Red Shift in Photoluminescence Emissions of ZnO Nanoparticles with Mg Incorporation

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***Abstract*— In this study, nanostructured ZnO-Mg samples were prepared by polymeric precursor method. Pure ZnO sample exhibits hexagonal symmetry of wurtzite structure. Samples with Mg content equal to 30 and 40 at. % exhibit the presence of secondary phase indexed as MgO. Photoluminescence spectra present typical emissions for ZnO. As the Mg content is incorporated exceeding the solubility limit, the relative intensity decreases for green emissions, which has been attributed to the formation of defects like Mg_i, inhibiting the formation of Zn_i and V_{Zn}. Thus, red shift tunable photoluminescence emission is observed with Mg incorporation, as depicted by CIE coordinates.**

Keywords*— *ZnO, Zinc oxide, Mg, magnesium, photoluminescence, polymeric precursor method, tunable color.

I. INTRODUCTION

Nanocrystalline phosphor semiconductors exhibit intermediary optical properties between individual molecules and larger bulk crystals, offering a fascinating array of diverse applications [1]. Researchers are drawn to these materials not just for their exciting new characteristics and potential technological uses, but also to better understand the fundamental physical and chemical processes that give rise to these unique characters.

One prominent example is zinc oxide (ZnO). This n-type semiconductor presents a wide band gap of roughly 3.3 eV and is well-known for its excellent luminescence, making it a interesting choice for green phosphors under high-energy excitation [2,3]. Wide-gap oxide semiconductors like ZnO are particularly appealing for phosphor applications since they can produce visible light from defects within their band gap [2,3]. However, the emissions produced by these defects are often difficult to reproduce consistently, as they are highly sensitive to the specific conditions under which the material is synthesized.

Although several reports at the literature have studied ZnO photoluminescence for decades, there is still a lot of debate about what causes many of its luminescent properties. Specifically, the centers and mechanisms behind its green emission remain controversial. Various models to explain this green light have been proposed, often involving several types of lattice defects [1]. These include oxygen vacancies V_O, oxygen interstitials (O_i), oxygen antisites (O_{Zn}), zinc antisites (Zn_O), zinc vacancies (V_{Zn}), and zinc interstitials (Zn_i). Since ZnO is modified through certain kind of substitutions, this green emission often intensifies [1]. However, there is no general agreement about the mechanism behind this emission enhancement. For instance, the increased intensity of green emission in $Zn_{1-x}Mg_xO$ (ZnO:Mg) compound has been ascribed to free-to-bound transitions involving Zn_i and V_{Zn}, V_O or impurities in the lattice, transition between V_O or O_{Zn} and donor-acceptor pair or V_O or donor-acceptor pair generated by Mg incorporation on Zn sites [1,4].

In our previous study [1], we report that the enhancement of this emission is associated with the recombination of electrons in Mg interstitials (Mg_i) donor states and holes at V_{Zn}. However, this previous study focused on samples with Mg compositions in which the solubility limit was not exceeded. Thus, the aim of present study is to investigate Mg compositions of ZnO;Mg system beyond the solubility limit in order to infer if the green emissions are affected by any change in the configuration of Mg_i due to large Mg content.

II. EXPERIMENTAL PROCEDURE

The polymeric precursor method, often called the modified Pechini method, is a popular sol-gel technique for synthetize oxide materials [5]. It works by first chelating metal cations with an α-hydroxycarboxylic acid (like citric acid) to form stable metal complexes. These complexes then polymerize with a polyhydroxy alcohol (such as ethylene glycol), resulting in a polymeric resin. This resin is then subjected to pyrolysis. This method offers several advantages, including its low toxicity, excellent compositional homogeneity, the ability to achieve doping at a molecular level in solution and a reduced tendency for metal ion segregation [5]. The polymeric precursor method has proven to be particularly effective for preparing both pure and doped zinc oxide (ZnO) nanoparticles. In this study, ZnO and $Zn_{1-x}Mg_xO$ samples were prepared using this methodology, with x = 0.30 (ZM30) and 0.40 (ZM40). Details of this preparation can be found elsewhere [1].

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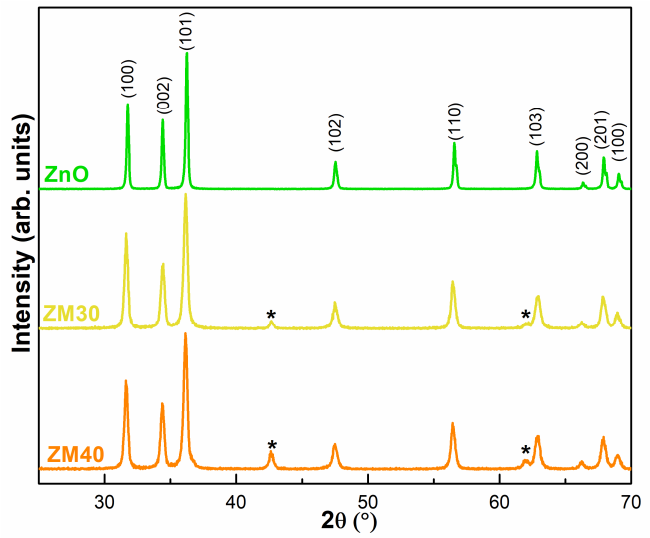

Fig. 1. X-ray diffraction patterns for ZnO:Mg samples.

Room-temperature X-ray diffraction (XRD) analysis was performed with measurements using a Rigaku Ultima 4 powder diffractometer. This instrument, configured in a θ–2θ geometry, was equipped with a rotating anode X-ray source emitting Cu-Kα radiation (λ=1.542 Å) and a scintillation detector. Data were collected with 0.02° step size and a 5-second dwell time per step. We collected room-temperature photoluminescence spectra using a Thermal Jarrel-Ash Monospec monochromator coupled with a Hamamatsu R446 photomultiplier. A krypton ion laser (Coherent Innova), set to an exciting wavelength of 350.6 nm and an output of 200 mW, was used as the excitation source.

III. Results and Discussion

XRD patterns for ZnO:Mg samples are presented in Fig. 1. As can be seen in this Fig., ZnO sample crystallized with broadened diffraction peaks relative to a nanoscaled structure, in agreement with reports at the literature of ZnO based samples prepared with the same route [1-3]. The observed peaks for this sample are indexed as diffraction planes for polycrystalline wurtzite ZnO with space group $P6_3mc$ [1]. Same diffraction patterns are identified for ZM30 and ZM40 samples, except fort two peaks of spurious phase labeled with asterisks at 42.7° and 62.1°, which are related with the formation of MgO phase [1]. It is worthy to mention that no these spurious peaks are not observed for 20 at. % of Mg in our previous study [1] and its intensity increases as Mg content increases, an indication that the solubility limit is less than 30 at. % of Mg.

Photoluminescence spectra for ZnO:Mg samples are presented in Fig. 2. All samples exhibit broad and asymmetrical spectrum, with multiple peaks, suggesting the involvement of various luminescence centers in its radiative processes. In order to understand the ZnO photoluminescence curve, a Gaussian curve fitting was applied, deconvoluting the spectrum into six radiative processes, which are labeled as (1), (2), (3), (4), (5) and (6) [1,6,7] in Fig. 2(a). According to our previous study, the Gaussian peak in the near-infrared region labeled as (1) have been attributed to the donor-acceptor transition between V_O and V_{Zn} [1,6,7]. The emission in red-orange region labeled as (2) has been explained in terms of the radiative transitions involve electrons trapped at a V_O^{++} donor level at 2 eV above the valence band [1,6]. The emission in green region labeled as (3) is also associated with oxygen vacancy, but in this case V_O.

The peaks labeled as (4) and (5) in blue region of the spectrum for ZnO sample have been ascribed to the transition of an electron from conduction band to a deep level hole at V_{Zn} and the recombination of an electron at Zn_i with a hole in

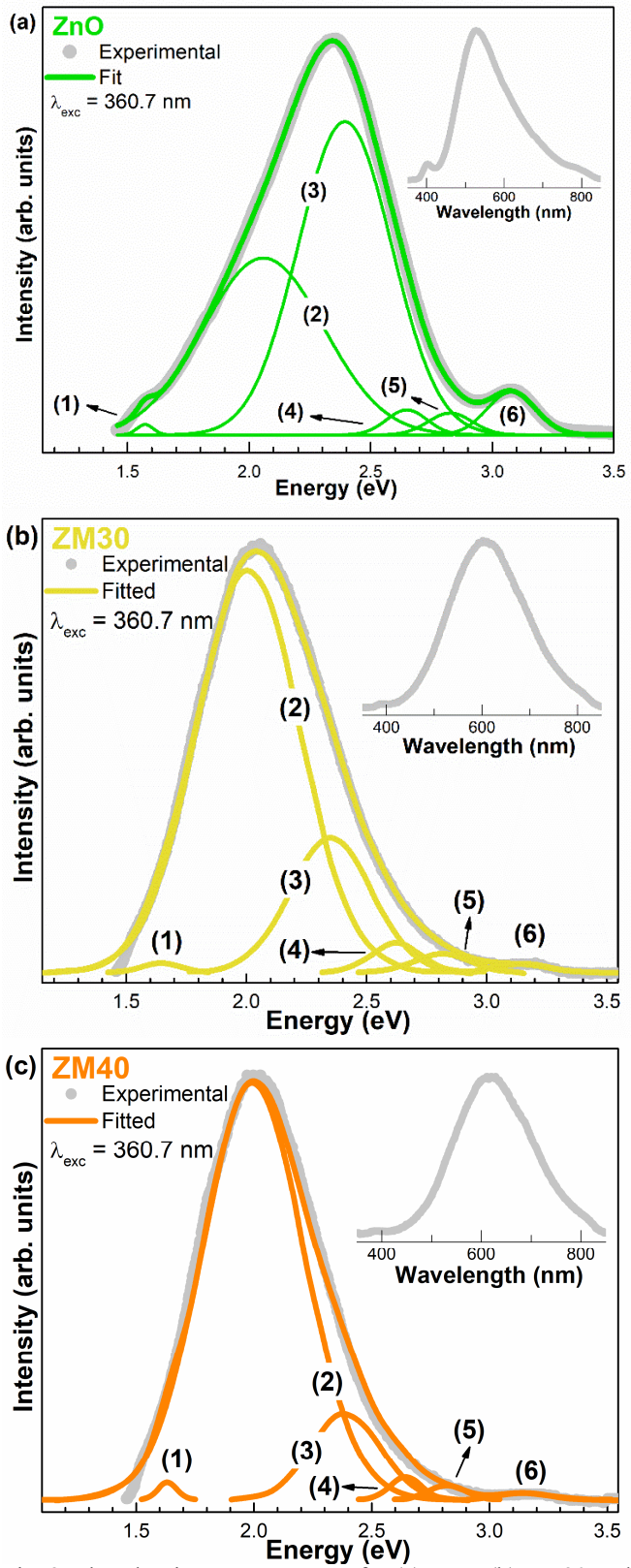

Fig. 2. Photoluminescence spectra for (a) ZnO, (b) ZM30 and (c) ZM40 samples.

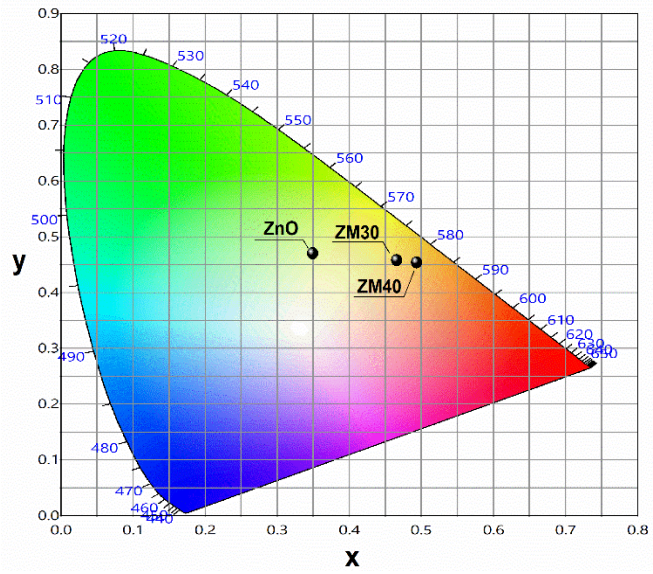

Fig. 3. CIE chromaticity diagram for ZnO:Mg samples.

the valence band [1,8]. Finally, the peak labeled as (6) in UV region has been related to near band-edge emission.

The statement that the defects originated by V_O states cause the emission labeled as (3) is consistent with the fact that synthesis conditions can increase the formation of V_O and intensifier this emission, as shown in our previous study. Furthermore, the substitution of Mg^{2+} ions for Zn^{2+} ions in ZnO up to the solubility limit also causes the intensity increasing of this green emission, which has been associated with free-to-bound type transitions between Zn_i and V_{Zn}. However, as Mg content is increased beyond the solubility limit, the relative intensity of green emission presents a remarkably decrease, as shown in Fig 2(b) and 2(c), although the position of the six emissions remains practically constant. Because of the changes in the emission in green region, the broaden and asymmetric spectrum for ZnO sample is centered around 529 nm, whereas around 607 nm and 621 nm for ZM30 and ZM40 samples, respectively.

The non-increasing of green emission as Mg ions are incorporated to ZnO lattice in the present study is consistent with the fact that Mg contents for ZM30 and ZM40 samples far exceed the solubility limit, even resulting in MgO secondary phase identified in XRD analysis. The additional Mg quantities result the formation of Mg_i, inhibiting the formation of Frenkel defect - in this case, the pair Zn_i and V_{Zn}, which originates the additional green emission. However, the comparison of Fig. 2(a) with Fig. 2(b) and 2(c) shows assuredly a decrease of the emissions in blue-green region of the spectra for pure ZnO sample. Thus, this region of the spectra should be not only associated with defects originated by V_O states since the substitution of Mg ions for Zn ions is homovalent and should not cause any change in the formation of vacancies due to the natural mechanism to preserve the electric neutrality of ZnO lattice. Zn_i and V_{Zn} must have influence on the emission in the green region of the spectra for ZnO pure sample.

The CIE coordinates (x, y) for ZnO:Mg samples were calculated from the emission photoluminescence spectra and CIE chromaticity diagram and chromaticity coordinates are presented in Fig. 3. As expected for a photoluminescence spectrum composed by several broadened emissions, CIE coordinates for ZnO sample represent bright shades in the green color emission. As the Mg content increases, the bright shades change into orange color direction (more pure color). This result is explained in terms of the emissions in green region of photoluminescence spectra whose relative intensity is decreased with Mg content as depicted in Fig 2.

IV. Conclusions

In this study, nanostructured ZnO:Mg samples were prepared by polymeric precursor method. Pure ZnO sample exhibits hexagonal symmetry of wurtzite structure. Samples with values of Mg content equal to 30 and 40 at. % exhibit the presence of secondary phase indexed as MgO. Photoluminescence spectra present typical six deconvoluted emissions for ZnO pure sample. As the Mg content is incorporated exceeding the solubility limit, the relative intensity decreases for green emissions, which has been attributed to the formation of defects like Mg_i, inhibiting the formation of Zn_i and V_{Zn}. Thus, red shift tunable photoluminescence emission is observed with Mg incorporation, as depicted by CIE coordinates.

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