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Sol-gel Auto Combustion Synthesis, Structural and Magnetic Properties of Mn doped ZnO Nanoparticles

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Abstract

Mn^{2+} doped ZnO nanoparticles were synthesized by sol–gel auto combustion technique. The effects of Mn^{2+} doping on the structural and magnetic properties of ZnO nanoparticles were investigated. Synthesized nanoparticles were characterized by X-ray diffraction technique (XRD), Fourier transform infrared spectroscopy (FTIR). The hexagonal wurtzite structure with single phase of Mn2+ doped ZnO nanoparticles were confirmed by XRD analysis. The average crystallite size determined by Scherrer's formula was found in the range 14–17 nm. It is observed that the lattice parameter, volume of unit cell, X-ray density, and atomic packing fraction increase with increasing Mn^{2+} content. FTIR analysis revealed a slight change in main absorption band of ZnO in the frequency range of 500-1000 cm^{-1}. Magnetic characterization was performed using vibrating sample magnetometer (VSM) and, which evidenced the properties of pure ZnO and Mn doped ZnO nanoparticles showed the diamagnetic and paramagnetic behaviour respectively.

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Keywords: *XRD; ZnO; FTIR, VSM*

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1. Introduction

From last few decades, the scientist and researchers have been looking intensively at the use of nanomaterials because of their excellent physical [1] and chemical properties [2] compared to bulk materials. Nowadays, nanostructures material are being used in the manufacturing of sensors, solar panel display, anti-graffiti coatings for walls, transparent sunscreens, stain-repellent fabrics etc. ZnO is one of the important and attractive nanostructure materials due to their optical and magnetic properties. ZnO material can be used to fabricate optoelectronic device due their wide energy band gap (3.37 eV) and large exciton binding energy (60 meV) [3, 4]. The development of novel nanostructure material in the form of thin films, nanoparticles, nanowire, nanowalls etc, it is an essential part of research as well as technology. In order to develop new technology, it is important to understand fundamental properties of nanomaterials. Fundamental properties of nanomaterials depend on size of nanoparticles, colour of nanoparticles, doping concentrations, sintering temperature, synthesis temperature etc. The properties of ZnO nanoparticles can be controlled by introducing the dopant element [5]. Doping of transition metal ions in the ZnO has lead to the enhancement of the band gap, optical, electrical and magnetic properties [6-8]. The transition metal ions have several advantages as a dopant that makes easy to incorporate into ZnO crystal structures and induced the magnetic as well as optical properties [9, 10].

Recently, the transition metal ions like Co^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, etc substitution in ZnO has received special attention [11]. The role played by the substituent in modifying the physical properties of ZnO and the mechanism behind reduce the size of nanoparticles and enhanced magnetic response is not widely studied. Furthermore, many theoretical and experimental evidences suggested that ZnO doped with transition metals is a promising semiconductor material exhibiting ferromagnetism when doped with transition metal ions like Co, Ni [12]. The control of chemical composition, purity, morphology, and particle size is very important to obtain suitable metal-ions doped ZnO powders for their desired applications. A number of synthesis methods have been devoted to the fabrication of transition metal doped ZnO nanoparticles, such as auto combustion method [13], ball milling method [14], co-precipitation method [15], hydrothermal process [16], solid state reaction method [17]. Among these synthesis methods, sol gel auto combustion method was used for the synthesis of Mn doped ZnO nanoparticles [18]. Using sol gel auto combustion method, reagents can be mixed at molecular level, easily control agglomeration of nanoparticles and reaction can be carried at low temperature [19].

In order to fabricate spintronic and optoelectronic device at room temperature, it is necessary to understand magnetic and optical properties of nanomaterials. These properties can be changed with doping of transition metal ions such as Ni^{2+}, Co^{2+}, Fe^{3+}, Mn^{2+}, Zn^{2+} etc. Among the transition metal ions, manganese is considered as a potential candidate because of its variable oxidation state, large solubility limit in ZnO matrix. In the present work, the effect of manganese ions on the structural and magnetic properties of ZnO nanoparticles has been investigated and the obtained experimental results are presented.

2. Experimental details

2.1 Synthesis of Mn doped nanoparticles

Nanocrystalline $Zn_{1-x}Mn_xO$ (x = 0.0, 0.06 and 0.12) samples were synthesized by a sol-gel auto-combustion technique. Analytical grade chemicals were used for synthesis of Mn doped ZnO nanoparticles. Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$, Sigma-Aldrich 99.999 %), manganese nitrate hexahydrate ($Mn(NO_3)_2.6H_2O$, Sigma-Aldrich 98.0 %), and citric acid monohydrate ($C_6H_8O_7.H_2O$, Sigma-Aldrich 99 %), were used. Double distilled water (Merck & Co., Inc.) was used as a solvent. Citric acid was used as a fuel. The fuel ratio was taken according to stoichiometric proportion of metal nitrate to oxidizer ratio (1:1). In a typical synthesis of $Zn_{1-x}Mn_xO$ samples, the appropriate proportion of $Zn(NO_3)_2.6H_2O$, $Mn(NO_3)_2.6H_2O$ and $C_6H_8O_7.H_2O$ were completely dissolved in a minimum amount of double distilled water to get the aqueous solution. The aqueous solution was then stirred for about 1 h in order to mix the solution uniformly. The mixed solution was evaporated to dryness by heating at 120° C on a hot plate with continuous constant stirring and finally formed a very viscous gel. The viscous gel was ignited by increasing temperature up to 200 ° C and the loose and burnt powder of the samples was obtained. Finally, the burnt powder was sintered at 600 ° C for 6 h to obtain manganese substituted zinc oxide nanoparticles. The resulting