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Investigation of phase segregation in yttrium doped zinc oxide

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Abstract

We report the effect of phase segregation on the structural, morphological, and optical properties of sol–gel synthesized $Zn_{1-x}Y_xO$ samples in dilute concentration of 1–5 %. X-ray diffraction patterns confirm that below 3% of Y doping, pure ZnO wurtzite structure phase is obtained and phase segregation of Y_2O_3 appears at $x \geq 0.03$. XRD results are well supported by the results obtained from scanning electron microscopy, Photoluminescence and Raman spectroscopy techniques. The difference in the charge states, ionic radii and the coordination numbers of host lattice and dopant ions leads to the phase segregation.

Keywords: Crystal structure; Rare earth doping; Phase segregation; Raman spectroscopy

1. Introduction

ZnO with a wide band gap (3.3 eV) and large exciton binding energy (60 meV) is the most studied material because of its wide range of applications in the field of optoelectronics devices [1–4]. Although ZnO had been widely studied material for the past decades, the renewed interests are focused on the modifications in various physical properties by rare earth dopants. It has been shown that doping rare-earth ions enable ZnO as a multifunctional system. For instance, Ce doping results in the reduction of band gap (red shift) [5] whereas Er doping enhances the band gap (blue shift) of the material [6]. Apart from band gap engineering, Anandan et al. [7] has reported the relatively high photonic efficiencies and improved photocatalytic activity for La doped ZnO samples. Further, the quenching of UV emission band and observation of strong visible emission at ~618 nm has been reported for Eu doped ZnO [8]. Above studies indicate that the desired modifications can be achieved by selecting suitable rare-earth dopants. However, in the context of realization of devices, it is important to understand the crystal structure and the optimization of the procedures as well as the extent of dopant up to which it is soluble in the host matrix. There are many reports on the structural and luminescence properties of rare earth doped ZnO [9,10] but there is hardly any report available on the effect of phase segregation. Even though, Yttrium does not directly belong to rare earth group, it exhibits the properties similar to rare-earth ions. It has been observed that there is an enhancement in defect-induced green–yellow visible emission which in turn is responsible for the enhanced magnetic performances in Y doped ZnO nanorods.

Present work aims to determine the optimum solubility of Y in the host ZnO and to understand the physical properties when Y ions are doped in dilute concentration of 5%. The sol–gel route is chosen in the present study for the synthesis because of low cost, high yield, high purity and relatively easier process as compared to other synthesis methods. Further, the effect of phase segregation on the structural and optical properties of Y doped ZnO samples are investigated by employing various techniques such as

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X-ray diffraction (XRD), Scanning electron microscopy (SEM), Photoluminescence (PL) and Raman spectroscopy.

2. Experimental details

Pure and yttrium doped zinc oxide ($Zn_{1-x}Y_xO$) samples with different Y concentrations (x=0.0, 0.01, 0.03 and 0.05, represented as Y0, Y1, Y3 and Y5) were synthesized using sol–gel method. $Zn(NO_3)_2\cdot 6H_2O$, $Y(NO_3)_3\cdot 6H_2O$, citric acid and ethylene glycol were used as the starting materials for the synthesis and were dissolved in distilled water. The mixed solution was heated at 80 °C with continuous stirring for 2 h in order to get the gel which was dried at 100 °C for overnight. The powder was further sintered at 1000 °C for 12 h to obtain the desired phase. Synthesized samples were then characterized to study their structural, morphological and optical properties. X-ray diffraction (XRD) study of synthesized samples was carried out using Bruker D8 X-ray diffractometer while surface morphology was investigated by scanning electron microscope (SEM), MIRA II LMH, TESCAN, with energy dispersive X-ray spectroscopy (EDX). Raman spectroscopy was performed on these samples with InVia Raman microscope (Renishaw) with Ar^+ ion laser beam having wavelength of 514 nm and 50 mw power.

3. Results and discussion

3.1. Structural properties

Fig. 1 shows the XRD patterns of $Zn_{1-x}Y_xO$ (x=0.0, 0.01, 0.03 and 0.05) samples. All the diffraction peaks are indexed to pure wurtzite phase of ZnO with hexagonal structure (JCPDS file 36-1451). It is observed that there were no detectable peaks of Y_2O_3 for 1% Y doping, which means that such a small amount of Y does not affect the wurtzite structure of ZnO. The analysis of the diffraction peaks of both pure and 1% Y doped ZnO, revealed that there is a shift in the diffraction peaks of doped ZnO towards lower angle as compare to the former. This is due to smaller ionic radii of Zn^{2+} ions (0.74 Å) as compared to the Y^{3+} ions (0.89 Å) [9]. Similar observation has also been reported in previous studies and the shifting of (002) peak is correlated with the change of lattice parameter [12]. The lattice constants for pure and 1% Y doped ZnO samples are found to be $a=3.233$ Å, $c=5.169$ Å and $a=3.250$ Å, $c=5.207$ Å, respectively. The increment in the doping concentration (for $x=0.03$ and 0.05 samples) leads to the formation of impurity peaks (corresponding to Y_2O_3 phase marked as $*$ in the Fig. 1). This indicates that the excess amount of Y cannot be incorporated in ZnO host lattice sites, giving rise to a separate phase under the experimental conditions. As evident from Fig. 1 that the intensity of peaks corresponding to impure phases increases with the increase in concentration of Y. It is observed that the c-axis lattice parameter value for 3% and 5% Y doped ZnO is smaller than 1% Y doped ZnO sample but larger than pure ZnO. Such kind of variation in lattice parameter is due to phase segregation (i.e. the appearance of Y_2O_3 phase) after 1% Y doping. It is contemplated that after certain doping concentration, Y ions causes deterioration in crystal structure i.e. distortion takes place in ZnO [13]. Also, the non uniform distribution of dopant atoms comes into the picture as the doping concentration exceeds certain value and causes decrement in the value of lattice parameter. Similar kinds of behaviour i.e. decrease in lattice parameter after particular doping concentrations have been reported by other researchers also [10,11].

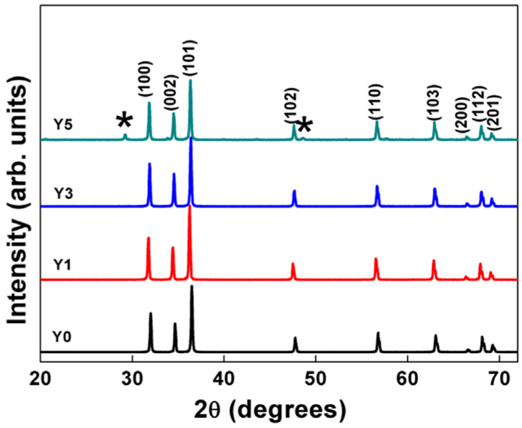

Fig. 1. XRD patterns of $Zn_{1-x}Y_xO$ samples (Y0, Y1, Y3 and Y5). Peaks corresponding to secondary phase of Y_2O_3 are marked as *.

Furthermore, the average crystallite size (D) of these samples is estimated using Scherrer's formula ($D\sim 0.89\lambda/\beta\cos\theta$, where λ is the wavelength of X-rays, β is the FWHM and θ is Bragg's angle) [14]. The crystallite size for pure ZnO was estimated to be ~9.13 nm, and found to vary from 9.13 nm to 10.58 nm by increasing the Y content (Table 1).

3.2. Morphological studies

Fig. 2 (a–d) shows the SEM images recorded for morphological studies. The well defined crystals of pure ZnO are observed as can be seen from Fig. 2(a). As the doping concentration increases, the well-defined crystals of pure ZnO changes to platelet like structures with a wide range distribution of size and shape. It has been observed that the average particle size for pure ZnO estimated from SEM was found to be increasing with the increase in Y content (up to 1% Y doping). The doping of 3% or higher concentration of Y exhibits some smaller particles along with well defined ZnO crystals and their concentration increases with the increment in Y concentration. The existence of smaller particles in the system may be attributed to the Y_2O_3 phase which clearly indicates the beginning of phase segregation for ($x\geq 3\%$). In order to confirm composition and the phase segregation effect, energy dispersive X-ray spectroscopy (EDX) measurement was

Table 1
Different parameters obtained from XRD data of $Zn_{1-x}Y_xO$ samples.

Samples	c-axis lattice parameter (Å)	a-axis lattice parameter (Å)	Crystallite size (nm)
Y0	5.169	3.233	9.13
Y1	5.207	3.250	9.67
Y3	5.187	3.243	10.58
Y5	5.197	3.243	9.15