**Synthesis and Characterization of Zn1-xAlxO oxide Nanomaterials**

**Abstract**

Aluminium (Al) substituted zinc oxide (ZnO) nanopowders with various proportions Zn1-xAlxO were synthesized by the co-precipitation method. All the samples were characterized using X-ray diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) confirming a single crystalline phase with a wurtzite structure. The effect of Al doping amount in ZnO samples has decreased average crystallite size and increased dielectric constant and electrical conductivity. The results of dielectric measurement indicate that the parameters dielectric constant, k, and dielectric loss, tanδ were decreasing with increasing of frequency.

*Keywords:* Nanostructures; Coprecipitation; Dielectric constant; Dielectric loss; Electrical conductivity;

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 has 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 exists in three crystalline structures, namely cubic zinc blend, rock salt, and hexagonal wurtzite, among which the hexagonal wurtzite-type structure is the most stable at room temperature.

Due to large energy band gap, transparency to visible light (400-700 nm), and some of the properties of ZnO such as optical, acoustic, and electrical, it is employed in many applications. ZnO has been synthesized by many methods including the wet chemical method, hydrothermal method, chemical vapor deposition, etc. 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 favourable properties like non-toxic, easy availability, environmental stability, cost-effectiveness, etc. The structural and morphological characterization was studied. The Al doping effect on electrical and dielectric properties was analyzed and reported.

1. Experimental

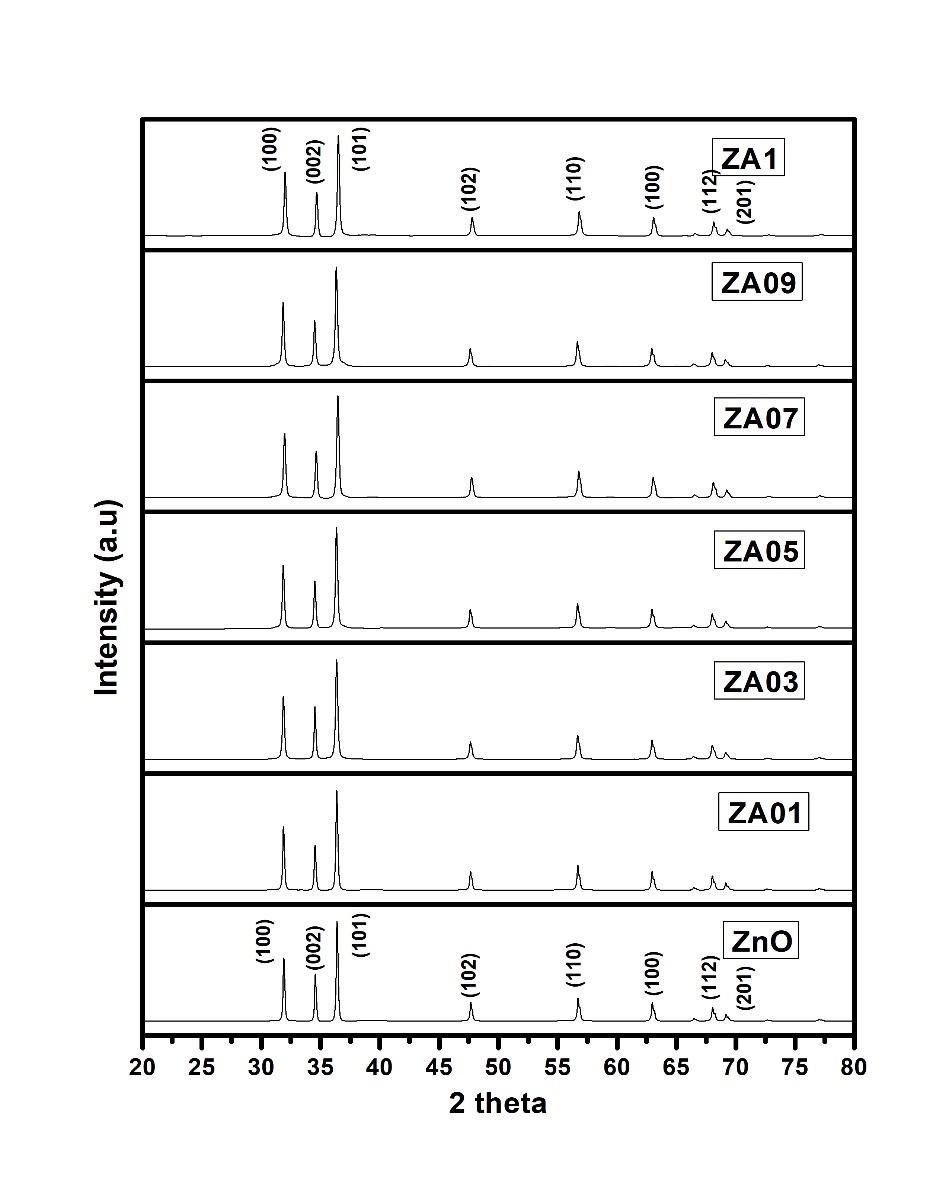
Samples of ZnO with Al dopant having proportions, (Zn1-xAlxO, x=0, 0.01, 0.03, 0.05, 0.07, 0.09, 0.1), were synthesized by co-precipitation method. The starting materials used were Zn (NO3)26H2O and NaOH solution. Zinc nitrate of 0.3 M solution was prepared by dissolving Zn (NO3)26H2O in 100 ml of distilled water by continuous stirring. 0.3 M NaOH solution was added, then, dropwise. The stirring process was continued for 2 h at 75oC and then cooled to room temperature. The resultant precipitate was filtered and washed with distilled water several times. Finally, the precipitate was again dried at 100oC for 24 h and then calcinated at 700oC for 3 h. Al (NO3)39H2O was added to zinc nitrate in different amounts from 0.01 to 1 mol%. The samples are named as ZnO, ZA01, ZA03, ZA05, ZA07, ZA09, and ZA1 for different wt% loading concentrations of Al (x=0, 0.01, 0.03, 0.05, 0.07, 0.09, 0.1), respectively. The doped samples were characterized using XRD (Philips PW-1730), FTIR (Brucker tensor 27), and SEM (LEICA, S440i, UK). The pellets of 10 mm diameter and 3 mm thickness were made from the sample powders and then sintered at 1100oC for 3 h. The two surfaces of sintered pellets were coated with silver paste and then studied dielectric properties using a PSM1700 meter frequency response analyzer, Newton 4th Ltd.

1. Results and Discussions

XRD patterns of ZnO samples doped with Al in different concentrations 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 Al2O3 or other impurities are observed which confirms the diffusion of Al3+ in ZnO. The figure depicts the shifting of diffraction characteristic peaks to higher angles with increasing dopant levels of Al3+. The crystallite size was calculated from relative intensity levels of peaks using the Scherrer equation.

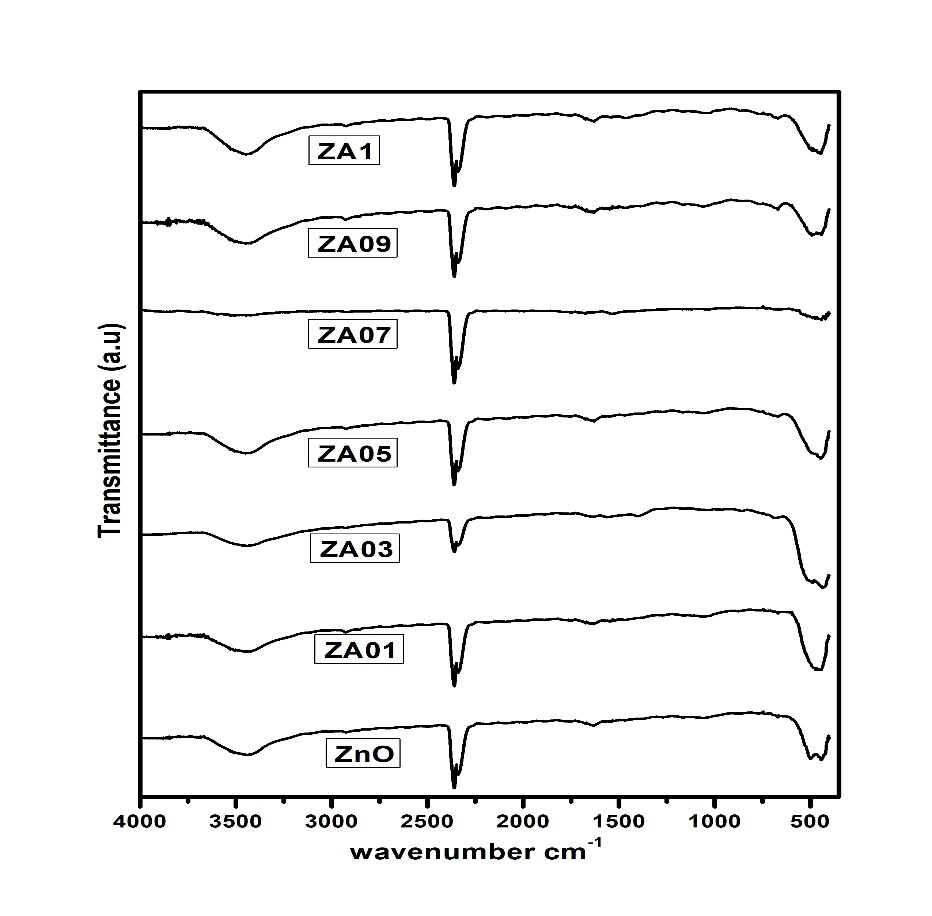
Where, D is the average crystallite size, 𝛽 is the full width at the half maximum of the diffraction peak, 𝛉 is the Bragg angle, 𝜆 is the wavelength of the X-ray used and k is a constant.

Table 1 gives the average crystallite size of all samples and lattice parameters. Average crystallite size was found to decrease with the increase of Al doping which reveals the fact that Al3+ ions replaced Zn2+ ions successfully in the ZnO crystal structure.



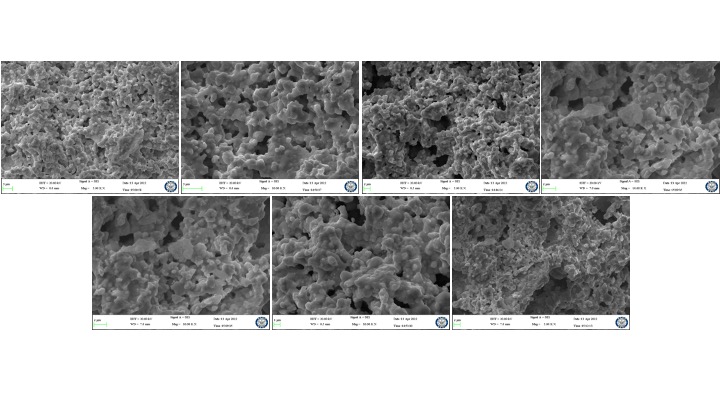
**Figure 1. XRD patterns showing ZnO and ZnO nano-particles doped with Al.**

ZnO doped with Al samples was analyzed by FTIR in the region 4000-400 cm-1 and the spectra are shown in the fig.2. The absorption band observed between 3417 and 3479 cm-1 , as seen from the fig., is attributed to OH group stretching vibrations which reveals the presence of H2O on the surface of the samples. Zn-O stretching vibration, which supports the ZnO wurtzite structure formation, corresponds to the band near 500 cm-1in the fig. The bands near 2350 cm-1 and 1445 cm-1are ascribed to CO2, which is absorbed by metal cations from the atmosphere. The band of Al-O can be seen near 683 cm-1in the fig. The shift in the spectra of doped samples, as shown in the fig., may be due to crystal perturbation created by Al atoms into the crystalline lattice sites. The band around 445 cm-1, can be assigned to the Zn-O bond which is seen in all the samples. The bands near 960 cm-1 with weak intensity and 1122 cm-1 with strong intensity are found to increase in intensity with Al doping level, as can be seen from the fig. These bands correspond to Al-O stretching vibrations.



**Figure 2. FTIR spectra of ZnO and ZnO nano-particles doped with Al.**

The analysis of the morphological structure was performed using SEM for all samples. And the picture is shown in Fig. 3. The formation of nanoparticles of ZnO and AZO was seen in these micrographs. The nanoparticles have a nearly spherical shape, and their morphology does not change after doping. It was discovered that as the concentration of Al rises, so does the agglomeration.



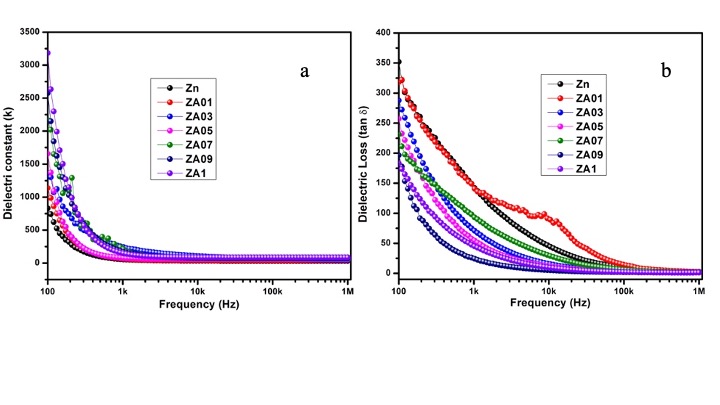
**Fig. 3: SEM micrographs of ZnO and Al-doped ZnO nanostructures.**

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 nanosamples.

Table 1 gives k values of all samples. The k is found to increase with Al doping amount which may be because the electro-negativity of Al (1.61) is less than that of Zn (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.

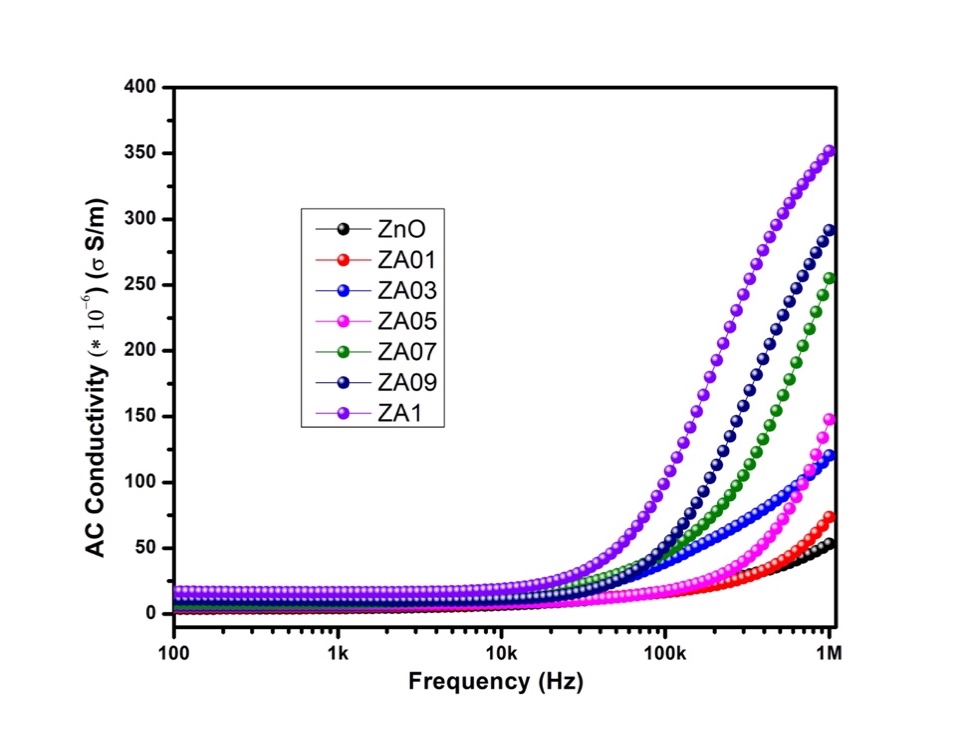
Figure 4b shows the frequency dependence of dielectric loss, tan𝛿. All samples exhibit the falling off dielectric loss with the increase of frequency at lower frequencies and at higher frequencies tan𝛿 become constant. This can be attributed to ionic hopping at low and moderate frequencies leading to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

At high frequencies, ionic vibrations are the only source that contributes to dielectric losses. The tan𝛿 values of Table 1 shows that the dielectric loss is highest for pure ZnO and decreases with the increase of the Al doping level. Hence, it is confirmed that doping of Al into ZnO increased the dielectric capability which is a desirable feature for high-frequency device applications.



**Fig. 4: Frequency variation of a) dielectric constant and b) dielectric loss (tan𝛿) of ZnO and Al-doped ZnO nanostructures.**

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 Al ions are doped in the ZnO lattice, more free charge carriers are present near grain boundaries, contributing to conductivity at high frequencies.



**Fig. 5: Frequency variation of AC conductivity of ZnO and Al-doped ZnO nanostructures.**

**Table 1.Structural, electrical and dielectric data of ZnO and Al-doped ZnO nanostructures.**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| 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 | 3.2353 | 5.6037 | 47.5×10-6 | 31 | 2.51 |
| ZA01 | 72 | 3.2381 | 5.6085 | 61.44×10-6 | 38 | 2.32 |
| ZA03 | 68 | 3.2394 | 5.6108 | 110.21×10-6 | 45 | 1.94 |
| ZA05 | 63 | 3.2405 | 5.6127 | 121.03×10-6 | 58 | 1.78 |
| ZA07 | 59 | 3.2298 | 5.5941 | 229.43×10-6 | 67 | 1.45 |
| ZA09 | 57 | 3.2415 | 5.6144 | 274.52×10-6 | 75 | 1.31 |
| ZA1 | 54 | 3.2249 | 5.5858 | 339.22×10-6 | 84 | 1.14 |

1. Conclusions

A series of samples of zinc oxide with aluminum doping, (Zn1-xAlxO, x=0, 0.01, 0.03, 0.05, 0.07, 0.09, 0.1), has been successfully prepared by co-precipitation method and confirmed by XRD, FTIR, SEM. It has proven that, the effect of Al doping in ZnO on dielectric and electrical properties of the prepared samples can show improvement in dielectric constant and electrical conductivity with low dielectric losses. These features are favourable for optoelectronics and spintronics devices.

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