Optical and Raman studies of Zn$_{1-x}$Mg$_x$O ceramic pellets

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**A B S T R A C T**

The undoped and Mg-doped ZnO ceramics have been successfully synthesized using the conventional solid state sintering method. The doping effect of MgO content on the structural properties of ZnO/MgO composites has been investigated by X-ray diffraction (XRD) and Raman spectroscopy. The XRD patterns reveal that all the samples are polycrystalline and have a prominent hexagonal crystalline structure with (002) and (101) as preferred growth directions. The formation of the hexagonal ZnMgO alloy phase and the segregation of MgO-cubic phase took place for an MgO composition $x > 20$ wt%. This finding is in good agreement with the Raman spectroscopy measurements which prove the existence of multiple-order Raman peaks originating from ZnO-like and MgO phonons. The band gap energy and the carrier concentration of ZnO pellets were found to be dependent upon the Mg doping whose values vary from 3.287 to 3.827 eV and from 1.6 $\times$ 10$^17$ to 5.2 $\times$ 10$^{16}$ cm$^{-2}$, respectively.

1. **Introduction**

Due to the ever-increasing need for short-wavelength photonic devices, high-power and high-frequency electronic devices, a great interest has been focused on the wide band gap semiconductors over the past decade [1]. Among these semiconductors we can mention the zinc oxide (II-VI semiconductor) which acquires a wide direct band gap (3.37 eV at room temperature), large exciton binding energy (60 meV), high optical gain and luminescence as well as piezoelectric properties [1]. Zinc oxide (ZnO) has been deeply studied and exploited in microelectronics as transparent conducting oxides (TCO) [2,3]. Moreover, ZnO was found to have similar properties as the gallium nitride (GaN). It is a very promising material which can be operated in several industrial applications such as gas sensors [4,5], spin electronics [6,7], light emitting diodes (LEDs) [8,9] and acoustic wave devices [10].

With the intention of expanding its optoelectronic application in infrared and ultraviolet wavelength regions, several researchers have used appropriate doped ions such as Cd, Co and Mg to modulate the band gap energy of ZnO material [11–17]. For instance, Makino et al. [18] reported that the band gap of ZnCdO could be tuned to the lower energy side by 0.3 eV at $x = 0.07$, in comparison with that of ZnO. Regarding Acharya et al. [11], they found that the optical band gap of wurtzite Zn$_1-x$Cd$_x$O ($x \leq 0.25$) grown on the glass substrates by the spray pyrolysis technique decreased from that of ZnO (3.25 eV) to 2.94 eV at Cd doping content $x = 25\%$. Concerning MgO, it has been used to grow Zn$_1-x$Mg$_x$O alloys that are expected to achieve high energy band gaps. Zn$_{1-x}$Mg$_x$O thin films have been prepared by many techniques such as pulsed-laser deposition (PLD) [19], molecular beam epitaxy (MBE) [20], metal-organic chemical vapor deposition (MOCVD) [21,22], and radio frequency (RF) magnetron sputtering [23]. According to the phase diagram of the ZnO–MgO binary system, the thermodynamic solubility limit of MgO in ZnO is less than 4 mol% due to the large lattice mismatch and the difference in crystal structure [24]. The reports have demonstrated that the ternary alloys Zn$_{1-x}$Mg$_x$O with a wide range of Mg$^2+$ from 0 to 36% maintain the hexagonal lattice structure due to the similar ionic radius of Mg$^2+$ (0.76 Å) and Zn$^2+$ (0.60 Å), and the corresponding energy band gap could be increased from 3.34 eV to 3.96 eV [25]. Ohtomo et al. [13] have reported that the solid solubility of MgO in ZnO is 33 mol% for the thin-film alloys grown under metastable conditions. With respect to Yang [26], he has evidenced the growth of epitaxial hexagonal Mg$_2$ZnO thin films on sapphire (0001) substrates with high single-crystalline quality. The band gap of these films can be tuned from 3.36 to 4.12 eV through the change of the Mg content. Furthermore, they observed that the increase of Mg content in the ZnO films reduces the defect emission and strongly improves the bright excitonic photoluminescence at room temperature. This paper investigates the structural and crystalline qualities of ZnO/MgO composite ceramics synthesized by the solid sintering method.

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2. Experimental details

The Zn$_{1-x}$Mg$_x$O composites were prepared by means of a conventional solid state sintering method. Different weight contents of MgO ($x = 0\%-40\%$) were added to ZnO powder (purity $\sim 99.9\%$) which homogenously milled in an agate mortar and then calcined in air at 500$^\circ$C for 3 h. The Zn$_{1-x}$Mg$_x$O powders were pressed into pellets (of 1 mm in thickness and 6 mm in diameter) and sintered at high temperature 1200$^\circ$C for 24 h with heating rate of 10$^\circ$/C/min. Pellets were then slowly cooled to room temperature. Next, X-ray diffraction (XRD) with Cu-K$\alpha$ radiation wavelength of 0.15406 nm was used to determine the crystal structure of the Zn$_{1-x}$Mg$_x$O samples in the scan range of 20 = 30$^\circ$-40$^\circ$. The optical properties of the ZnMgO pellets were examined in the wavelength range 200–1800 nm by using the UV–Vis–NIR spectrophotometer (SHIMADZU UV-3101PC). We used Tauc’s procedure to evaluate precisely the optical band gap. The free carrier concentration is determined. The structural properties of the sintered pellets were examined in the wave number range of 50–3000 cm$^{-1}$ by using the micro-Raman spectroscopy Horiba HR 800 recorded at room temperature. The excitation source was a He-Ne laser emitting at 633 nm and the photo collection of the signal was made in a confocal microscope.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of doped ZnO samples with different MgO contents ($0 \leq x \leq 40\%$). All the samples exhibit a poly-crystalline hexagonal structure. For the undoped ZnO sample, three prominent diffraction peaks were noted at 20 = 31.81$^\circ$, 34.47$^\circ$ and 36.31$^\circ$, which can be attributed to the (100), (002) and (101) plane reflections of hexagonal wurtzite ZnO (JCPDS card 36–1451), respectively. It can be seen that the ZnO growth appears to be randomly oriented along the (101) and (002) planes. For doped ZnO samples, the hexagonal structure remains unchanged despite the addition of MgO contents. However, secondary phases are formed at higher concentrations. The texture coefficient ($TC(hkl)$) and the percentages of oriented crystallites in the <hkl> direction have determined by using the following formula [27]:

$$TC(hkl) = \frac{I(hkl)/I_{0(hkl)}}{N\sum_{i} I(hkl)/I_{0(hkl)}}$$

where $I(hkl)$ and $I_{0(hkl)}$ are the measured relative intensity and standard intensity of a plane <hkl> taken from JCPDS data respectively, N is the reflection number. As shown in Fig. 1(c), we found that the growth of ZnO grains is more favoured towards the (002) and (101) orientation with texture coefficient about 41% and 27%, respectively. With doping content up to $x=20\%$, a

![Fig. 1. (a) XRD patterns of Zn$_{1-x}$Mg$_x$O (b) Enlarged detail of peaks (002) and (c) Texture coefficient of oriented crystallites in <hkl> direction versus MgO doping content.](image-url)
diffraction peak can be seen at 36.7°, corresponding to (111) plane of cubic MgO phase according to the standard JCPDS data card No.78-0430. The intensity of this rock-salt cubic peak is found to increase extensively as the content of MgO raises. This result indicates a considerable segregation of the MgO phase in the ZnO wurtzite structure. Recently, Jaafar et al. [28] have shown that the limit solubility of MgO in the ZnO host is found to be x = 10%, which is in good agreement with that obtained by Kumar et al. [29] in Zn1-xMgO (x < 20%) systems synthesized by sol-gel method. Outside this critical composition, two phases coexist with texture coefficients depending on the doping level. Indeed, doping favors firstly the preferential growth of ZnO grains following the directions (101) and (002), and secondly the grain nucleation MgO with a texture coefficient that increases from 0 to 15% (see Fig. 1(c)).

As shown in Fig. 1(b), another diffraction peak appears at 2θ = 34.68°, which is identified at the (002) direction of hexagonal ZnMgO alloy structure [3–7]. It reveals that the doping increases the texture coefficient of the wurtzite ZnMgO phase which reach 15% for MgO doping rate x = 0.34. Zheng et al. [5] showed the appearance of this diffraction peak around 2θ = 34.7° in a single-crystalline wurtzite structure of Zn0.51Mg0.49O films. Besides, it is reported that the formation of ZnMgO alloy phase takes place above 15 mol% of MgO [30]. Recently, Singh et al. [31] have obtained single-wurtzite Zn1-xMgO thin films for Mg content x ≤ 25% by sol-gel method. Actually, a mixed phase of hexagonal and cubic crystal structure is detected beyond this concentration phase and the segregation of the phases is initiated. In our case, a slight shift of the (002) peaks to the higher angles was also noted when the MgO content increased, which indicates a lattice compression along the c axis. But, the oriented peaks in the (100) direction are slightly shifted to the small angles. These facts provide strong evidence for the MgO incorporation in ZnO phase. The small changes in lattice parameters are probably due to the similar ionic radius of Zn2+ (0.60Å) and Mg2+ (0.57Å). Moreover, we have studied the effect of MgO doping content on the line-widths of diffraction peaks, the grain size, the lattice strain, the residual stress, the band gap energy and the free carrier concentration of Zn1-xMgO. The average ZnO grain size is calculated using the Scherer’s equation [32] and results are illustrated in Table 1:

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]

(2)

where D is the grain size, \( \lambda \) is the wavelength of the X-ray radiation used, \( \beta \) is the FWHM of the diffraction peak (002) and \( \theta \) is the Bragg diffraction angle of the XRD peak.

The crystalline quality is deteriorated with the increase of MgO content (x = 0–0.4), which is demonstrated by the decrease of the average grain size from 109.55 nm to 42.97 nm.

In our case, the residual stress \( \sigma_{zz} \) in the grown Zn1-xMgO samples are estimated using the following expressions [33]:

\[
\sigma_{zz} (\text{GPa}) = -226.8 \frac{c - c_0}{\epsilon_0}
\]

(3)

where \( c \) and \( c_0 \) are the lattice parameters of the prepared and unstrained ZnO, respectively [34]. The biaxial stress (\( \sigma_{zz} \)) along the c-axis increased from 0.35 to 1.03 GPa as the doping concentration varied from 0 to 40%. On the one hand, this degradation of the crystal quality with MgO doping could be partly due to the compression of the c-axis crystal unit cell caused by the substitution of Zn by Mg atoms. On the other hand, this may be accredited to the incorporation of the Mg atoms in interstitial Zn sites, which causes lattice distortion and enhances the segregation phenomenon. In recent paper [28] we have found that this substitution of Zn by Mg as well as the existence of intrinsic defects in ZnO such as zinc interstitial and oxygen vacancies can lead to the increase of the carrier concentration from \( 1.6 \times 10^{16} \) to \( 5.2 \times 10^{19} \) cm\(^{-3} \) for the undoped ZnO and doped sample (x = 40%), respectively.

We have also determine the values of the band gap energy (E\(_g\)) from the intercept of extrapolated linear portion of plots (x0\( \chi \))2 versus the photon energy axis (See Fig. 2). As observed from Table 1, the optical band gap broadened from 3.287 to 3.827 eV when the MgO content increased until x = 4 wt% [28]. Nidhi Adhikara and al [35] have reported similar results for doped ZnO samples with MgO concentrations between 0 and 50%. Since the texture coefficient of hexagonal ZnMgO phase is very low (<15%), the alloying effect could not caused this band gap broadening. Also, the grain size is found in the range 43–110 nm, which the hypothesis of confinement effect of the charge carriers in the nanoparticles should be excluded. In our case, the increase in the energy gap with doping is probably due to the Burstein-Moss effect [36–39] rather than the alloying effect and/or the confinement effect of the charge carriers in the nanoparticles [40]. Similar results are obtained by several authors [39–41]. Shan et al. [37] have demonstrated that the doping of Mg in ZnO causes a considerable increase in the concentration of free carriers as well as a broadening of the energy gap.

Raman microscopy is a spectroscopic technique used to study vibrations, rotations and other low-frequency modes in a system. In fact, it is a suitable tool to elucidate minerals, polymeric materials, ceramic materials, cells and proteins. This technique is important especially for alloy semiconductors in which the alloy-induced disorder disturbs the interaction between the lattice vibrations and electronic states. It introduces localized excitons in the forbidden gap shown as sharp resonance features in resonant Raman scattering (RRS) [42]. Fig. 3 shows the Raman spectra of pure zinc oxide sample. Several modes of vibration can be noted and their characteristics are summarized in Table 2. The E\(_2\) (Low) mode is weak and non-polar [43]. It is located at 90 cm\(^{-1}\) and associated with the Zn subnet vibration. Nonetheless, the E\(_2\) (High) corresponds to the non-polar optical phonons [43–44] whose vibration is centered at about 430 cm\(^{-1}\) and includes only the oxygen atoms [45]. It is well-known that this mode can exhibit a big change in frequency when the isotopic masses of ZnO molecules are modified or when a homogeneous distribution of impurities is recognized [46]. It could also be associated with a compressive stress in the layer. As regards E\(_1\) (LO) mode, it is

<table>
<thead>
<tr>
<th>MgO (at%)</th>
<th>FWHM(002) (°)</th>
<th>D (nm)</th>
<th>( \epsilon_0 ) (u.a)</th>
<th>( \sigma_{zz} ) (GPa)</th>
<th>E(_g) (eV)</th>
<th>N (cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0793</td>
<td>109.55</td>
<td>-0.00156</td>
<td>0.355</td>
<td>3.287 ± 0.013</td>
<td>1.6 \times 10^{16}</td>
</tr>
<tr>
<td>20</td>
<td>0.0864</td>
<td>100.620</td>
<td>-0.00444</td>
<td>1.017</td>
<td>3.414 ± 0.015</td>
<td>2.554 \times 10^{19}</td>
</tr>
<tr>
<td>34</td>
<td>0.1793</td>
<td>48.465</td>
<td>-0.00484</td>
<td>1.016</td>
<td>3.495 ± 0.122</td>
<td>8.708 \times 10^{19}</td>
</tr>
<tr>
<td>40</td>
<td>0.2022</td>
<td>42.978</td>
<td>-0.00482</td>
<td>1.092</td>
<td>3.827 ± 0.123</td>
<td>5.196 \times 10^{20}</td>
</tr>
</tbody>
</table>
considered as a longitudinal mode with $E_1$ symmetry [44,47], which appears around 610 cm$^{-1}$. It is associated with lattice defects such as oxygen vacancies and interstitial zinc [48,49].

At ~374 cm$^{-1}$, ~981 cm$^{-1}$ and ~1136 cm$^{-1}$, the existence of modes labeled as $A_1$ (TO), 2TO and $A_1$ (2LO), respectively [43,44] can be noted. Moreover, there are peaks that are attributed to the vibrational modes of the phonon replicas, already mentioned in the interval 1200–3000 cm$^{-1}$. Before doping ZnO with MgO component, the FWHM (Full Width at Half Maximum) of different Raman peaks is between ~1.5 and ~7 cm$^{-1}$ (thin peaks), which reflects the high structural quality of our sample. Fig. 4 shows that the MgO doping leads to the appearance of additional peaks, whose intensities decrease and line widths broaden. This behavior can be correlated to the structural degradation induced by the increase of lattice stress as evidenced by the XRD analysis.

In order to understand the influence of MgO doping, we have analyzed quantitatively the observed Raman spectra 4(a), 4(b) and 4(c) by using Lorentz fitting. It is worthwhile to mention the existence of intense multi-phonon peaks, corresponding to the third and forth longitudinal (LO) and transverse (TO) optical phonons of ZnO wurtzite structure [50]. With increasing MgO content from 20 to 40%, the first peak shifted from 1750 cm$^{-1}$ to 1727 cm$^{-1}$ while the second one broadened from 2328 cm$^{-1}$ to 2339 cm$^{-1}$. It can also be seen some vibration modes related to MgO cubic structure around 684–695 cm$^{-1}$ (denoted by $v_7 + v_8$) and at 830 cm$^{-1}$ (denoted by $v_3 + v_9$) [51,52].
Table 2
Position, intensity and FWHM of ZnO vibration modes.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Position (cm⁻¹) ± 0.012</th>
<th>Intensity (counts)/(mW min)</th>
<th>FWHM (cm⁻¹) ± 0.002</th>
</tr>
</thead>
<tbody>
<tr>
<td>E₂ (Low)</td>
<td>90.131</td>
<td>1412.069</td>
<td>3.237</td>
</tr>
<tr>
<td>E₂M</td>
<td>322.315</td>
<td>524.990</td>
<td>2.809</td>
</tr>
<tr>
<td>A₁ (TO)</td>
<td>373.911</td>
<td>561.876</td>
<td>3.731</td>
</tr>
<tr>
<td>E₂ (High)</td>
<td>430.285</td>
<td>1101.247</td>
<td>6.419</td>
</tr>
<tr>
<td>E₁ (LO)</td>
<td>609.918</td>
<td>671.020</td>
<td>7.131</td>
</tr>
<tr>
<td>2TO</td>
<td>980.648</td>
<td>3199.612</td>
<td>3.867</td>
</tr>
<tr>
<td>A₁ (2LO)</td>
<td>1136.388</td>
<td>614.722</td>
<td>4.510</td>
</tr>
<tr>
<td>A₁ (TO)</td>
<td>1317.937</td>
<td>531.039</td>
<td>3.420</td>
</tr>
<tr>
<td>A₁ (4TO)</td>
<td>1466.993</td>
<td>508.303</td>
<td>1.484</td>
</tr>
<tr>
<td>A₁ (7TO)</td>
<td>2642.247</td>
<td>482.293</td>
<td>2.646</td>
</tr>
<tr>
<td>E₁ (6LO)</td>
<td>3471.613</td>
<td>404.808</td>
<td>2.237</td>
</tr>
</tbody>
</table>

An additional peak is appeared at 1010.77 cm⁻¹ (denoted by AM) assigned to the mixed mode of the ZnMgO phase. This mode originates from the Mg-related local vibrational mode (LVM) in ZnO [53]. By using \( \omega \left( \text{ZnO}_{2\text{E2(High)}} \right) \approx 860.57 \text{ cm}^{-1} \) measured from ZnO nanowires and the effective reduced masses \( \mu = (1/M + 1/m)^{-1} \) of ZnO and the LVM, we can access to the Mg-related LVM frequency [54]:

\[
\nu_{\text{LVM}} = \sqrt{\mu_{\text{ZnO}}} = \sqrt{\mu_{\text{LVM}}} \tag{4}
\]

We obtain LVM frequency about 1011.8 cm⁻¹. This result confirms that the LVM mode is a signature of the Mg incorporation in ZnO leading to crystallization of ZnMgO alloy phase confirmed by XRD analysis.

Fig. 5 presents the evolution of Raman intensity and line width of the principal modes \( A₃ (2LO) \) and \( A₁ (4TO) \) with the MgO doping concentration. It is worthwhile to note that the intensities of all these modes decrease for Mg-doped pellets. In addition, with Mg incorporation, the phonon scattering becomes weak, thus broadening their line shapes. This result agrees well with what was reported by Kong [55]. This behavior is related to the segregation effect and the degradation of the crystal quality due to the Mg inclusion in the ZnO lattice.

4. Conclusion

This paper presents a modest contribution about the characterization of \( \text{Zn}_1-x\text{Mg}_x\text{O} \) composites obtained by the conventional solid state sintering method. All adopted experimental techniques have jointly analyzed the structural qualification of defects in our prepared samples. With MgO doping between 0% and 40%, it was observed that the crystal structure of all composites are maintained (hexagonal polycrystalline wurtzite structure of ZnO). However, the segregation of cubic and hexagonal phases occurs at a doping level \( x \geq 20\% \), thus inducing the degradation of the crystal quality which is confirmed by the decrease of the grain size. The band gap of the \( \text{ZnO}/\text{MgO} \) composites tuned from 3.28 to 3.82 eV via changing the Mg content. This blue shift in the band gap is found to depend on the electron concentration as suggested by the Burstein-Moss effect. Our structural characterization is completed by Raman spectroscopy at room temperature. It indicates the presence of several vibrational modes of hexagonal ZnO such as \( E₂ \) (LO) mode which is associated with lattice defects (such as oxygen vacancy and interstitial zinc), the \( E₂ \) (High) mode which contains only the oxygen atoms and the resulting compressive stress in the pellets and the \( A₁ \) (TO) mode that is a transverse optical second order mode with A1 symmetry. It was found that the FWHM of these modes are very thin (1.5−7 cm⁻¹) to pure ZnO. They broadly expand the doping levels under 20%, beyond which they start decreasing. This behavior is essentially attached to the segregation caused by an incorporation of Mg as well as the degradation of the crystal quality.

Acknowledgments

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Fig. 5. Evolution of Raman modes (a) $A_1(2LO)$ and (b) $A_1(4TO)$ with the MgO doping concentration.

References


