

Study on the Frequency and Temperature Dependent Electrical Properties of MnO and PbO Doped ZnO Nanoceramics

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Abstract

This work reports the temperature and frequency dependence microstructure, electrical of MnO and PbO doped ZnO nanoceramic synthesized by solid state reaction method. The as-sintered ceramic varistors with different compositions have been characterized via laboratory X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and electrical measurements. It has been observed that MnO and PbO doping on ZnO plays a remarkable role in improving its structural, electrical and dielectric properties (XRD) pattern confirmed the single-phase hexagonal wurtzite structure of the samples without having any other intermediate phases. AC resistivity has been found to be decreased while the conductivity increased with the increase in doping.

Keywords: Zinc oxide; Doping; Dielectric properties; Nano-composite

Introduction

ZnO is environmental friendly and its low cost makes it unique material which attracts the interest among researchers and technologists for device applications. It has a lot of application in various recognized field such as, solar cell, photolytic degradation organic dyes, antibacterial activity, and cancer treatment as well. Due to lack of center of symmetry, ZnO is also used in actuators and piezoelectric transducers [1,2].

The wurtzite structure of ZnO has intrinsic defects such as oxygen vacancies and zinc interstitials and considered as an n-type semiconductor material with both good electrical and optical properties [3]. Nevertheless, such instability in ZnO limits its application in some other fields. Properties of ZnO can be modified by doping metal atoms which make drastic changes in electrical, optical, and magnetic properties of ZnO by altering its electronic structure to fit specific need and applications [4].

Doping is a suitable and facile method to tune the electrical, optical, magnetic, piezoelectric and electronic properties of ZnO [2].

For example, doping of ZnO with Ga, and Al advances both electrical and optical properties for transparent high power electrical devices. Again, for the improvement of photocatalytic performance some other metal like Al, Ta, Cr, La, Ag have been used [5].

Multidoping of ZnO forms a multicomponent system separated by distinct interfaces usually produce superior material properties [6]. The performance of such multicomponent system found to be depends on the composition and processing temperature [7]. Again, the microstructure of such polycrystalline material largely depends on the number; size, shape and rate of formation of various phases present [8]. Sintering a ternary system of ZnO above 800°C showed that

formation of liquid phase reactions promoting the densification of the ceramics and the growth of ZnO grains [9].

The electrical properties of ZnO based ceramics are very sensitive to the grain boundary because the varistors nonlinear coefficient and breakdown voltage depends on the grain boundary. Therefore, numerous studies are suggesting the grain boundary phenomena Of ZnO-Bi₂O₃ and ZnO-V₂O₅ based ceramic systems studied the influence of MnO₂, PbO and a mixture of MnO₂, PbO and B₂O₃ on electrical and dielectric properties of ZnO-V₂O₅ ceramics by alternating current (AC) impedance and variable temperature dielectric spectroscopy and found that the Schottky barrier present at grain boundary is much more important for varistor performance [10-12]. The electrical conductivity of Mn doped and Co doped ZnO-Bi₂O₃ varistors were investigated using complex plane modulus analysis and found that the ratio of grain boundary to grain resistance of Mn doped samples is higher than that of Co doped samples [13].

A number of methods have been devoted for the fabrication of doped ZnO nanoparticles, such as solid-state reaction, co precipitation, sol-gel process, hydrothermal route, and so on [3]. Among these methods, solid state reaction method is of great interest because of its simplicity and low cost.

Here we report the result of effect of sintering temperature and frequency on the electrical and magnetic properties of MnO and PbO doped ZnO nanoceramic through solid state reaction method.

Experimental Methods

ZnO (99.95%) doped PbO/MnO (99.99%) samples with 1%, 1.5%, 2.0% and 2.5% were prepared in ceramic form by solid-state reaction (all chemicals are from GFC, Canada) as shown in Table 1. Powders of ZnO/PbO/MnO were mixed in stoichiometric proportions thoroughly grinding these powders in an agate mortar and then by ball milling for 24 hours. The resulting powders were dried in oven at 90°C and calcined at 850°C for 8 hours with a heating rate of 10°C/min using air atmosphere. Polyvinyl alcohol (5% PV A solution) was mixed as binder

with the calcined powder to provide some green strength for subsequent handling. Then, it is dried in an oven for 24 hours to evaporate excess PVA. The pellets were prepared using a universal testing machine (UTM) (FS - 300 KN, Testometric, England) at 25°C with 1.5 g of powder for every sample to maintain uniformity in thickness. The pellets made by UTM placed in a Z 18-14 of Micropyretics Heaters international, high temperature furnace for sintering. Sintering schedule was varied from batch to batch. Here, sintering is carried out at 850°C, 1000°C and 1050°C in air atmosphere. However, for every sintering schedule all samples with similar composition were put in the furnace at the same time.

| Composition | ZnO(g) | MnO (g) | PbO (g) | Total (g) |
|---------------------------|--------|---------|---------|-----------|
| 95% ZnO+2.5% MnO+2.5% PbO | 19 | 0.5 | 0.5 | 20 |
| 96% ZnO+2% MnO+2% PbO | 19.2 | 0.4 | 0.4 | 20 |
| 97% ZnO+1.5% MnO+1.5% PbO | 19.4 | 0.3 | 0.3 | 20 |
| 98% ZnO+1% MnO+1% PbO | 19.6 | 0.2 | 0.2 | 20 |

Table 1: Composition of prepared sample.

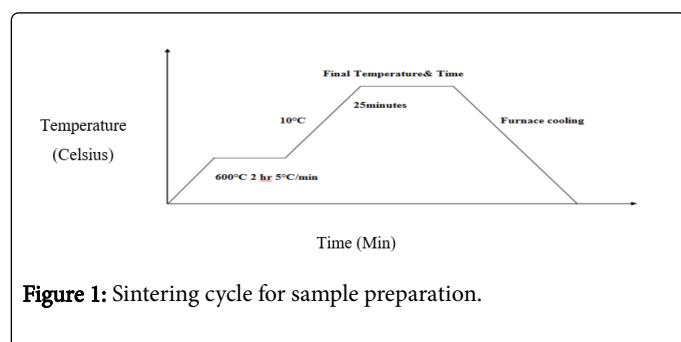


Figure 1: Sintering cycle for sample preparation.

X-ray diffraction experiments were performed after the powders were obtained in order to identify the main crystalline phase of SrTiO₃ powders recording the diffractogram from 10°C to 90°C (Figure 1) using Bruker's D 8-Discover X-ray diffractometer with Cu K α radiation. The microstructure of the powders was studied by a JEOL FE-SEM-760°F Scanning Electron Microscopy (SEM). Densities of sintered samples were measured by the Archimedes principle method [2]. Dielectric properties of ferrites were carried out by using Keithley Electrometer and Hewlett Packart Impedance Analyzer (WAYNE KERR 6500 B). For dielectric measurements, the pellet shaped samples were prepared. Later on, the samples were well polished to remove any roughness and the surfaces of each pellet were coated with silver paste as contact material. Dielectric measurements have been done as a function of frequency in the range of 10 Hz to 120 MHz at room Temperature.

Characterizations

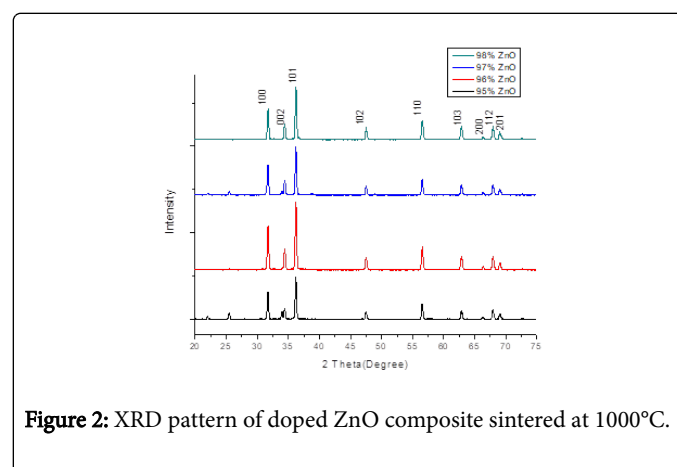


Figure 2: XRD pattern of doped ZnO composite sintered at 1000°C.

At 1000°C, with different percent concentrations (95-98 wt %) of ZnO loading in the matrix, the XRD pattern reveals that there is a little change in XRD peak positions. The peak of highest intensity as shown in Figure 2 occurs at 2 thetas=36.250 with crystallite size of 25.42 nm for each ZnO loading. The peak left and right side of the highest peak described above indicates that particle size must be nanometer size at different 2-theta values such as 2-theta=31.80 for which particle size 23 nm. At higher temperatures above or below 1000°C, no change in particle size but uniform distribution of ZnO in the matrix because cluster of nano-particles releases more free nano-particles to become distributed evenly and thereby, more crystalline structure. The peak at 2-theta values of about 36.50 represents the PbO peak and peak at 73.9°C represents the MnO peak.

SEM images of ZnO and composites show that higher at different magnifications is obtained for ZnO nanoparticles and uniform distribution of ZnO in the matrix which is essential for good mechanical properties. It is worth noting that the filler was more or less evenly distributed within the matrix, but some particles are aggregated. It could be ascribed to the strong interaction between the ZnO and matrix. The Figure 3-4 shows that, sample comprising each 2.5% doping exhibits relatively large crystal size and small pore size whereas the sample with each 1% doping revealed a small crystal size and large pore size. So that, maximum doping low porosity and minimum doping high porosity. For the lower temperature the particle size is found almost constant everywhere which can be around 1 μ m which shows a high dielectric constant along with high capacitance. The grain formation is quite obvious here, but the grain size is much lower than found for the highest sintering temperature. In the higher temperature grain formation is higher and grain coarsening is also prevalent.

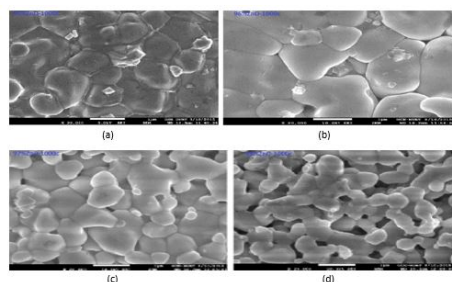


Figure 3: SEM image(X=20.000) of microstructure of MnO, PbO doped on ZnO at various composition sintered at 1000°C. (a) 95% ZnO+2.5% MnO+2.5% PbO, (b) 96% ZnO+2% MnO+2% PbO (c) 97% ZnO+1.5% MnO+1.5% PbO, (d) 98% ZnO+1% MnO+1% PbO.

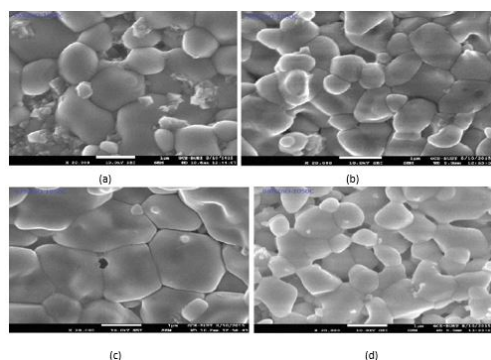


Figure 4: SEM image (X=20.000) of microstructure of MnO, PbO doped on ZnO at various composition sintered at 1050°C. (a) 95% ZnO+2.5% MnO+2.5% PbO, (b) 96% ZnO+2% MnO+2% PbO (c) 97% ZnO+1.5% MnO+1.5% PbO, (d) 98% ZnO+1% MnO+1% PbO.

Densification

The theoretical density of ZnO, PbO and MnO are 5.61 gm, 9.53 gm/cc and 5.37 gm/cc respectively. Whenever, we dope any high-density compound into low density substance it will increase the density of low density substance. Maximum doping contains highest percentage of PbO which density is more than two others. That's why, with increase of doping increase the percentage densification

Figure 1 depicts the percentage of densification of the samples as a function of doping content and sintering temperature. From the Figure 5, it is observed that, with increasing amount of doping, percentage densification is also increased. Highest densification is found at 95% ZnO which contains highest amount of doping (2.5% MnO+2.5% PbO). On the other hand, lowest densification is found at 98% ZnO (1% MnO+1% PbO). But with the increase in sintering temperature decrease in densification is observed. The reasons for decreasing densification at higher temperature may be because of reduction in the rate of diffusion mechanisms due to increasing the liquid layer thickness (SEM Image). Differently, due to the increased amount of

liquid content, the capillary force between particles decreases resulting in the deceleration densification during sintering [14].

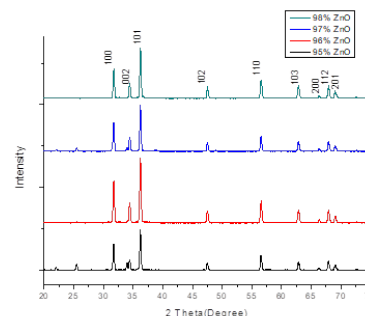


Figure 5: % Densification of sample after sintering.

Results of dielectric constant

Following Figure 6 shows the variation of the dielectric constant with frequency at room temperature for Manganese and lead oxide (each 2.5%, 2%, 1.5%, 1%) doped on ZnO at sintering temperature at 850°C, 1000°C and 1050°C for one hour.

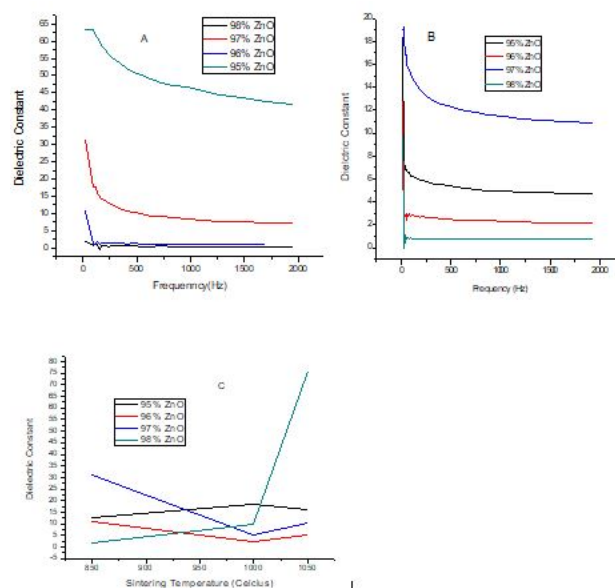


Figure 6: A) Dielectric constant with frequency at 1000°C B) Dielectric constant with frequency at 1050°C C) Dielectric constant with sintering temperature.

From the three Figures it is shown that, with rising frequency the dielectric constant decreases. Dielectric constant of the samples is high at lower frequencies, decreases with increase of frequency by approaching approximately a more or less constant value. This is because mechanisms of polarization have varying time response capability to an applied field frequency. For the frequency range between 1 kHz and 120 MHz, the total contribution of polarization is arising from electronic displacement, ionic displacement, dipole

orientation and space charge displacement. But the graphical representation has been shown from frequency 20 Hz-2000 Hz for clear understanding. It is also observed that, dielectric constant increases with the sintering temperature due to the grain growth and enhanced crystallinity but with increasing percentage of doping dielectric constant decreases.

Conductance Analysis

A-C conductivity has been measured by impedance analyzer, where conductance was taken from 20 Hz to 120 MHz. All measurement has been carried out at room temperature. We will discuss frequency dependent conductivity starting from 20 Hz to 1947.71 Hz for better understanding.

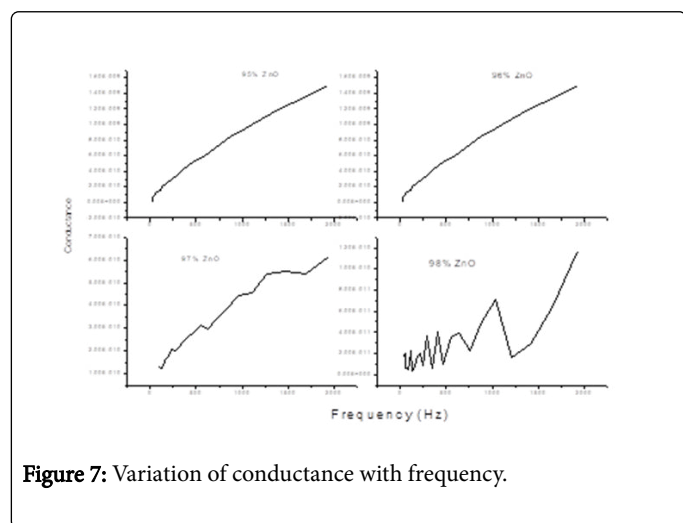


Figure 7: Variation of conductance with frequency.

From Figure 7, it can be seen that the highest amount of conductance is obtained for Each 1% MnO, PbO doped on ZnO sintered at 1050°C. Here, conductance declined sharply with rising sintering temperature from 850°C to 1000°C and rose again slightly at 1050°C. For pellets sintered at 1050°C, is smaller than the pellets that are sintered at 1000°C and 1050°C due to increasing conductance of the pellets. This is because, when those pellets were subjected to a sintering process at 1050°C, volume of pore space between the particle is reduce. Thus, there are larger grain grows at the expense of smaller grains. Therefore, the energy barrier is reduced and rapidly increases the diffusion of atoms to another grain which means the diffusion coefficient is increase. Hence, the conductance is increase with increasing of mobility, indicates the pellets sintered at 1050°C possess a conductor behavior (Figure 8).

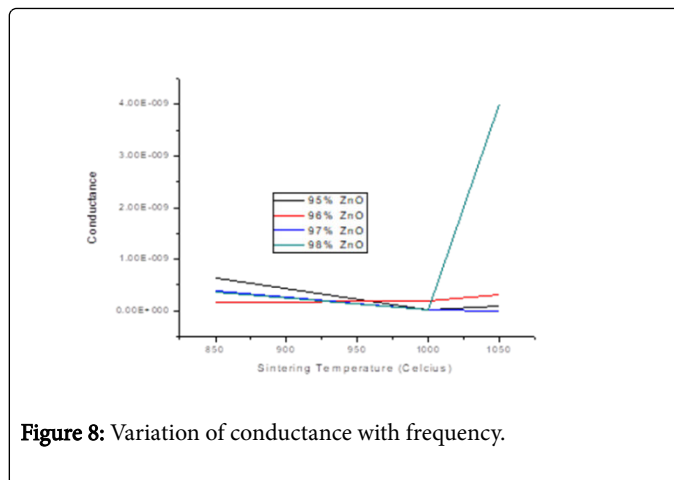


Figure 8: Variation of conductance with frequency.

Resistance

Resistivity of ceramics depends upon the method of preparation, chemical composition, grain size and sintering conditions. Figure 9 A represents the variation of AC resistivity of MnO, PbO doped on ZnO as a function of frequency at room temperature. According to the resistivity data, it has been noticed that with the addition of doping material, AC resistivity of ZnO decreases. It has also been found that at lower frequency region the randomness of resistivity is observed as comparing to the higher frequency region and at much higher frequency the resistivity of the ZnO becomes almost independent of frequency. But lowest doping showed the lowest resistance at highest sintering temperature shown in Figure 9 B. Resistivity of semiconductors decrease with increase in temperature. As the temperature of the semi-conductor is increased, the electrons in the valence band gain sufficient energy to escape from the confines of their atoms. As a result, in higher temperatures, a semi-conductor's valence electrons are free resulting in decrease in resistivity. Again, at high temperature (above 400 K or higher) carrier concentration is intrinsic and mobility is dominated by lattice scattering resulting in the decrease in resistivity [15,16].

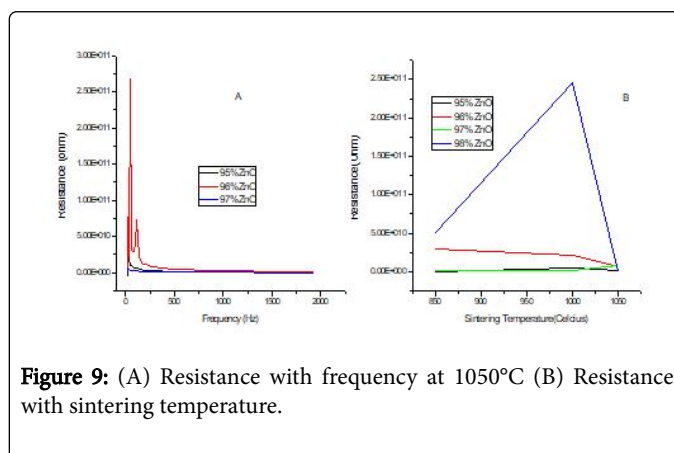


Figure 9: (A) Resistance with frequency at 1050°C (B) Resistance with sintering temperature.

Conclusions

In our investigations, it has been observed that MnO, PbO addition on ZnO plays a remarkable role in improving its electric and dielectric properties. The percentage densification of the samples increases with

the increase in doping. In XRD studies, the XRD pattern confirmed the single-phase hexagonal wurtzite structure of the samples without having any other intermediate phases. The dielectric constant decreases with the increase in frequency, which is faster at lower frequencies and slower at higher frequencies. It is also observed that, dielectric constant increases with the sintering temperature due to the grain growth and enhanced crystallinity but with increasing percentage of doping dielectric constant decreases. AC resistivity also observed to be decreased with the addition of doping material. The minimum resistivity occurred when the frequency of the hopping charge carriers is equal to the applied field frequency termed as resonance frequency.

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