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Synthesis of ZnO nanostructures and its effect on linear-nonlinear optical properties

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Zinc oxide (ZnO) nanostructures with nanoparticle morphology have been synthesized at ambient pressure and different temperatures using [OMIM]Br ionic liquid as solvent by ionothermal method. The products were characterized by field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), and Z-scan technique. The average crystallite size of ZnO was between 15-23 nm. The band gaps of products are 3.19, 3.25, and 3.32 at 65, 90, and 120 ^{o}C, respectively. The Z-scan technique was proposed to detect the nonlinear optical (NLO) properties at 532 nm wavelength. Temperature effect on third order NLO responses of ZnO nanostructures is studied. The results show that higher annealing temperature in ionic liquid produced ZnO nanoparticles with decreased crystalline and enlarged band gap. Also, this process leads to produce ZnO nanoparticles with increasing NLO responses by altering vacancy distribution.

Keywords: Zinc oxide; Nanoparticle; Ionic Liquid.

1. INTRODUCTION

Metal oxides have been studied for wide applications such as energy conversion/storage, photovoltaic application, clean energy production, sensors, biological uses, environmental remediation, catalysts, and solar cells. Zinc oxide in other metal oxide is important due to nontoxicity, easy to high chemical stability, transparency in visible range of spectrum and relatively low cost. Also, as a wide-band-gap semiconductor (~3.37 eV) has been extensively for various applications, photocatalysis, sensors, solar cells, supercapacitors, etc. Some strategies such as, changing the morphology, coupling with other metal, functionalize with noble metals, nanocarbon material and doping with transition metal ions or nonmetal ions have been employed to enhance zinc oxide performances [1].

Creating the defect is one of strategies that modify optical properties of ZnO nanostructures. It could be controlled by modifying synthetic conditions such as temperature, pressure, time, etc. Annealing as a heat treatment process softness improve electrical, magnetic, photocatalytic, machinability and optical properties in nanostructures [2].

In this research, ionothermal method using ionic liquid (IL) enables production of ZnO nanostructure at different temperatures. IL, (1-octyl-3-methylimidazolium bromide), [OMIM]Br due to high polarity, high thermal stability and low vapor pressure is employed as both the template and the solvent in the ionothermal method (Scheme 1). We further demonstrate Cu dopant of ZnO samples synthesized in ionic liquids (ILs) more efficient than their morphology in nonlinear optical coefficient results [3].

2. EXPERIMENTAL

Zn(CH3COO)2·2H2O (99%, Aldrich), sodium hydroxide (99%, Merck), 1-bromooctane, (99%, Fluka), N-methylimidazole (99%, Sigma-Aldrich), EtOAc (Merck) and ethyl alcohol (98%, Merck) were used in our experiment. The IL, [Omim]Br, was prepared by the method reported in the literature. In a typical reaction in this work, 2 mmol of Zn)OAc)2·2H2O (438 mg) was dissolved in 2.5 g It under stirring at room temperature for 20 min in the flask. Then 2 mmol of fine powder of sodium hydroxide (320 mg) was gradually added to the mixture, stirred for 20 min at r.t and the temperature were increased to 65 oC. The reaction was allowed to continue for 4 h at definite temperature. After cooling to r.t, the product was separated from the reaction mixture by washed with ethanol (96%) and water several times. The white powder product, T1, was prepared after drying in the air. Preparation of T2 and T3 samples are like to preparation of T1 except the temperature is 90 and 120 ℃, respectively (Scheme 2).

3. RESULTS AND DISCUSSION

Figure 1 illustrates the XRD patterns of the products (T1-3). The XRD result revealed that obtained ZnO nanostructures were composed of hexagonal wurtzite structure with excellent crystallinity. All the peaks correspond to the pure phase of zinc oxide which can be indexed in Figure 1. According to XRD patterns of samples, the crystallinity index of T1-3 is 73.35%, 74.75%, and 75.27%, respectively. The Debye–Scherrer equation was used to calculate the size of the crystallite, and presented**.** Increasing the synthesized temperature causes to decrease the crystallite size of products.

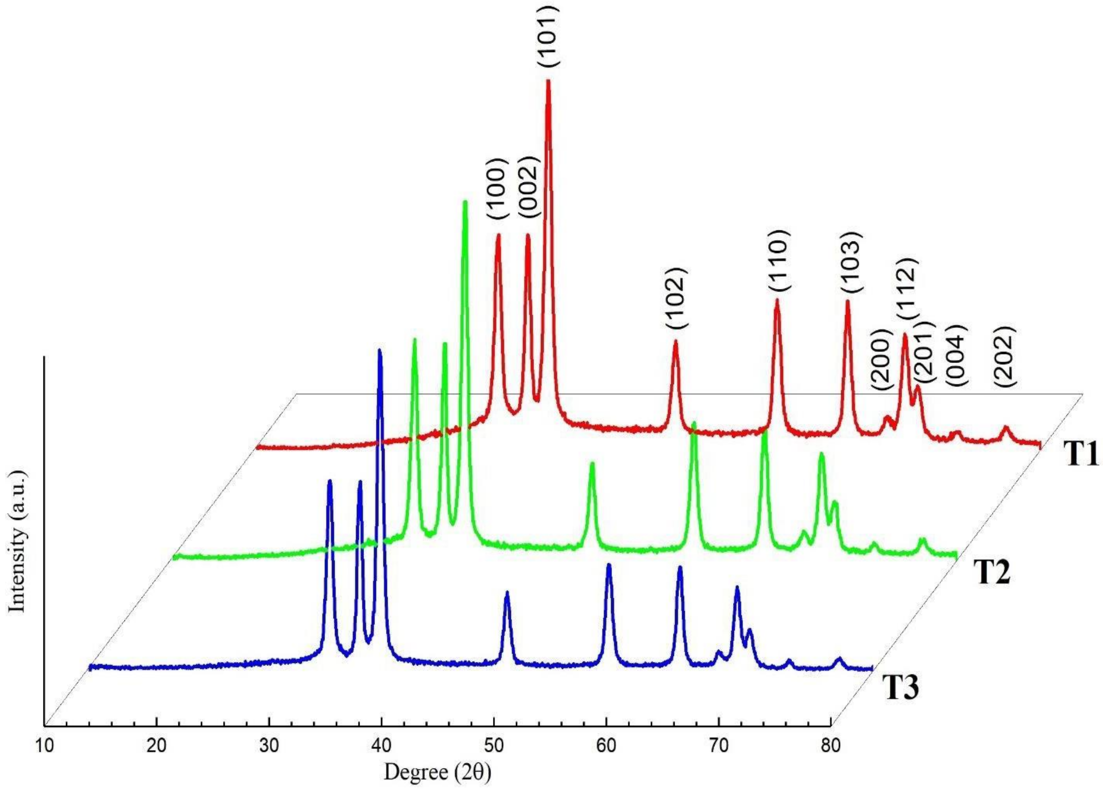

Figure 1 XRD pattern of the ZnO nanostructures.

FESEM observations showed the morphology of the ZnO nanostructures (Figure 2). Zero dimension of nanoparticles without any special morphology was created in ionothermal method in the presence of [OMIM]Br as an IL in different temperatures. IL inhibits the agglomeration of the particles. This is due to the interactions between [OMIM]Br and nucleus. It seems the role of the cation is considered more important as hydrogen bonds as well as π-π-stack interactions can be formed [4].

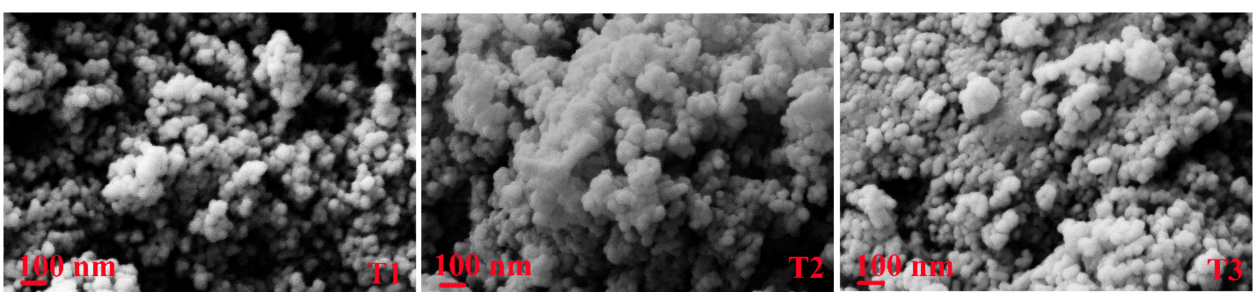

Figure 2 SEM of the products.

Considering Kubelka-Munk relation and diffuse reflectance spectra (DRS), the band-gap of synthesized samples were calculated [5]. The obtained band-gap of T1, T2, and T3 are 3.19, 3.25, and 3.32 eV, respectively. As shown in Figure 3, it is obvious that by increasing synthesized temperature, the band-gap increases. The band-gap of bulk ZnO is 3.37 at room temperature. The other probability for band-gap related to presence of defect formation and disorders at the grain boundaries [6]. According to related research, this is due to existence of oxygen vacancy in ZnO structure [7]. With increasing the synthesized temperature, the band-gap energy increases which may be because of Moss-Burstein band filling effect [8]. The decreasing the crystallite size and increasing the band-gap related to quantum confinement effect [9]. Due to quantum confinement in the semiconductor nanoparticles, electronic energy levels are discrete. Then the excited electrons in semiconductors with different frequencies because of size- dependent frequency [10].

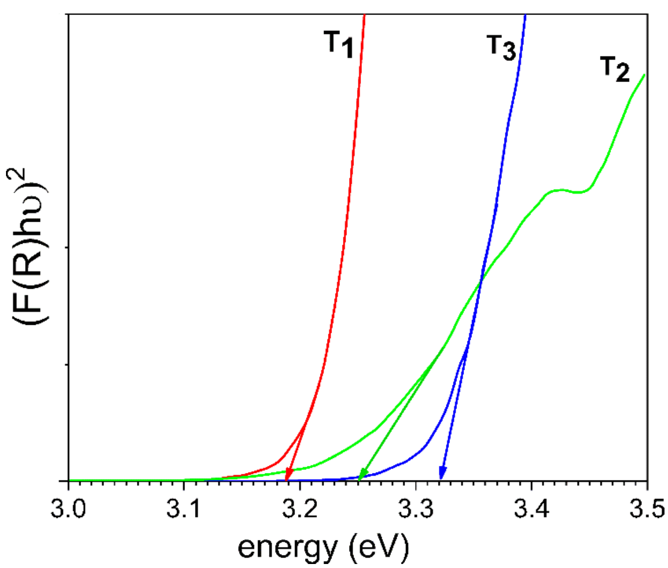

Figure 3 Band-gap calculation of **T1-3**

A Z-scan test was done at 532 nm from a Nd:YAG laser was utilized to evaluate the third-order nonlinear optical properties of the samples. Closed-aperture (CA) and open-aperture (OA) z-scan indicate nonlinear refraction and nonlinear absorption coefficient of specimens, respectively. The nonlinear refraction (NLR) index, n_2 was recorded by CA z-scan measurement with linear transmission of S= 0.26-0.28. Other hand, the valley followed by the peak, to negative n_2 and self-defocusing effect in the synthesized samples.

Figure 4 demonstrate the increasing ratio of n_2 and β of different synthesized temperature. The NLR and NLA coefficients of T1-3 are in the order of 10^{-8} cm^2/W and 10^{-5} cm/W, respectively. Considering increased temperature, the increasing ratio of NLR is more than NLA. Since the NLR increased five times, in comparison the NLA coefficient increased two times.

According to XRD and DRS results, the increase in annealing temperature causes to increase the band-gap and decrease the crystallite size of the synthesized products. The crystallite size of samples is related to the quantum confinement effect of the samples that is confirmed in another research. Decreasing band-gap and effect of it on the increasing nonlinearity responses also reported in the scientific reports. Susceptibility is related to light-matter interaction, nonlinearity responses of materials, and improvement of optical applications of materials. The order of calculated both parts of susceptibility of samples are 10^{-6} esu. Increasing synthesized temperature causes to increase the crystallinity index, decrease the crystallite size, and increase the susceptibility of the samples about four times. The increasing ratio of susceptibility is more than the increasing ratio of NLR and NLA coefficient in similar temperature. In our previous research, Cu-doped ZnO was prepared by ionothermal synthesis. In that research, after doping Cu, the nonlinearity responses were increased the increasing ratio of Cu-doped ZnO is less than ZnO synthesized under various temperatures in this study.

The figure of merit (FOM) of synthesized samples was defined as FOM= $|Im\ (\chi^3)\ |/\alpha$. The relation between $\chi^{(3)}$ (esu) and $\chi^{(3)}$ (m^2/V^2) are $\chi^{(3)}$ $(m^2/V^2)=1.4\times10^{-8}$ $\chi^{(3)}$ (esu). The FOM demonstrate the nonlinear absorption ratio to linear absorption of samples that are calculated and tabulated. The incremental process is observed in FOM values by adding synthesized temperature. The reported FOM value research smaller than reported value in this study.

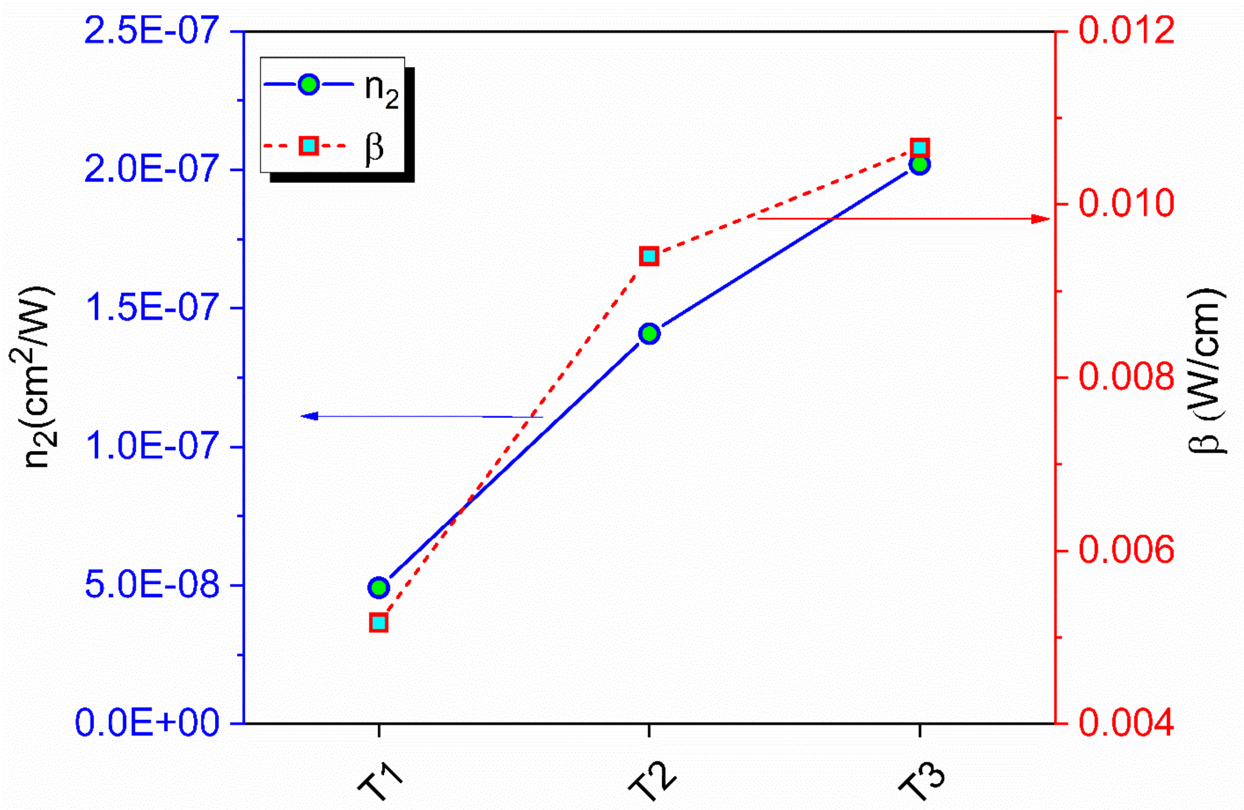

Figure 4 Nonlinear absorption coefficient (dotted line) and nonlinear refractive index (continuous line) of T1-3

The CW laser propagating through the samples causes the thermal spatial distribution in the samples and produces the thermal lens effect in which maybe one of the NLR responses of samples. The thermally induced nonlinearity responses reveal that the refractive index changes temporally. These changes because of the effect of producing acoustic waves from laser heating on the density of the samples. This is because of using CW lasers, long-pulse lasers, or high-pulse repetition rate lasers. According to the DRS data and band-gap of samples, the increasing band-gap causes to increase NLO properties. This is because of band- t o - b a n d nonradiative transition and its energy that is to band-gap energy. By decreasing crystallite size, the surface of samples has many atomic vacancies that act as trap states. These trapped states lead to change in the NLR index. On the other hand, He et al. demonstrated high-annealing temperature causes to the produce oxygen vacancy on the surface and through the balk of ZnO. Ayand et al. evaluated the third order NLO properties of ZnO thin film that the order of β was 10^{-9} cm/W. They confirmed that oxygen vacancy is one of the on improved nonlinearity. In another study, the NLA coefficient increased from 2.9×10^{-6} for 300 °C to 1.0×10^{-4} m/W for 1050 °C in ZnO thin films. In this case NLO response is smaller than our results whereas was done in higher temperatures in with our experiment. It seems another factor affected on increasing the NLO response too. Li et al. show the hydrogen bonds created between ZnO nuclei and the imidazolium based IL by study of the stretching vibration of C(2)–H of imidazole ring in FTIR spectrum. They show strong interactions between imidazolium ILs and the oxygen atoms of ZnO crystal cores (Scheme 3). Thus, oxygen vacancy can during the growth of ZnO crystal nuclei and after that with higher temperature conditions.

It seems and temperature show synergistic effects in increasing the defects in ZnO structure. As could be concluded, the ZnO structure has some defects and oxygen vacancy that cause nonlinearity increase. The results reveal that this synthesized method for ZnO nanostructure is more suitable for nonlinearity application than the usual synthesized method.

4. CONCLUSIONS

Promising ionothermal method to ZnO nanostructures in [OMIM]Br as ionic liquid with an annealing step is reported here. Ionic liquid acts as both solvent and template in this process. The order of NLR, NLA, and $\chi^{(3)}$ were 10^{-8} cm^2/W, 10^{-5} cm/W, and 10^{-6} esu, respectively.

References

[1]D.R. Miller, S.A. Akbar, P.A. Morris, Sens. Actuators B 204 (2014) 250.
[2]N. Neugebohrn, N. Osterthun, M. Götz-Köhler, K. Gehrke, C. Agert, Nanoscale Res Lett 16 (2021) 566
[3]M. P. Nikolova, M. S. Chavali, Biomimetics 5 (2020) 27.
[4]A.B. Djurisic, Y.H. Leung, A.M.C. Ng, Mater. Horiz. 1 (2014) 400
[5]G. Wang, Y. Yang, D. Han, Y. Li, Nano Today 13 (2017) 23
[6]D.-Y. Son, J.-H. Im, H.-S. Kim, N.-G. Park, J. Phys. Chem. C 118 (2014) 16567
[7]C. B. Ong, L. Y. Ng, A. W. Mohammad, Renew. Sust. Energ. Rev. 81 (2018) 536.
[8] Alvin Luis, Tadres Mauricio, Exp. Theo. NANOTECHNOLOGY 5 (2021) 157
[9] B. D. Kim, T. Pan. J. G. Kim, Exp. Theo. NANOTECHNOLOGY 5 (2021) 163
[10] S. Nandi, S. Kumar, A. Misra, Mater. Adv. 2 (2021) 6768