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Structural, optical and morphological properties of La, Cu co-doped SnO_2 nanocrystals by co-precipitation method

S. Nilavazhagan, S. Muthukumaran *, M. Ashokkumar

PG and Research Department of Physics, H.H. The Rajah's College, Pudukkottai 622 001, Tamilnadu, India

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ABSTRACT

$Sn_{0.96-x}La_{0.04}Cu_xO_2$ ($0 \leqslant x \leqslant 0.03$) nanocrystals have been successfully synthesized by employing a simple co-precipitation method. The crystal structure of the synthesized nanocrystals was found to be tetragonal rutile of tin oxide by using X-ray diffraction technique and was not affected by doping. The change in lattice parameters was discussed based on the secondary phase formation and presence of Cu^{2+}/Cu^{3+} in La—SnO_2 lattice. The variation in size and shape of the nanocrystals by Cu-doping was discussed using scanning electron microscope. The chemical stoichiometry of Sn, Cu, La and O was confirmed by energy dispersive X-ray spectra. The best optical transparency and lower absorption observed at $Sn_{0.97}La_{0.02}Cu_{0.01}O_2$ nanocrystals seems to be optimal for industrial applications especially as transparent electrode. The initial blue shift of energy gap from 3.65 eV (Cu = 0%) to 3.78 eV (Cu = 1%) ($\Delta E_g \approx 0.13$ eV) is due to the distortion in the crystal structure of the host compound and generation of defects. The red shift of energy gap after Cu = 1% is due to the charge-transfer transitions between the metal ions d-electrons and the SnO_2 conduction or valence band. Lattice mode of SnO_2 at 686 cm^{-1} in $Sn_{0.98}La_{0.02}O_2$ nanocrystals and anti-symmetric Sn—O—Sn stretching mode of the surface bridging oxide around 634–642 cm^{-1} in Cu doped $Sn_{0.98}La_{0.02}O_2$ nanocrystals was confirmed by Fourier transform infrared spectra.

1. Introduction

Tin oxide (SnO_2) is one of n-type wide-band-gap semiconductor material (3.6 eV) and has large exciton binding energy (130 meV) [1]. It has been widely used as a gas sensor material [2,3] and also investigated for use in transistors, electrode materials [4] and solar cells due to their fascinating electronic, catalytic and optical properties. Among the different nanostructures of SnO_2 viz. namely nano-crystals, nano-wires, nano-belts, nanotubes, nanocrystals are technologically important due to their size dependent properties.

For most of those applications, doping of impurities is needed to modify its conductivity, optical absorption and gas sensitivity. The additives like La, Ce and Y [5] stabilize the SnO_2 surface and lead to decrease the grain size. Carreno et al. [5] studied the nanosized SnO_2 powders doped with La and concluded that a supersaturated solid solution yields a nanosized metastable material that will undergo rare earth cation segregation to the outer surface. This process can effectively be used to control the surface chemistry and subsequently grain growth inhibition. In the present investigation, among the two additives, La is used as one of the additives with 2% to avoid the secondary phase formation. Li et al. [6] described the better electrochemical performance, cycling performance and reduced particle size by La-doping (La = 1%, 5% and 10%) in SnO_2 samples. The crystal structure and the gas sensing property of Zn and Cu doped SnO_2 were studied by Rai [7]. He concluded that the compounds have negative temperature coefficient of resistance. Fe et al. explained the change in microstructure of La-doped SnO_2 nanopowders with various dopant concentrations prepared by chemical co-precipitation technique [8]. They discussed the detailed crystallite growth process with different La concentrations between 0 and 10 at.%.

The grain size is typically 20–40 nm, which is highly dependent on the synthesis technique, temperature, doping level, etc. [9]. The optoelectronic properties such as photoluminescence and optical band gap of SnO_2 can also be improved by transition metal (TM) doping. Yu and choi [10] reported that addition of CuO and ZnO abruptly decreased the conductivity of SnO_2. Mishra et al. [11] demonstrated the Cu doping induced modifications in the structural, photoluminescence and gas sensing behavior of SnO_2 nanocrystals. The structural and optical changes in SnO_2 system was discussed using density functional theory [12] by introduction of Cu in a SnO_2. Cu is very good electrical and thermal conducting material so it doped with SnO_2 to improve the electrical and

* Corresponding author. Tel.: +91 04322 221558; fax: +91 04322 230490.
E-mail address: drsmk123@yahoo.co.in (S. Muthukumaran).

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thermal conducting property of the materials. Therefore, to improve the optical, structural and morphological properties Cu is used as the second doping element.

Nanosized doped SnO_2 nanocrystals are successfully synthesized by different methods. Various methods, including molten-salt synthesis [13] sol–gel [14], microwave technique [15], carbo-thermal reduction [16], chemical precipitation [17], laser-ablation synthesis [18], hydrothermal method [19], chemical co-precipitation method [20] and sono-chemical [21] have been developed to synthesize SnO_2 nanostructures. Among these different methods, co-precipitation method is one of the most important techniques to prepare nanocrystals. Co-precipitation is the name given by analytical chemists to a phenomenon whereby the fractional precipitation of a specified ion in a solution results in precipitation not only of target ion but also of other ions existing side by side in the solution.

Most of the literature expressed that La-doped and Cu-doped SnO_2 are studied separately [5–12]. The detailed study of the structural, morphological and optical properties of Cu and La co-doped SnO_2 nanocrystals is still scanty. Doped SnO_2 dealt mainly with gas sensitivity and conductivity of SnO_2 doping systems and less care has been devoted to the microstructure and optical parameters. Therefore, in the present investigation, the major objective is to prepare La doped and Cu, La co-doped SnO_2 ($Sn_{0.98-x}La_{0.02}Cu_xO_2$, $0 \leqslant x \leqslant 0.03$) nanocrystals by co-precipitation method. The effect of Cu substitution on its structural, optical and morphological properties has been studied extensively. Further, the size dependent properties of the nanocrystals are correlated with band gap.

2. Materials and experimental procedure

2.1. Synthesize of $Sn_{0.98-x}La_{0.02}Cu_xO_2$ ($0 \leqslant x \leqslant 0.03$) nanocrystals

$Sn_{0.98-x}La_{0.02}Cu_xO_2$ ($0 \leqslant x \leqslant 0.03$) nanocrystals were prepared by chemical co-precipitation method. For the synthesis of $Sn_{0.98-x}La_{0.02}Cu_xO_2$ sample, tin chloride pentahydrate ($SnCl_4{\cdot}5H_2O$), lanthanum chloride heptahydrate ($LaCl_3{\cdot}7H_2O$), copper chloride dihydrate ($CuCl_2{\cdot}2H_2O$) and sodium hydroxide (NaOH) were used as precursors without further purification. All the used chemicals are highly pure and AR grade from Merck. The appropriate amount of $SnCl_4{\cdot}5H_2O$, $LaCl_3{\cdot}7H_2O$ and $CuCl_2{\cdot}2H_2O$ were dissolved in 50 ml double distilled water and kept stirring until get clear solution. NaOH solution was prepared separately by dissolving appropriate amount of NaOH in 50 ml double distilled water. The prepared NaOH solution was added drop wise to the initial solution to increase the pH to 9. To ensure the completion of reactions, the system was stirred continuously for 3 h at room temperature. The precipitations were filtered and then washed several times using double distilled water and ethanol to eliminate the impurities and chlorine ions from precipitates.

The collected precipitates were dried in an oven at 90 °C for 18 h. The precipitates were collected and grounded using an agate mortar. Finally, the synthesized powders were annealed at 550 °C in air atmosphere for 4 h followed by furnace cooling. The same procedure is repeated for the remaining samples synthesized with nominal compositions of $Sn_{0.98-x}La_{0.02}Cu_xO_2$ ($0 \leqslant x \leqslant 0.03$) nanocrystals.

2.2. X-ray diffraction (XRD) and energy dispersive X-ray (EDX) studies

The crystal structure of $Sn_{0.98-x}La_{0.02}Cu_xO_2$ nanocrystals were determined by powder X-ray diffraction. XRD patterns were recorded on a RigaKu C/max-2500 diffractometer using Cu Kα radiation (λ = 1.5406 Å) operated at 40 kV and 30 mA in the wide angle region from 20° to 70°. The topological features and the composition of Sn, O, La and Cu were determined by energy dispersive X-ray spectrometer on K and L lines. The difference between the measured and predicted peak position ($\Delta 2\theta$) should be kept <0.015° to be able to perform lattice parameters measurements with an accuracy $\geqslant$0.0001 Å.

2.3. Scanning electron microscope (SEM) studies

SEM technique was used to study the grain sizes, rough morphology and distribution of the particles within the matrix. The surface morphology of the samples was studied using a scanning electron microscope (SEM, Philip XL 30).

2.4. UV–Visible optical absorption studies

The UV–Visible optical absorption and transmittance spectra of La-doped and Cu and La co-doped SnO_2 nanocrystals have been carried out with a view to explore their optical properties. The spectral absorption spectra were recorded using UV visible spectrophotometer (Model: Lambda 35, Make: Perkin Elmer) in the wavelength ranges from 300 to 700 nm using cm^{-1} quartz cuvettes at room temperature. Halogen and deuterium lamp are used as sources for visible and UV radiations, respectively at room temperature.

2.5. Fourier transforms infrared (FTIR) studies

The presence of chemical bonding of La-doped and Cu and La co-doped SnO_2 nanocrystals was studied by FTIR spectrometer (Model: PerkinElmer, Make: Spectrum RX I) in the range of 400–4000 cm^{-1}. The sample used for this measurement is in the form of pellets prepared by mixing the nanopowder with powdered KBr in the concentration range of 2% per weight. Resulting disks are placed in sample holder in the measurement chamber.

3. Results and discussion

3.1. X-ray diffraction (XRD) – structural studies

XRD is one of the important tools to analyze the structure of the crystalline materials. XRD pattern of $Sn_{0.98-x}La_{0.02}Cu_xO_2$ ($0 \leqslant x \leqslant 0.03$) nanocrystals are shown in Fig. 1. The XRD pattern shows the close agreement with the standard JCPDS file for SnO_2 (JCPDS 41-1445, lattice constants $a = b = 0.4743$ nm and $c = 0.3198$ nm). All the diffraction peaks are assigned to tetragonal rutile crystalline phases of tin oxide. The diffraction peaks in the XRD pattern of $Sn_{0.98}La_{0.02}O_2$ nanocrystal clearly illustrates the crystalline nature with peaks corresponding to the position 26.64° (110), 33.96° (101), 38.05° (200), 52.32° (211), 55.31° (220), 58.28°(002), 61.69° (310), and 63.02° (112) for $Sn_{0.98}La_{0.02}O_2$ nanocrystal. There are no other characterization peaks corresponding to oxides of Sn/Cu/La or Cu/La related secondary and impurity phases which may be attributed to the incorporation of Cu and La instead of Sn lattice site. The facts indicate that the level of impurity in the sample is low. All the available reflections of the present XRD phases have been fitted with Gaussian distribution.

The enlarged image of the diffraction peak corresponding to (101) plane of $Sn_{0.98-x}La_{0.02}Cu_xO_2$ nanocrystals between 32.7° and 35.2° is shown in Fig. 2a which is used to study the Cu doping effect on peak position and peak intensity. Fig. 2b shows the variation of peak intensity and full width at half maximum (FWHM) as a function of Cu concentrations from 0% to 3% along (101) plane. The peak intensity is increased and the peak position is shifted towards higher 2θ side ($\Delta 2\theta \sim 0.1°$) when 2% of Cu is introduced into the Sn—La—O lattice. Further increase of Cu-doping concentration, beyond 2%, the peak position is shifted towards the lower 2θ