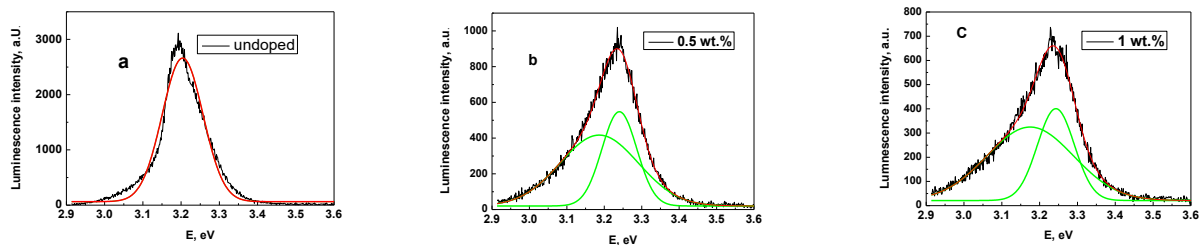


Figure 3. The results of decomposition of luminescence band into Gaussian components for undoped (a) and In-doped (b and c).

3.3 Luminescence decay kinetics in ZnO:In NC

The ZnO:In is considered as a promising material for fast scintillators, so the scintillation decay time estimation is important. In Fig.4 the decay kinetics for undoped NCs and ZnO:In with 0.5 and 1.0 wt.% concentration are shown. The decay process is not exponential, and this can be explained by the two luminescence centers (Fig.4). Doping concentration affects the decay time which decreases with an increase of In-concentration.

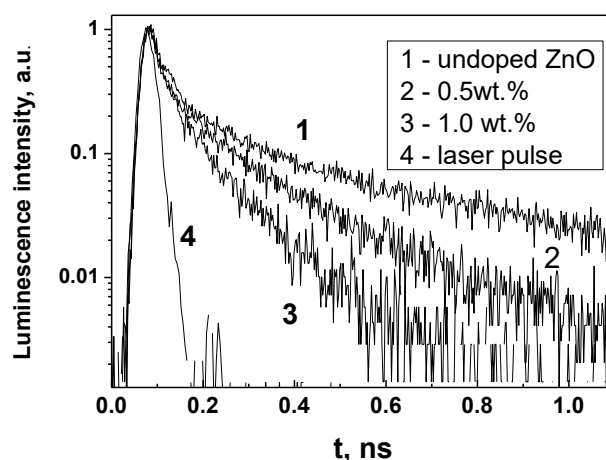


Figure 4. Luminescence decay kinetics of ZnO and ZnO:In NC in spectral region 3.24 eV.

4. Summary

The electronic processes in In doped nanocrystals are significantly different from those in the single crystal. Excitonic bands of ExD^0 and $1LOFEx$ in ZnO:In are hidden under the edge of fundamental absorption and under a wide band associated with the In-doping. The additional fast luminescence peak was obtained in In-doped NC and explains the effect of scintillation peak broadening in doped samples. The luminescence decay time depends on In concentration in NC and is significantly less in ZnO:In when compared with undoped NC

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