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Tweaking electrical and magnetic properties of Al–Ni co-doped ZnO nanopowders

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Abstract

The preparation of pure ZnO, doped [$(Zn_{0.99}M_{0.01})O$] and co-doped [$(Zn_{0.99}Al_{.01-x}Ni_x)O$: $x=$ .005, .007] materials, where M = Al, Ni has been carried out by co-precipitation route. The results of various characterizations such as X-ray diffraction (XRD), Vibrating Sample Magnetometer (VSM) and dc conductivity measurements on these samples have been reported. The temperature variation of dc conductivity has been used to delineate the changes in the activation energy. A unique plot depicting the variation of activation energy with temperature has been obtained. These results show the potential of aluminium and nickel co-doped ZnO for spintronic applications.

Keywords: A. Sintering; B. X-ray diffraction; C. Electrical conductivity; D. ZnO; Spintronics

1. Introduction

Zinc oxide has received considerable attention due to its optical and electrical properties. It is a semiconducting material suitable for various technological applications such as varistors, gas sensors, catalysts, transparent conducting films, etc. [1–5]. The non-toxicity and wide band gap (3.437 eV at 2 K) of ZnO make it a valuable electronic and photonic material [6–8]. Nanocrystalline ZnO also possesses excellent chemical and thermal stability. The physical and chemical properties of ZnO could be easily altered by doping with various dopants which has widened its scope of applications. Many researchers are working to improve the electrical and optical properties of ZnO by doping with different metallic ions such as Ga, In, Sn, Al, and Y [9–12] and magnetic properties by Ni, Co, and Mn dopant ions [13–15]. In recent years, substantial amount of research work has been carried out to tune the desired electrical and magnetic properties in the same host compound in bulk as well as in thin film forms [16–17]. ZnO doped with transition metals such as Ni and Co can acts as a ferromagnetic material. Ferromagnetism in transition metal-doped ZnO has been theoretically predicted by Sato and Katayama-Yoshioda [18]. Predominantly, n-type conductivity is exhibited by doped ZnO based varistors. A lot work has already been reported on ZnO based varistors with different dopants [19–24]. The electrical and magnetic properties of ZnO could be altered by variation in microstructural properties, such as grain size, density, morphology and the distribution of second phases. The effect of doping on electrical and magnetic properties of ZnO has been studied by many researchers [25–30], although minimal work has been reported on the simultaneous tuning of electrical and magnetic properties [31]. In the present work, undoped ZnO, aluminium and nickel doped ZnO nanopowders were prepared by a simple and inexpensive co-precipitation method having compositions as ZnO (PZ), $Zn_{0.99}Ni_{0.01}O$ (ZN1), $Zn_{0.99}Al_{0.01}O$ (ZA1), $Zn_{0.99}Al_{0.005}Ni_{0.005}O$ (ZAN55) and $Zn_{0.99}Al_{0.003}Ni_{0.007}$ (ZAN37). The effect of doping has been studied on structural, electrical and magnetic properties. The electrical conductivity measurements were used to calculate the activation energies at various temperatures and a plot showing variation of activation energy with temperature has been obtained for all the samples.

2. Experiment

The co-precipitation method was used for preparation of the ZnO based ceramic nanopowders [32]. Precipitation was conducted

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by adding NaOH (1 M) to the 0.5 M aqueous solution of zinc nitrate hexahydrate. Aluminium nitrate nonahydrate and nickel nitrate hexahydrate were used as the doping sources. Undoped ZnO, doped [($Zn_{0.99}M_{0.01}$) O] and co-doped [($Zn_{0.99}Al_{0.01-x}Ni_x$), O: $x=0.007$, 0.005] samples were prepared by co-precipitation route where M = Al, Ni. The collected white precipitate was calcined at 700 °C for 3 h in a muffle furnace and the resultant powders were used to prepare pellets having a diameter of 7 mm. The pellets were sintered at 850 °C for 3 h with a heating rate of 150 °C/h. The structural investigations of these powders were done with an X-ray diffractometer (Bruker, D8 advanced diffractometer, Germany) using a CuKα radiation and Transmission Electron Microscope (TEM) of TECNAI $(G)^2$ T30 U-TWIN, FEI make. The magnetic studies were carried out by VSM (Micro Scene EV9, USA) at room temperature. Electrical studies of the prepared samples were done by using Keithley 2400 Source Meter at room temperature as well as in the temperature range of 30–200 °C. The conductivity was measured on the pelleted samples with silver coating on both sides to form metal–semiconductor–metal structure.

3. Result and discussion

3.1. Structural analysis

The effect of aluminium and nickel doping on structural properties of ZnO has been studied. Fig. 1 shows the XRD pattern of undoped and doped (ZA1, ZN1, ZAN55, ZAN37) samples of ZnO sintered at 850 °C for 3 h. The observed peaks were found in good agreement with the wurtzite hexagonal structure of ZnO (JCPDS-36-1451). No additional peak was found in undoped ZnO, which confirms the formation of pure crystalline phase of zinc oxide. Fig. 1 shows no extra peak corresponding to Al doping, however, XRD pattern shows the appearance of two low intensity peaks corresponding to NiO phase in ZnO:Ni (ZN1 and ZAN37) sample at 42.9° (200) and 36.96° (111). It is to be noted that no major high intensity diffraction peak was observed corresponding to Al or Ni dopings, indicating that Al and Ni doped ZnO have been synthesised without formation of any secondary phases. The most prominent XRD peak observed corresponding to 101 plane. Fig. 2 shows the comparison for 101 planes of undoped and doped samples. It has been observed (Fig. 2) that the diffraction pattern of doped samples shows a slight right shift in 2theta values relative to undoped ZnO. The maximum shift was observed for ZN1. These shifts in peak position give evidence for doping. The shift in 2theta values has already been studied by various workers [33–38]. In some cases, the shift to the higher 2theta values has been attributed to doping by smaller ions as in our case Al^{3+} and Ni^{2+}. This shift is an evidence of the formation of internal compressive microstress [39]. Doping leads to the creation of compressive microstress (σ_{st}) which results in the structural strain ($\epsilon_s = -\Delta\theta_{(101)}\cot\theta_{(101)}$). Doping in any compound leads to the formation of structural strain which could be co-related to the shift in peak positions. The compressive microstress can be calculated as

$$\sigma_{st} \approx (3\epsilon_s)B \quad (1)$$

where B is the Bulk modulus for ZnO which is about 143 GPa [40]. As mentioned in Table 1, ZN1 shows the maximum compressive microstress and correspondingly results in maximum peak shift of 101 plane Table 2.

Debye Scherrer's formula is used to calculate the crystallite size, according to the formula [41]

$$\text{Crystallite size } (D) = 0.9\lambda/\beta \cos\theta \quad (2)$$

where $\lambda(=1.5418$ Å) is the wavelength of incident X-ray, β is the full width half maxima of maximum intensity peak (101) and θ is the angle at which maximum peak occur.

The calculated average crystallite size for undoped ZnO is around 26.69 nm. The lattice constants 'a' and 'c' were calculated by using well known analytical method [42]. The a/c ratio for undoped sample was found to be 0.6250 which is identical with standard value [43].

The TEM image of undoped ZnO shows a hexagonal shape while that of co-doped sample ZAN55 represents reduced particle size with a marked change in the shape (Fig. 3).

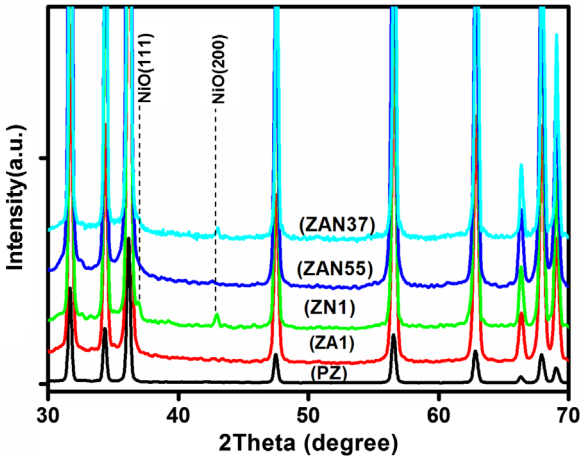

Fig. 1. XRD pattern of undoped and doped (ZA1, ZN1, ZAN55, ZAN37) samples of ZnO compound sintered at 850 °C.

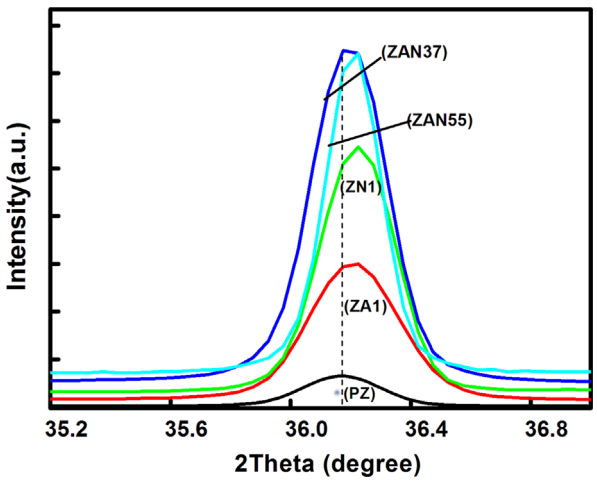

Fig. 2. Comparison for 101 planes of undoped and doped ZnO samples.