Materials Research Bulletin 74 (2016) 1–8

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Origin of giant dielectric constant and conductivity behavior in $Zn_{1-x}Mg_xO$ ($0 \leq x \leq 0.1$) ceramics

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ARTICLE INFO

Article history:
Received 23 March 2015
Received in revised form 18 September 2015
Accepted 5 October 2015
Available online 9 October 2015

Keywords:
A. Semiconductors
A. Ceramics
C. X-ray Diffraction
C. Impedance Spectroscopy
D. Dielectric Properties

ABSTRACT

$Zn_{1-x}Mg_xO$ ($\leq x \leq 0.1$) ceramics were fabricated by conventional solid-state reaction of co-precipitated zinc oxide and magnesium hydroxide nanoparticles. Structural and morphological properties of the fabricated ceramics were studied using X-ray diffraction and scanning electron microscopic analysis. The dielectric measurements of the ceramics were carried out as a function of frequency and temperature respectively. Interestingly, Mg doped ZnO (MZO) samples exhibited colossal dielectric response ($\sim 1 \times 10^4$ at 1 kHz) with Debye like relaxation. The detailed dielectric studies and thermal analyses showed that the unusual dielectric response of the samples were originated from the defected grain and grain boundary (GB) conductivity relaxations due to the absorbed atmospheric water vapor (moisture). Impedance spectroscopy was employed to determine the defected grain and GB resistances, capacitances and which supported Maxwell–Wagner type relaxation phenomena.

1. Introduction

Zinc Oxide (ZnO) is known for its wide variety of device applications such as solar cells, transparent conducting oxides (TCOs), light emitters, sensors, varistors, detectors etc. The wide optical band gap (3.2 eV), large exciton binding energy (~60 meV) and favorable electron mobility provided an incentive to the research and development especially on the synthesis and properties of zinc oxide [1–6]. ZnO almost exhibits strong n-type conductivity, with electrons in the conduction band as the charge carriers [7]. Relatively small concentrations of defects (vacancies, interstitials, antisites etc.) and impurities in ZnO can significantly affects the electrical and optical properties. Generally, the metallic impurities can easily tailor the properties of ZnO, for example dopants like B, Al and Cu shows enhanced conducting properties [8–10], whereas Mn, Ni, Co, Cr shows an induced magnetic and improved piezoelectric properties [11–14], Cd and Mg can tune the band gap of ZnO narrow and wider [15], and other rare earth materials effectively modifies the optical property of ZnO [16,17].

The Mg doped ZnO (MZO) is an interesting system due to their ability to tune band gap (from 3.2 to 7.7 eV) with respect to the doping concentrations. Since, ionic radii of Mg (0.65 Å) and Zn (0.74 Å) are quite closer, which may dope by significant replacement of one another and exhibits an enhanced optical properties [18–21]. A large number of works have been reported on $Zn_{1-x}Mg_xO$ system owing to their advantages and attractive properties for possible applications in optoelectronic and electronic devices. Apart from their optical properties, Mg doped ZnO shows an anomalous dielectric constant at low temperature similar to that observed in Li doped ZnO and reported as ferroelectric like behavior [22,23]. But, there exists no proper experimental evidences for explaining the ferroelectric transition of wurzite-ZnO structure. However, the possibility of the pseudo-ferroelectric behavior for this type of system (Li and Mg doped ZnO) have been reported theoretically [24]. Recently, Soukiassian et al. [25] have experimentally studied the origin of anomalous dielectric constant (so called ferroelectric transition) exhibited in Li and Mg doped ZnO ceramics and affirmed as the contribution from absorbed moisture in the microporous of ceramic. Recently, the same anomalous dielectric constant was also observed in high pressure treated porous ZnO ceramic. By studying the dielectric response with respect to sintering temperature and size of microstructure, they confirmed that the giant dielectric values were originated from the resistance difference between the grain and grain boundary due to the Maxwell–Wagner type of relaxation mechanism [26,27].

In this present work, Mg doped ZnO ceramics were fabricated using chemically co-precipitated ZnO and $Mg(OH)_2$ nanoparticles.

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http://dx.doi.org/10.1016/j.materresbull.2015.10.006
0025-5408/

We observed an unusually colossal dielectric constant value especially for the MZO ceramics. To unravel the origin of MZO dielectric behavior, the detailed dielectric, thermal, impedance and conductivity studies were carried out along with the possible underlying mechanisms are described.

2. Experimental

$Zn_{1-x}Mg_xO$ ceramics were fabricated by conventional solid state reaction utilizing the chemically co-precipitated ZnO and $Mg(OH)_2$ nanoparticles. Initially the co-precipitation technique was performed by dissolving zinc chloride dihydrate (Merk) and magnesium chloride hexahydrate (Merk) separately in distilled water and few drops of ammonium hydroxide solution were added to precipitate as their hydroxides. The precipitates were thoroughly washed and transferred into a flask fitted with a water condenser and refluxed at 90–100 °C under constant stirring for 6 h. After refluxing, the crystalline nanoparticles were filtered, dried at 100 °C for 12 h in oven and used for the ceramic fabrications. Polycrystalline ceramic powder of $Zn_{1-x}Mg_xO$ was prepared via conventional solid-state reaction. In this process, the stoichiometric amounts of as prepared ZnO and $Mg(OH)_2$ nanoparticles were thoroughly mixed in an acetone medium and heated treated at 500 °C for 10 h in air. Then the polycrystalline powder was cold pressed into pellet of 10 mm in diameter and ~2 mm thickness at a pressure of 300 kg cm^{-2} using 10% PVA as a binder. The pressed green pellets were slowly heated treated up to 600 °C to remove the binder and sintered at 950 °C for 12 h in air. The density obtained for the pellets were about 93–95% of its theoretical value.

The crystallinity and structural properties of the samples were studied using powder X-ray diffraction analysis (JDX-8030, JEOL) recorded by Cu $k_{\alpha 1}$ radiation in the 2θ range from 20° to 80°. Microstructural aspects and the grain size distribution of the ceramic was observed using a scanning electron microscope (QUANTA-ESEM). The dielectric and impedance measurements were carried out as functions of frequency (100 Hz–1 MHz) and temperature (223–373 K) using an impedance gain phase analyzer (HP4194A) at a signal strength of 0.5 V_{rms}. For these measurements, the opposite faces of the pellets were silver coated, thus forming a parallel plate capacitor and copper leads were bonded using silver epoxy as the connecting electrodes.

3. Results and discussion

3.1. Structural and micro-structural features

The X-ray diffraction patterns of co-precipitated zinc oxide and magnesium hydroxide nanoparticles are shown in Fig. 1a. The diffraction peaks of each samples were indexed to the hexagonal structure of $Mg(OH)_2$ and hexagonal wurzite structure of ZnO with the lattice constants comparable to the values of JCPDS 7-239 and JCPDS 36-1451 respectively. The significant peak broadening of the diffraction patterns indicate that the synthesized samples possessed nanosized particles . The mean crystallite size of ZnO (~20 nm) and $Mg(OH)_2$ (~17 nm) were calculated using the Scherrer relation [28]. The XRD pattern of fabricated polycrystalline $Zn_{1-x}Mg_xO$ ceramics are depicted in Fig. 1b. The diffraction patterns show a single-phase polycrystalline ZnO with hexagonal wurtzite structure up to $x \leq 0.1$. For higher ($x > 0.1$) Mg content several additional peaks were appeared due to the formation of secondary phase of MgO. SEM image of the 0.5% MZO pellet sintered at 950 °C for 12 h is shown in Fig. 2. The image reveals well sintered nature of the pellet with different grain sizes distribution ranging from 0.5 to 2.5 μm. Inset of Fig. 2 shows the Energy dispersive X-ray spectrum (EDAX) of the 0.5% MZO sample, which confirms the presence of Mg ions in the synthesized sample.

3.2. Frequency and temperature dependent dielectric properties

The frequency dependence dielectric constant (ε') and dielectric loss ($\tan\delta$) of the $Zn_{1-x}Mg_xO$ ceramics are shown in Fig. 3a and b. The dielectric constant (ε') exhibited a Debye-like relaxation curve, with large dielectric relaxation strength ($\Delta\varepsilon \approx 9900$) at room temperature. The highest value of dielectric constant was observed in $x = 0.05$ (5% MZO) samples and are particularly used for further detailed studies to understand the colossal dielectric constant response and relaxation phenomena.

Temperature dependent dielectric properties were performed to understand the unusually large $\Delta\varepsilon$ value of MZO ceramics. The resultant dielectric constant and loss of 5% MZO are shown in Fig. 4a and b for the heating cycle. From the graph it is observed that ε_r shows a step like rise at ~95 °C, 170 °C and 225 °C and the similar behavior was noticed in the dielectric loss plot (represented by arrow marks). The measurements were repeated while cooling the sample and the step like rise of ε_r observed in the heating cycle

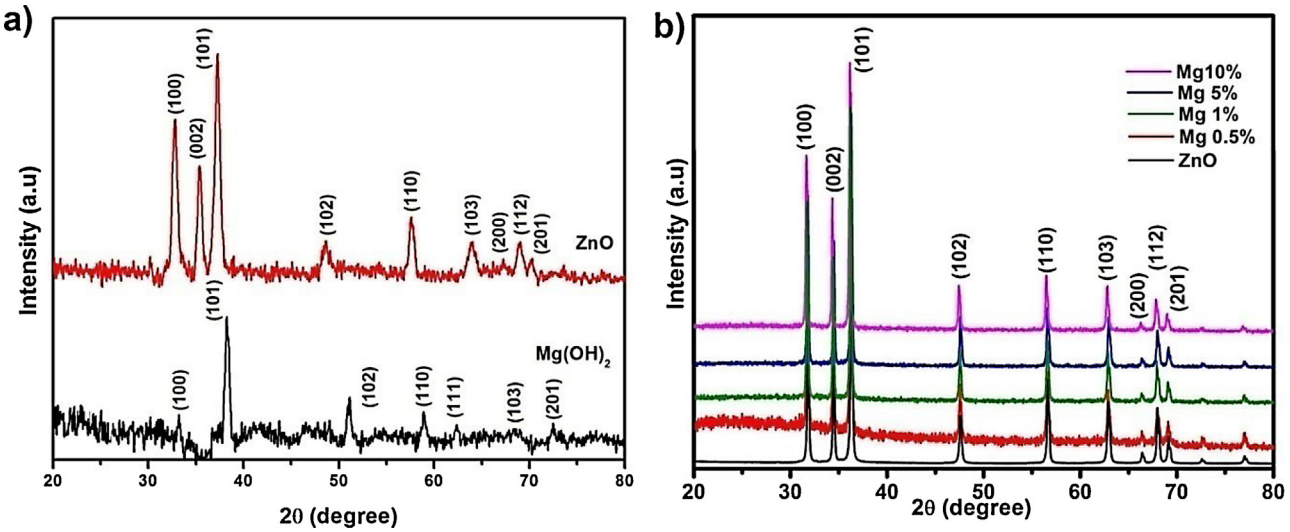

Fig. 1. a) X-ray diffraction pattern of co-precipitated $Mg(OH)_2$ and ZnO; b) X-ray diffraction pattern of $Zn_{1-x}Mg_xO$ ($0 \leq x \leq 0.1$) ceramics.