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Studies on the synthesis and characterization of co-precipitated nanocrystalline Zn–Pb–O

Sumayya I. Inamdar [a], Aappasaheb R. Babar [b], Sambhaji S. Shinde [c], Kesu Y. Rajpure [a,*]

[a] Electrochemical Materials Laboratory, Department of Physics, Shivaji University, Kolhapur 416004, India
[b] Shankarrao Mohite Mahavidyalaya, Akluj 413101, India
[c] Korea Research Institute of Standards and Science (KRISS), Daejeon, South Korea

HIGHLIGHTS

- Zinc lead oxide nanopowders are synthesized by co-precipitation method.
- Effect of sintering temperature on structure, dielectric and electrical properties.
- Conduction mechanism by complex impedance measurements.

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ABSTRACT

Zinc lead oxide (Zn_2PbO_4) nanopowders were synthesized by a simple co-precipitation method using zinc nitrate and lead nitrate precursors in 2:1 proportion by carefully controlling the preparative parameters. Ammonium hydroxide was used to precipitate Zn^{2+} and Pb^{4+} cations simultaneously. X-ray diffraction study of prepared samples indicates both orthorhombic and tetragonal phase formation of Zn_2PbO_4. The microstructural features are examined by scanning electron microscopy. Frequency dependent dielectric constant (ε') shows the usual dispersion behavior, while linear variation of AC conductivity (σ_{AC}) with frequency confirms the conduction due to small polaron. The DC resistivity decreases with increase in temperature indicating semiconducting behavior of samples. To understand the conduction mechanism, complex impedance measurements are carried out.

1. Introduction

The ZnO [1] and PbO [2] are among the most studied and extensively used photoconductive materials. ZnO, in addition to being a semiconductor, exhibits photonic and electronic applications due to its unique properties such as direct wide band gap (3.3 eV) and large exciton binding energy (60 meV) [3]. PbO_2 decomposes below 400 °C, well below normal solid state reaction temperature at atmospheric pressure. For this reason, zinc lead oxide compounds have not previously been studied [4]. Therefore, the studies on influence of reaction conditions such as reaction temperature and time on formation of Zn_2PbO_4 is of great importance. The order of magnitude of conductivity greatly influences the dielectric and electric behavior of the oxide and depends on the type of preparation method [5]. In co-precipitation method, it depends on the pH of solution, annealing temperature and time. Co-precipitation is a chemical route which plays a crucial role in preparing the final product by minimizing problems associated with diffusion, impurities and agglomeration. Keester and White [4] studied the phase relations in the system PbO–ZnO–O at 4 kbars oxygen partial pressure. They discovered ternary phases viz. Zn_2PbO_4, and $Zn_xPb_{1-x}O$ which were characterized by using X-ray powder diffraction data. Zhou et al. [6] reported ZnPbO nanowires and studied the influence of Pb doping on the optical properties of ZnO nanowires. It was observed that ZnO nanowires show strong redshift as Pb content increases. Yousefi et al. [7] reported Pb-doped ZnO nanowires grown by thermal evaporation method and concluded that optical properties and crystallinity of the Pb-doped ZnO nanowires decreased with increasing Pb concentration from PL and Raman analysis. The studies on synthesis and physical properties of Zn–Pb–O nanoparticles are more useful due to its high dielectric constant and co-existence of various phases which may be applied in various applications.

In the present investigation, we have made an attempt to prepare well crystallized Zn–Pb–O samples from zinc nitrate and

* Corresponding author. Tel.: +91 231 2609227; fax: +91 231 2691533.
E-mail address: rajpure@yahoo.com (K.Y. Rajpure).

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lead nitrate precursors with simple and economical co-precipitation method. Effect of sintering temperature on the phase composition, dielectric and electrical properties of Zn–Pb–O system has been studied.

2. Experimental details

Co-precipitation method was employed to synthesize Zn–Pb–O samples so as to have better control on chemical homogeneity and stoichiometry. Aqueous solutions of Zinc nitrate and Lead nitrate were initially prepared. Both the solutions were mixed together (2:1 M ratio) and a clear solution was obtained. All cations were then co-precipitated using NH_3 solution as a precipitating agent. The precipitate was washed with water and dried at 100 °C for 8 h to get white powders. The white powders were sintered (in separate experiments) at 400 °C, 600 °C, 800 °C and 1000 °C (at the rate of 5 °C/min) for 4 h followed by natural cooling down to room temperature inside the furnace. These samples were further mixed with polyvinyl alcohol as a binder and pressed into pellets having 15 mm diameter and 2–4 mm thickness using a hydraulic press. The flow chart of the synthesis process is depicted in Fig. 1.

Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) of as prepared zinc lead oxide powder was carried out for determination of decomposition temperature of Zn_2PbO_4 with DSC–TGA machine, TA Instruments model SDT 2960. The powders were characterized by X-ray diffractometer (Philips, Model PW-3710) using Cu Kα radiation ($\lambda = 1.54056$ Å) for structural analysis especially to verdict the structure. The surface morphology was investigated using a JEOL JSM-6360 scanning electron microscope (SEM). The frequency dependence of dielectric permittivity (ε') and dissipation factor ($\tan\delta$) in the range from 20 Hz to 1 MHz were studied using a precision LCR meter bridge (HP 4284 A). By using this data the dielectric constant (ε') was estimated using the relation [5],

$$\varepsilon' = \frac{C_p t}{\varepsilon_0 A} \quad (1)$$

where C_p is the capacitance of the pellet, t the thickness of the pellet, A the area of cross section of the pellet and ε_0 the permittivity of free space (8.854×10^{-12} F m^{-1}).

The AC conductivity (σ_{AC}) of the samples was estimated from the dielectric parameters using the relation,

$$\sigma_{AC} = \omega\varepsilon'\varepsilon_0 \tan\delta \quad (2)$$

where ω the angular frequency and $\tan\delta$ is the dissipation factor. The impedance parameters namely Z' and Z'' for all the samples were measured at room temperature in the frequency range 20 Hz–1 MHz using a precision LCR meter bridge (model HP 4284 A).

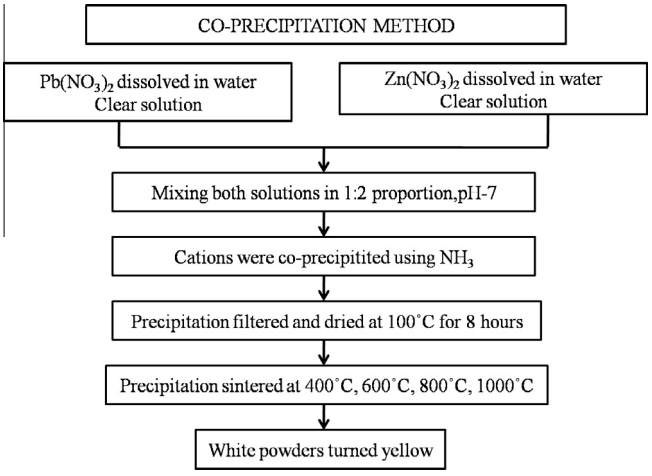

Fig. 1. Flow chart of the synthesis process.

3. Results and discussion

3.1. Thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA)

TGA–DTA is important in studying the transformation of a solid sample in a thermal process [8,9]. TGA measures the change in mass of a sample as a function of time or temperature in an inert or oxidative atmosphere. DTA is a calorimetric technique, recording the temperature and heat flow associated with thermal transitions in a material. In order to predetermine the appropriate temperature for the decomposition of Zn_2PbO_4, the TGA and DTA studies have been carried out. The thermogram recorded for mixture of $Zn(NO_3)$ and $Pb(NO_3)$ powders is shown in Fig. 2. TGA showed a weight loses in the temperature ranges 75–150 °C and 400–500 °C and correspondingly DTA showed one endothermic peak at these temperatures. Initially minor weight loss in the temperature range 75–100 °C is observed which corresponds to removal of hydroxide phases and adsorbed water molecule. A rapid weight loss, found in temperature range of 400–500 °C, is a consequence of removal of the nitrate group (in the form of NO_2 and O_2) from the precursor, resulting in the formation of Zn_2PbO_4 phase. After 500 °C, the TGA trace is stable with no further weight loss indicating the stability of phase. Therefore as prepared samples were sintered at 400 °C, 600 °C, 800 °C and 1000 °C in ambient atmosphere for further studies.

3.2. X-ray diffraction studies

X-ray diffraction spectra of zinc lead oxide samples sintered at different temperatures are shown in Fig. 3. The intensity and number of diffraction peaks depend on the density of the electrons in particular plane and amount of corresponding phase respectively. Diffraction patterns reveal that the (Zn_2PbO_4) phase is observed at 400 °C with good crystallinity. The data is analyzed by making use of JCPDS data card nos. 23-1496 (orthorhombic Zn_2PbO_4) and 23-1497 (tetragonal $Zn_xPb_{1-x}O$). Diffraction pattern reveals that samples contain mixed ternary phases viz. Zn_2PbO_4 and $Zn_xPb_{1-x}O$. The relative amount of Zn_2PbO_4 phase is more than $Zn_xPb_{1-x}O$. Characteristic peaks viz. (130), (300), (221) and (212) of Zn_2PbO_4 have been detected. Number of peaks of both phases decreases with sintering temperature. This is due to crystal reorientation effect occurred due to sintering. Peak intensity of (130) reflection

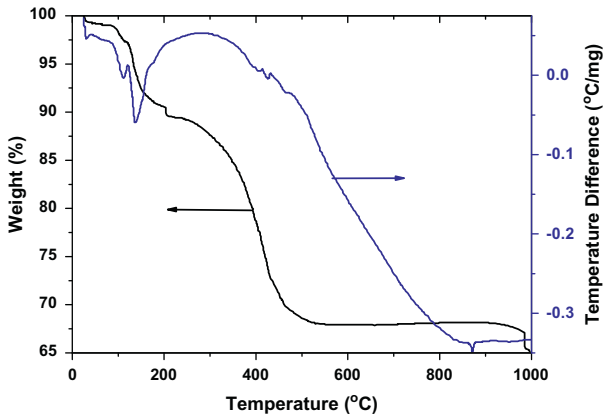

Fig. 2. TGA–DTA thermographs for the mixture of $Zn(NO_3)_2$ and $Pb(NO_3)_2$ powders.