SYNTHESIS AND CHARACTERIZATION OF ZN_{1-X} AL_XO OXIDE NANOMATERIALS

Abstract

Zinc Oxide (ZnO) nanopowders with different ratios of zinc oxide replaced with aluminum (Al) through the process of co-precipitation, $Zn_{1-x}Al_xO$ were formed. X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) analyses of all the samples supported the presence of a single crystalline phase with a hexagonal wurtzite structure. The average crystallite size in ZnO samples has decreased as a result of Al doping, while electrical conductivity and the dielectric constant have increased. According to the results of the dielectric measurement, the parameters k, or the dielectric constant or relative permittivity, and tanδ, or the dielectric loss, both decreased with increasing frequency.

Keywords: Nanoparticles; Coprecipitation; Relative permittivity; Dielectric loss; Electrical conductivity;

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I. INTRODUCTION

The field of nanotechnology plays a dominant role in several areas like electronics, medical technologies, etc. The changes in material properties at the nanometer scale have been explained in several ways by many researchers, that are used to develop novel, multifunctional nanomaterials suitable for device applications. Zinc oxide material attracted many researchers due to its several optical applications, such as solar cells, LEDs, photodetectors, spintronics, sensors, photocatalysis, etc. ZnO is made up of three different crystalline structures: cubic zinc blend (ZM), rock salt, and wurtzite. The wurtzite type is the most stable and stable at room temperature.

Due to the large energy band gap, transparency to visible light (400-700 nm), and some of the properties of ZnO such as electrical, optical, and acoustic, it is employed in many applications. ZnO has been prepared by various methods including the wet chemical method, hydrothermal method, chemical vapor deposition, etc. Unfortunately, pure ZnO conductivity is unstable thermally. The third group elements (B^{3+}, Ga^{3+}, Al^{3+}, In^{3+}) improve optical, electrical, thermal, and magnetic properties when they are doped in place of Zn^{2+} ions. Transparent conducting materials such as indium oxide with other dopants have been developed so far, for many optical applications.

As an alternative approach, Al-doped ZnO has been developed in the current work due to its favorable properties like non-toxic, easy availability, environmental stability, cost-effectiveness, etc. Their structural, morphological, electrical, and dielectric properties were analyzed and reported.

II. EXPERIMENTAL

Co-precipitating method was employed to synthesize samples of ZnO containing Al dopant proportions ($Zn_{1-x}Al_xO$, x = 0, 1%, 3%, 5%, 7%, 9%, 10%). The primary raw materials used were $Zn(NO_3)_26H_2O$ and sodium hydroxide solution. The 0.3 M zinc nitrate solution was initially prepared by dissolving the corresponding proportions of zinc and Al dopant in 100 mL of double distilled water, by continuous stirring. Subsequently, 0.3 M of NaOH solution was dropwise added, and the stirring process continued for a period of two hours at 75^oC before cooling to room temperature. The resultant precipitate was filtered and washed with double distilled water many times. Finally, the precipitate was again dried at 100^oC for 24 h and then calcinated at 700^oC for 3 h. Al $(NO_3)_39H_2O$ was added to zinc nitrate in different amounts from 1 to 10 mol%. The samples are named as ZnO, ZA01, ZA03, ZA05, ZA07, ZA09, and ZA1 for different wt% loading proportions of Al (x=0, 1%,3%, 5%,7%, 9%, 10%), respectively. The doped samples were characterized using XRD (Philips PW-1730), FTIR (Brucker tensor 27), and SEM (LEICA, S440i, UK). The sample powders were formed into pellets measuring 10 mm in diameter and 3 mm in thickness, which were then sintered for three hours at 1100°C. Newton 4th Ltd. applied the silver paste to the two surfaces of sintered pellets before analyzing the dielectric characteristics with a PSM1700 meter frequency response analyzer.

III. RESULTS AND DISCUSSIONS

X-Ray Diffraction patterns of Zinc Oxide samples substituted with aluminum in different proportions are shown in Fig. 1. The fig. shows characteristic peaks of zinc oxide

with indexing (100), (002), (101), (102), (110), (103), (112), and (201) which correspond to hexagonal wurtzite structure of ZnO. In the fig., no XRD peaks related to secondary phases of Al_2O_3 or other impurities are observed which confirms the diffusion of Al^{3+} in ZnO. The figure depicts the shifting of diffraction characteristic peaks to higher angles with increasing dopant levels of Al^{3+}. The size of the crystallite was calculated from the relative intensity levels of peaks using the Scherrer equation.

$$D = k\lambda/(\beta\, cos\theta)$$

Where D is the average size of the crystallite; β = the full width at half the diffraction peak; $\boldsymbol{\theta}$ = the Bragg angle; λ = the wavelength of the x-ray source; and k is the constant.

Table 1 provides an overview of the average size of crystallite for all samples, as well as the lattice parameters. It was observed that the average size decreased with the elevation of Al doping, suggesting that Al^{3+} ions were able to successfully replace Zn^{2+} ions in the structure of ZnO.

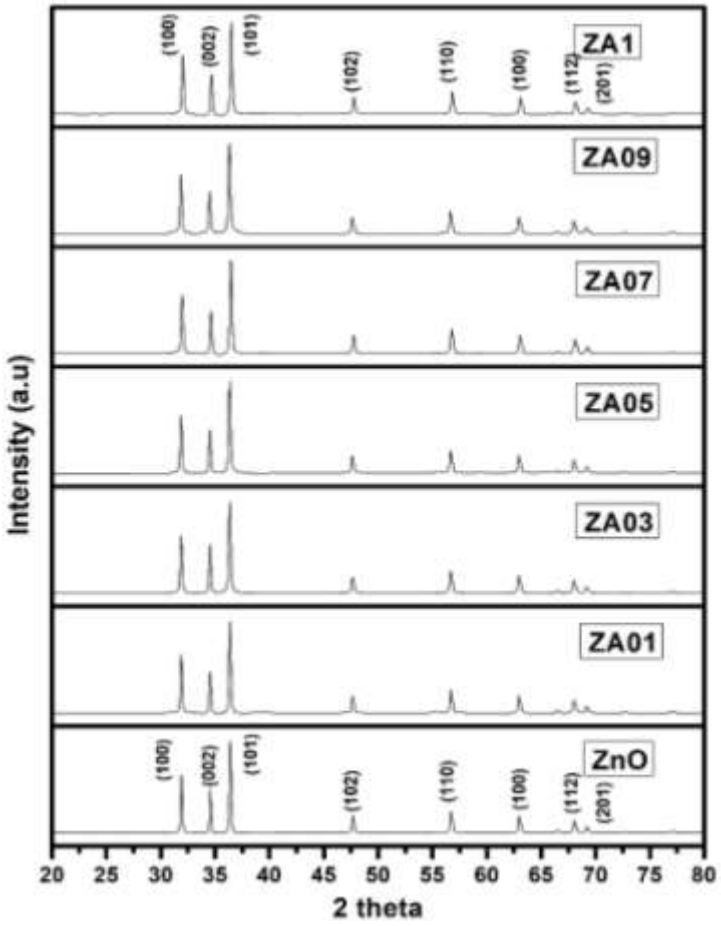

Figure 1: XRD Patterns Showing Zinc Oxide and ZnO Nano-Particles Substituted with Aluminum

The FTIR spectra of the ZnO samples doped with Al ranged from 4000 to 400 cm^{-1}, as illustrated in Figure 2. Figure 2 indicates that the absorption band in the range 3417-3479 cm^{-1} results from the stretching vibrations caused by the OH group, indicating that H_2O is

present on the sample surfaces. The band near 500 cm^{-1} in figure 2 corresponds to the Zn-O stretching vibration, which aids in the production of the ZnO hexagonal wurtzite structure. Metal cations from the environment absorb CO_2, which is attributed to the bands between 2350 cm^{-1} and 1445 cm^{-1}. In Fig., the Al-O band is visible close to 683 cm^{-1}. The change in the spectra of the doped samples depicted in fig. may be the result of Al atoms introducing crystallographic disturbance into the crystalline lattice locations. The Zn-O bond, which is present in all the prepared samples, may be identified by the band at 445 cm^{-1}. As can be observed from the fig, it is discovered that the strength of the bands between 960 cm^{-1} with feeble intensity and 1122 cm^{-1} with high intensity increases with Al doping level. These bands match the stretching vibrations of Al-O.

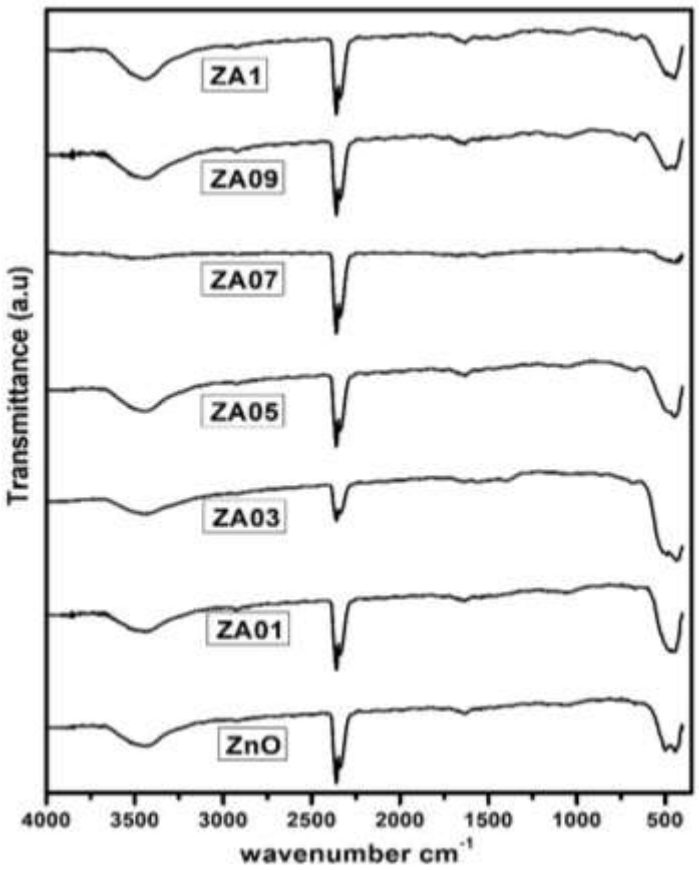

Figure 2: Fourier Transform Infrared Spectra of Zinc Oxide and Al-doped Zinc Oxide Nanoparticles**.**

The analysis of the morphological structure was performed using SEM for all samples. And the picture is shown in Fig. 3. ZnO and ZAO nanoparticles formation was seen in these micrographs. The shape of the nanoparticles is approximately spherical, and the morphology of the nanoparticles does not change after doping Al with ZnO. It has been demonstrated that agglomeration increases with the concentration of Al.

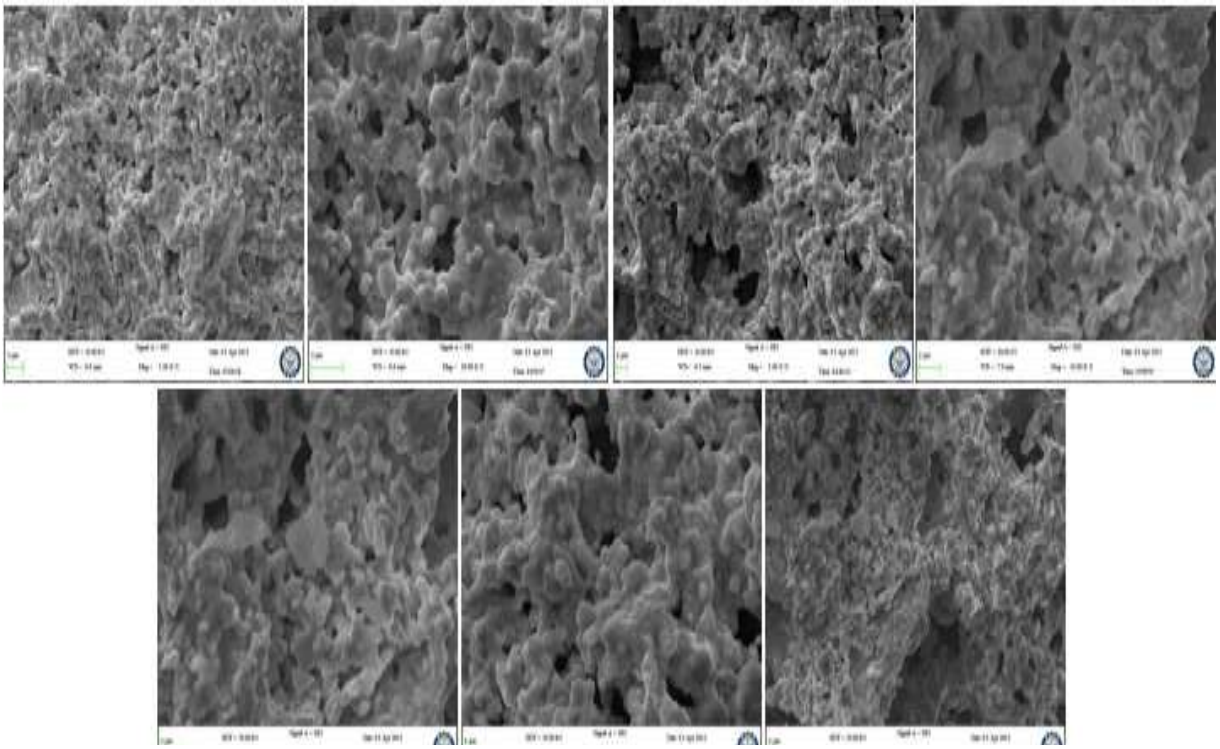

Figure 3: Scanning Electron Microscopy images of Zinc Oxide and Al-doped Zinc Oxide Nanoparticles.

The plots of dielectric constant k and loss versus frequency are shown in Fig. (4). The fig shows that k decreases rapidly in lower frequencies and the fall off k is slow in higher frequencies. This feature is common for all oxide nano samples.

Table 1 gives k values of all samples. The k is found to rise with Al doping amount which may be because the electro-negativity of Aluminum (1.61) is less than that of Zinc (1.78). This results in the weaker ionic bond of Zn-O-Al as compared with the Zn- O-Zn bond, which causes the increase of ionic polarization and hence dielectric constant. The average crystallite size decreases with Al concentration as noted in the table 1.

Figure 4b shows the frequency dependence of dielectric loss, tanδ. All samples exhibit the falling off dielectric loss with the increase of frequency at lower frequencies and at higher frequencies tanδ become constant. This can be attributed to ionic hopping at low and moderate frequencies leading to ionic polarization or charge carrier-induced conduction losses.

At very high frequencies, ionic vibrations are the single source that contributes to dielectric losses. Table 1 shows that dielectric losses are greatest for pure zinc oxide (ZnO) and decrease as the Al doping concentration increases. Hence, it is confirmed that doping of Al into ZnO increased the dielectric capability which is a desirable feature for high-frequency device applications.

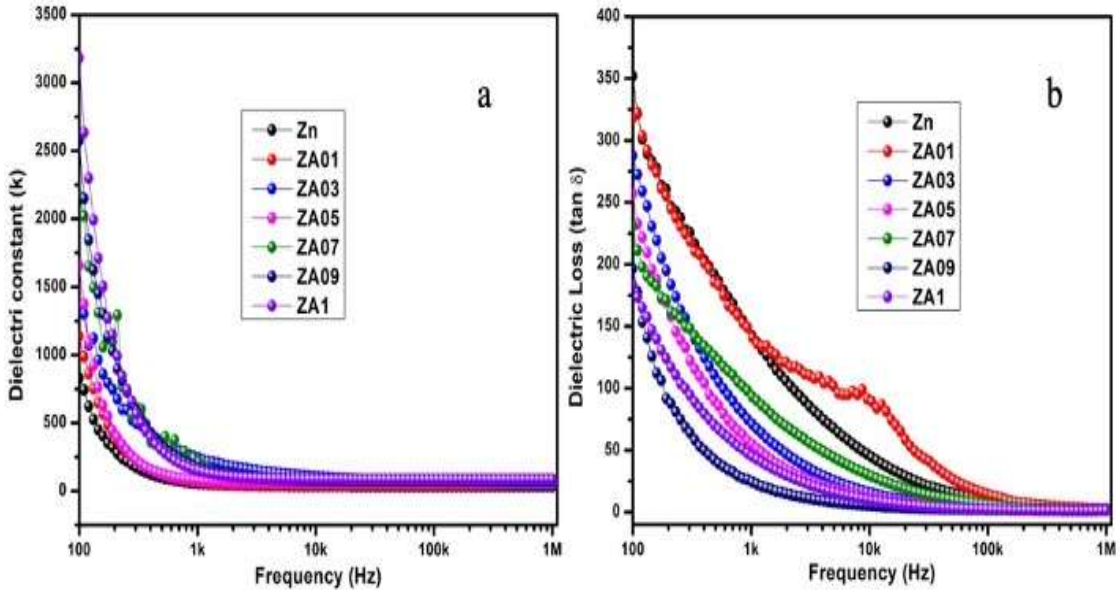

Figure 4: Variation of the Frequency with a) Dielectric Constant and b) Dielectric Loss (tanδ) of Zinc Oxide and Al-doped Zinc Oxide Nanoparticles.

AC conductivity variation with frequency is plotted for all samples and shown in Fig. 5. As frequency increases, the number of electrons hopping cases near grain boundaries also increases which reflects an increase in AC conductivity, as seen from the fig. It can be noted from the table 1 that conductivity increases with Al doping in ZnO samples. When the Al ions are excited in the lattice of ZnO, the abundance of free charge carriers near the grain boundaries increases, resulting in high-frequency conductivity.

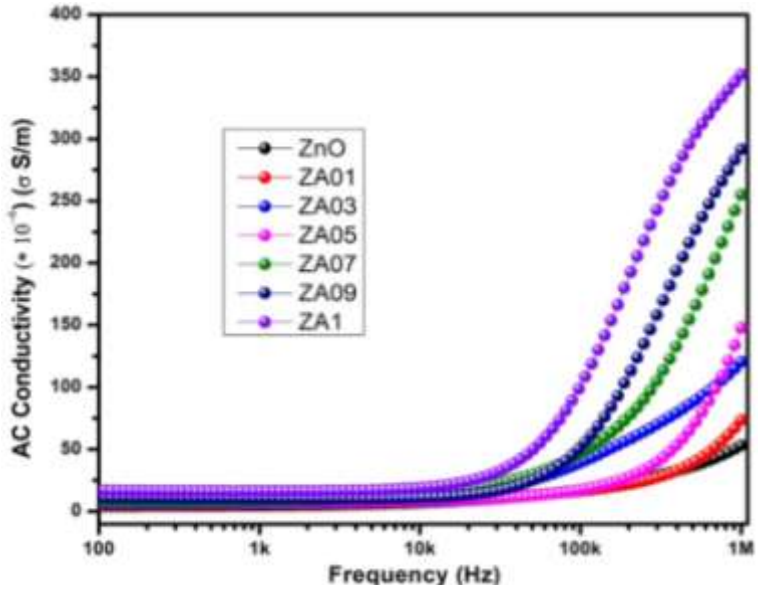

Figure 5: Variation of the Frequency with AC Conductivity of Zinc Oxide and Al-doped Zinc Oxide Nanoparticles.

Table 1: Detailed Information on the Structure, Electrical Conductivity, and Dielectric Properties of Zinc Oxide and Al-doped Zinc Oxide Nanoparticles.

Sample	Crystallite Size (nm)	Lattice parameter a (Å)	Lattice parameter c (Å)	Conductivity (S/m) at 800 kHz	Dielectric constant at 800 kHz	Dielectric Loss at 800 kHz
ZnO	79	3.235	5.603	47.51×10^{-6}	31	2.51
ZA01	72	3.238	5.608	61.42×10^{-6}	38	2.32
ZA03	68	3.239	5.61	110.2×10^{-6}	45	1.94
ZA05	63	3.24	5.612	121.01×10^{-6}	58	1.78
ZA07	59	3.229	5.594	229.41×10^{-6}	67	1.45
ZA09	57	3.241	5.614	274.51×10^{-6}	75	1.31
ZA1	54	3.224	5.585	339.21×10^{-6}	84	1.14

IV. CONCLUSIONS

A series of samples of zinc oxide with aluminum doping, ($Zn_{1-x}Al_xO$, x=0, 1%, 3%, 5%, 7%, 9%, 10%), has been successfully made by co-precipitation method and confirmed by XRD, FTIR, SEM. Al doping in zinc oxide (ZnO) has been shown to improve the dielectric constant (DC) and electrical conductivity (electrical conductivity) of prepared samples with minimal dielectric losses. These features are favorable for optoelectronics and spintronics devices.

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