Doping effect of Ag⁺, Mn²⁺ ions on Structural and Optical Properties of ZnO nanoparticles

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Abstract: Pure ZnO and co-doped (Mn, Ag) ZnO nanoparticles have been successfully prepared by chemical co-precipitation method without using a capping agent. X-ray diffraction (XRD) studies confirms the presence of wurtzite (hexagonal) crystal structure similar to undoped ZnO, suggesting that doped Mn, Ag ions are substituted to the regular Zn sites. The morphology of the samples were studied by scanning electron microscopy (SEM). The chemical composition of pure and co-doped ZnO nanoparticles were characterized by energy dispersive X-ray analysis spectroscopy (EDAX). Optical absorption properties were determined by UV-vis Diffuse Reflectance Spectrophotometer. The incorporation of Ag⁺, Mn²⁺ in the place of Zn²⁺ provoked to decrease the size of nanocrystals as compared to pure ZnO. Optical absorption measurements indicates blue shift in the absorption band edge upon Ag, Mn ions doped ZnO nanoparticles.

Keywords: Pure ZnO, co-doped ZnO nanoparticles, co-precipitation method, SEM, EDAX, DRS.

1. Introduction:
Zinc oxide (ZnO) is an important electronic and photonic material which has been studied extensively in the past few years due to its technological importance [1]. It has a wide band gap (Eg=3.37eV), large excitation energy of 60 meV, high chemical stability, good piezoelectric properties, nontoxicity and biocompatibility. To synthesize ZnO nanoparticles with transition metals by different routes such as wet chemical methods like sol-gel [2], co-precipitation [3], combustion [4] etc. It has been used in a wide range of applications such as sensors, varistors, piezoelectric, transducers, surface acoustic wave devices, phosphors, transparent conducting oxides, optoelectronic devices, ferromagnetic devices, and heterogeneous photo catalysts [5-9]. ZnO possesses n-type conductivity due to its native defects such as Zinc interstitials and oxygen vacancies, and silver doping is found to be effective for the fabrication of p-type ZnO. On irradiation, the high density free electrons oscillate, which is known as Surface Plasmon Resonance (SPR), and also, recently SPR based Nobel metal semiconductor nanocomposites have become a popular research topic because of their improved optical properties [10]. In this paper, we report that the morphology induced by two different ions such as silver and manganese ions of equal concentrations (x = 0.00 and 0.05) in ZnO nanocrystals was systematically studied. By
using chemical co-precipitation method pure ZnO and Zn$_{1-x}$Mn$_x$Ag$_x$O nanoparticles were synthesized and their structural, morphology and optical properties have been investigated.

2. Experimental:
All the chemicals used in the experiment are of analytical grade purity and purchased from Merck, Mumbai, India. Pure ZnO and manganese, silver doped ZnO nanoparticles were synthesized by chemical co-precipitation method at room temperature and for silver and manganese doping silver nitrate (AgNO$_3$), and manganese acetate tetra hydrate Mn(CH$_3$COO)$_2$.4H$_2$O were used. Zn$_{1-x}$Mn$_x$Ag$_x$O (x=0.00, 0.05) nanostructures were prepared at room temperature as the procedure described below. Initially 0.2 M solution was prepared by using Zinc acetate and KOH. For dopants, AgNO$_3$ and manganese acetate have been added drop wise to the above solution in equal concentrations such as 0.00, 0.05 under continuous stirring for 8 hrs. Hence, the precipitate was formed and it was filtered out separately, and repeatedly washed with deionized water to remove unnecessary impurities formed during the preparation process. Ag and Mn doped ZnO nanopowders were obtained after drying at 100 $^\circ$C for 5 hrs. Then the final products were grinded and annealed at 400 $^\circ$C in the furnace for 1 hr.

The synthesized nanostructures were characterized by X-ray diffraction technique using BRUKER D8-advance powder X-ray diffractometer (Germany) with source of 2.2 kW Cu anode, Ceramic X-ray tube. Morphology of the samples was analyzed using scanning electron microscopy (SEM) technique. Concentration of dopants in ZnO was estimated by energy dispersive X-ray analysis spectroscopy (EDAX) attached with SEM (Model: CARL-ZEISS EVOMA-15). The optical properties were estimated from the UV-vis diffuse reflectance spectroscopic studies with a model Varian Cary- 4000 spectrophotometer.

3. Results and Discussion:
The prepared Pure and Ag, Mn doped ZnO nanopowders possesses hexagonal wurtzite structure. Fig.1 shows the X-rd pattern of Zn$_{1-x}$Mn$_x$Ag$_x$O (x = 0.00, 0.05) powder samples at 400 $^\circ$C. The diffraction patterns of samples can be indexed to the hexagonal wurtzite structure of ZnO (JCPDS data card No: 36-1451). It should be pointed that in the XRD patterns except diffraction peaks of ZnO, no peak of additional phase was observed. The crystalline sizes of the synthesized powders were determined using Debye-Scherer’s equation, $D = \frac{0.89 \lambda}{\beta \cos \theta}$, the increasing Mn solubility in ZnO is due to decreasing particle size, as discussed by Straumal et al. [11]. In our study, we observed that for 5 mol% of Ag, Mn doped ZnO nanoparticles of size decreases than pure ZnO. Thus, we may conclude that the lattice constants and particle sizes decreased for the following reason. Silver can also exist in Ag$^{2+}$, Ag$^{3+}$ in addition to Ag$^+$. The ionic radii of Ag$^+$ (0.75 Å), Ag$^{2+}$ (0.94 Å) are nearly equal size of Zn$^{2+}$, but the ionic radii of Mn$^{3+}$ (0.58 Å) and Mn$^{4+}$ (0.53 Å) are smaller than Zn$^{2+}$. In the doped ZnO, substitution of Zn$^{2+}$ by Mn$^{3+}$ and Mn$^{4+}$ brings about the lattice constant decreases as noted by Bhatti et al. [12], and for 5 mol% of Ag, Mn doped ZnO nanoparticles sizes are 17 nm, the corresponding lattice constants are $a = 0.32551$ nm, $c = 0.52164$ nm respectively, which are lesser than the sizes of pure ZnO nanoparticles (size ~ 23 nm). The intensity of pure ZnO shows higher diffracted intensity than that of 5 mol% of Mn, Ag doped ZnO.
Scanning electron microscope (SEM) was used to investigate the morphology of the samples as shown in the Fig. 2. Pure ZnO shows clusters of tiny particles and 5 mol% of Ag, Mn doped ZnO image [Fig. 2(b)] appears like hexagonal structures, these structures agree with the X-rd results. The energy dispersive X-ray spectroscopic analysis of the pure ZnO and co-doped ZnO confirms the presence of Ag and Mn in the prepared oxide as shown in Fig. 3.

The optical absorption spectra of pure ZnO and Zn$_{1-x}$Mn$_x$Ag$_x$O (x = 0.00, 0.05) samples are studied by diffuse reflectance spectrometer (DRS) in the range of 200 to 800 nm. From Fig. 4, it can be seen that the excitonic absorption peak for undoped ZnO appears around 363 nm and 5 mol% of Ag, Mn doped ZnO nanoparticles shows that the one excitonic peak at 240 nm and other broad peak is observed, which is centered at 336 nm. It is clearly observed that the
absorbance of the co-doped ZnO samples decreased for 5 mol% of Ag, Mn concentration. From Fig. 4, blue shift is observed for 5 mol% of Ag, Mn concentration in ZnO nanoparticles, because of the quantum confinement effect [13,14].

![Absorption Spectra](image)

**Fig. 4.** UV-vis absorption spectra of (a) pure ZnO and (b) 5 mol% of Ag, Mn doped ZnO nanoparticles.

4. Conclusions:
Nanocrystals of pure ZnO and Zn$_{1-x}$Mn$_x$Ag$_x$O were successfully synthesized by using a chemical co-precipitation method. The crystalline structure, optical properties were determined by XRD and UV-visible diffuse reflectance spectrophotometer respectively. XRD analysis shows the hexagonal phase and SEM image shows (5 mol% of Ag, Mn doped ZnO) hexagonal structure. The average particle sizes, lattice parameters ‘a’ and ‘c’ of nanoparticles decreased for 5 mol% of Ag, Mn doped ZnO nanoparticles as compared to undoped ZnO nanoparticles. Optical absorption measurements indicate the blue shift in the absorption band edge upon 5 mol% concentration of Ag, Mn doped ZnO nanoparticles.

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