



Photoluminescence emission at room temperature in zinc oxide nano-columns



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ABSTRACT

Hydrothermal microwave method (HTMW) was used to synthesize crystalline zinc oxide (ZnO) nano-columns at the temperature of 120 °C with a soaking time of 8 min. ZnO nano-columns were characterized by using X-ray analyses (XRD), infrared spectroscopy (FT-IR), thermogravimetric analyses (TG-DTA), field emission gun and transmission electron microscopy (FEG-SEM and TEM) and photoluminescence properties (PL). XRD results indicated that the ZnO nano-columns are free of any impurity phase and crystallize in the hexagonal structure. Typical FT-IR spectra for ZnO nano-columns presented well defined bands, indicating a substantial short-range order in the system. PL spectra consist of a broad band at 590 nm and narrow band at 480 nm corresponding to a near-band edge emission related to the recombination of excitons and level emission related to structural defects. These results show that the HTMW synthesis route is rapid, cost effective, and could be used as an alternative to obtain ZnO nano-columns in the temperature of 120 °C for 8 min.

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1. Introduction

Order and disorder of the material are the keys to many unsolved structural issues and unexplained structure-related properties in solid materials. In particular, structural order-disorder are always present in real materials and may play an important role in technological applications by altering their electronic and optical properties.

Zinc oxide (ZnO) is an important multifunctional material with applications such as LED's [1,2], gas sensors [3,4], SAW devices [5], solar cells [6,7], catalysts [8,9] and specially as the most promising semiconductor material host, which exhibits ferromagnetism when doped with most of the transition metals including Co, Ni, etc. [10]. The various applications of ZnO are due to specific chemical, surface and microstructural properties of this material [5]. This oxide can form three distinct structures: cubic zinc blende, rocksalt and the thermodynamically stable phase zincite, with the

wurtzite crystal structure, which can be described as a number of alternating planes composed of tetrahedrally coordinated oxygen anions and zinc cations stacked alternately along the *c*-axis [11]. The rocksalt structure is only observed in relatively high pressures about 10 GPa [12].

Besides the potential applications of ZnO nanostructures in a range of subjects, they also present photoluminescence properties that are useful to investigate structural defects and impurities [13]. The characteristic photoluminescence peaks in the UV band are observed due to direct recombination of electrons in Zn 4p conduction band with holes in O 2p valence band, while the broad visible emission band has been suggested due to the presence of many point defects, such as oxygen vacancies [14,15]. In hydrothermal synthesis the formation of crystal nuclei begins when the concentration of ZnO reaches super saturation, due to the dehydration of Zn(OH)⁻²₄ ions, which acts as the growth unit of ZnO nanostructures [16–18], as a result, the fast growing of ZnO nanostructures lead to smaller surface areas, and the faces whose normal directions correspond to slow growing dominate the final morphology [19–21]. Lima et al. [22] obtained ZnO single crystals, using microwave-hydrothermal method, with reaction times ranging from 15 min to 2 h. Results of the PL emission of ZnO crystalline structures recorded with a 488 nm wavelength argon-ion laser indicated broad

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luminescence behavior in the visible-range spectra. In the case of samples annealed at 2 h, presenting high crystallinity (long-range order), ZnO powders exhibited low emission of the red PL component and blue PL component (498 nm, blue). The powder annealed at 15 min using the conventional hydrothermal method also presented a low blue PL emission. Besides the common use of microwave-hydrothermal method to obtain ZnO, it proved to be effective in the synthesis of other metal oxides, such as CuO, PdO, Nd₂O₃, CeO₂, gadolinium-doped CeO₂ and others, obtained by authors of this group [23–26].

In a conventional heating oven, the heat first reaches the surface of the material. As the heating is kept, the temperature inside the sample gradually increases to equilibrate with the surface, and the equilibrium is reached. In the liquid phase preparation of inorganic nanostructures, most of the synthesis are carried out by conductive heating with an external heat source, like an oil bath, heating mantle or a furnace, which are very slow and rather inefficient, because they depend on convection currents and on the thermal conductivity of the various materials that have to be penetrated, and often the temperature of the reaction vessel is considerably higher than of the reaction mixture. Microwave irradiation, on the other hand, produces efficient internal heating, increasing the temperature of the whole volume simultaneously and uniformly. This technique can provide the following advantages in comparison to conventional heating for chemical synthesis: high heating rates, thus increasing the reaction rates, no direct contact between the heating source and the reactants and/or solvents, excellent control of the reaction parameters, which is not only important with respect to the quality of the product, but also addresses a serious safety issue, selective heating if the reaction mixture contains compounds with different microwave absorbing properties, better selectivity due to reduced side reactions, improved reproducibility, automated and high throughput synthesis. In addition to these numerous advantages, microwave chemistry also has some significant limitations such as short penetration depth of microwave irradiation into the liquid medium, limiting the size of the reactors, which is a serious problem for scale-up, besides the difficulty to monitor nanostructure formation in situ under reaction conditions [27–35].

de Moura et al. [36] have obtained zinc oxide (ZnO) architectures by an efficient microwave-assisted hydrothermal (MAH) method using a cationic surfactant, cetyltrimethylammonium bromide (CTAB), as the structure-directing template. The ZnO nanostructures were obtained under hydrothermal conditions at 130 °C for 30, 60, 120 and 180 min. Wire-like and flower-like ZnO nanostructures and microstructures were easily prepared using a CTAB structure-directing template MAH method at a short time and a low temperature as compared to the conventional hydrothermal process. PL spectra consist of two bands related to the recombination of excitons and level emission related to structural defects. Macario et al. obtained BaZrO₃ microcrystals using the microwave assisted hydrothermal method at 140 °C for 40 min. The authors have obtained nanostructures free of impurities at lower temperature and reaction time, proving its efficacy [37].

The present work focuses on the photoluminescent behavior of ZnO nano-columns, investigating the role of MAH and the mineralizer agent (KOH) on the PL emission in the absence of CTAB (a cationic surfactant), which decreases the energy needed to form ZnO phase. This research involves four critical steps: (1) synthesis of the nano-columns; (2) structural characterization; (3) establishing the purity of the ZnO phase; and more importantly, (4) revealing the relationship between structural defects and the PL properties at lower soaking time compared with previous results obtained via hydrothermal microwave method.

2. Experimental procedure

Zinc acetate dihydrate ((CH₃CO₂)₂Zn·2H₂O) was dissolved in a solution of ethyl alcohol and acetylacetone (CH₃COCH₂COCH₃) at 60 °C for 1 h. ZnO nano-columns were synthesized by a hydrothermal microwave route. Zinc acetate dihydrate (5 × 10⁻³ mol L⁻¹, 99.9% purity) was dissolved in 80 ml of deionized water under constant stirring for 15 min at room temperature. Subsequently, 2 M KOH (p.a, Merck) was slowly added in the solution until the pH 10. The resulting solution was transferred into a sealed Teflon autoclave and placed in a hydrothermal microwave (2.45 GHz, maximum power of 800 W). The reactional system was heat treated at 120 °C for 8 min with a heating rate fixed at 10 °C/min. The pressure in the sealed autoclave was stabilized at 1.2 atm. The autoclave was cooled to room temperature naturally. ZnO nano-columns were collected and washed with acetone several times and then dried at 80 °C in an oven until pH 7.

Thermal effect was investigated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in the apparatus STA 409, Netzsch, Germany. Synthetic air flow (30 cm³/min) with a constant heating rate of 5 °C/min from room temperature up to 1200 °C was used. The obtained nano-columns were characterized by X-ray powder diffraction (XRD) using a (Rigaku-DMAX/2500PC, Japan) with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range from 20 to 80° with 0.2°/min. The crystallite size (d) of ZnO was calculated using Scherrer equation $d = k\lambda/\beta \cos \theta$, where k is constant, λ is wavelength of X-rays and β is the full width at half maximum (FWHM) for (1 1 1) reflection measured from slow scan where θ is the diffraction angle of the main peak. A 1064 nm YAG laser was used as the excitation source, and its power was kept at 150 mW. The FT-IR spectra were recorded with a Bruker Equinox-55 instrument. Infrared spectroscopy was used for monitoring the structural changes occurring during the synthesis process with the KBr pellet technique. The morphology of as-prepared samples was observed using a high resolution field-emission gun scanning electron microscopy FEG-SEM (Supra 35-VP, Carl Zeiss, Germany). Specimens for TEM were obtained by drying droplets of as-prepared samples from an ethanolic dispersion which had been sonicated for 5 min onto 300 mesh Cu grids. TEM, HRTEM images and SAD patterns were then taken at an accelerating voltage of 200 kV on a Philips model CM 200 instrument. PL properties were measured with a Thermal Jarrel-Ash Monospec27 monochromator and a Hamamatsu R446 photomultiplier. The excitation source was 350.7 nm wavelength of a krypton ion laser (Coherent Innova), keeping their power at 200 mW. All measurements were performed at room temperature.

3. Results and discussion

3.1. Thermal analyses

Having in mind that ZnO powder obtained at 120 °C for 8 min contains slight traces of impurity, we have performed TG-DTA analyses (Fig. 1). TG/DTA curves of the ((CH₃CO₂)₂Zn·2H₂O) precursor solution obtained from room temperature up to 1200 °C using a heating rate of 5 °C/min is shown in Fig. 1. The existence of three stages corresponding to the weight and energy change can be observed. The first region (25–200 °C) corresponds to the loss of physisorbed water; the second between 200 and 350 °C corresponds to the loss of surface hydroxyl groups, and finally, the weight loss above 500 °C is due to CO₂ released from the decomposition of carbonate species. DTA curve shows a strong exothermic peak around 270–350 °C, correlated to a weight loss that must be considered as the crystallization of the residual

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