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# X-ray excited luminescence of Ga- and In-doped ZnO microrods by annealing treatment

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ABSTRACT

Ga- and In-doped ZnO microrods were prepared by low temperature hydrothermal process, and the effect of annealing temperature on morphology, crystallization, photoluminescence and X-ray excited luminescence were deeply researched. The results showed that both Ga- and In-doped ZnO microrods were possessed of a good crystalline quality and exhibited an intense visible emission band with a blue-shift under X-ray excitation. This blue-shift of the visible luminescence could be ascribed to the different contributions of the defect emissions, i.e. the increase in the oxygen vacancy ($V_O$) emission and the decrease of the oxygen interstitial ($O_i$) emission. Moreover, a strong ultraviolet luminescence was also obtained by further hydrogen annealing. It is expected that Ga- and In-doped microrods are promising candidates for development of fast and high-spatial-resolution X-ray imaging detectors.



## 1. Introduction

To develop a high-spatial-resolution and fast X-ray imaging detector, it is crucial for manufacturing a structural scintillator layer with fast decay time [1,2]. The spatial resolution of the detector is mostly determined by the geometry and morphology of the scintillator layer. A proper way to enhance the spatial resolution of the detector is to prevent optical crosstalk between neighboring pixels by using segmented scintillators, such as microrod array and micro-columnar structure [3]. As a scintillator material, ZnO has the richest family of the nanostructures, for instance, nanorods or microrod [4], nanowires [5], nanobelts [6], nanopropellers [7] etc., and the growth of vertically aligned ZnO microrod array is conveniently [8]. ZnO scintillator has two luminescence bands, i.e. ultraviolet and visible bands, which correspond to excitonic recombination and defect luminescence, respectively [7]. The decay times of both bands are in the picosecond- and nanosecond-scale, respectively, belonging to fast luminescence decay [9]. Experimental and simulation results demonstrated that the vertically aligned ZnO microrod arrays could be one of the hopeful candidates for ameliorating the image quality and spatial resolution of the X-ray detector [1,3]. From the application perspective, it is urgent and important to improve the intensity of X-ray excited luminescence (XEL) for ZnO microrods.

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Ga- and In-doped ZnO scintillators exhibited more excellent XEL than pure ZnO and were widely developed in the forms of powders and transparent ceramics [10,11]. The luminescence characterizations of the ZnO materials are closely related to their morphologies and dramatically affected by the annealing treatment [12]. As a consequence, it is necessary to understand the influence of the annealing treatment on the XEL characterizations of the microrod-like ZnO. Hydrothermal process has been demonstrated to be a good choice for synthesizing the doped ZnO microrods and annealing treatment is an appropriate rout for optimizing the luminescence properties of the ZnO materials [13]. Although, some works had mentioned the influence of the annealing treatment on XEL of ZnO nanoparticles or ceramic scintillators [14,15], there are still lack of detailed investigations on the XEL performance of the doped ZnO microrods.

In this work, Ga- and In-doped ZnO microrods were prepared by hydrothermal technique and were post-annealed in air atmosphere. The effect of the annealing temperature on the morphology, crystallization and luminescence performance (including PL and XEL) of the microrods were deeply studied.

## 2. Experimental details

Ga- and In-doped ZnO microrods were synthesized by low temperature hydrothermal approach. The molar concentration of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99.0%) in aqueous solutions was 0.025 mol/L, and the molar ratio of $Zn(NO_3)_2 \cdot 6H_2O$ and hexamethylenetetramine ($C_6H_{12}N_4$, HMT, 99.0%) was 1:1. Appropriate amount of gallium nitrate hydrate ($Ga(NO_3)_3 \cdot xH_2O$, 99.9%) or indium nitrate hydrate ($In(NO_3)_3 \cdot 6H_2O$, 99.9%) was added into the above aqueous solution. The nominal doping concentrations of Ga and In were 1 and 10 mol%, respectively, which were optimized in our previous work [16]. The mixed solution was then transferred into a reaction kettle, and the temperature of the reactor was kept in 95 °C for 3 h. Lastly, the microrods were taken out and cleaned several times with alcohol and deionized water. The Ga- and In-doped ZnO microrods were separately annealed at 500, 750 or 1000 °C for 2 h in a muffle furnace, and then cooled down to room temperature.

The morphology was examined by field emission scanning electron microscopy (FE-SEM, XL30, Philips). The structure of the microrods were measured by an X-ray diffractometer (XRD, DX-2700, Haoyuan Instrument Co., Ltd., Dandong, PR China), and the diffractometer was operated at 40 kV and 30 mA. PL spectrum was recorded by a fiber spectrometer with a FFT-CCD (PG2000-Pro-Ex, Ideaoptics Instrument Co., Ltd., Shanghai, PR China) under excitation of 266 nm laser (MPL-F-266, Changchun New Industries Optoelectronics Technology Co., Ltd., Changchun, PR China). XEL spectrum was obtained by an X-ray excited spectrometer, where X-ray was obtained form an F30-III X-ray tube (W anticathode target, 80 kV, 4 mA), and emission spectrum was measured by Hamamatsu PMTH-CR131 photomultiplier and Zolix SBP300 monochromator. PL and XEL spectra were measured with the same quality and volume of the sample under identical test conditions for several times at room temperature.

## 3. Results and discussion

Fig. 1 exhibits the FE-SEM images of Ga- and In-doped ZnO microrods before and after annealing treatment. It is clearly illustrated that all microrods have a hexagonal structure. The average diameter of Ga and In-doped ZnO microrods are about 0.2 and 1 μm, respectively, while the length of those microrods are about 2 and 10 μm, respectively. In addition, it is obvious to see the size of In-doped ZnO microrods is distinctly larger than that of Ga-doped ZnO microrods, though they were grown under the same conditions except for the doping concentration. This is due to a high doping concentration of In, which promotes the growth of the ZnO microrods at the doping concentration larger than 1 mol% [17]. Additionally, lightly surface etching in the morphology of the sample appears after annealing at 1000 °C in comparison with annealing at 500 and 750 °C. This surface blurring can be understood by the polar lattice structure of ZnO. It is known that the structure of ZnO is comprehended as hexagonal close arrangement of zinc and oxygen atoms, and the polar and nonpolar faces are metastable. The surface of the microrods will appear slight thermal decomposition after annealing at high temperature. The similar phenomena was reported by Wang et al. [18], where great and even essential morphology changes had been revealed in their samples. However, not only the morphology is basically maintained in our microrods, but also the PL and XEL of the annealed microrods are optimized as discussed below.

For the sake of analyzing the effect of the annealing temperature on the structure of the microrods, the XRD patterns of Ga- and In-doped ZnO microrods are given in Fig. 2. It depicts that all diffraction peaks are consistent with the standard data (JCPDS No. 36-1451), which means all microrods are hexagonal wurtzite structure without any secondary phases, and no evident change was observed except for the (100) peak. The intensity of the (100) peak appears an obvious increase with the annealing temperature, and reaches a maximum intensity for Ga- and In-doped microrods after annealing at 750 and 500 °C, respectively, and then decreases until the temperature up to 1000 °C. It could imply that the Ga- and In-doped microrods annealed at 750 and 500 °C, respectively, have a better crystalline quality. Meanwhile, comparing Fig. 1(d) and (h) with Fig. 2(a) and (b), it indicates that the hexagonal wurtzite structure of the microrods is not damaged by high temperature annealing, although slight thermal decomposition has appeared on the surface of the microrods.

Fig. 3 shows the normalized PL spectra of Ga- and In-doped ZnO microrods. There are two luminescence bands in typical PL spectrum, i.e. ultraviolet peak located at about 389 nm and visible band located at 450–750 nm, which attribute to the near-band-edge and deep level emission, respectively [7]. In order to better reveal the evolution of ultraviolet and visible emissions of the sample, the dependence of the peak intensity ratio of ultraviolet to visible emission ($I_{UV}/I_{VIS}$) on the