Investigation on the path process of M doped ZnO (M = Gd, Mg) via the sol-gel method from dried gel to stable nanostructure powder

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Abstract. Doping is one of the effective methods to modify the physical properties of ZnO material in order to extend its applications. An investigation on Zn_{1-x}M_xO (M = Gd, Mg and x = 0.00, 0.03) nanopowders that have been synthesized by sol-gel method and sintered at 600 °C for 2 hours was reported. The decomposition process of the dried gel system was investigated by thermal gravimetric analysis (TGA) and the nanopowders with different heating temperature were studied using FT-IR spectroscopy. The crystal structure of the nanopowders after sintering at 600 °C was obtained using X-ray diffraction (XRD). The TGA curves of the samples showed the various weight loss regions corresponding to the removal of starting materials and no weight loss was observed in the temperature range of 300 to 800 °C which corresponded to the phase-crystallization step. The FTIR spectra showed that ZnO band was assigned to the stretching frequency at 669 cm$^{-1}$ while Gd/Mg doped ZnO was at 668 cm$^{-1}$ and 666 cm$^{-1}$. From the XRD studies, the crystal structure of the samples indicated single phase ZnO crystalline and confirmed hexagonal wurtzite structure (space group of P6$_3$mc).

1. Introduction
Multiferroic materials show simultaneously ferromagnetic and ferroelectric properties. They lead to a variety of promising future device applications in spintronics and sensors [1]. ZnO materials show ferroelectric properties but possess mainly antiferromagnetism at room temperature. Due to the ferroelectric properties in ZnO, further research for suitable multiferroic materials is interesting in relation with this materials.

ZnO is known as an n-type semiconductor material which has direct band gap of 3.37 eV and exciton binding energy of 60 meV [2]. It is a good candidate for applications in the field of lasers, gas sensors, solar cells, optoelectronic devices and luminescent screens. Certain element doped to ZnO also show ferromagnetic materials [3-6]. Undoped or doped ZnO is also very attractive due to its unique properties and versatile applications, such as ultraviolet light emitters, piezoelectric devices, chemical sensors, and spintronics [7-11].

Different physical or chemical synthetic methods have been used to synthesize the ZnO nanoparticles such as thermal decomposition, thermolysis, chemical vapour deposition, sol gel, spray pyrolysis, precipitation, vapour phase oxidation, thermal vapour transport, condensation, co-precipitation, and hydrothermal [12-18]. The ferromagnetism in ZnO can be related to vacancies like Zn or O defects, Zn interstitial sites and lattice distortions [19]. However, ferroelectricity rises due to
off-center distortion of hexagonal structure. In order to achieve room temperature ferromagnetism, the doping of various transition metals has been carried out in ZnO [20].

The different in saturation of magnetization values by non-magnetic ion dopants has been reported. Lin et al. [21] in 2007 studied the co-doping of Li and Co in ZnO films. It was observed that Li co-doping led to the increase in ferromagnetism due to the Li defects that mediated indirect exchange interactions. Yang et al. [22] in 2008 reported the multiferroic properties of Cr-doped ZnO films. Lim et al. [23] in 2013 studied the coexistence of both ferromagnetism and ferroelectricity in Mg-doped ZnO. Sharma et al. [24] in 2014 observed the multiferroicity and magnetoelectric coupling in (Li, Ni, and Mg) doped ZnO. The observation of multiferroic behavior in non-magnetic ion-doped ZnO will be an important step towards fundamental understanding and novel applications.

In this paper, we studied the synthetic path using thermal analysis, FTIR, X-ray diffraction to obtain chemical information and crystal structure for Zn\(_{1-x}\)M\(_x\)O (M = Gd, Mg and x = 0.00, 0.03), which were synthesized by sol–gel method.

2. Materials and methods
Zn\(_{1-x}\)M\(_x\)O (M = Gd, Mg and x = 0.00, 0.03) has been synthesized by sol–gel method. An appropriate amount of zinc acetate Zn(CH\(_3\)COO)\(_2\).2H\(_2\)O, magnesium acetate tetrahydrate Mg(CH\(_3\)COO)\(_2\).2H\(_2\)O, and gadolinium nitrate Gd(NO\(_3\))\(_3\).3H\(_2\)O have been dissolved in ethanol. The resulting solution was stirred at 80 °C for 2 hours until gel was formed. The obtained gel was then dried in heating oven at 150 °C for 1 hour and then grounded with mortar and pestle to obtain fine powder. The powder was then sintered at 600 °C for 2 hours.

The gel has been investigated by Thermal Analysis (TGA/DTA) with nitrogen at 20 ml/min and the temperature ranged from 50 to 1000 °C. Dried samples were studied by FTIR spectrometer in the range of 300-4000 cm\(^{-1}\). Meanwhile, the crystal structure of the samples were investigated by X-ray diffraction (XRD) in which the 2\(\theta\) was from 20 to 80° with Cu-K\(\alpha\) radiation source having wavelength of 1.54060 Å.

3. Results and discussion
3.1. Thermal analysis
As shown in figure 1, the exothermic reaction with the largest weight loss in the temperature range between 200 and 300 °C could be assigned to the collapse of gel. No more weight loss observed in the temperature range of 300-800 °C corresponded to the phase crystallization step. For temperature higher than 800 °C, undoped ZnO showed exothermic reaction while Gd or Mg doped ZnO showed endothermic reaction.

![Figure 1](a) The pattern of Zn\(_{1-x}\)M\(_x\)O (M = Gd, Mg and x = 0.00, 0.03) analysed by (a) TGA and (b) DTA.
3.2. FT-IR studies

FTIR is a technique used to obtain information regarding chemical bonding in a material. The band positions and number of absorption peaks depend on crystalline structure, chemical composition and also morphology. FT-IR spectra of samples ZnO after drying at 150 °C are shown in figure 2(a) and IR peaks for the ZnO are shown in table 1. After heating at 600 °C, absorption band around 395 cm\(^{-1}\), which correspond to Zn-O peak, occurred as shown in figure 2(b).

The absorption band at 3062 cm\(^{-1}\) corresponded to the O-H stretching vibration of water presence in ZnO. The broad transmission bands at 1556 cm\(^{-1}\) and 1425 cm\(^{-1}\) in both the samples were due to the carbonyl group of the carboxylate ions, which might remain adsorbed on the surface of ZnO. The ZnO band was assigned to the stretching frequency at 669 cm\(^{-1}\) for pure ZnO, 668 cm\(^{-1}\) for Gd-doped ZnO, and 666 cm\(^{-1}\) for Mg-doped ZnO. The vibration mode above 600 cm\(^{-1}\) was weak. The stretching of band appearing at 479 cm\(^{-1}\) confirmed the formation of rod shaped ZnO particles [25]. The strong vibrational mode observed at 525 cm\(^{-1}\) was assigned to the stretching vibration of ZnO [26]. The appearance of peaks in three different positions depending on the shapes of ZnO has been reported by Ashokkumar et al. [27] and Muthukumaran et al. [28].

![Figure 2(a)](image1)

![Figure 2(b)](image2)

**Figure 2.** FT-IR spectra of Zn\(_{1-x}\)M\(_x\)O (M = Gd, Mg and x = 0.00, 0.03) (a) before and (b) after heating at 600°C.
Table 1. IR peak of Zn$_{1-x}$M$_x$O (M = Gd, Mg and x = 0.00, 0.03)

| Assignments                  | ZnO  | Zn$_{0.97}$Gd$_{0.03}$O | Zn$_{0.97}$Mg$_{0.03}$O |
|------------------------------|------|------------------------|-------------------------|
| O-H stretching               | 3062 | 3060                   | 3205                    |
| Adsorbed surface of ZnO      | 1556 | 1555                   | 1555                    |
| Zn-O stretching (before heating) | 669  | 668                    | 666                     |
| Zn-O stretching (after heating 600ºC) | 449  | 372                    | 365                     |

The characteristic IR peaks below 1000 cm$^{-1}$ are very important to study the presence of Zn-O/Mg-O bonds. In addition, functional groups and absorption bands observed in the range of 420-600 cm$^{-1}$ are attributed to the stretching modes of Zn-O [26].

3.3. XRD Analysis

The typical XRD diffraction peaks of Zn$_{1-x}$M$_x$O (M = Gd, Mg and x = 0.00, 0.03) are shown in figure 3. The diffraction peaks in the XRD pattern clearly showed the crystalline with peaks corresponding to (100), (002), (101), (102), (110), (103), (200), and (112) planes. The diffraction peaks showed the crystal structure of Zn$_{1-x}$M$_x$O (M = Gd, Mg and x = 0.00, 0.03) to be hexagonal wurtzite structure (space group P6$_3$mc) with preferred orientation along (101) plane for all the samples, which is the most stable phase of ZnO. ZnO$_{1}$ corresponded to the ZnO commercial and ZnO$_{2}$ corresponded to synthesized ZnO.

![Figure 3. XRD pattern of ZnO$_{1}$, ZnO$_{2}$, and Zn$_{1-x}$M$_x$O (M = Gd, Mg, x = 0.03).](image)

The existence of broad peaks indicated that the average crystal size (D) was in the order of nanometer scale. It was evident from the XRD spectra that there were no extra peaks corresponding to Gd/Mg related secondary and impurity phases, which might be attributed to the incorporation of Gd$^{3+}$ and Mg$^{2+}$ instead of Zn$^{2+}$ lattice site. The changes in cell parameters and peak shift towards higher 2θ value was observed in XRD analysis, thereby indicating successful substitution of Gd and Mg in host ZnO nanopowders. The determination of average crystal size for all samples were using Debye-Scherer’s formula [29].

$$D = \frac{0.9 \lambda}{\beta \cos \theta}$$ (1)
where \( \lambda \) is the wavelength of X-ray used (1.54060 Å), \( \beta \) is the full width at half maximum (FWHM) of (101) plane peak of ZnO and \( \theta \) is Bragg’s diffraction angle. The crystal size decreased with doping of Gd and Mg on ZnO. This can be related to the larger ionic radii of Gd\(^{3+}\) (94 pm) and Mg\(^{2+}\) (72 pm) as compared to that of Zn\(^{2+}\) (74 pm). The average crystal sizes calculated from X-ray diffraction were 65.25 nm for ZnO, 51.97 nm for Gd-doped ZnO, and 58.06 nm for Mg-doped ZnO. These results suggested that the doping inhibited crystallite growth as observed in other systems [30]. The 20 value, FWHM, cell parameters, c/a ratio, d-value, and average crystal size (D) are tabulated in table 2.

Table 2. The 20 value, FWHM, cell parameters, and c/a ratio, d-value, and average crystal size (D) of Zn\(_{1-x}\)M\(_x\)O (M = Gd, Mg)

| Samples         | 20 (°) | FWHM (°) | cell parameters (Å) | c/a ratio | d-value (Å) | Average crystal size D (nm) |
|-----------------|--------|----------|---------------------|-----------|-------------|-----------------------------|
| ZnO             | 36.25  | 0.2790   | 3.2493              | 5.2057    | 1.6021      | 2.4755                      | 65.25                      |
| Zn\(_{0.97}\)Gd\(_{0.03}\)O | 36.23  | 0.2024   | 3.2498              | 5.2060    | 1.6019      | 2.4757                      | 51.97                      |
| Zn\(_{0.97}\)Mg\(_{0.03}\)O | 36.00  | 0.2509   | 3.2503              | 5.2073    | 1.6020      | 2.4780                      | 58.06                      |

4. Conclusion
Zn\(_{1-x}\)M\(_x\)O (M = Gd, Mg and x = 0.00, 0.03) nanopowders have been successfully synthesized by sol-gel method and sintered at 600 °C for 2 hours. Sintering at temperature between 400 to 800 °C gave a stable crystalite size. Doping process reduced particle size and ion OH in ZnO. The XRD investigation revealed the hexagonal wurtzite structure, which indicated single phase of ZnO nanopowders.

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References
[1] Ramesh R and Spaldin N A 2007 Nat. Mater. 6 21
[2] Kim Y S, Tai W P and Shul S J 2005 Thin Solid Films 491 153
[3] Gao D, Zhang Z, Fu J, Xu Y, Qi J and Xue D 2009 J. Appl. Phys. 105 113928
[4] Liu C, Yun F and Morkoc H 2005 J. Mater. Sci. Mater. Electron. 6 555
[5] Cullity B D 1978 Elements of X-ray Diffraction (Massachusetts: Addison-Wesley Publishing Company, Inc)
[6] Motaung D E, Mhlongo G H, Nkosi S S, Malgas G F, Mwakikunga B W, Coetsee E and Swart H C, Abdallah H M, Moyo T and Ray S S 2014 ACS Appl. Mater. Interfaces 6 8981
[7] Goldberger J, He R, Zhang Y, Lee S, Yan H, Choi H-J and Yang P 2003 Nature 422 599
[8] Yan H, He R, Pham J and Yang P 2003 Adv. Mater. 15 402
[9] Nomura K, Ohta H, Ueda K, Kamiya T, Hirano M and Hosono H 2003 Science 300 1269
[10] Lee S Y, Shim E S, Kang H S, Pang S S and Kang J S 2005 Thin Solid Film 437 31
[11] Konenkamp R and Word R C 2004 Appl. Phys. Lett. 85 6004
[12] Harima H 2004 J. Phys. Condens. Matter. 16 55653
[13] Niasari M S, Davar F and Khansari A 2011 J. Alloy. Compd. 509 61
[14] Yang J, Feia L, Liua H, Liu Y and Yanga L 2011 J. Alloy. Compd. 509 3672
[15] Yang Y, Chen H, Zhao B and Bao X 2004 J. Cryst. Growth 263 447
[16] Hu J Q, Li Q, Wong N B, Lee C S and Lee S T 2002 Chem. Mater. 14 1216
[17] Lao J Y, Huang J Y and Wang D Z 2003 Nano Lett. 3 235
[18] Chauhan R, Kumar R and Chaodharya R P 2010 J. Chem. Pharm. Res. 2(4) 178
[19] Savu R, Parra R, Jancar B and Elizario S A 2009 J. Cryst. Growth 311 4102
[20] Kumar P, Kumar Y, Malik H K, Annapoorni S, Gautam S, Chae K H and Asokan K 2014 J. Appl. Phys. 114 453
[21] Lin Y H, Ying M, Li M, Wang X and Nan C W 2007 Appl. Phys. Lett. 90 222110
[22] Yang Y C, Zhong C F, Wang X H and He B 2008 J. Appl. Phys. 104 064102
[23] Oh J Y, Lim S C, Ahn S D, Lee S S, Cho K K, Koo J B, Choi R and Hasan M 2013 J. Phys. D Appl. Phys. 46 285101
[24] Sherma N, Gaur A, Kumar V and Kotnala R K 2014 Superlatt. Microstruct. 65 308
[25] Raja K, Pamesh P S and Geetha D 2014 Spectrochim. Acta A 131 183
[26] Singhal R, Voyles Y, Zhu Y, Jia W and Tomar M S Nanotechnology 18 315606
[27] Ashokkumar M and Muthukumaran S 2014 Opt. Mater. 37 671
[28] Muthukumaran S and R Gopalakhrisnan 2012 Opt. Mater. 34 1946
[29] Kathirvel P, Manoharan D, Mohan S M and Kumar S 2009 J. Optoelectron. Biomed. Mater. 1(1) 25
[30] Ueda K, Tabata H and Kawai T 2001 Appl. Phys. Lett. 79 988