Synthesis, characterization and properties of Mn-doped ZnO nanocrystals

R K Sharma, Sandeep Patel and K C Pargaien

Space Applications Centre, Ahmedabad-380015, India
E-mail: rakeshs@sac.isro.gov.in

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Abstract
In this work ZnO and Mn-doped ZnO nanocrystals were synthesized by one-step aqueous solution method. X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive x-ray (EDX) analysis and photoluminescence (PL) spectroscopy have been used to characterize the samples in detail. The XRD studies revealed that the ZnO and Mn-doped ZnO had wurtzite structure (hexagonal). The composition analysis by EDX indicated the presence of small amounts of Mn. A strong and wide ultraviolet emission has been observed for the ZnO and Mn-doped ZnO nanocrystals as evidenced by the photoluminescence spectra at a wavelength of 384 and 389 nm respectively. As-synthesized ZnO and Mn-doped ZnO nanocrystals have a good crystal quality. ZnO and Mn-doped ZnO nanocrystals show diamagnetism at room temperature.

Keywords: zinc oxide, doping, nanocrystals, photoluminescence, band-edge emission

Classification numbers: 4.02, 4.03

1. Introduction
The study of nanostructures with controlled shapes, size and morphology is essential and an important aspect for developing materials with novel properties and tailorable functions. Different types of semiconducting nanomaterials have been attracting much attention because of their exceptional properties, which are different from bulk materials [1, 2]. Zinc oxide (ZnO), one of the very important and versatile semiconductors with direct band gap of \(\sim 3.37 \text{ eV} \) [3] and a large exciton binding energy of \(\sim 60 \text{ meV} \) [4] at room temperature (RT) is a promising candidate for functional components of devices and materials in photonic crystals [5], gas sensors [6], light emitting diodes [7], solar cells [8, 9], lasers [2], varistors [10] and photoelectrochemical cells [11].

Over the past few years, ZnO nanomaterials with various interesting structures and properties have been synthesized, such as nanoparticles [12], nanorods [13], nanobelts [1], nanocomb [14], nanowires [15], and tetrapod nanostructures [16]. It is well known that doping a selective element into ZnO is the primary method for controlling the properties of the semiconductor such as band gap or electrical conductivity, and to increase the carrier concentration for electronic applications where a higher carrier concentration is required. Recently, many studies have focused on the doping of transition metals (TMs) such as Mn, Ni, Fe, Co and Cr into ZnO due to the potential applications in spintronics [17]. ZnO materials are believed to be non-toxic, biosafe and biocompatible [18] and have been used in many applications of daily life, such as drug carriers, cosmetics and fillings in medical materials [19, 20]. Based on these properties, the doped and undoped ZnO nanostructures have the possibility of being applied for nanodevices to detect chemical and gas because the response to different gases is related to a great extent to the surface state and morphology of the material. Moreover, to overcome the limitations of sensors with micrometer dimensions such as limited surface-to-volume ratio determines a limited gas response to low concentration of tested gases and requirement of elevated temperatures for operation to reach a desired gas response, nanostructured materials and approaches have been investigated for their gas response, selectivity and possible application in sensors with better characteristics [21–25].

In the present work, we report the structural, optical and magnetic properties of ZnO and Mn-doped ZnO...
nanocrystals prepared by aqueous solution method for sensor application.

2. Experimental method

Undoped and Mn-doped zinc oxide nanocrystals have been synthesized in aqueous solutions by using zinc acetate (Zn(CH₃COO)₂·2H₂O), manganese acetate (Mn(CH₃COO)₂·2H₂O) and potassium hydroxide (KOH) as the starting materials. 1.975 g of Zn(CH₃COO)₂·2H₂O and 0.079 g of Mn(CH₃COO)₂·2H₂O were dissolved in 100 ml of ultra-pure water from a millipore water purification system in a flask. 0.28 g of KOH was dissolved in 10 ml of ultra-pure water. Aqueous solution of zinc acetate and copper acetate at room temperature was stirred for about 30 min using a magnetic stirrer. Then the KOH solution was added slowly drop wise to aqueous solution of zinc acetate and copper acetate at 80–85 °C under constant stirring. After 3 h of reaction, the white precipitate deposited in the bottom of the flask was collected and washed with ethanol and deionized water. Finally, the precipitate was centrifuged with spinning speed of 3000 rpm and dried over 50 °C for 6 h in order to remove water molecules to obtain ZnO nanocrystal in powder form. The samples were stored at room temperature to study photoluminescence, structural and magnetic properties.

Prepared samples have been characterized by a powder x-ray diffractometer XPERT with CuKα x-ray radiation (λ = 0.15496 nm). The crystalline nature of ZnO samples is confirmed by sharp intense peaks. The surface morphology of the sample is observed by a scanning electron microscopy (SEM, JEOL, JSM-67001). The composition of elements like Zn, O and Cu is confirmed by energy dispersive x-ray (EDX) spectra. The room temperature photoluminescence (PL) spectrum of ZnO is recorded with a fluorescence spectrometer (FLS920) using an Xe lamp as the excitation source at excitation wavelength (λex = 325 nm). The magnetization behavior of the Mn-doped ZnO nanocrystals was also investigated using a vibrating sample magnetometer (VSM).

3. Results and discussion

Figure 1 shows the XRD patterns of undoped and Mn-doped ZnO nanocrystalline powder. The sharp intense peaks of ZnO confirms the good crystalline nature of ZnO and the diffraction peaks can be indexed to a hexagonal wurtzite structured ZnO, whereas the centers of all diffraction peaks have a slight shift compared with undoped NC samples (the spectra of undoped ZnO NCs are shown with red lines in figure 1). As for Mn-doped NCs, the lattice parameter c calculated from the (002) peaks of the samples is 5.186 Å, and that for the undoped ones is 5.210 Å. The decrease of the lattice parameter (about 0.024 Å) indicates that Mn is introduced into the ZnO crystal lattice and substitutes for the Zn²⁺ site. Furthermore, compared with the undoped ZnO, introduced manganese ions shift the diffraction peaks to higher angles by 0.17°. Such changes are indeed to be expected if Mn ions replace Zn ions in the lattice, as the Mn ions have smaller ionic radii (0.66 Å) than Zn ions (0.74 Å). The shift degrees indicate decrease of lattice parameters. The XRD result confirms the synthesis of Mn-doped ZnO nanocrystals without any phase-segregation. Figures 2(a) and (b) show the SEM images of ZnO and Mn-doped ZnO nanocrystals prepared by aqueous solutions method. The figure clearly indicates the morphology of the nanocrystals to be hexagonal with homogeneous uniform particle size distribution. EDX spectra displayed in figures 3(a) and (b) demonstrate the presence of various elements in the prepared doped and undoped samples. The EDX analysis provided precise composition of the elements. The EDX spectra in figure 3 clearly show peaks corresponding to elements Zn, Mn and O.

Figure 4 shows the photoluminescence (PL) emission of undoped and Mn-doped ZnO nanocrystals dispersed in
double distilled water at room temperature. A strong and wide ultraviolet emission peak for both undoped and Mn-doped ZnO nanocrystals is observed at 384 and 389 nm, respectively, which can be attributed to the exciton transitions [26]. The UV emission peak of doped nanocrystals exhibits a redshift of 5 nm in comparison with the PL emission of undoped nanocrystals, usually observed in the undoped ZnO nanowires [15] and ZnO films [27]. The redshift emission is related to the change of band gap \( E_g \). This change in the band gap is due to the presence of Mn in ZnO crystal.

On the other hand, the deep level emission, centered at 509 nm (2.44 eV) and also known to be related to the structure defects [28], is absent. The blue-green emission at 468 nm probably ascribed to oxygen vacancies and to the presence of dopant Mn is also quite weak. The sharp excitonic emission and weak deep level emission peaks indicate that the ZnO nanocrystals have a lower concentration of oxygen vacancies and high optical property.

An unusual but interesting feature of our PL spectra is that the deep level emission (DLE) is very weak. This result is in good agreement with the reports of Satoh Kobayanti [29] and Wu et al [30], in which they had mentioned that the Cr doping in ZnO had a significant effect on the quenching of DLE of ZnO. DLE has been attributed to the oxygen vacancy \( (V_O) \) and the zinc vacancy \( (V_{Zn}) \) [31, 32]. From the conclusion of Studenikinm [33], both green and orange PL peaks related to the oxygen vacancy are also absent. Therefore, the results show that the Mn doping decreases the quantity of the defect.
Figure 5 shows the field-dependent magnetization curves of ZnO and Mn-doped ZnO nanocrystals at 300 K, respectively. The origin of ferromagnetism (FM) in transition metal (TM)-doped ZnO samples is still underdetermined. A number of studies indicate that the FM in TM-doped ZnO may come from the precipitation of magnetic clusters or from the secondary magnetic phases [34]. In addition, several groups have found that the point defects play crucial roles in the FM of ZnO-based dilute magnetic semiconductors [35]. Zhuge et al [36] have found that the magnetization in their Cr-doped ZnO films is correlated to the $V_{Zn}$. Hong et al [37] ascribed the FM in Cr-doped ZnO films to the $V_{O}$. Double exchange mechanism between $d$ states of TM elements is another possible candidate to induce ferromagnetism in magnetic oxide [37]. But the results of XRD and PL exclude the possibility of the existence of the secondary phases $V_{Zn}$ and $V_{O}$ defect in our samples. Both pure and Mn-doped ZnO nanocrystals exhibit diamagnetism as shown in figures 5(a) and (b). More detailed work is essential in order to understand the magnetic behaviors of these materials.

4. Conclusion

In summary, highly crystalline pure and Mn-doped ZnO nanocrystals were prepared from the mixture of zinc acetate, manganese acetate and potassium hydroxide aqueous solutions method. The dopant is substituted onto zinc sites in the wurtzite lattice uniformly, with no detectable phase impurities or clustering. A strong near-band-edge gap emission was observed. It is found that a green band most likely due to oxygen vacancies located on surfaces is absent. This could be important for UV light-emitting applications. Mn-doped nanocrystals display diamagnetism at room temperature. More detailed work is essential in order to understand the magnetic behaviors of these materials.

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