The effects of Cr and Ni Doping on the Structural, Optical, and Magnetic Properties of ZnO

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Zinc oxide (ZnO) is II-IV semiconductor, with a wide band gap (2.83 eV [1]). It has been the centre of much research in semiconducting material [2] as a candidate for the development of diluted magnetic semiconductors (DMS) [3] which exhibit multi-functional properties such as magnetic, semiconducting, and optical properties with potential application in spin-based electronics [1] and optoelectronic devices [4]. In these materials, a fraction of ions of the host material has been substituted for by magnetic ions (typically $3d$ transition metals) [2]. The *sp-d* exchange interaction between the charge carriers of the host and the dopant ions gives rise to unique structural, optical, and magnetic properties [5]. In the present work, we report the sol-gel synthesis of $(\mathrm{Zn}_{1-x}\mathrm{Cr}_x)\mathrm{O}$ ($x = 0$, 0.005, 0.01, 0.03) and $(\mathrm{Zn}_{1-(x+y)}\mathrm{Cr}_x\mathrm{Ni}_y)\mathrm{O}$ ($x = y = 0.005$ and $x = 0.025$, $y = 0.005$). The samples were calcined prior to characterization using X-ray diffraction (XRD), Transmission electron microscopy (TEM), Ultraviolet-visible (UV-VIS) spectroscopy, and Vibrating sample magnetometer (VSM). The hexagonal wurtzite structure of ZnO was confirmed from XRD data. The crystal size calculated using Williamson-Hall analysis [6] and were found to be between 73 nm and 99 nm. The crystal size increased with increasing Cr concentration from $x = 0.005$ to $x = 0.01$ followed by a decreased for $x = 0.03$. Doping ZnO with Cr and Ni decreased the crystallite size of ZnO from 90.59 nm to 83.49 nm for $(\mathrm{Zn}_{0.97}\mathrm{Cr}_{0.025}\mathrm{Ni}_{0.005})\mathrm{O}$ and 73.72 nm for $(\mathrm{Zn}_{0.99}\mathrm{Cr}_{0.005}\mathrm{Ni}_{0.005})$. TEM revealed that the ZnO, as well as all the doped samples prepared in this study form agglomeration of the crystallites. The size of the band gap of ZnO decreased with increasing Cr concentration from $x = 0.005$ to $x = 0.01$, while the band gap increased with increasing Cr concentration to $x = 0.03$, contrary to previous reports. The simultaneous doping of ZnO with Ni and Cr decreased the optical gap. Low field ferromagnetism and high field diamgnetism was observed in all samples and they did not show magnetic saturation. Ferromagnetism in ZnO was attributed to the possible presence of oxygen vaccancies in the samples. In the doped samples, ferromagnetism originates from the $\mathrm{ZnCr_2O_4}$ phase obserevd in XRD data and possoble formation of bound magnetic polarons (BMPs) as reported by other authors. High field diamagnetism observed was linked to the bulk like nature of the samples.

References:

[1] K. Haq *et al.*, J. Semicond. **39** (2018).
[2] M.A. Garcia *et al.*, Nano lett. **7** (2007).
[3] R. Seshadri, Current Opinion in Solid State and Material Science. **9** (2005).
[4] T. Pandiyarajan and B. Karthikeyan, J. Nanopart Res. **14** (2012).
[5] K. Ando *et al.*, Journal of Applied Physics. **89** (2001).
[6] V. D. Mote *et al.*, Journal of Theoretical and Applied Physics. **6** (2012).

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