

Enhanced Room Temperature Ferromagnetism in Polyethylene Glycol Capped $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ Nanoparticles

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Abstract — $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x=0.00, 0.01, 0.03, 0.05$ and 0.07) nanoparticles were synthesized by simple chemical co-precipitation method using polyethylene glycol (PEG) as a surfactant for the first time. EDAX spectra confirmed the presence of Cr and Cu in the host material with near stoichiometric ratio. The results from XRD studies indicated that the synthesized samples had a single phase rutile type tetragonal crystal structure as that of ($P4_2/mnm$) SnO_2 . TEM analysis revealed that the average particle size lies in the range of 8-10 nm. Optical absorption spectra and corresponding Tauc's plots showed a blueshift in optical absorption band edge, the bandgap widening with increasing Cu concentration in $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ nanoparticles can be well explained in terms Burstein–Moss effect. From magnetization measurements it is noticed that the saturation magnetization increases for 1% of Cu doping, then decreased with increasing the Cu concentration. The observed magnetic behavior is well supported with the bound magnetic polarons (BMPs) model.

Keywords: Cu co-doping, chemical synthesis, Burstein–Moss effect, FTIR spectra, Room temperature ferromagnetism.

I. INTRODUCTION

Dilute magnetic semiconductors (DMSs) are promising materials for the new functionality of memory devices, detectors, light emitting sources and possible use in next generation spintronic devices with enhanced functionalities such as spin valve transistors, spin light emitting diodes, non-volatile storage and logic devices, since they possess charge and spin degrees of freedom in single substance [1-4]. Recently, extensive research has been performed on transitional metal doped oxide based dilute magnetic semiconducting systems, with the major focus on creating room temperature ferromagnetic semiconductors at above the room temperature [5-9]. Among the family of oxide based semiconductors, SnO_2 is a technologically versatile and important semiconducting material for many applications especially in nanocrystalline form such as gas sensors, optoelectronic devices, dye based solar cells, liquid crystal display transistors and secondary lithium batteries owing to its wide bandgap (3.6 eV at 300 K), relatively large excitation binding energy and good optical transparency in the visible region [10-15]. Further, up to now a numerous results are reported by several research groups on single transition metal ion doped SnO_2 DMS nanoparticles synthesized by different methods [5, 16-21], but doping of two different kinds of ions simultaneously in a host material generates magnetic property which is quite different from the magnetic property

developed due to presence of single transition metal ion, this property is very useful for spintronic applications [22, 23]. Further, co-doping is a fairly simple and effective method to amend the number of vacancies and interstitial host metal atoms, which is useful to explore the mechanism of RTFM. On the other hand, co-doping under appropriate conditions can modify the intrinsic point defects of the TM-doped DMS and influence the properties of the carriers to regulate the magnetism [22, 23]. Moreover to the best of our knowledge, very few co-doped SnO_2 systems have also been reported with expectation that co-doping can lead to remarkable changes in the properties of the materials. K. Nomura et al. [22] found enhanced room temperature ferromagnetism in Fe and Co co-doped SnO_2 . Jun Okabayashi et al. [23] reported enhanced room temperature ferromagnetism in Fe and Mn co-doped SnO_2 . Jasneet Kaur et al. [24] reported electrical and magnetic properties of Co and Fe doped SnO_2 nanorods by Ce co-doped. S. Dalui et al. [25] observed room temperature ferromagnetism in (Co, Mo): SnO_2 films prepared by pulsed laser deposition. In the previous work, we have reported a systematic study on the structural, optical and magnetic properties of Cr doped SnO_2 nanoparticles and observed well defined RTFM hysteresis loop for 1% Cr concentration [26]. In order to study the effect of Cu co-doping, in this paper we report the synthesis, structural, optical and magnetic properties of $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x=0.00, 0.01, 0.03, 0.05$ and 0.07) nanoparticles by the simple chemical co-precipitation method using polyethylene glycol (PEG) as a template. Here we chose Cr and Cu as doping elements, because unlike many other metals, Cr itself is anti-ferromagnetic and an extrinsic ferromagnetism cannot be induced even if Cr clustering occurs [27]. In addition, Cu is a preferred choice to avoid controversies since the secondary phases such as CuO, Cu_2O or Cu related clusters could not contribute to the room temperature ferromagnetism [28], as well as the ionic radii of Cr^{3+} (0.063 nm) and Cu^{2+} (0.065 nm) metal ions are very close to the ionic radius of Sn^{4+} (0.069 nm) metal ion. Among the different kinds of capping agents, here the water soluble PEG was used as a capping agent, it has attracted great attention, because polymer molecules adsorbs to the nanoparticle surface, is generally added both to control the size of the nanoparticles and to prevent the agglomeration of the synthesized particles and it is bio-compatible [29].

Revised Manuscript Received on November 2014.

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II. EXPERIMENTAL

$\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x=0.00, 0.01, 0.03, 0.05$ and 0.07) nanoparticles capped with PEG were synthesized by simple co-precipitation method. All the chemicals $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ and NH_4OH used in the present study are of AR grade (Sigma Aldrich 99.99%) and used without further purification. Aqueous solutions of precursors (0.2M) were separately prepared as per stoichiometric ratio and stirred for 30 min. In this solution NH_4OH (28%) solution was added drop wise in very controlled manner to maintain the chemical homogeneity. The addition of NH_4OH was stopped when pH of the solution reached to 9 at room temperature and added 2ml of surfactant (PEG-400) under vigorous stirring for 8 hr. The precipitate was filtered out separately and washed with de-ionized water to remove unnecessary impurities formed during the synthesis process. The obtained product was placed in oven for 14 hr at 60°C and the dried samples were grounded for half an hour and then annealed at 450°C for 3 hr to obtain $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ nanoparticles. The samples of $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x=0.00, 0.01, 0.03, 0.05$ and 0.07) were subjected to various characterization studies. Structural investigations were done by “Seifert 3003 TT X-ray Diffractometer” with Cu-K α radiation with a wavelength of 1.542 \AA . Crystal structure and crystallite size were obtained from XRD data. The particle size and structure confirmations were done by Phillips TECHNAI FE 12, Transmission Electron Microscope (TEM). The optical absorption measurements were performed in (JASCO-V-670) spectrophotometer. FTIR studies were carried out using Thermo Nicolet FTIR-200 thermo Electron Corporation. Room temperature magnetization was recorded using a Lakeshore Vibrating Sample Magnetometer, VSM 7410.

III. RESULTS AND DISCUSSION

A. Elemental Analysis

In order to confirm the presence of Cr and Cu ions in the host material, the EDAX spectra of co-doped samples were recorded. Fig.1 shows the EDAX spectra of $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x=0.01$) nanoparticles. The EDAX spectra exhibited signals corresponding to Sn, O, Cr and Cu only, indicated that the nanoparticles are made up of tin, oxygen, chromium and copper and no other impurity elements are found within the detection limit of the instrument.

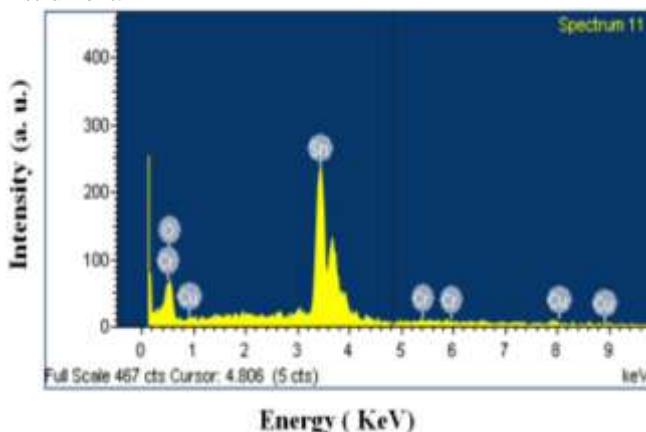


Fig. 1 EDAX Spectra of $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x=0.01$) Nanoparticles

B. Structural Analysis

The as synthesized samples were subjected to XRD studies to obtain information about the crystallinity, size and phase of the $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x=0.00, 0.01, 0.03, 0.05$ and 0.07) nanoparticles. Fig. 2 represents the XRD patterns of $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x=0.00, 0.01, 0.03, 0.05$ and 0.07) nanoparticles and all the peaks could be indexed to the rutile type tetragonal crystal structure of SnO_2 with space group ($P4_2/mnm$). The peaks observed in the XRD patterns match well with the standard JCPDS file no. (41-1445) of SnO_2 . No additional peaks corresponding to the possible impurity phases were observed in the XRD pattern. It is also found that the XRD peaks become gradually sharper with increasing the doping concentration indicating the increase of particle size. The average crystallite size of $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x=0.00, 0.01, 0.03, 0.05$ and 0.07) nanoparticles were determined from XRD broadening using the Debye-Scherrer formula, $D=0.89\lambda/\beta\cos\theta$, where λ is the wavelength of X-ray radiation, β is the full width at half maximum of the peak at diffraction angle θ [30] and the average grain sizes are found to be in the range of 6-8 nm. The increase of crystallite size with increasing the doping concentration may be attributed to the micro structural changes due to non uniform stress or strain during the grain growth or to the existence of local structural disorder in the material at the time of formation. Jun Okabayashi et al. [23] also reported similar increase in crystallite size by co-doping of (Fe, Mn) ions in SnO_2 .

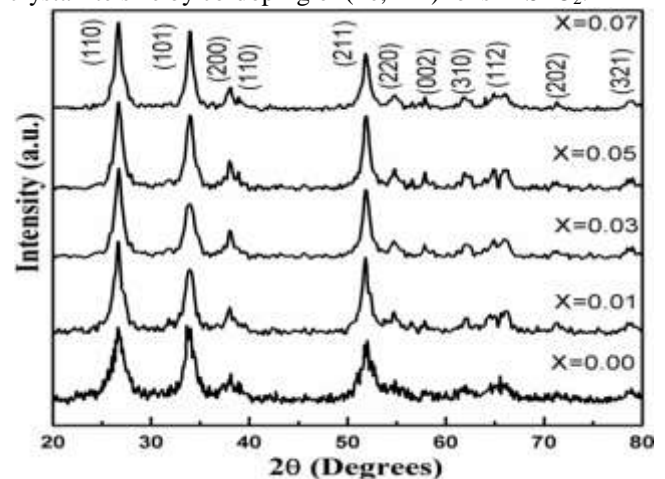


Fig. 2 XRD Patterns of $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ Nanoparticles

C. TEM, HRTEM and SAED Analyses

To obtain the particle size and the information about the nanostructures by direct measurement, TEM is a powerful instrument, it can reveal the size and morphology of the nanoparticles. Fig. 3 shows typical TEM images of $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x=0.00, 0.01, 0.03,$ and 0.05) nanoparticles. Powder samples were dispersed in ethanol and sonicated in ultrasonic bath for 15 min for TEM analysis. It was obvious from the TEM micrograph that the morphology of the particles are found to be nearly spherical in shape and from the images it is also evident that in the present synthesized samples agglomeration was decreased with uniform distribution of particles by the addition of PEG to the host matrix.

The average size of nanoparticles obtained from TEM analysis is about 10 nm which is good agreement with the XRD results and it was clearly confirmed by particle size distribution plots as shown in Fig. 4. Fig. 5 (a-c) show the HRTEM image of $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x=0.00, 0.03$ and 0.05) nanoparticles are about 5 nm with clear lattice fringes. Fig. 5 (d) explore the selected area electron diffraction (SAED) pattern of the $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x=0.01$) sample and all crystalline rings could be indexed to a rutile type of SnO_2 tetragonal crystal structure.

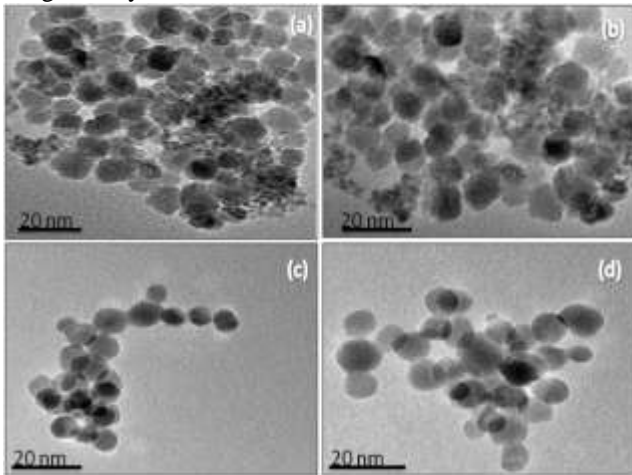


Fig. 3 (a-d) TEM Images of $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x=0.00, 0.01, 0.03$ and 0.05) Nanoparticles

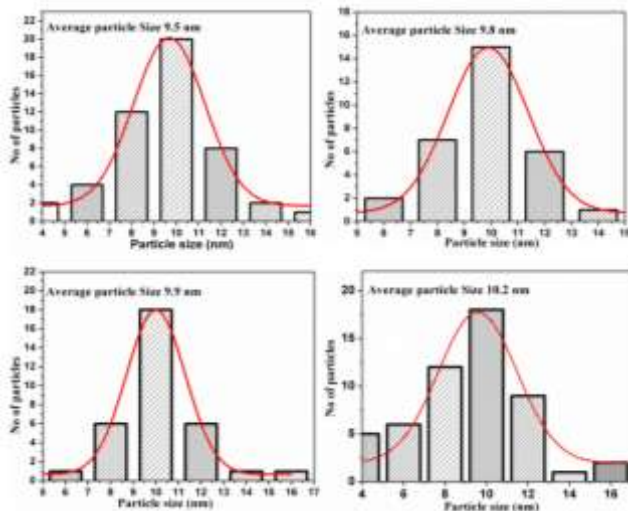


Fig. 4 Particle Size Distribution Graphs for $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x=0.00, 0.01, 0.03$ and 0.05) Nanoparticles

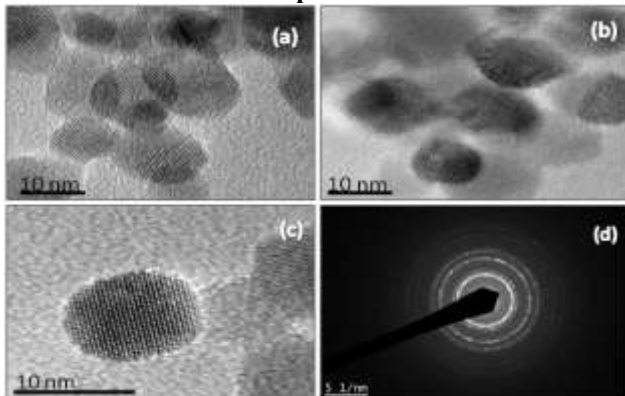


Fig. 5 (a-c) HRTEM Images of the $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x=0.00, 0.03$ and 0.05) Nanoparticles. (d) SAED Pattern of $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x=0.01$) Nanoparticles

D. Optical absorption studies

UV-vis optical absorption spectroscopy is a constructive technique for the characterization of synthesized DMS nanoparticles to get the information of optical bandgap values. The optical absorption spectra and corresponding Tauc's plots of $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x=0.00, 0.01, 0.03, 0.05$ and 0.07) nanoparticles are shown in Fig. 6 and Fig. 7 respectively. Absorption spectra shows an ultraviolet cut-off wavelength around 285–305 nm, which can be different samples varies as the concentration of Cu in the $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ nanoparticles varies. In order to calculate the direct bandgap, we used the Tauc's relation, $\alpha h\nu = A(h\nu - E_g)^n$, Where α is the absorption coefficient, A is a constant and $n=1/2$ for direct bandgap semiconductor. An extrapolation of the linear region of a plot of $(\alpha h\nu)^2$ vs $h\nu$ gives the value of the optical band gap. The measured bandgap was found to be 4.21 eV for 1% Cr doped SnO_2 nanoparticles, which is higher than the reported value of the bulk SnO_2 (3.6 eV) [31]. This can be attributed to the strong quantum confinement of the nanoparticles. On doping of Cu in to the $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ system, the bandgap energy increases, even though the particle size increases. Estimated bandgap values of $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ nanoparticles with $x=0, 0.01, 0.03, 0.05$ and 0.07 are 4.21 eV, 4.23 eV, 4.24 eV, 4.26 eV and 4.32 eV respectively. Widening of bandgap with increasing Cu content can be well explained in terms of the so-called Burstein–Moss effect that the Fermi level merges into the conduction band with the increasing carrier concentration [32]. S. Dalui et al. [25] reported similar widening of bandgap in (Co, Mo): SnO_2 films prepared by pulsed laser deposition. There is no data available on optical bandgap studies of $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x=0.00, 0.01, 0.03, 0.05$ and 0.07) nanoparticles for comparison.

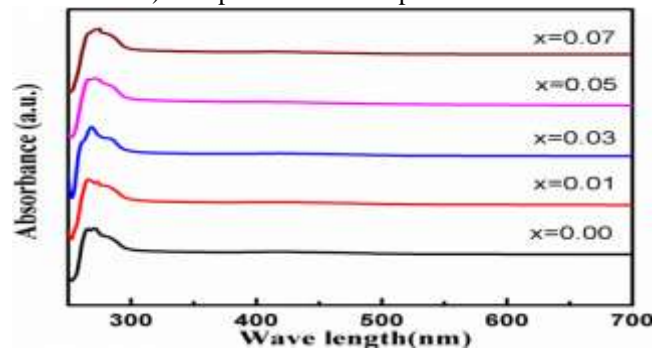


Fig. 6 Optical Absorption Spectra of the $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x=0.00, 0.01, 0.03, 0.05$ and 0.07) Nanoparticles

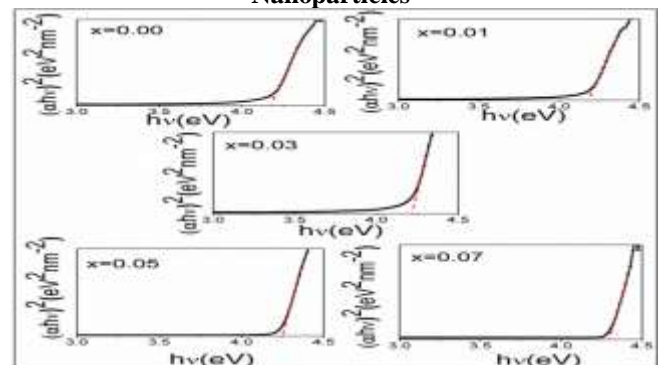


Fig. 7 Tauc's Plots of the $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x=0.00, 0.01, 0.03, 0.05$ and 0.07) Nanoparticles

E. FTIR Analysis

In order to confirm the phase purity of the investigated samples, FTIR was recorded in the range of 500 to 4000 cm^{-1} . Due to larger probing depth of IR, this technique is more sensitive than X-ray diffraction and Raman spectroscopy in the characterization of phases and lattice distortions. Fig. 8 shows FTIR spectrum of $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x = 0.00, 0.01, 0.03, 0.05$ and 0.07) nanoparticles capped with PEG. All the samples exhibited absorption bands at 3741 cm^{-1} , 3614 cm^{-1} , 2943 cm^{-1} , 2310 cm^{-1} , 1672 cm^{-1} , 1508 cm^{-1} , 1095 cm^{-1} and 680-590 cm^{-1} . The spectral bands at 3741 cm^{-1} , 3614 cm^{-1} and 1672 cm^{-1} are attributed to characteristic absorption of O-H stretching vibrations of H_2O molecule. The presence of these bands in synthesized nanoparticles may be due to the adsorption of atmospheric water content. A small absorption peak observed at 2943 cm^{-1} was due to C-H stretching vibrations. The spectral band at 2310 cm^{-1} is related with the N-H^{2+} asymmetric stretching vibrations of amines. The absorption peaks found at 1508 cm^{-1} and 1095 cm^{-1} are assigned to the asymmetric and symmetric C-O stretching vibrations. Finally broad peak at around 680-590 cm^{-1} in Cr doped and (Cr, Cu) doped SnO_2 samples in the infrared spectra is due to the stretching vibrations of O-Sn-O it confirms the bonding of metal-oxygen as present in SnO_2 [33-36]. Fig. 9 shows FTIR spectra for uncapped SnO_2 nanoparticles. The peaks are only located at 610 cm^{-1} , 1656 cm^{-1} and 1550 cm^{-1} . These peaks are related to metal-oxygen and hydroxyl compound. We have not observed any modes corresponding to the Cr and Cu, since it is located in the interior of the nanoparticle not on the surface. It is further indicated that Cr and Cu is completely doped into SnO_2 . Further above considerations perceptibly confirmed that the surface of SnO_2 : (Cr, Cu) nanoparticles were capped by PEG.

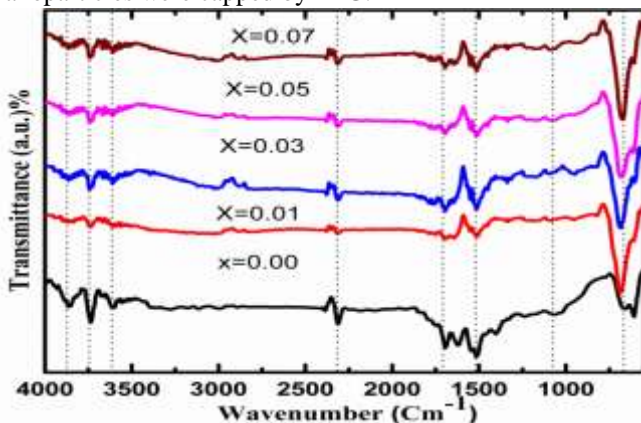


Fig. 8 FTIR Spectra of $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x = 0.00, 0.01, 0.03, 0.05$ and 0.07) Nanoparticles

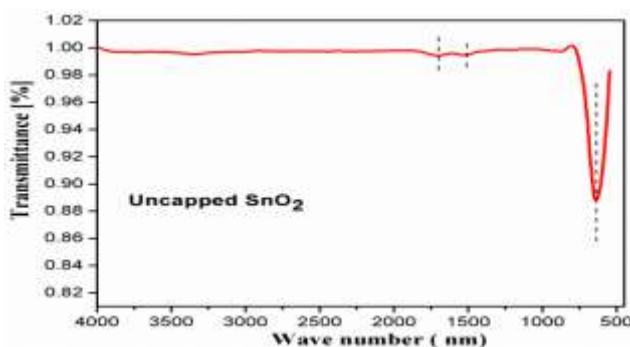


Fig. 9 FTIR Spectra of Uncapped SnO_2 Nanoparticles

F. Magnetic Studies

Magnetization measurements were carried out at room temperature for $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x = 0.00, 0.01, 0.03, 0.05$ and 0.07) nanoparticles as shown in Fig. 10. It is interesting to note that all the samples of the present investigation are found to exhibit room temperature ferromagnetism (RTFM). The room temperature ferromagnetism in Cr and Cu co-doped SnO_2 nanoparticles could arise by the number of secondary phases such as magnetic phase of CrO_2 or anti-ferromagnetic phases of Cr_2O_3 , Cr_3O_4 or CuO , Cu_2O and Cu clusters. In fact no trace of Cr metal clusters and Cu related clusters was detected by XRD measurements in the synthesized nanoparticles, moreover none of them exhibited room temperature ferromagnetism above room temperature. Consequently it may conclude that the observed ferromagnetism in the present samples is not due to the presence of any secondary phases, and it is attributed to the doping of Cr, Cu metal ions and presence of oxygen vacancies in SnO_2 lattice. In case of $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x = 0.00, 0.01, 0.03, 0.05$ and 0.07) nanoparticles, the origin of ferromagnetism is very complex. Although different mechanisms might be responsible, an endeavor has been made to explain the phenomenon using bound magnetic polarons (BMPs) model [37, 38].

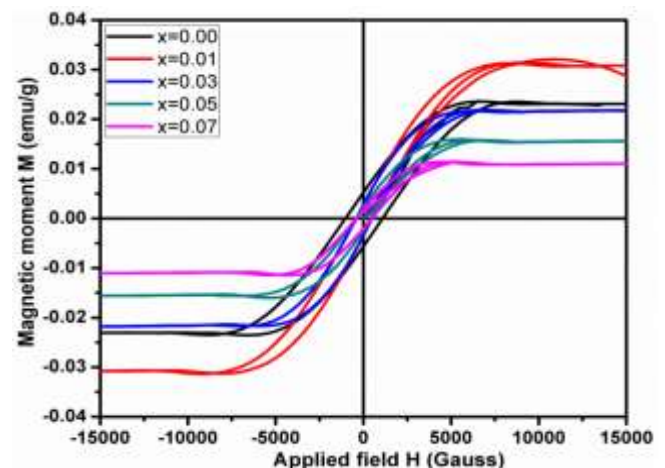


Fig. 10 Room Temperature M-H Plots of $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x = 0.00, 0.01, 0.03, 0.05$ and 0.07) Nanoparticles

According to BMP model, the localized spins of the dopant ions interact with the charge carriers which are bound to a small number of defects such as oxygen vacancies, resulting in a magnetic polarization of the surrounding local moments. In the samples of present investigation, due to the substitution of Cr^{3+} and Cu^{2+} for Sn^{4+} , a large number of free charge carriers and oxygen vacancies might have been introduced to maintain the charge neutrality leading to the formation of BMPs. Particularly in $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x = 0.01$) doped system enhanced ferromagnetism was observed, on the other hand for $x \geq 0.01$ the magnetization parameters were decreases with increasing Cu concentration, it may be due to interactions among these Cr^{3+} - Cu^{2+} and Cu^{2+} - Cu^{2+} ions becomes anti-ferromagnetic (AFM) in nature. The enhanced anti-ferromagnetic (AFM) interaction arising from the increased volume fraction of Cu ions, suppresses the

ferromagnetic ordering at higher doping concentration. The values of the saturation magnetization (M_S), residual magnetization (M_R) and coercive field (H_C) of the present samples were obtained from the hysteresis loops and are given in Table 1. The table 1. indicates that the magnetization increases with the doping concentration of 1 at% of Cu and the values of saturation magnetization (M_S), residual magnetization (M_R) and coercive field (H_C) are continuously decrease with increasing doping concentration.

Table. 1 Magnetic parameters of $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ ($x=0.00, 0.01, 0.03, 0.05$ and 0.07) nanoparticles.

Parameter	Sample				
	$x=0.00$	$x=0.01$	$x=0.03$	$x=0.05$	$x=0.07$
M_S (emu/g)	23.13×10^{-3}	30.75×10^{-3}	21.31×10^{-3}	15.61×10^{-3}	10.78×10^{-3}
M_R (emu/g)	5.03×10^{-3}	29.03×10^{-4}	20.51×10^{-4}	18.66×10^{-4}	15.37×10^{-4}
H_C (Gauss)	910	640	589	540	520

IV. CONCLUSIONS

In summary, we have investigated structural, optical and magnetic properties of the chemically synthesized Cr and Cu co-doped SnO_2 DMS nanoparticles. EDAX spectra confirmed the presence of Cr and Cu in the SnO_2 host matrix. The XRD studies revealed that particles are crystallized in single phase rutile type tetragonal crystal structure ($P4_2/mnm$) of SnO_2 . TEM analysis suggested the formation of nanometric particles with average particle sizes are in the range of 8-10 nm. Optical absorption spectra and corresponding Tauc's plots showed that a blueshift in optical absorption band edge and related bandgap widening with increasing Cu concentration in $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ nanoparticles can be well explained in terms Burstein–Moss effect. FTIR studies recognized that strong oxide bridge functional group in all present samples. All the Cu co-doped $\text{Sn}_{0.99-x}\text{Cu}_x\text{Cr}_{0.01}\text{O}_2$ nanoparticles exhibited strong room temperature ferromagnetism with nominal doping concentrations, further magnetization parameters were decreased with increasing the doping concentration. The BMP model is a reasonable explanation for observed RTFM. Hence the present synthesized material has good potential to be used in new generation spintronic devices.

ACKNOWLEDGMENTS

The authors are grateful to the University Grants Commission, New Delhi, Government of India, for financial support. The authors are thankful to Mr. N. Sivarama krishnan and Mr. Muttu kumar, SAIF, IIT Madras, Chennai for extending the VSM facility.

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