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Characterization, sintering and dielectric properties of nanocrystalline zinc oxide prepared by a citric acid-based combustion route

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ABSTRACT

Nanosized zinc oxide has been synthesized through a novel single step solution combustion route using citric acid as fuel. The X-ray diffraction (XRD) analysis revealed that the synthesized ZnO nanopowder has the pure wurtzite structure. The phase purity of the nanopowder has been confirmed using differential thermal analysis (DTA), thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FT-IR). The morphology and crystalline size of the as-prepared nanopowder characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed that the powder consisted of a mixture of nanoparticles and nanorods. The nanocrystalline ZnO could be sintered to ~97% of the theoretical density at 1200 °C in 4 h. The dielectric constant (ε_r) and dielectric loss (ε_i) of sintered ZnO pellets at 5 MHz were 1.38 and 9×10^{-2}, respectively, at room temperature.
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1. Introduction

Zinc oxide (ZnO), a representative II–VI compound semiconductor, has attracted considerable attention over the last few years. Its many attractive properties, such as the direct wide bandgap of about 3.37 eV, large exciton binding energy of 60 meV at room temperature, good piezoelectric characteristics, chemical stability and biocompatibility, suggest a host of possible practical applications, notably in the area of ultraviolet/blue emission devices [1–8]. So far, nanocrystalline ZnO with different particle morphologies and sizes has been obtained by several preparation approaches, including thermal decomposition [9], vapor chemical deposition [10–13], sol–gel method [14], wet chemical synthesis [15], mechanochemical [16], electrodeposition [17], gas-phase reaction [18], hydrothermal synthesis [19] and so on. Among other established synthesis methods, simple and cost effective routes to synthesize nanocrystalline ZnO by utilization of cheap, nontoxic and environmentally benign precursors are still the key issues.

Solid-state synthesis, a well known method for synthesizing the oxide powders, has difficulties on fine particle distribution because of abnormal grain growth at high temperature. Among the above methods to prepare ZnO, wet chemical synthesis such as sol–gel [20,21] and precipitation method [22,23] have the merits of uniform particle distribution as well as lower processing temperature, but induce impurities in the particles from starting materials and metal ions having a different melting temperature. In comparison with other oxide preparation techniques the combustion method is a low temperature synthesis route, which can produce a more uniform particle distribution. In recent times this method has received much attention because of its simple and rapid preparation process, which yields homogeneous, fine and agglomeration free crystalline powders.

Noori et al. [24] reported the synthesis of zinc oxide nanopowder by the gel combustion method. But the as-prepared powder was amorphous in nature and a calcination temperature of 500 °C was desired to change amorphous particles to a crystalline phase. In the present case, we have synthesized single phase nanoparticles of ZnO using a single step auto-ignition combustion route employing citric acid as fuel. The phase purity and crystallinity of the as-prepared powder indicates that phase formation is completed during the combustion process itself without the need for any calcination step. In this paper, we report the combustion synthesis, characterization and sintering of ZnO nanopowders. The as-synthesized powders were characterized by XRD, FT-IR, TG/DTA, SEM and TEM. Dielectric properties of the sintered specimen were also investigated.

2. Material and methods

In a typical experiment, all the reagents were analytically pure (99.9%) and used without further purification. 5 g of zinc nitrate tetrahydrate was dissolved in 25 ml of distilled water to obtain a

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zinc nitrate solution (0.76 M), and 7.87 g of anhydrous citric acid was dissolved in 25 ml of distilled water to form a citric acid solution (1.64 M). The solutions were mixed and homogenized on a magnetic stirrer at room temperature, keeping citric acid to cation ratio unity. Subsequently, nitric acid and ammonium hydroxide were added to the system to adjust the oxidant/fuel ratio. The solution containing the complex precursor at neutral pH, having an oxidant/fuel ratio unity, was then heated to about 250 °C on a hot plate. The solution boils on heating and forms a syrupy liquid, which undergoes dehydration followed by decomposition leading to smooth deflation producing foam. The foam gets ignited by itself on persistent heating, giving voluminous and fluffy product of combustion. The combustion product was subsequently characterized as phase pure nanocrystals of ZnO.

Room temperature powder X-ray diffraction (XRD) was carried out on the combustion synthesized powder for phase identification and crystallite size estimation using a X-ray diffractometer (Model Bruker D-8) with nickel filtered CuKα radiation (λ=1.54056 Å). To determine whether there is any phase transition or solid-state reaction, differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the combustion product were carried out using a Perkin-Elmer TG/DT thermal analyzer in the range 40–1000 °C at a heating rate of 20 °C/min in nitrogen atmosphere. To check whether any carbonaceous impurity was left in the as-prepared powder, FT-IR spectrum of the as-prepared powder was recorded. The infrared (IR) spectra of the samples were recorded in the range 400–4000 cm^{-1} on a Thermo-Nicolet Avatar 370 Fourier transform infrared (FT-IR) spectrometer using the KBr pellet method. The morphology of the nanocrystallites was inspected using a transmission electron microscope (TEM, JEOL 2010Fas) at an accelerating voltage of 200 kV. For TEM observation, the powder samples were dispersed in methanol and sonicated for 30 min to obtain a better particle dispersion and a drop of this was dried on a carbon-coated copper grid. The shape and grain size of the as-prepared powders and sintered specimen were evaluated using a scanning electron microscope (JEOL, Model-JSM-6390LA, Analytical SEM).

To study the sinterability of the ZnO nanoparticles obtained by the present combustion method, the combustion derived powders were mixed with polyvinyl alcohol (5% aqueous solution) as binder and uniaxially pressed in the form of circular disks of 14 mm diameter and ~2 mm thickness at a pressure of about 350 MPa using a hydraulic press. The binder was removed by heating the pellet at 600 °C for 30 min. Then the binder burnt-out components were sintered at 1200 °C for 4 h in a programmable furnace in air at a heating/cooling rate of 10 °C/min. The density of the sintered specimen was measured using the Archimedes method with distilled water as the liquid medium. The microstructure of sintered samples after thermal etching was investigated by scanning electron microscopy. For dielectric measurements, silver electrodes were attached on either sides of the sintered pellet and dried at 80 °C for 15 min. The capacitance measurements were carried out in the frequency range 1 kHz–5 MHz at room temperature using an LCR meter (HIOKI 3532-50). The sample was about 11.91 mm in diameter and about 1.45 mm in thickness.

3. Results and discussion

The XRD pattern of as-prepared powder is shown in Fig. 1a. All of the diffraction peaks can be indexed within experimental errors as hexagonal ZnO phase with wurtzite structure with lattice constants a=0.3251 nm and c=0.5207 nm in comparison

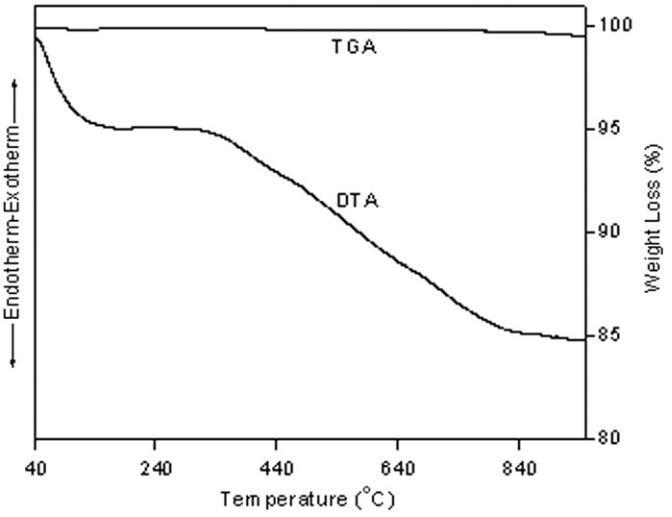

Fig. 2. DTA and TGA curves of as-prepared ZnO nanopowder.

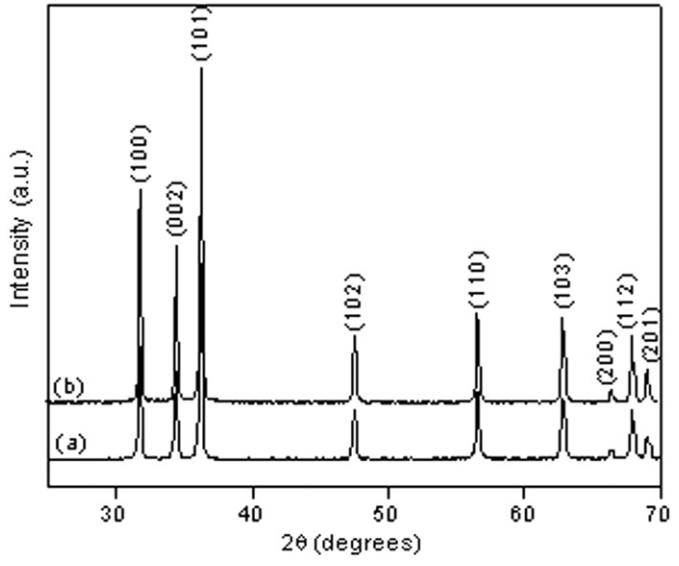

Fig. 1. XRD patterns of (a) as-prepared ZnO nanopowder and (b) ZnO annealed at 600 °C.

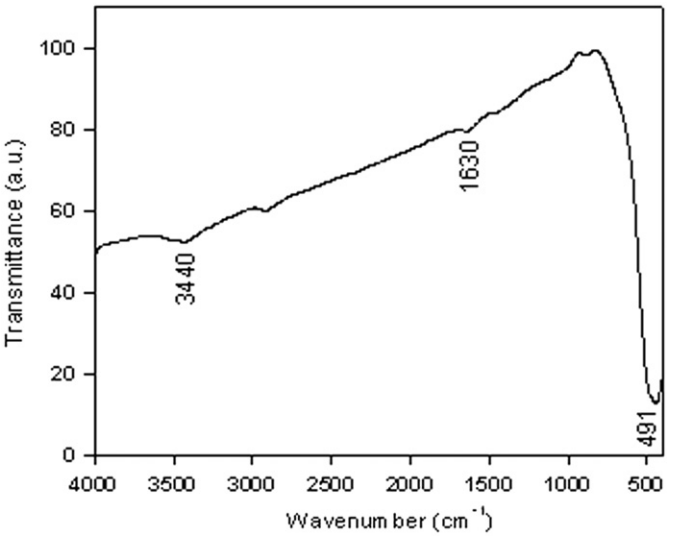

Fig. 3. FT-IR spectra of as-synthesized ZnO nanopowder.

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