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Structural and Dielectric Properties of Zn_{1-x}Mo_xO Nanoparticles

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Abstract: In this work, samples of zinc oxide nanoparticles doped by molybdenum $(Zn_{1-x}Mo_xO \text{ with } 0 \le x \le 0.1)$ were prepared by using the wet co-precipitation method. The characterization of the prepared samples was carried out by means of X-ray powder diffraction (XRD). The samples reserved their hexagonal wurtzite structure with Mo doping and showed a decrease in the crystallite size up to x = 0.04 followed by a further increase. On the other hand, dielectric measurements were performed using an LCR meter. The effect of frequency and temperature on the dielectric properties such as the real and imaginary parts of dielectric constant (ε' and ε'' , respectively), dielectric loss (tan δ) and acconductivity (σ_{ac}) of Mo-doped zinc oxide samples, was studied in the frequency range (100 Hz - 1 MHz) and at temperatures (300 - 773 K). The values of room temperature dielectric parameters were found to be strongly dependent on the Mo-doping. However, the increase in temperature caused an enhancement in the values of the dielectric parameters, particularly at 773 K.

Keywords: Zinc oxide, XRD, Dielectric constants, Ac-conductivity.

Introduction

Among diluted semiconductors, extensive research was employed to study ZnO due to its interesting features, such as wide direct band gap, large exciton binding energy and high transparency in the visible region [1]. Thanks these interesting features, ZnO has been employed in various applications as light emitting diodes, piezoelectric devices, solar cells and gas sensors [2]. Research has shown that doping ZnO with transition metals enhances their structural, optical and electrical properties, which is useful in the fabrication of optoelectronic devices. Studies have reported the effects of transition metal doping on ZnO properties [3-6]. Sundar and John [7] investigated the dielectric properties of ZnO doped with Mn. The dielectric properties increased with temperature, confirming the space-charge contribution in the charge transport process and polarizability. Belkhaoui et al. [8] studied Mn-doped ZnO nanoparticles. The acconductivity was decreased with Mn addition, which is attributed to the increase of defects. Boukachem et al. [9] explored the effect of Mo on ZnO thin films. The high-frequency dielectric constant and plasma pulsation showed a decrease with Mo content. Gosh et al. [10] studied the impact of Ni on ZnO prepared by precipitation method and reported the decrease in dielectric constant with the increase in Ni-doping percentages.

Doping with Mo is favorable, since it has multiple valence states and hence produces free carriers by single doping. Furthermore, the ion scattering effect is reduced due to the difference in the valence electrons between Mo and Zn ions. Therefore, the aim of this work is to study the structural, as well as dielectric properties of Zn_{1-x}Mo_xO (0.00 $\leq x \leq 0.10$) nanoparticles prepared by the co-precipitation method.

Experimental Techniques

Nanoparticles of general formula $Zn_{1-x}Mo_xO$ were prepared by the wet chemical coprecipitation method as reported previously for $Zn_{1-x}Er_xO$ [11]. The structure of the samples was examined by room temperature X-Ray powder diffraction using Shimadzu-7000 advance powder diffractometer with Cu-K_a radiation ($\lambda =$ 1.54056 Å) in the range $25^\circ \le 2\theta \le 75^\circ$. The dielectric properties were measured as a function of frequency and temperature using HIOKI 3532- 50 LCR Hi-tester.

Results and Discussion

Structural Properties

XRD Zn_{1-x}Mo_xO The patterns of nanoparticles with $0 \le x \le 0.10$ are shown in Fig. 1. The diffraction peaks of the pure and Modoped samples confirmed the formation of a hexagonal wurtzite structure. No additional phase was observed in the XRD patterns of the Mo-doped ZnO samples up to doping value x =0.04. However, a diffraction peak corresponding to MoO₃ was observed in the XRD pattern for the samples with x = 0.06 and x = 0.1. Table 1 depicts the values of the lattice parameters (a and c), the unit cell volume (v), the crystallite size

(D) and the Zn-O bond length (l) for pure and Mo-doped samples. It is noticed that both lattice parameters a and c show a decrease with x up to 0.06 and then increase for x > 0.06. The decrease in lattice parameter c is probably due to the fact that Mo⁶⁺ ions have smaller ionic radii than Zn²⁺ and a higher valence state. This causes a contraction of the unit cell and hence a decrease in its volume. The lattice parameter c increases for x > 0.06 and reaches the value of pure ZnO. A reasonable interpretation might be the migration of smaller Mo⁶⁺ ions from ZnO lattice to form MoO₃ impurity as confirmed by the XRD patterns for samples with $x \ge 0.06$. The values of the crystallite size D was obtained from the stress-starin plots. They show a decrease with x up to 0.04 and then increase to 30.11 nm for x = 0.1. The decrease in D might be attributed to the lowering of nucleation and decreasing growth rate of ZnO crystals resulting from the deformation of the ZnO lattice by Mo⁶⁺-doping. At high substitutions of Mo⁶⁺, the migration of Mo⁶⁺ from the ZnO matrix to form MoO₃ reduces the deformation of the lattice, changing back the value of crystallite size to that of pure ZnO sample. The Zn-O bond length decreased with x due to the substitution of Zn²⁺ ions by Mo⁶⁺ ions.



FIG. 1. XRD patterns of $Zn_{1-x}Mo_xO$ nanoparticles with $0 \le x \le 0.1$.

 TABLE 1. Lattice parameters, unit cell volume, crystallite size and Zn-O bond length as functions of x.

X	a (A°)	c(A°)	$v (A^{\circ})^{\beta}$	D(nm)	$l(A^{\circ})$
0.00	3.24	5.22	47.68	31.85	1.978
0.02	3.24	5.21	47.53	27.09	1.976
0.04	3.23	5.18	47.09	26.46	1.970
0.06	3.22	5.16	46.48	29.60	1.961
0.10	3.25	5.20	46.01	30.11	1.955

Dielectric Properties

Fig. 2(a - d) shows the dependence of the real and imaginary parts of the dielectric constants $(\varepsilon'), (\varepsilon'')$, dielectric loss tangent $(\tan \delta)$ and acconductivity (σ_{ac}) at room temperature of pure and Mo-doped ZnO nanoparticles. For all samples, the dielectric constant (ε') (Fig. 2.a) shows a sharp decrease at low frequencies followed by a marginal decrease to obtain constant values up to a frequency of 1 MHz. This behavior is explained by the Maxwell-Wagner model [12] which agrees with Koop's phenomenological theory [13]. The samples consist of strongly conducting grains surrounded by weakly conducting grain boundaries. Upon the application of an external field, the charge within the grains migrate carriers and accumulate at the grain boundaries. This high accumulation causes large polarization and consequently high dielectric constants. Another reason behind the high dielectric constant at low frequencies is the contribution of interfacial/space polarization which arises due to the inhomogeneous dielectric structure. Furthermore, as the frequency increases, the hopping between the different metal cations $(Zn^{2+} and Mo^{6+})$ cannot follow the applied field anymore and this explains the frequency independence of the dielectric constant at high frequencies. The variation of ε' with Mo doping shows an unsystematic decrease with x up to 0.06 followed by an increase for x = 0.1. Research has shown that polarization in nanoparticles varies by doping according to several factors, including crystallite size, cation distribution, defect density, inhomogenieties, porosity of samples, number of oxidation states of the dopant element, lattice distortions and variation of bond length [14–16].



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For the samples under study, the variation of the crystallite size with doping, as shown in Table 1, causes a variation in the surface to volume ratio and hence the variation of interfaces and boundary defects, at which polarization takes place, which results in a variation in the dielectric constant. Again, the incorporation of Mo ions gives rise to lattice distortion and a decrease of bond lengths, as shown in Table 1, which varies polarizability and thus dielectric constant.

Finally, the interaction between different Mo ions found in different valence states and distributed randomly over different crystallographic sites changes the polarizability and the dielectric constant.

The values of ε " (Fig. 2.b) for all samples show a decrease with frequency for all samples. The values of ε'' are high at low frequency due to high resistivity of grain boundaries at this range of frequency, which requires more energy for polarization, resulting in a high energy loss. As frequency increases, the effect of the grain boundary decreases, accordingly less energy will be required for the hopping process. Thus, less energy is dissipated for polarization, which results in lower dielectric losses. Higher doping caused a sharp decrease in the dielectric loss at higher frequencies. The migration of Mo ions from the grain boundaries to form the MoO_3 phase reduces their contribution in dielectric losses and hence we obtain a dcerarse in ε'' . Therefore, one can conclude that the doped samples might be used in high-frequency device applications [17].

Tan δ displayed in Fig. 2.c represents the ratio of the dielectric loss to the dielectric constant and exhibits a similar trend, such that it decreases with frequency increase and increases with temperature increase, confirming Koop's theory.

For all samples, σ_{ac} (Fig. 2.d) shows a gradual increase with frequency, with a faster increment at higher frequencies. As the frequency increases, more charges can migrate between

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grains as they acquire enough energy to overcome the poor conducting- grain boundary barrier [18]. Moreover, the values of σ_{ac} decrease with Mo doping. So, Mo doping hinders the hopping mechanism and hence decreases the value of σ_{ac} . This might be linked to the enhancement of zinc interstitials and oxygen vacancies by Mo doping [3]. These defects segregate at grain boundaries and assist the formation of the barrier resulting in a decrease in conductivity [13]. The small values of σ_{ac} are attributed to the space charge contribution to the charge transport process and polarizability. When the grain size is smaller than the electron mean free path, grain boundary scattering dominates and hence electrical resistivity is increased.

Fig. 3(a-d) represents the temperature dependence of all the dielectric parameters at a fixed frequency equal to 10^5 Hz. All the parameters showed an increase with temperature. This can be attributed to the increase in the number of accumulated charges at the grain boundaries due to temperature increase, which consequently leads to polarization increment and hence to an increase in dielectric constants. At lower temperatures, the charge carriers possess a weak contribution to the dielectric response. As a result, they cannot orient themselves with respect to the direction of the applied field [19]. However, as temperature increases, the drift mobility of these charge carriers increases causing an enhancement in the dielectric parameters. The contribution from space charge polarization depends on the purity and perfection of the crystal structure, which in turn are strongly dependent on temperature [20]. Hence, the large values of dielectric parameters obtained at higher temperatures may be ascribed to the creation of crystal defects as the temperature increases leading to the dominance of space charge polarization contribution [21]. It is remarkable to note that the sample of highest Mo doping possesses the highest dielectric constants with temperature.



FIG. 3. Variation of $\epsilon'(a)$, $\epsilon''(b)$, $\sigma_{ac}(c)$ and tan $\delta(d)$ versus T at f=10⁵ Hz.

Conclusion

ZnO Mo-doped nanoparticles were successfully prepared using the wet chemical coprecipitation method. XRD measurements revealed that Mo substituted Zn without altering hexagonal crystal structure. the Room temperature dielectric measurements showed a non-systematic decrease in dielectric constant

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with frequency due to electron exchange interaction. The dielectric loss was found to decrease with Mo-doping, indicating that Modoped ZnO nanoparticles are important for highfrequency applications. At a fixed frequency, all dielectric parameters showed an increment with the increase in temperature for both pure and doped samples.

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