



LUMINESCENCE ENHANCEMENT OF CO-DOPED SnO₂ NANOPARTICLES

M.Umadevi

Department of Physics, Sri Parasakthi College for women, Courtallam India.

ABSTRACT From the optical properties of the samples the band gap (E_g) is found to be reduced from 3.79 to 3.62 eV with increasing Co dopant concentration due to the defect of oxygen vacancies. From PL spectra, the oxygen vacancy is one of the active luminescent centre, thus, it greatly influences in the PL emission intensity. The intrinsic defects such as oxygen vacancies can also act as luminescent centers by formation of defect levels located inside the energy gap and trap electrons from the valence band. The chemical compositions of the prepared samples have been studied using the energy dispersive X-ray analysis.

KEYWORDS : Optical, EDAX, doping.

1. INTRODUCTION

Oxide based diluted magnetic semiconductors have been attracting passionate interest to the current researchers due to their potential applications in Spintronics. The materials can exploit both charge and spin degrees of freedom of electrons to create new functionalities beyond conventional semiconductors. The most common approach to drive a semiconductor ferromagnetic is that of diluted magnetic semiconductors (DMSs), which is obtained by doping a non-magnetic semiconductor with a few atomic percent of transition metal (TM) elements (V, Cr, Mn, Fe, Co, Ni and Cu). Recently, magnetic semiconductors have been studied extensively with the doping of magnetic transition metal ions (Co, Mn, Cr and Ni) for multidisciplinary magneto electronic devices. Further the diluted magnetic semiconductors with high T_c is needed for real life advanced spintronics device fabrication technology.

2. EXPERIMENTAL DETAILS

2.1 Preparation of Co doped SnO₂ nano particles

SnO₂ nano particles doped with three different concentration of Co 2%, 4% and 6% were prepared by chemical co-precipitation method. The precursors for dopant and host were cobalt nitrate hexahydrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and tin chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) respectively.

3. Result and Discussion

3.1 EDAX analysis

Figures 1 (a, b and c) shows the selected area electron diffraction images of 4% Co and doped SnO₂. Selected area electron diffraction pattern is used to study about the crystal properties of a particular region. The presence of rings with discrete spots suggests that the prepared SnO₂ is made of small particles of uniform size. Ring patterns in the image correspond to the planes (1 1 0), (1 0 1), (2 1 1), (2 0 2) and (3 2 1) are in consistent with the peaks observed in XRD patterns. The distance from centre to each ring (moving from smallest to larger ones) is measured to be 2.68, 4.33, 6.156, 6.862 and 6.99 nm nano particle for Co doped SnO₂ nano particles.

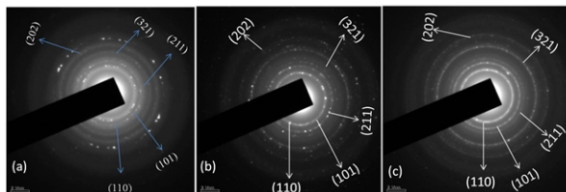


Figure 1. Selected area electron diffraction images of (a) 4% Mn doped SnO₂, (b) 4% Co doped SnO₂, (c) 4% Cr doped SnO₂

Table 1. Calculated 'd' spacing value of different planes of Co doped SnO₂ nano particles

Calculated 'd' values from TEM Å	Reported 'd' value (JCPDS) Å	Planes (hkl)
3.1	3.347	(1 1 0)
2.54	2.6427	(1 0 1)
1.71	1.7641	(2 1 1)
1.32	1.3220	(3 2 1)
1.22	1.2147	(2 0 2)

The EDAX spectra of Co doped SnO₂ nano particles are shown in figures 1, and 2. In the figures, there are peaks for O, Co relatively sharper peak for Sn. Qualitatively, it can be predicted that oxygen deficiency is there in the samples, which, in turn, makes these nano particles n-type semiconductors. However, a proper explanation for this can be provided only after a quantitative chemical analysis. This is attributed to fact that during the crystallization of samples, the oxygen species get de-absorbed and trapped electrons are released, which, in turn, corresponds to the increase in number of oxygen vacancies (Ke et al 2011).

The atomic percentages of Sn, O and Co elements present in the prepared 2%, 4% and 6% Co doped SnO₂ powder is found from the EDAX analysis. The composition of 2% Co doped SnO₂ nano particle is Sn = 33.63 at %, O = 64.37 at % and Co = 2 at %. The 4% Co doped SnO₂ nano particle has a composition of Sn = 29.59 at %, O = 66.49 at % and Co = 3.92 at % and 6% Co doped SnO₂ nano particle has a composition of Sn = 26.05 at %, O = 67.95 at % and Co = 6 at %.

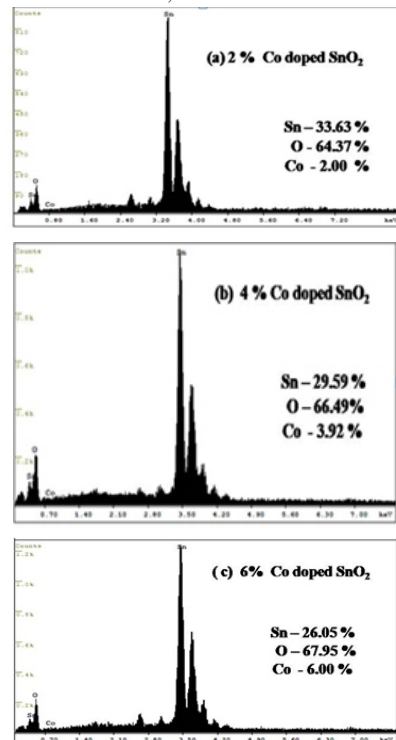


Figure 2 EDAX Spectra of (a) 2% Co doped SnO₂, (b) 4% Co doped SnO₂, (c) 6% Co doped SnO₂

3.2.1 OPTICAL STUDIES

3.2.2 Optical Absorption UV-Studies

Figure.3 shows the absorption spectra of Co doped SnO₂ and the spectra has a sharp absorption edge around 327nm (3.7eV) for 2% Co doped SnO₂ which corresponds to the band gap (E_g) of bulk tetragonal

SnO₂ (3.6 eV). The 4%, 6% Co doped SnO₂ have the absorption edges at 327, 337 and 343 nm. The band gap (E_g) is found to be reduced from 3.79 to 3.62 eV with increasing Co dopant concentration. Such a decrease of the band gap (E_g) is induced by transition metal (Co and Mn) doping in SnO₂. It has been ascribed to the sp-d exchange interactions between the band electrons and the localized d electrons of the transition metal ions substituting for Sn ions. The band gap energy decreases with increasing Co²⁺ dopant concentration which may be attributed to the absorption of trapped electrons and d-d transitions of dopant Co²⁺ ions respectively (Kravets & Poperenko 2008). Moreover, in all absorption spectra, no typical peak corresponding to Co₃O₄ was detected, because the Co²⁺ ions only substituted for Sn⁴⁺ ions rather than creation of oxide impurities.

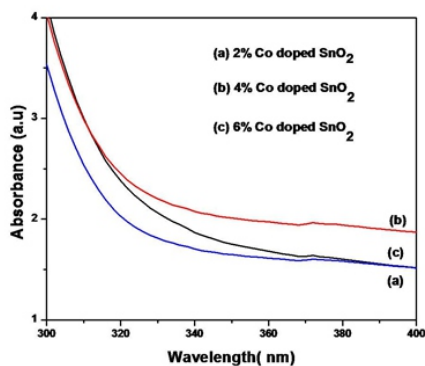


Figure.3 Absorption spectra of (a) 2% Co Doped SnO₂, (b) 4% Co Doped SnO₂, (c) 6% Co Doped SnO₂

Table.2: Band gap of (a) 2% Co doped SnO₂, (b) 4% Co doped SnO₂, (c) 6% Co doped SnO₂

S.No	Samples	Absorption Edge wavelength (nm)	Bandgap (eV)
1	2% Co doped SnO ₂	327.16	3.79
2	4% Co doped SnO ₂	337.27	3.68
3	6% Co doped SnO ₂	343.05	3.62

From the UV-absorbance spectra of Co doped SnO₂, it is observed that 6% of Co doped SnO₂ nano particles shows better optical behaviour compared to various other dopant concentrations. UV absorption edge around 360 nm is associated to the photo exciton of charges from the conduction band to valence band (Tian et al 2008). When the Co concentration increases, the absorption edge shifted towards higher wavelength corresponds to increase in crystalline size. This shift in the absorption edge is directly related to the transition of charges from valence or conduction band of SnO₂ to 4f electrons of transition metal ions. Dopant concentration dependent blue shift of absorption edge is observed in UV-VIS absorption spectra. The potential application of the Co doped SnO₂ nano particles with narrow band gap are in optoelectronic devices. The measured E_g values are lower than the bulk SnO₂ (3.6 eV), which is directly related to the surface structure, particle size and morphology. The E_g values are found to be in the range of 3.4 eV to 3.7 eV for Co doped SnO₂ nano particles. The band gap values are decreased, when there is an increased concentration of dopants completely incorporated into Sn lattice. This leads to the strong UV-VIS emission in the PL spectra. Further, the variation in band gap energy substantiates the presence of additional energy band within the SnO₂ energy bands, which arises from dopants.

3.2.1 Photoluminescence Studies

The room temperature PL spectra of the Co doped SnO₂ samples were recorded using an excitation wavelength (λ_{exc}) of 385 nm and is shown in Figure.5. PL spectra exhibits only a broad emission peak in the range of 420–540 nm. The Co-doping does not bring about new energy levels in the band structure to produce new emission. It also indicates that the Co²⁺ ions substitute for Sn⁴⁺ ions without the formation of other additional energy levels. As the emission energies are lesser than the band gap (E_g) of all the samples, such the emissions cannot be assigned to direct recombination of electrons in Sn⁴⁺ conduction band and holes in O²⁻ valence band where as it is usually related to the oxygen vacancies. In Co doped SnO₂, the Co²⁺ ion substitute for the Sn⁴⁺ and charge imbalance might influence not only the local disorder but also

the concentration and distribution of the oxygen vacancies. It is understood that the Co substitutes at the Sn site in SnO₂ matrix with +2 charge state and does not form metallic clusters and other oxide phases. The intrinsic defects such as oxygen vacancies can also act as luminescent centers by formation of defect levels located inside the energy gap and trap electrons from the valence band. In oxide nano particles, oxygen vacancy is known to be the most common defect and usually acts as a radiative center in the luminescence (Dharmaraj et al 2006).

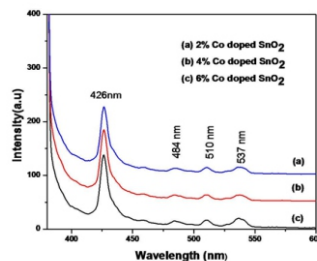


Figure.4 PL Emission spectra of (a) 2% Co doped SnO₂, (b) 4% Co doped SnO₂, (c) 6% Co doped SnO₂

Photoluminescence spectra of the Co doped SnO₂ nano particles excited at 385 nm shows strong UV-VIS emission band. The blue emission at 427 nm and the corresponding energy is 2.9 eV, which is lower when compared to the bulk SnO₂ (3.6 eV). It is ascribed to the direct electronic transition between donor level to valence band. In particular, in SnO₂ semiconductor nano systems, the oxygen vacancy is one of the active luminescent centre, thus, it greatly influences in the PL emission intensity (Gu et al 2003). The occurrence of PL band at 427 nm is associated to luminescent centres and dangling in the SnO₂ nano particles. When the concentration of Co is increased, it exhibits strong blue emission with high intensity hump of about 427 nm - 540 nm in PL spectra. This confirms the influences of dopants in luminescent behavior of SnO₂ nano particles. It is clear that the blue shift, in the PL spectra with Co doped SnO₂, is due to the appearance of new unoccupied states located near the SnO₂ conduction band.

4. CONCLUSION

Detailed investigations have been carried out on Co doped SnO₂ chemical co precipitation method. There are a few reports describing the chemical precipitation method. In the present work the effect of concentration on the optical and magnetic properties of Co doped SnO₂ nano particles has been investigated in detail. Nano particles of basic composition 2%, 4% and 6% Co doped SnO₂ have been prepared by the chemical precipitation method. The doping of Co in SnO₂ brought significant changes in the physical properties of the samples. It is observed that the average crystallite size, lattice constant and increased with Doping. Magnetization measurement shows that saturation magnetization increased with doping which is attributed to large amount of induced defects and oxygen vacancies formed in the sample. The present investigation clearly points out that on the doping dependent properties and the vacancy induced ferromagnetism in Cobalt doped SnO₂.

5. REFERENCES

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