Structural characterisation of aluminium and yttrium co-doped tin oxide

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Abstract. The sol gel technique was successfully used to synthesize the nanocrystals of tin dioxide (SnO_2), co-doped with aluminium (Al) and yttrium (Y). The powders were preheated at different temperatures ranging from 200 to 1000 ˚C. The effects of temperature and dopants on the structure of tin dioxide nanoparticles were investigated. X-ray powder diffraction (XRD) and Raman spectroscopy were used to probe the structural properties. The average crystallite sizes were found to be in the range between 2.5 – 8 nm in the temperature range studied. Both techniques confirm that at higher temperatures there is a high temperature reaction resulting in the formation of yttrium stannate.

Introduction

SnO_2 is an important semiconducting material due to its dipole forbidden direct band gap of 3.6 eV at room temperature [1]. It has multiple applications and such are in the fields of gas sensing [2], solar energy conversion [3] and catalysis [4]. The multifunctionality of nanostructured SnO_2 is due to its high surface to volume ratio, larger band gap energy and high exciton binding energy. It is also mechanically, thermally and chemically stable [5]. SnO_2 has remarkable resistivity variation in gaseous environment and this property is important in gas sensing technology. Optoelectronic properties of SnO_2 depend on the presence of impurities.

Introducing metal dopants has been found to reduce grain growth and also improve the absorption capabilities of nanocrystalline oxides [6]. Co-doping or introducing suitable amounts of more than one type of metals has recently been found to further improve the photocatalytic properties of metal oxides [7]. In this contribution, aluminium (Al) and yttrium (Y) metal cations have been simultaneously introduced in SnO_2 using sol-gel method. The aim of the study is to investigate the effects of combinational doping on the structural properties of SnO_2 using X-ray diffraction (XRD) and Raman scattering spectroscopy. Their effect on the crystallite growth is also examined.

Experimental details

The sol gel preparation method of Ansari et al. [8] was followed in the present work. To prepare Y and Al doped nanocrystalline tin oxide, appropriate amounts of tin chloride octahydrate and water soluble metal salts (yttrium chloride hexahydrate and aluminium trichloride hexahydrate) were dissolved in 40 ml of distilled water to prepare a 0.1 M solution. To this solution, 0.5 ml of aqueous ammonia was gently added and the resulting white precipitate recovered by evaporation. This was followed by

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washing with distilled water to remove the by-product, ammonium chloride. The resulting sample was oven dried at 100 ˚C for overnight followed by a thorough grinding to make fine nanoparticles. The samples were prepared with dopant concentrations of 10 wt % of Al and 10 wt % of Y. Portions of the sample were heated at various temperatures ranging from 200 to 1000 ˚C.
XRD patterns of the samples were recorded in an ambient environment using a Panalytical XPERT PRO diffractometer equipped with a Cu Kα tube (λ = 1.5406 Å) monochromatic radiation source operating at 35 kV and 40 mA.
Raman spectra of all the samples were recorded using the HORIBA Jobin Yvon T64000 spectrometer equipped with an Olympus BX-40 microscope. The spectra were excited using the excitation wavelength of 514.5 nm from an argon ion laser.

Results and discussion
The XRD profiles of the Al/Y-SnO_2 preheated at different temperatures are shown in figures 1(a) and 1(b). For the 200 ˚C sample, three main peaks along (110), (101) and (211) planes are clearly observed indicating that the material is polycrystalline in nature. These diffraction peaks are assigned to tetragonal rutile crystalline phases of tin oxide and are consistent with the values in the standard card (JCPDS 77-0452). As the temperature rises, more peaks associated with SnO_2 become evident indicating the improvement in crystallinity. No characteristic peaks associated with impurities or additional phases are observed for all samples up to 600 ˚C. However, at 800 ˚C new peaks at $2\theta = 30^0$, 36^0, 48^0 and 57^0 associated with the (222), (400), (440) and (622) planes, respectively, start to develop and as can be seen in figure 1(b), at 1000 ˚C the new peaks are intense. These new peaks are associated with yttrium stannate ($Y_2Sn_2O_7$) phase [9] suggesting that at higher temperatures tin dioxide reacts with yttrium to form yttrium stannate. In our earlier paper [10], we used extended x-ray absorption fine structure (EXAFS) to study SnO_2 singly doped with Y and the results showed Y preferred the surface layers. The technique also revealed the formation of yttrium stannate at higher temperatures which is consistent with the present work on the double doped sample. SnO_2 singly doped with Al was also investigated [11, 12] and like in the present work no peaks associated with Al metal or alumina were found, indicating that Al substitutes for Sn in the SnO_2. The lattice parameters and crystallite sizes are shown in table 1. The lattice parameters were determined from the interplaner spacing equation and Bragg's law using the X-ray diffraction peaks of the (101) and (110) crystal planes. As seen from the table, the addition of dopants caused no significant changes in the lattice parameters confirming that Y (with a larger ionic radius than the host ion) has not entered into the matrix. The results of the SnO_2 singly doped with Y [10] showed that heating caused the crystallites to grow to about 40 nm at 1000 ˚C. In the present work, heating to 1000 ˚C resulted in nanocrystals of ~ 8 nm indicating that double doping resulted in considerable pinning of growth.

Table1: Crystallite sizes and lattice parameters of Al/Y co-doped SnO_2

Sample	Temperature (˚C)	Crystallite size (nm)	Lattice parameters (Å)		
			a	*b*	*c*
Pure SnO_2 [13]	Ambient	-	*4.738*	*4.738*	*3.188*
Al/Y - SnO_2	200	2.6	*4.810*	*4.810*	*3.158*
	400	3.2	*4.810*	*4.810*	*3.198*
	600	4.5	*4.747*	*4.747*	*3.080*
	800	6.0	*4.747*	*4.747*	*3.065*
	1000	8.0	*4.706*	*4.706*	*3.012*

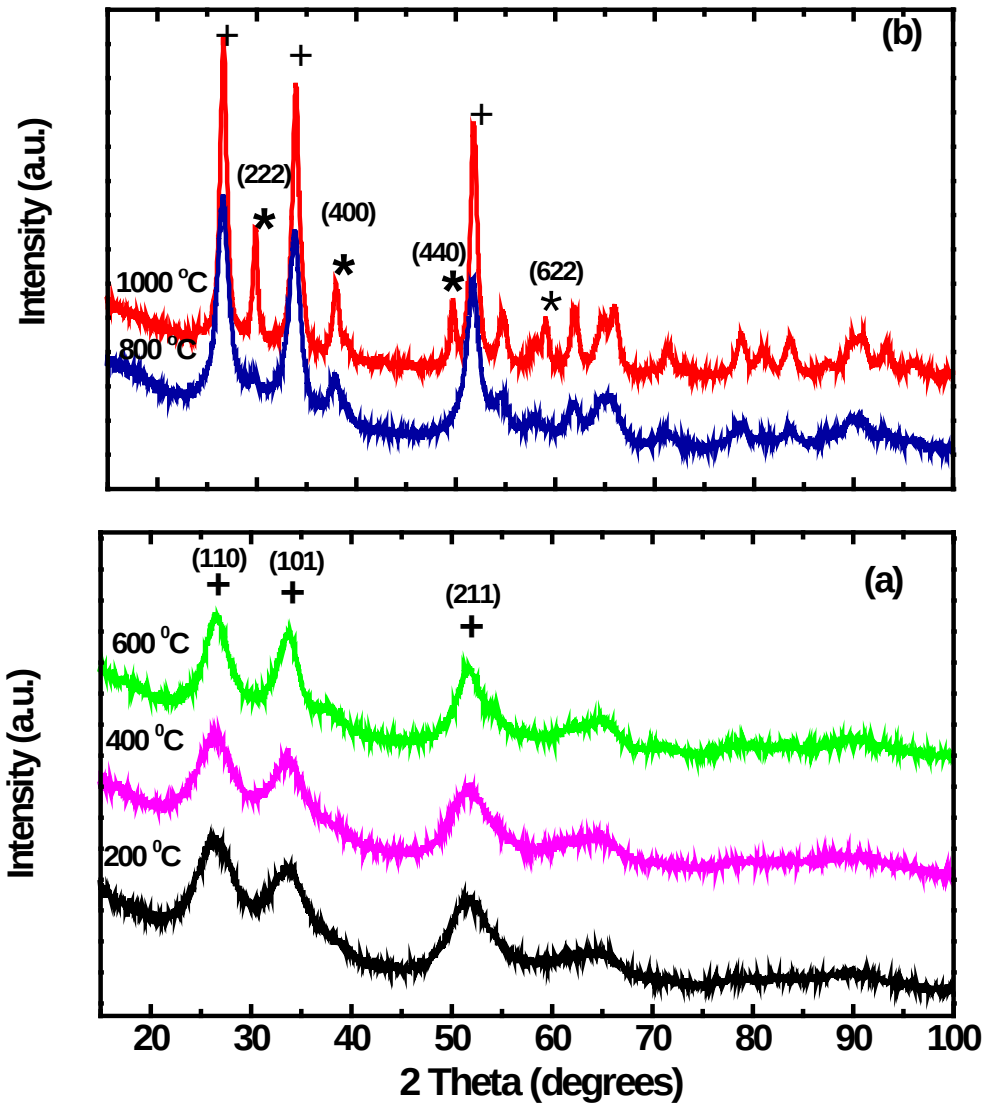

Figure 1: XRD profiles for Y/Al co-doped SnO_2 at (a) 200 ˚C, 400 ˚C and 600 ˚C and at (b) 800 ˚C and 1000 ˚C, where peaks associated with SnO_2 are indicated by (+) and those associated with $Y_2Sn_2O_7$ are indicated by (*).

SnO_2 is expected to display three main Raman bands, i.e. A_{1g} (630 cm^{-1}), B_{2g} (774 cm^{-1}) and E_g (472 cm^{-1}) [14]. Figure 2 shows the Raman spectra of Al/Y co-doped nanocrystalline SnO_2 at various temperatures. The Raman spectrum of the sample heated at 200 ˚C is similar to the as prepared (not shown) and it displays a broad Raman band at 572 cm^{-1} associated with the amorphous tin (IV)-hydrous oxide [15]. The 572 cm^{-1} band is still observed at 400 ˚C although peaks associated with the SnO_2 start to develop at 630 cm^{-1} and 774 cm^{-1}. Above 400 ˚C, the amorphous phase is no longer visible and at 800 ˚C the three Raman active modes i.e. A_{1g}, B_{2g} and E_g are observed although only the A_{1g} band is clearly visible due the particle size being small. At 1000 ˚C, all the three bands are clearly visible with the A_{1g} being the most intense. In addition to those associated with SnO_2, more Raman bands at 508 cm^{-1}, 412 cm^{-1} and 311cm^{-1} associated with yttrium stannate ($Y_2Sn_2O_7$) [16] are observed.

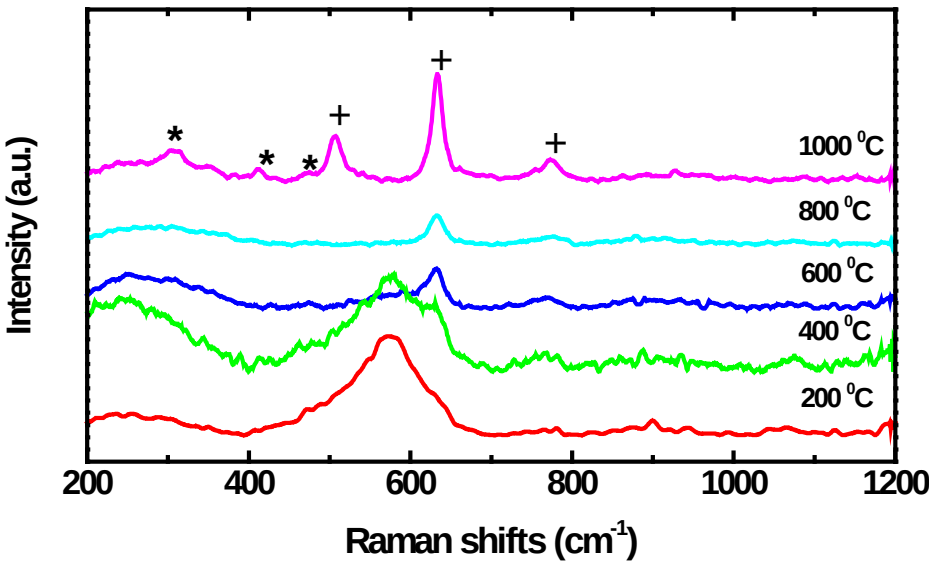

Figure 2: Raman spectra of Al/Y SnO_2 at different temperatures, where peaks associated with SnO_2 are indicated by (+) and those associated with $Y_2Sn_2O_7$ are indicated by (*).

Conclusions

The sol gel technique was successfully used to synthesize the nanocrystals of tin dioxide (SnO_2) co-doped with aluminium and yttrium. The samples were characterised by XRD and Raman. The Raman results show that at lower temperatures there is an amorphous phase although not clearly shown by XRD. The results reveal that double doping significantly reduces the crystallite growth of SnO_2. There was no evidence of an Al metal or alumina in the sample indicating that Al may have substituted for Sn atom in the SnO_2. Y is probably on the surface layers. Both XRD and Raman results consistently show that at high temperatures SnO_2 chemically reacts with Y to form yttrium stannate.

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