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Structural and Magnetic Properties of Cr Doped SnO₂ Nanopowders Prepared by Solid State Reaction

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ABSTRACT. Chromium-doped tin oxide nano powders (Sn_{1-x}Cr_xO₂, x = 0.00, 0.03, 0.05 and 0.07) were prepared using simple low cost solid state reaction and followed by vacuum annealing at 900 °C and studied the effects of Cr dopant concentration on structural and magnetic properties. The X-ray diffraction (XRD) studies confirmed that all the diffracted peaks were polycrystalline rutile structure of SnO₂ phase. FT-IR analysis gave additional supports of formation of O-Sn-O and Cr-Sn-O the system. Magnetic studies revealed that all the powder samples were ferromagnetic at room temperature. Further the saturation magnetization increased with increase of doping concentration.

Introduction. Since the discovery of room temperature ferromagnetism in Mn doped GaP and ZnO by Deitl et. al. [1] and the discovery of room temperature ferromagnetism in Co doped TiO₂ by Mastumoto et al [2], intense research work has been carried out on doping of different semiconductors with different impurities. An extensive research work has been carried out on wide band gap oxide semiconductors such titanium oxide, zinc oxide, copper oxide, tin oxide and gallium nitrate systems [3-9]. These semiconductors possess wide band gap of the order of 3.5 eV, high electrical conductivity, high optical transmittance in visible region and high stability. The discovery of high temperature ferromagnetism in Co doped SnO₂ thin films by Ogale et. al. [10] prompted a large number of experimental investigations on pure and transition metal doped tin oxide [11]. Among the other wide band gap oxide, tin oxide is one of the best material due to its wide band gap (3.5 eV), n-type conductivity and high transmittance in visible region of the electromagnetism spectrum and finds many applications such as solar cells, gas sensors, photo detectors etc.[12-14]. Different synthesis methods were adopted for the synthesis of undoped and impurity doped metal oxides. Among the other synthesis methods, solid state reaction method is the one of the best techniques by which one can get nanoparticle with uniform size. The synthesis of nanoparticles such as indium oxide, tin oxide and indium tin oxide were studied and reported the room temperature ferromagnetic

properties in these. An effort is made here for the synthesis of Cr doped SnO₂ nanoparticles using simple solid state reaction method and studied their structural and magnetic properties [6, 15, 16]

Experimental details. Chromium doped tin oxide Sn_{1-x}Cr_xO₂ (x = 0.00, 0.03, 0.05 and 0.07) concentrations were prepared by a solid state reaction followed by vacuum annealing. Commercially available SnO₂ and Cr₂O₃ (M/S Sigma-Aldrich 99.99 % pure) were accurately weighed in required proportions and were mixed and ground thoroughly using an Agate mortar and pestle to convert to very fine powders. The grinding of the mixtures was carried out for 16 hours for all the powder samples. The ground powder samples were loaded into a small one end closed quartz tube of diameter 10 mm and length of 10 cm, which was enclosed in a bigger quartz tube of diameter of 2.5 cm and length of 75 cm with provision to allow unwanted vapors to escape from the reaction chamber and evacuated at 2×10^{-3} mbar using a rotary pump was used for the synthesis of the present samples. The complete set up was placed in horizontal tubular microprocessor controlled furnace and fired for several hours at different temperatures. The firing temperature and firing periods were optimized at 900 °C and 10 hours. X-ray diffraction (X-ray diffractometer, D8 Advance, BRUKER) was used to establish structural aspects. Energy dispersive analysis spectroscopy (EDS) (OXFORD instrument inca penta FET X3) was used to carry out elemental analysis. Magnetic measurements were carried out using Vibrating sample magnetometer (Lake Shore-7410)

Results and discussion

Structural properties. Fig.1 shows the XRD pattern of chromium oxide (Cr₂O₃). The diffraction peaks such as (0 1 2), (1 0 4), (1 1 0), (1 1 3), (0 2 4), (1 1 6), (2 1 4) and (3 0 0) were observed among with (1 0 4) as the most predominant orientation. All these diffraction peaks were exactly coincided with α -crystalline Cr₂O₃ [JCPDS card: 74-0326]. The other stable phases of chromium (Cr) such as CrO, Cr₂O, CrO₂ and Cr₃O₄ were not found in the present X-ray diffraction pattern, indicating the absence of other phases of Chromium.

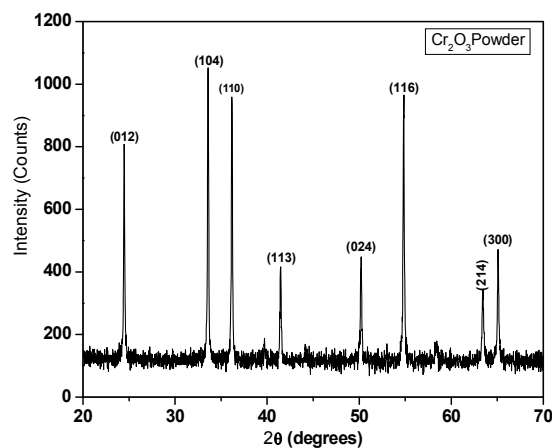


Fig. 1. XRD profile of bulk Cr₂O₃.

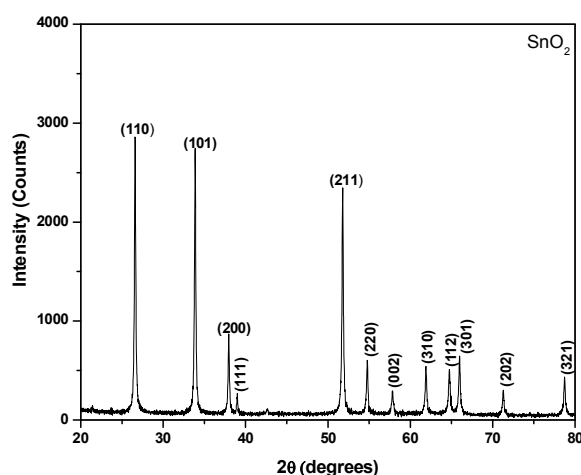


Fig. 2. XRD profile of bulk SnO_2 .

Fig. 2 shows the XRD profiles of bulk SnO_2 . The diffraction peaks were found at diffraction angles of 26.62° (110), 33.89° (101), 37.98° (200), 39.09° (111), 42.65° (210), 51.80° (211), 54.79° (220), 57.85° (002), 61.92° (310), 64.75° (112), 65.98° (301), 71.39° (202) and 78.73° (321) were exactly coincided with tetragonal structure of SnO_2 [JCPDS No. 411445]. Among the above orientations, (110) was the predominant orientation. No other diffraction peaks related to tin in other phases such as SnO or tin (Sn) metal clusters were identified in XRD within detectable limit of XRD. The same diffraction peaks were observed for the Cr doped SnO_2 nanoparticles and no diffraction peaks related to either Cr or Cr_2O_3 were observed in XRD. All the diffraction peaks were exactly coincided with tin oxide XRD profiles. The crystallite size (G) was calculated by using the Debye-Scherrer formula:

$$G = k \lambda / \beta \cos \theta,$$

where k is particle geometry dependent constant (for spherical shape $k \sim 1$), λ is the wavelength of used ($\lambda = 1.5406 \text{ \AA}$), β is the full width-at-half maximum (FWHM) and θ is the diffracted angle, respectively.

The estimated average crystallite size is found to be 47 nm. The same was confirmed by elemental analysis and spectroscopic studies. It confirms the doping of Cr into the SnO_2 lattice.

Optical properties. Fig. 3 shows the optical band gaps of the Cr doped SnO_2 nanoparticles. The optical band gap was obtained by plotting $(\alpha h\nu)^2$ versus the photon energy ($h\nu$) and by extrapolating of the linear region of the plots to zero absorption ($\alpha = 0$). The optical band gap of the powder samples decreases from 3.58 eV to 3.63 eV when the Cr doping concentration increased from $x = 0.03$ to $x = 0.07$.

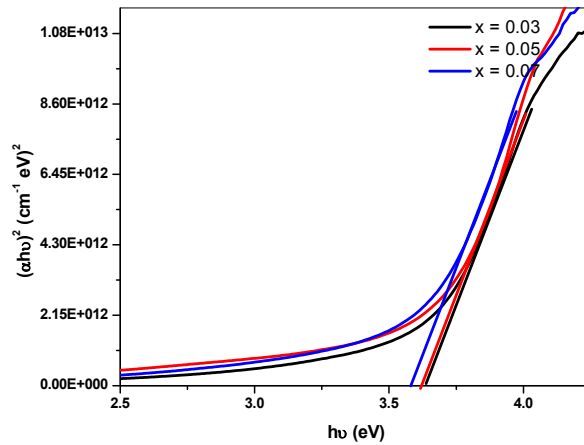


Fig. 3. Optical band gaps of Cr doped SnO₂ nanoparticles.

Magnetic properties. Fig.4. shows the magnetic measurements, which were carried out for all the samples including pure SnO₂ and Cr₂O₃. The SnO₂ nanoparticles exhibit the weak ferromagnetism at low magnetic fields and converted to paramagnetic at higher applied magnetic fields. The Cr₂O₃ nanoparticles exhibited antiferromagnetic behaviour. By doping Cr impurity of 3 at.%, 5 at.% and 7 at.%, the nanoparticles exhibited weak ferromagnetism without saturation even at high applied magnetic fields. From this it conclude that the observed ferromagnetism is an intrinsic in nature rather than any impurities as no impurity phase was observed from XRD and other spectroscopic studies.

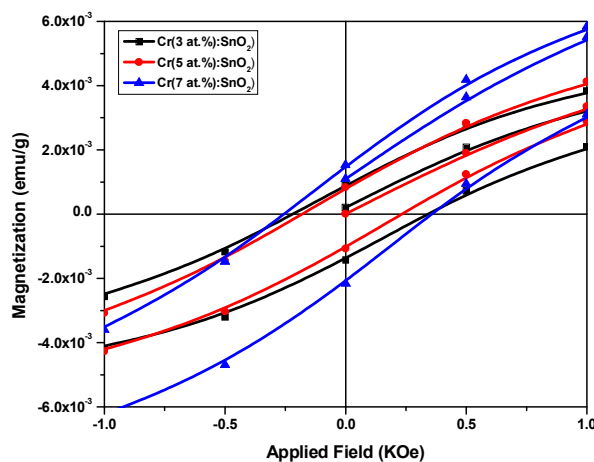


Fig. 4. M-H loops of Cr doped SnO₂ nanoparticles at different doping concentrations.

Summary. Chromium doped SnO₂ nanoparticle were synthesised using simple solid state reaction method and studies their structural, optical and magnetic properties. The structural studies indicated that the synthesised nanopowders were in rutile structure and particle size was of the order of 47 nm. From the optical studies, it was found that the optical band gap of the nanoparticle decreased with the increase of doping concentration. From the magnetic studies it was found that the nanoparticles exhibited ferromagnetism at low external magnetic fields the strength of magnetization increased with the increase of doping concentration. It seems that the observed ferromagnetism is an intrinsic in nature.

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