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Investigation of Solvent Effect on the Structural Morphological and Optical Properties of ZnO Doped Mg Elaborated by Sol-Gel Method

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Abstract

This work aims to study the solvent's effect on the structural, morphological, and optical properties of Mg-doped zinc oxide (MZO) thin films. The results of the XRD analysis revealed that the 2-methoxyethanol solvent imparts a preferential orientation to the MZO samples, following the (002) plane, with a maximum value observed at 2% Mg. In contrast, the samples prepared using methanol show no preferential orientation. SEM analysis corroborated that the use of 2-methoxyethanol results in an orderly distribution of MZO crystallites. The optical characterization indicated that the transmittance of MZO thin films reached a maximum value of 90% for Mg concentrations ranging from 2% to 3%. At the same time, the refractive index showed its lowest value of 1.46. In contrast, the use of methanol as a solvent resulted in a maximum transmittance of 80% at 4% Mg, accompanied by a minimum refractive index value of 1.96.

Keywords

ZnO, ZnO Doped Mg, Methanol, 2-Methoxyethanol, Preferential Orientation, Optical Properties, Sol-Gel

1. Introduction

For many years, the main applications of zinc oxide have been used in the chemical and pharmaceutical industries. Nowadays, new avenues of research in optoelectronics are arousing great interest in this material due to its multiple properties. ZnO is a semiconductor with a large band gap (~3.37 eV), high bond energy (60 meV), and transparency in the visible and near-infrared range. It is considered a "twin" of GaN material [1], which makes it interesting for potential applications in the fields of photovoltaics [2], light-emitting diodes for lighting [3], transparent conductive oxides (TCO) [4], photonics or sensors [5]. It also has special properties from the II-VI family: hardness, exciton stability, piezoelectricity, and thermochromicity… [6].

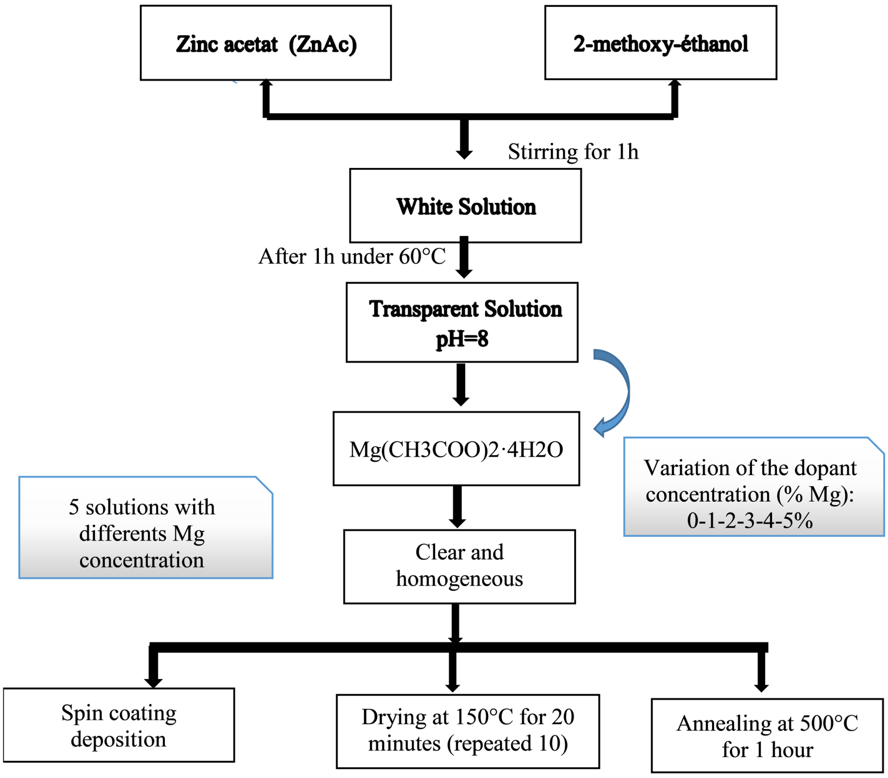
For the design and realization of ZnO-based devices, one of the major problems in having an efficient TCO is finding adequate doping that offers the TCO material both high conductivity and high transmittance. A concentration of carriers with a value of 10^{19} cm^{-3} or more, and a band gap energy greater than 3 eV are generally required for high conductivity and transmittance [7]. Fortunately, ZnO thin films are a promising alternative to the commonly used ITO, which are nontoxic and less expensive than ITO [8]. One of the major challenges of optimizing the optical properties of ZnO is the incorporation of doping ions into the ZnO lattice. Many researchers have reported that the optical properties of ZnO can be modified by doping ZnO by elements from group II as Mg [9] [10]. In this case, Mg-doped ZnO thin films are elaborated by two different solvents named 2-methoxy ethanol and methanol to realize an enhancement of the optical properties of TCO devices with affecting the lattice parameters, under the influence of difference electronegativity achieved by replacing Zn^{2+} ions by Mg^{2+}. The variation in the optical properties of materials when changing solvents is influenced by two crucial parameters: the dielectric constant and the boiling temperature. Understanding how these factors interact is essential for optimizing the performance of optical materials in various applications. In this study, we focus on two solvents that exhibit a significant disparity in these parameters: 2-methoxyethanol, with a dielectric constant of 16.93 and a boiling temperature of 126.4˚C, and methanol, which has a dielectric constant of 32.35 and a boiling temperature of 64.7˚C.

The primary objective of this work is to investigate how the differences in dielectric constant and boiling temperature between these solvents affect the optical properties of ZnO when doped with group II elements. By comparing the effects of these two solvents, we aim to gain insights into how solvent properties influence doping efficiency and, consequently, the resulting optical characteristics. This research could provide valuable guidance for selecting appropriate solvents in the synthesis of optical materials, ultimately enhancing their performance in practical applications.

2. Experimental Method

The samples are undoped and Mg-doped ZnO thin films were prepared on glass using a sol-gel process followed by spin coating. A homogenous solution was prepared by dissolving zinc acetate dehydrate $[Zn(CH_3OO)_2{\cdot}2H_2O]$ as a starting material and the 2-methoxyethanol ($C_3H_8O_2$) was used as the solvent with monoethanolamine (MEA) as the stabilizer. The zinc precursor solution was prepared with the MEA stabilizer at a ratio of 1:1. The Mg content was taken at 0%, 1%, 2%, 3%, 4%, and 5% using magnesium acetate $[Mg(CH_3COO){\cdot}2.4H_2O]$ as a doping element.

The same procedure is redone, but with the methanol solvent to study the effect of the solvent on the optical properties of these samples. Each film layer was deposited using a spin coater operating at 3000 rpm for 30 seconds, after cleaning ultrasonically glass substrates in acetone and rinsed in deionized water. After, the films were air-dried at 150˚C. This process of drying was repeated 10 times for each film. Finally, the films were annealed at 500˚C for one hour as illustrated in the following diagram.



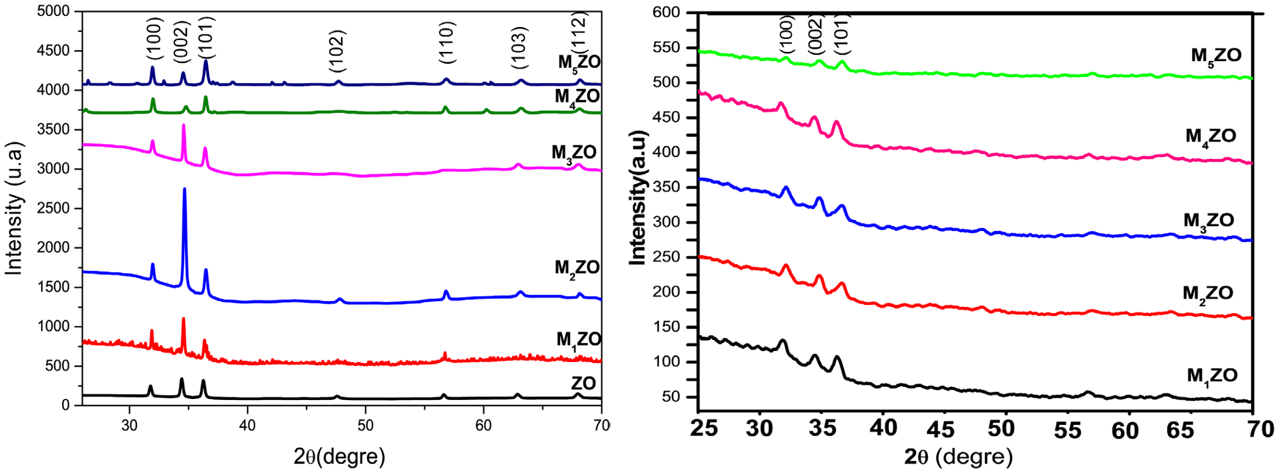
The same procedure is repeated using methanol as the solvent, except that during the drying step, we maintain a temperature of 80˚C for 20 minutes.

Films were analyzed using an X-ray diffraction (XRD, D/Max-2400) to analyze their crystal structure. A scanning electron microscope (SEM, JSM-6701F) was used to explore the morphological surface. The transmittance spectra of the UV-visible light passing through the films were measured by a UV-visible spectrophotometer (Lambda35 UV/VIS) to study the optical properties of the studied samples.

3. Result and Discussion

3.1. Structural and Morphological Characterizations

X-ray diffraction was used to determine the crystal's structure, the crystal's orientation, and the crystal size. Figure 1 shows that the samples of ZnO doped with Mg elaborated with two different solvents namely 2-methoxy-ethanol and methanol crystalized with wurtzite structure and exhibit tree peaks characteristic of ZnO correspond to (100), (002), and (101) peaks. Except, the samples prepared by 2-methoxy-ethanol showed more intense peaks with the appearance of secondary peaks compared to those synthesized with the methanol solvent.



(a) (b)

0% Mg = ZO, 1% Mg = M_1ZO, 2% Mg = M_2ZO, 3% Mg = M_3ZO, 4% Mg = M_4ZO, and 5% Mg = M_5ZO.

Figure 1. (a) X-ray pattern of Mg-doped ZnO thin films deposited on glass substrates by sol-gel at various percentages elaborated 2-methoxy ethanol solvent; (b) X-ray pattern of Mg-doped ZnO thin films deposited on glass substrates by sol-gel at various percentages elaborated by methanol solvent.

To analyze the orientation of the crystallites for each solvent, the texture coefficient TC (hkl) for each diffraction peak was calculated following this equation [11]. To analyze the orientation of the crystallites for each solvent, the texture coefficient TC (hkl) for each diffraction peak was calculated following this equation [11], the results of the calculations are shown in Table 1.

$$T_{C(hkl)} = \frac{\dfrac{I_{(hkl)}}{I_{0(hkl)}}}{\dfrac{1}{n}\sum \dfrac{I_{(hkl)}}{I_{0(hkl)}}} \tag{1}$$

Table 1. Texture coefficient of Mg doped ZnO thin films deposited on glass substrate by sol-gel elaborated with two different solvents: 2-methoxy ethanol and methanol.

Mg concentration	0%	1%	2%	3%	4%	5%
TC (002) 2-methoxy ethanol	1.28	1.47	2.16	1.92	0.71	0.93
TC (002) methanol	-	0.891	1.11	0.96	1.36	1.11

We note that the texture coefficient of all the samples prepared by methanol solvent is around 1, which confirms that the crystallites have a disordered distribution. Since the preparation with 2-methoxyethanol gave a texture coefficient greater than 2 for 2% Mg. We can conclude that the elaboration with 2-methoxyethanol gives the crystallites a better crystallinity compared to the samples prepared by methanol. Indeed, the methanol has a boiling point equal to 64.7˚C, it evaporates quickly leaving a disorder in the distribution of crystallites, while 2-methoxyethanol has a larger boiling point equal to 126.4˚C. In this case, evaporation takes place slowly, giving the crystallites enough time to have a preferred orientation. R Bekkari *et al.* [12] indicated that in the solvents with a low boiling point, the evaporation is faster and forces the material to develop in other directions and generally behaves like an amorphous material.

The calculated average crystallite size was obtained from the Scherrer relation (2) associated with the (002) peak for each solvent (**Table 2**).

$$D_{crystallite} = \frac{0.9\lambda}{\beta \cos(\theta)} \tag{2}$$

Table 2. Crystallite size of Mg-doped ZnO thin films deposited on glass substrate by sol-gel elaborated with two different solvents: 2-methoxyethanol and methanol.

Mg concentration	0% Mg	1% Mg	2% Mg	3% Mg	4% Mg	5% Mg
D (nm) (2-methoxy ethanol)	33.52	65.6	80.70	75.5	35.66	35.66
D (nm) (methanol)	-	35.6	42.91	53.679	53.42	35.82

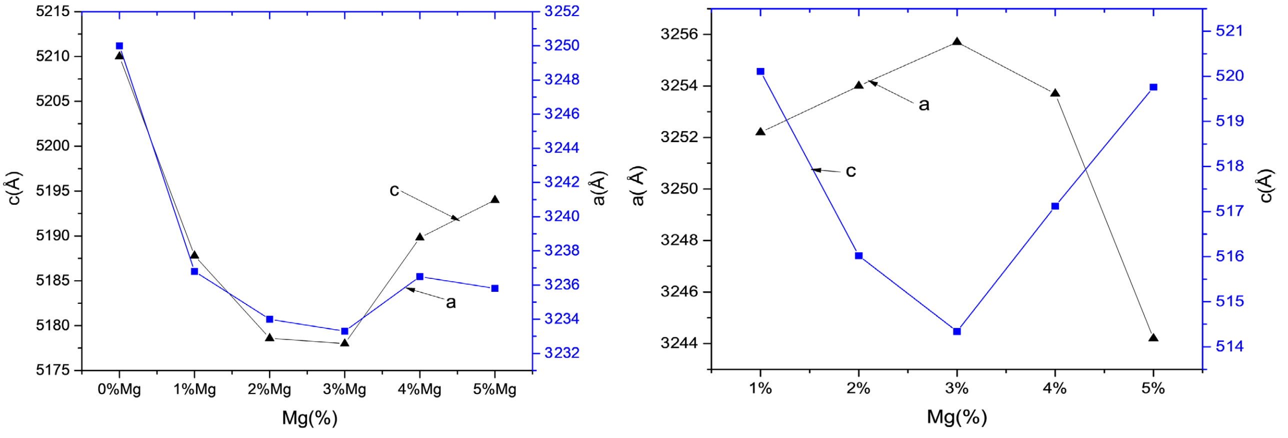
The crystallite size for samples prepared with the 2-methoxyethanol reaches a maximum value of 80.70 nm at 2% Mg and it begins to decrease. For the samples elaborated with the methanol solvent, the crystallite size varied slightly between 35 nm and 53 nm, which in all cases remains much smaller than those obtained with 2-methoxyethanol. This difference in size can be attributed to the difference in the dielectric constant and the boiling point of the two solvents. Indeed, the values of these magnitudes are (32.35˚C, 64.7˚C) for methanol and (16.93˚C, 126.4˚C) for 2-methoxyethanol. In this context, D.P. JOSHI *et al.* [13] have shown that the larger the dielectric constant is, the smaller the crystallite size is.

The lattice parameters a and c are calculated by the equation:

$$\frac{1}{d_{hkl}^2} = \frac{4}{3a^2}\left(h^2 + hk + k^2\right) + \frac{l^2}{c^2} \tag{3}$$

In the case of the 2-menoxyethanol, the lattice parameters a and c decrease simultaneously with increasing Mg concentration up to 3% Mg, then they increase (**Figure 2**).

This result may be due to the occupation of the substitutional sites by Mg atoms for concentrations ranging from (1% to 3%) Mg, under the influence of a large difference in the electronegativity between the Zn^{2+} (1.65) and Mg^{2+} (1.31) ions. While, the re-increase results of occupying the substitutional sites by Mg atoms [14]. On the other hand, the parameter "*c*" in the case of methanol solvent undergoes a remarkable variation and reaches a minimum value of 3% Mg. Conversely, the parameter "*a*" increases and reaches a maximum value at the same percentage of doping. This phenomenon can be explained by the presence of an intern stress during the insertion of Mg into the structure of ZnO. Indeed, the samples, produced by methanol, with a low boiling temperature, have a poor crystallinity and are more likely to contain more constraints than the ones elaborated by 2-methoxy-ethanol.



(a) (b)

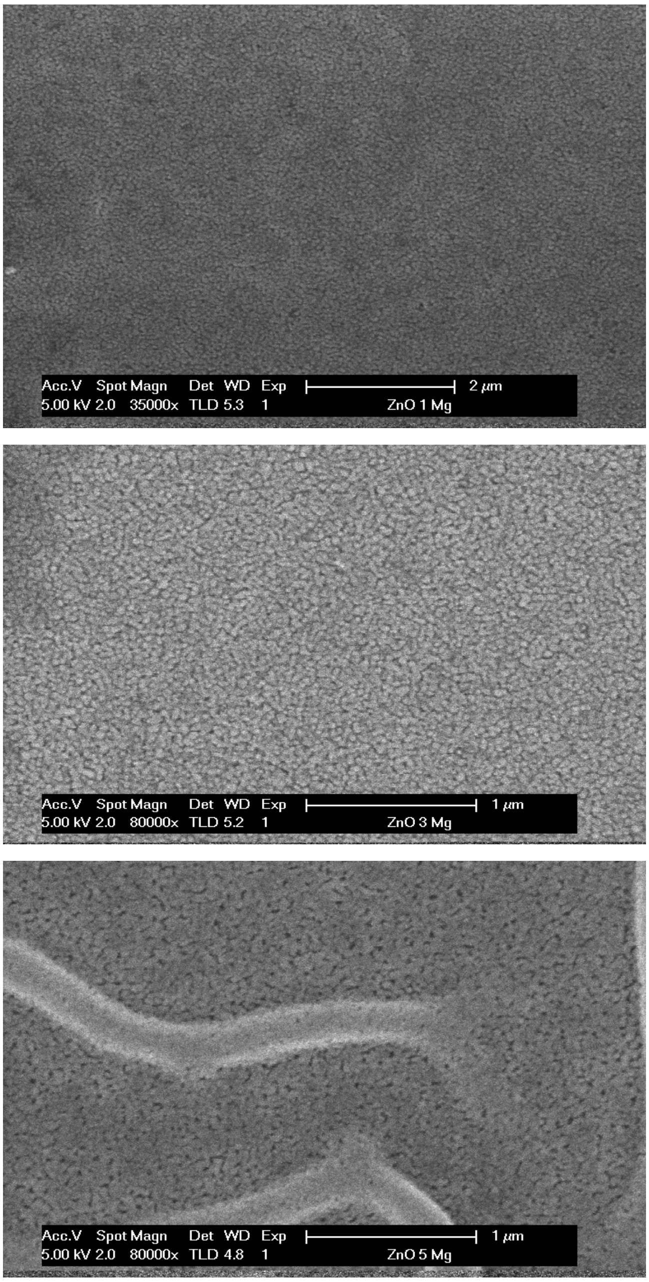
Figure 2. (a) Lattice parameters versus different concentrations of Mg-doped ZnO films deposited on glass substrates by sol-gel elaborated with 2-methoxy ethanol solvent; (b) Lattice parameters versus different concentrations of Mg-doped ZnO films deposited on glass substrates by sol-gel elaborated with methanol solvent.

Table 3 shows that these constraints reach their maximum at 3% Mg with a significant value of 5.4GPa to compare with 2.4 GPa for ZnO: Mg produced by 2-methoxy-ethanol, which causes an extremum of lattice parameters "*a*" and "*c*".

Table 3. Stress of Mg-doped ZnO thin films deposited on glass substrate by sol-gel elaborated with two different solvents: 2-methoxyethanol and methanol.

Mg concentration	0% Mg	1% Mg	2% Mg	3% Mg	4% Mg	5% Mg
σ(GPa) (2-methoxyethanol)	−0.33	1.55	2.33	2.42	1.38	0.95
σ(GPa) (methanol)	-	0.4	3.95	5.4	3	0.72

Some additional characterizations of SEM (scanning electron microscopy) are essential to obtain more detailed and precise information on the grains' size, shape, or distribution. The SEM images of the MZO samples prepared by 2-methoxy-ethanol (**Figure 3(a)**) show that the samples had a nanoscale crystalline microstructure with a uniform and dense distribution. It was also observed that the grain size increased from a concentration of 1% Mg to 3% Mg. On the other hand, the MZO samples prepared by methanol (**Figure 3(b)**) present nanowires of different orientations and shapes, presenting the agglomerations of grains. As has already been reported, this difference in morphology can be attributed to the difference in the dielectric constant and the boiling point between methanol and 2-methoxyethanol. The thermal decomposition of zinc acetate to form ZnO nuclei is more spontaneous in solvents with a high dielectric constant [15].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Acc.V Spot Magn Det WD Exp 1 μm
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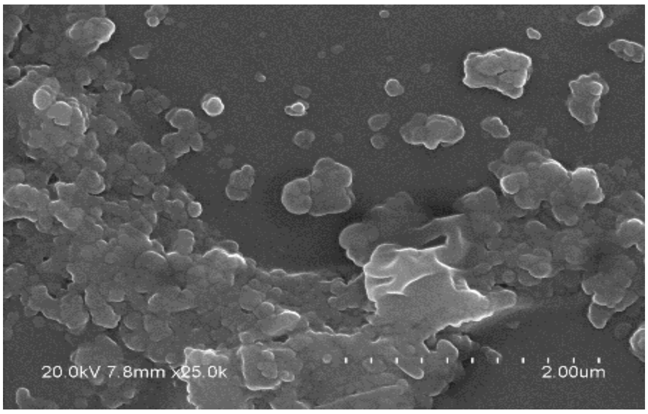
Acc.V Spot Magn Det WD Exp 1 μm
5.00 kV 2.0 80000x TLD 4.8 1 ZnO 5 Mg

(a)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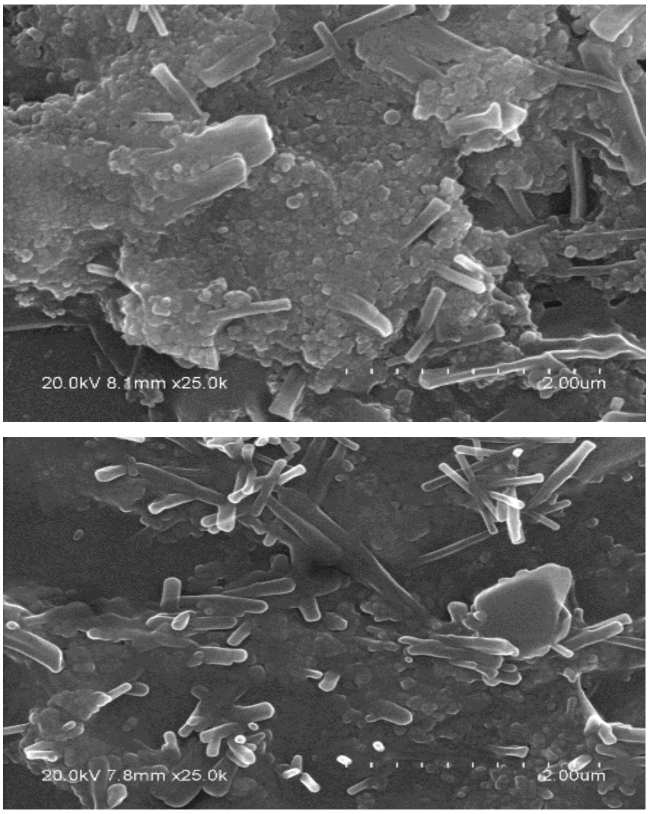


(b)

1% Mg = M_1ZO, 3% Mg = M_3ZO, and 5% Mg = M_5ZO.

Figure 3. (a) SEM images of Mg-doped ZnO films deposited on glass substrate by sol-gel at various concentrations of Mg elaborated with 2-methoxy ethanol solvents; (b) SEM images of Mg-doped ZnO films deposited on glass substrate by sol-gel at various concentrations of Mg elaborated with methanol solvent.

3.2. Optical Properties

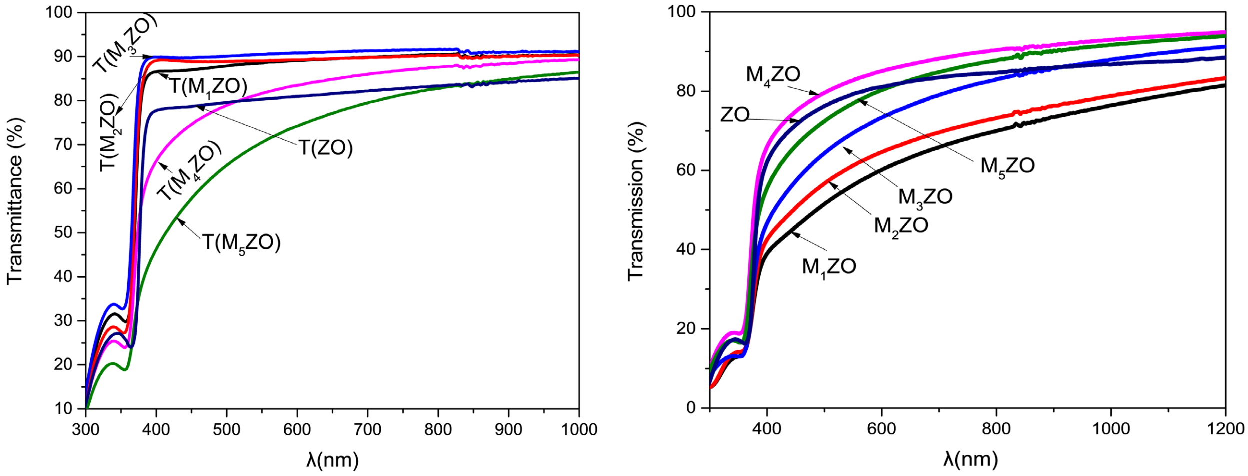
Figure 4 shows the optical transmission spectra of MZO films at various percentages prepared with two different solvents in the range of 300 - 1000 nm.

For the methanol solvent, the transmittance of the MZO samples decreases upon the introduction of Mg, then increases to a value of 80% at a Mg concentration of 4%. An opposite phenomenon is observed with the use of 2-methoxy-ethanol. In this case, the transmittance increases, reaching a maximum value of over 90% at 3% Mg, which corresponds to a high texture coefficient of 1.96. Conversely, for samples prepared with methanol, the M4ZO sample also exhibits a relatively high texture coefficient of 1.26. Consequently, we believe that the evolution of transmittance is linked to crystallinity, particularly to the preferential orientation of the samples along the (002) plane.

From the transmittance spectra, the optical gap E_g was deduced of the MZO films, by applying the following equation:

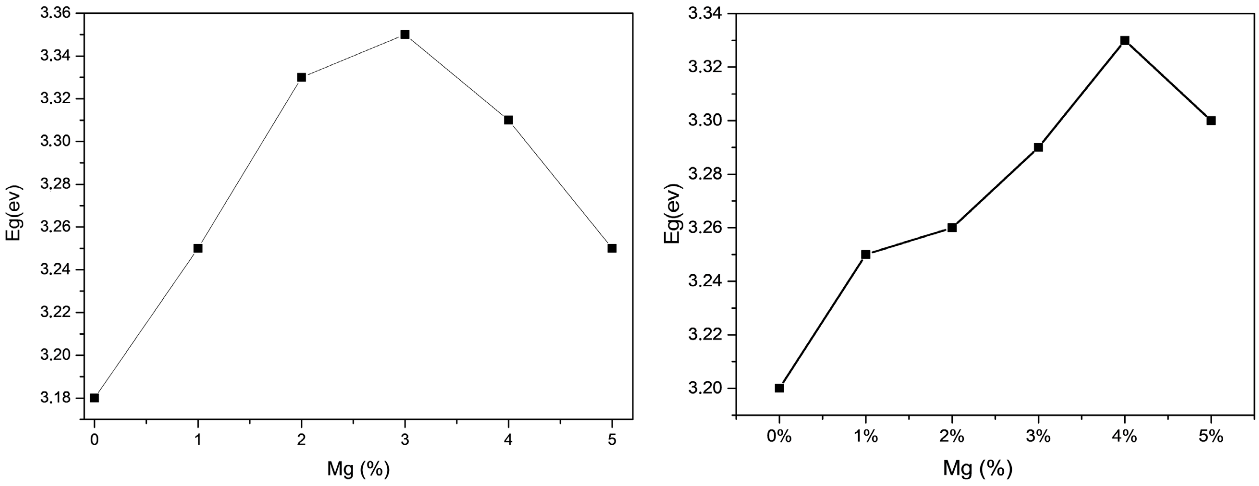
$$\alpha(h\nu) = A\left(h\nu - E_g\right)^{\frac{1}{2}} \tag{4}$$

where α is the absorption coefficient, and A is a constant. Figure 5 shows the evolution of the optical band gap as a function of Mg concentration for methanol and 2-methoxyethanol solvents.



(a) (b)

Figure 4. (a) Transmission spectra vs. wavelength for Mg-doped ZnO films deposited on glass substrate by sol-gel at various concentrations of Mg elaborated with 2-methoxy ethanol solvent; (b) Transmission spectra vs. wavelength for Mg-doped ZnO films deposited on glass substrate by sol-gel at various concentrations of Mg elaborated with methanol solvent.



(a) (b)

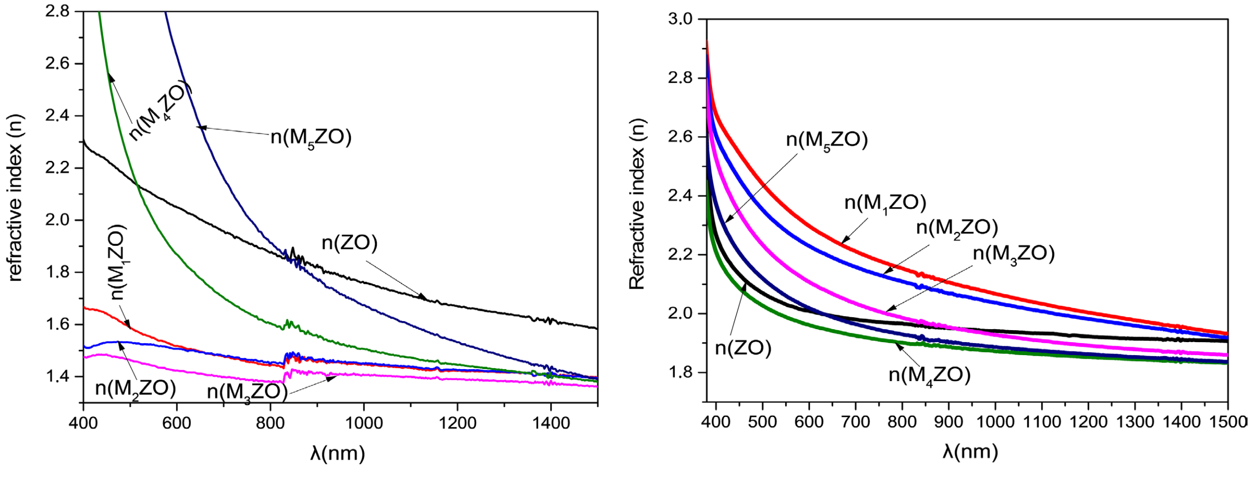
Figure 5. (a) Band gap versus different concentrations of Mg-doped ZnO films deposited on glass substrates by sol-gel elaborated with 2-methoxy ethanol solvent; (b) Band gap versus different concentrations of Mg-doped ZnO films deposited on glass substrates by sol-gel elaborated with methanol solvent.

For the methanol solvent, the band gap increases, reaching a maximum value of 3.33 eV at 4% Mg. In contrast, the maximum value for the 2-methoxyethanol solvent occurs at 3% Mg, with a value of 3.35 eV. It is noteworthy that the energy of the optical band gap varies similarly for both solvents, with a displacement of the maximum at 4%. The refractive index $n(\lambda)$, is related to reflectance, transmittance, and extinction coefficient $k(\lambda)$ by [16].

$$n=\frac{2-T}{T}+\sqrt{\frac{4\left(1-T\right)}{T^{2}}-k^{2}} \tag{5}$$

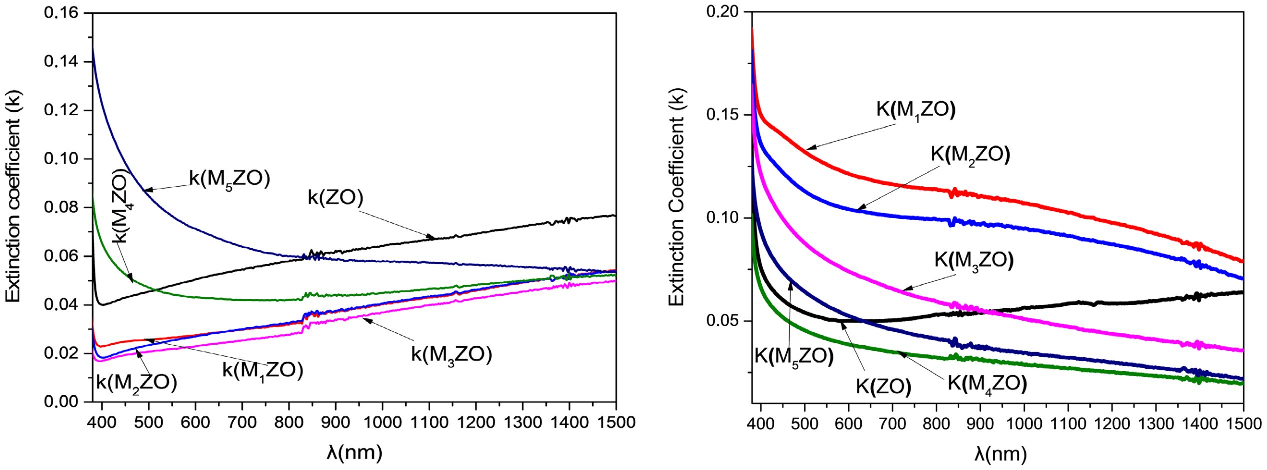
where k is the extinction coefficient ($k = \alpha\lambda/4\pi$) and T is the transmittance.

Figure 6, Figure 7 show the refractive index n (λ) and extinction coefficient k (λ) of MZO thin films at different percentages of Mg doping prepared with two different solvents in the range of 380 - 1500 nm.



(a) (b)

Figure 6. (a) Refractive index for different concentrations of Mg-doped ZnO films deposited on glass substrates by sol-gel elaborated with 2-methoxyethanol solvent; (b) Refractive index for different concentrations of Mg-doped ZnO films deposited on glass substrates by sol-gel elaborated with methanol solvent.



(a) (b)

Figure 7. (a) Extinction coefficient for different concentrations of Mg-doped ZnO films deposited on glass substrates by sol-gel elaborated with 2-methoxyethanol solvent; (b) Extinction coefficient for different concentrations of Mg-doped ZnO films deposited on glass substrates by sol-gel elaborated with methanol solvent.

These optical constants exhibit an exponential decrease with increasing (λ), therefore, we have grouped in Table 4, Table 5 their values for λ = 600 nm, to cipher their evolution with Mg concentration.

Table 4. Refractive index values determined for λ = 600 nm of Mg doped ZnO thin films deposited on glass substrate by sol gel elaborated with two different solvents: 2-methoxyethanol and methanol.

Mg concentration	0%	1%	2%	3%	4%	5%
n (2-methoxy ethanol)	2.04	1.56	1.55	1.46	1.9	2.66
n (methanol)	-	2.30	2.23	2.1	1.96	2.01

Table 5. Extinction coefficient values determined for λ = 600 nm of Mg doped ZnO thin films deposited on glass substrate by sol-gel elaborated with two different solvents: 2-methoxy ethanol and methanol.

Mg concentration	0%	1%	2%	3%	4%	5%
k (10^{-2}) (2-methoxyethanol)	5	2.7	2.7	2.2	4	7
k (10^{-2}) (methanol)	-	13	11	8.7	4	6

These results show that the refractive index increases as soon as the Mg is introduced, taking values greater than $n = 2$ recorded for undoped ZnO, then decreasing at 4% Mg taking a minimum value of 1.96. The increase can be caused by a disorder in the structure, changes in stochiometry, or the creation of internal tension caused by the increase in polarizability [17] [18]. This behavior contrasts with MZO samples prepared by 2-methoxyethanol, which makes the refractive index take a minimum going up to 1.46 for 3% Mg. This proves that the elaboration of MZO thin films with 2-methoxy ethanol solvent gives the samples better transparency compared to those prepared by methanol solvent. It can be concluded that the choice of solvent can modify the optical properties of ZnO-doped Mg. The extinction coefficient takes high values in the case of methanol for the percentages 1%, 2% Mg, and 3% Mg compared to the undoped ZnO, then it decreases taking a minimum value of 0.04 at 4% Mg. This increase is mainly due to the increase in absorption. While with the 2-methoxyethanol, k (λ = 600 nm) achieved its minimum value of 0.022 at 3% Mg. It can be concluded that the best TCO obtained, is the one of M_3ZO and M_2ZO prepared by 2-methoxyethanol solvent.

4. Conclusion

Mg-doped ZnO nanocrystalline thin films have been prepared by sol-gel method with two different solvents named 2-methoxyethanol and methanol. Structural characterization using X-ray diffraction for the samples elaborated with 2-methoxyethanol has been reported as a preferential orientation according to the (002) plan taking a maximum value of 2% Mg. While, the samples prepared by methanol solvent show no preferential orientation, which confirms that the crystallites have a disordered distribution. These results are corroborated by SEM analysis. The optical studies exhibit that the elaboration of MZO samples highly improves the optical transmission, which reaches a maximum value of 90% for (2% to 3%) Mg.

Accompanied by a minimum value of refractive index (1.46) lower than the undoped ZnO (2). Whereas, with the methanol solvent an opposite phenomenon to that obtained using 2-methoxyethanol is registered, reaching a maximum value of 80% at 4% Mg in transmittance, accompanied by a minimum value of refractive index (1.96).

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] Mohammed Nahhas, A. (2018) Review of GaN/ZnO Hybrid Structures Based Materials and Devices. *American Journal of Nano Research and Applications*, **6**, 34-53. https://doi.org/10.11648/j.nano.20180602.11

[2] Janfeshan, B., Sadeghimakki, B., Jahed, N.M.S. and Sivoththaman, S. (2014) Liquid Junction Quantum Dot Solar Cells Based on ZnO Nanowires Arrays. 2014 *IEEE* 40*th Photovoltaic Specialist Conference* (*PVSC*), Denver, 8-13 June 2014, 1051-1055. https://doi.org/10.1109/pvsc.2014.6925094

[3] Hwang, D., Kang, S., Lim, J., Yang, E., Oh, J., Yang, J., *et al.* (2005) *P*-ZnO/N-GaN Heterostructure ZnO Light-Emitting Diodes. *Applied Physics Letters*, **86**, Article ID: 222101. https://doi.org/10.1063/1.1940736

[4] Pearton, S. (2012). GaN and ZnO-Based Materials and Devices (Vol. 156). Springer.

[5] Kim, J.S., Park, W.I., Lee, C.H. and Yi, G.C. (2006) ZnO Nanorod Biosensor for Highly Sensitive Detection of Specific Protein Binding. *Journal of the Korean Physical Society*, **49**, 1653-1639.

[6] Özgür, Ü., Hofstetter, D. and Morkoç, H. (2010) ZnO Devices and Applications: A Review of Current Status and Future Prospects. *Proceedings of the IEEE*, **98**, 1255-1268. https://doi.org/10.1109/jproc.2010.2044550

[7] Nolen, J.R., Runnerstrom, E.L., Kelley, K.P., Luk, T.S., Folland, T.G., Cleri, A., *et al.* (2020) Ultraviolet to Far-Infrared Dielectric Function of n-Doped Cadmium Oxide Thin Films. *Physical Review Materials*, **4**, Article ID: 025202. https://doi.org/10.1103/physrevmaterials.4.025202

[8] Ali, M.K., Ibrahim, K., Hamad, O.S., Eisa, M.H., Faraj, M.G. and Azhari, F. (2011) Deposited Indium Tin Oxide (ITO) Thin Films by DC-Magnetron Sputtering on Poly-Ethylene Terephthalate Substrate (PET). *Romanian Journal of Physics*, **56**, 730-741.

[9] Ivetić, T.B., Dimitrievska, M.R., Finčur, N.L., Đačanin, L.R., Gúth, I.O., Abramović, B.F., *et al.* (2014) Effect of Annealing Temperature on Structural and Optical Properties of Mg-Doped ZnO Nanoparticles and Their Photocatalytic Efficiency in Alprazolam Degradation. *Ceramics International*, **40**, 1545-1552. https://doi.org/10.1016/j.ceramint.2013.07.041

[10] Saleem, M., Manzoor, A., Zaffar, M., Hussain, S.Z. and Anwar, M.S. (2016) Tailoring of ZnO with Selected Group-II Elements for LED Materials. *Applied Physics A*, **122**, Article No. 589. https://doi.org/10.1007/s00339-016-0118-4

[11] Shaikh, S.K., Ganbavle, V.V., Inamdar, S.I. and Rajpure, K.Y. (2016) Multifunctional Zinc Oxide Thin Films for High-Performance UV Photodetectors and Nitrogen Dioxide Gas Sensors. *RSC Advances*, **6**, 25641-25650. https://doi.org/10.1039/c6ra01750a

[12] Bekkari, R., Jaber, B., Labrim, H., Ouafi, M., Zayyoun, N. and Laânab, L. (2019) Effect of Solvents and Stabilizer Molar Ratio on the Growth Orientation of Sol-Gel-Derived ZnO Thin Films. *International Journal of Photoenergy*, **2019**, Article ID: 3164043. https://doi.org/10.1155/2019/3164043

[13] Joshi, D.P., Pant, G., Arora, N. and Nainwal, S. (2017) Effect of Solvents on Morphology, Magnetic and Dielectric Properties of (α-Fe_2O_3@SiO_2) Core-Shell Nanoparticles. *Heliyon*, **3**, e00253. https://doi.org/10.1016/j.heliyon.2017.e00253

[14] Sagheer, R., Khalil, M., Abbas, V., Kayani, Z.N., Tariq, U. and Ashraf, F. (2020) Effect of Mg Doping on Structural, Morphological, Optical and Thermal Properties of ZnO Nanoparticles. *Optik*, **200**, Article ID: 163428. https://doi.org/10.1016/j.ijleo.2019.163428

[15] Kunjara Na Ayudhya, S., Tonto, P., Mekasuwandumrong, O., Pavarajarn, V. and Praserthdam, P. (2006) Solvothermal Synthesis of ZnO with Various Aspect Ratios Using Organic Solvents. *Crystal Growth & Design*, **6**, 2446-2450. https://doi.org/10.1021/cg050345z

[16] Gautam, S.K., Singh, R.G., Siva Kumar, V.V. and Singh, F. (2015) Giant Enhancement of the N-Type Conductivity in Single Phase *P*-Type ZnO: N Thin Films by Intentionally Created Defect Clusters and Pairs. *Solid State Communications*, **218**, 20-24. https://doi.org/10.1016/j.ssc.2015.05.011

[17] Sharma, P. and Katyal, S.C. (2010) Linear and Nonlinear Refractive Index of As-Se-Ge and Bi Doped As-Se-Ge Thin Films. *Journal of Applied Physics*, **107**, Article ID: 113527. https://doi.org/10.1063/1.3428441

[18] Kaphle, A. and Hari, P. (2017) Variation of Index of Refraction in Cobalt Doped ZnO Nanostructures. *Journal of Applied Physics*, **122**, Article ID: 165304. https://doi.org/10.1063/1.5001713