

Dielectric Properties of Er³⁺ Doped ZnO Nanocrystals

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Abstract

Erbium doped ZnO nanocrystals were synthesized through solid state reaction route. A detailed structural study was carried out by using X-ray diffraction (XRD) data. This work investigates the changes occurred to the hexagonal wurtzite crystal lattice of ZnO due to the incorporation of Er³⁺ based on crystalline size. The chemical composition of the samples was confirmed using Energy Dispersive Spectra (EDS) data analysis. Decrease in average crystallite size with increase in rare earth concentration was observed in XRD. The frequency dependence of dielectric constant (ϵ_r), dielectric loss ($\tan\delta$) and AC conductivity of pure and rare earth doped ZnO were calculated and well explained with Maxwell-Weigner model.

Keywords

Solid State Reaction, XRD, Crystallite Size, Bond Length, Dielectric Constant, AC Conductivity

1. Introduction

The nontoxicity, excellent chemical and thermal stability, specific electrical and optical properties make ZnO an attractive compound for researchers. Growth conditions, environment, the type and purity of dopants have very important role in the determination of structural and dielectric properties of ZnO. It has potential applications in electro-optic, acousto-optic, ultraviolet (UV) light emitters, chemical sensors, piezoelectric materials and high power optoelectronic devices [1]. The endless requirement of materials with high dielectric constant in the field of microelectronics makes the study on the development of new dielectric materials more relevant. Dielectric constant and Loss tangent are the most important parameters determining the dielectric behaviour of materials [2]. Dielectric loss of a dielectric material is the inherent dissipation of electromagnetic energy into heat. It can be expressed in terms of either the loss angle δ or the corresponding loss tangent $\tan\delta$. Zinc oxide possesses

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semiconductor behaviour; it can be a dielectric at low temperature and can be a conductor at high temperature [3].

Rare earth (RE^{3+}) doped ZnO has the speciality of co-existence of semiconducting, electrochemical and optical properties, which motivates the researchers to work with these materials. The improvement of dielectric properties of ZnO via doping has been reported several times. Since the ionic radius of Zn^{2+} ions is very small compared with RE^{3+} ions, the incorporation of trivalent RE^{3+} ions in ZnO makes distortions in the ZnO matrix, which leads to asymmetry in the electronic environment of the system [4]-[18]. Thus electrical conductivity and other physical properties of the semiconductor can be controlled by the incorporation of RE^{3+} impurities into semiconductor lattices. Dielectric properties of erbium doped ZnO are rarely reported and this report opens a path for large scale production of dielectric materials with low dielectric loss.

The synthesis methods have prominent role in the properties of the materials. There are several methods like sol-gel method, co-precipitation method, electrochemical crystal growth, hydrothermal method, solid state reaction method, etc., which can be adapted for the preparation of samples. Each method has its own advantages and limitations. Compared with conventional methods, solid state reaction method facilitates the production of large quantity of high pure samples at low cost.

This report is unique in such a way that, this is first time reporting the production of perfectly doped ZnO within the solubility limit of erbium in ZnO via solid state reaction method. Thus this opens a door to the large scale production of RE doped ZnO with high dielectric constant and low dielectric loss. An important observation of this work is the frequency dependence of the dielectric constant of the samples with erbium concentration 0.6 wt% and 0.9 wt% and the frequency independent behaviour of dielectric constant of samples with 0.3 wt% and 1.2 wt% erbium incorporation. This observation will be very useful in the practical applications of these materials.

Aim of present study is (i) to synthesise Erbium doped ZnO via solid state reaction route and (ii) to study the structural and dielectric properties in detail. This work focuses on the development of dielectric material with low dielectric loss.

2. Experimental Details

2.1. Synthesis

Er^{3+} doped ZnO powders were prepared via controlled solid state reaction route at high temperature. The samples were prepared by thorough mixing of ZnO (Sigma aldrich product –99.99% purity) and Er_2O_3 (Sigma aldrich product –99.99% purity) and made in to slurry by adding $\text{LiOH}\cdot\text{H}_2\text{O}$ (merck product –99.99% purity) and ethanol (merck product –99.99% purity). In this study LiOH act as a heat transfer medium. The slurry then dried at 100°C in an oven. Then obtained powder sample was well ground for 1hr using a mortar and pestle and made in to pellets using hydraulic pelletizer at a pressure of 8 Torr. The pellets were packed in a quartz boat and fired at 900°C. The heat treated pellets were again ground for 15 minutes and used as the sample. Five batches of samples were prepared by varying the wt% of erbium as 0.3 wt%, 0.6 wt%, 0.9 wt% and 1.2 wt% of total amount of the powder sample.

2.2. Characterization

The phase purity and structural informations were obtained by using Rigaku Miniflex 600 machine with $\text{Cu K}\alpha$ radiation (1.5406 Å). The powder X, PDXL: Integrated powder X-ray diffraction software and ICDD data base were used for phase determination, peak reflection assignments and to analyse variations in peak positions and intensities. The purity of samples was confirmed with Energy Dispersive X-ray Analysis (EDAX) equipment of Hitatchi. The dielectric studies were done with Hioki 3532-50 LCR HiTESTER.

3. Results and Discussion

3.1. X-Ray Diffraction Analysis

The crystallinity and structure of the synthesised samples were analysed by X-ray diffraction data recorded. The intensity data was collected over a 2θ range of 10° - 90°. Powder X-ray diffraction patterns of undoped and Er-doped ZnO samples plotted in the Figure 1. All patterns are well matched with the standard X-ray diffraction pattern indicating hexagonal wurtzite structure of bulk ZnO. Diffraction peaks corresponding to reflections from

planes (100), (002), (101), (102), (110), (103), (112) of Wurtzite ZnO structure, which are consistent with the standard ICDD Card no.01-074-9940. When the concentration of erbium was increased further, extra phase related to Er_2O_3 arises and is observed in **Figure 2**. It indicates that at this concentration the solubility limit of erbium in ZnO has exceeded. And thus multiphase formation occurs at this concentration.

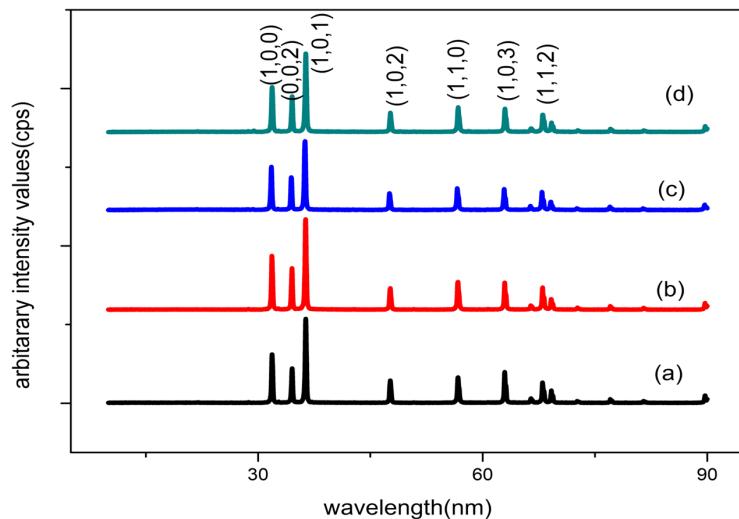


Figure 1. XRD pattern of samples (a) heat treated pure ZnO (b) 0.3 wt% Er doped ZnO (c) 0.6 wt% Er doped ZnO (d) 0.9 wt% Er doped ZnO (e) 1.2 wt% Er doped ZnO.

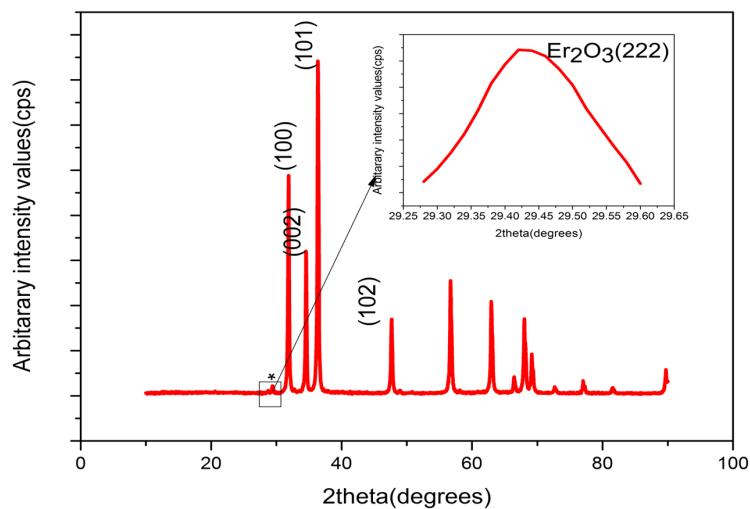


Figure 2. XRD pattern of 1.2 wt% Er doped ZnO sample.

Using Scherrer formula, $D = 0.9\lambda/\beta\cos\theta$, where λ is the wavelength of $\text{CuK}\alpha$ radiation (1.514 \AA), θ is the peak position and β is the FWHM, the average crystallite size of the samples was estimated [5]. It is found that average crystallite size decreases with increase in doping concentration. The average crystallite size of pure ZnO nanoparticle was 57.71 nm . It is decreased to 45.26 nm with 1.2 wt% doping of erbium. The decrease in crystallite size is due to the distortion of host ZnO lattice by RE^{3+} ions, which actually reduces the nucleation and subsequent growth rate of ZnO crystals.

3.2. Chemical Compositional Confirmation

In order to confirm the chemical composition of the samples, Energy Dispersive Spectra were taken. The

samples were cleaned by Ar⁺ ion beam sputtering to remove surface contamination if any. **Figure 3(a)** is the energy dispersive spectra of undoped ZnO. **Figure 3(b)** is the energy dispersive spectra of doped (Er^{3+} – 1.2 wt%) ZnO ceramics. From **Figure 3(a)**, the purity of parent sample is confirmed. There are no impurities in the parent ZnO sample. The incorporation of Er³⁺ ions in ZnO crystal lattice are confirmed from the **Figure 3(b)**.

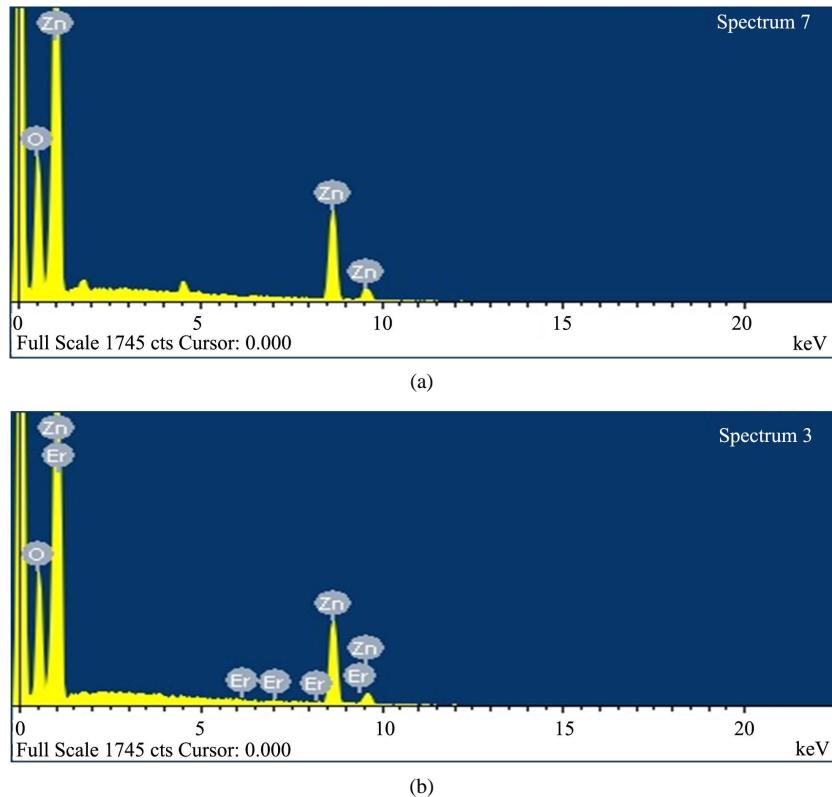


Figure 3. (a) (b) EDS spectra of pure and Er doped ZnO respectively.

3.3. Dielectric Properties

Dielectric measurements of the undoped and erbium doped ZnO were carried out as a function of frequency at room temperature using an LCR meter. The samples were pelletized by using a hydraulic press and this pellet was placed between the electrodes. The dielectric constant (ϵ_r) is calculated using the relation $\epsilon_r = Cd/\epsilon_0 A$ and the ac conductivity is calculated by the relation, $\sigma_{ac} = \epsilon_0 \epsilon_r \omega \tan(\Delta)$, where C is the capacitance, d is the thickness, A is the area of cross section of the pellet and $\tan(\Delta)$ is the dielectric relaxation of the sample. It is observed that the dielectric constant decreases with increasing frequency for all samples. This is evident in the low frequency region and is shown in **Figure 4**. At high frequencies the dielectric constant becomes frequency independent. Maxwell-Weigner model can be used to explain the dielectric properties of the homogeneous double structure systems. According to this model the dielectric medium is made of well conducting grains with poorly conducting or resistive grain boundaries. Thus by the application of external electric field, the charge carriers easily moves, but will be accumulated at the grain boundaries. This process causes large polarization and high dielectric constant produced by the sample. At low frequency, the small conductivity of grain boundary contributes to the high value of dielectric constant. The interfacial/space charge polarization due to inhomogeneous dielectric structure can also be considered as the reason for high dielectric constant. Beyond certain level of frequency of external field, the hopping between different metal ions (Zn^{2+} , Er^{3+}) can not follow the alternating field [2]. This is why the dielectric constant becomes frequency independent beyond certain limit. The decrease in dielectric constant with increase in frequency in the lower frequency range can be considered as a natural phenomenon because any species contributing to polarizability is found to show lagging behind the applied field at higher and higher frequencies.

In order to investigate further the effect of erbium doping, the dielectric constant of material is re plotted in

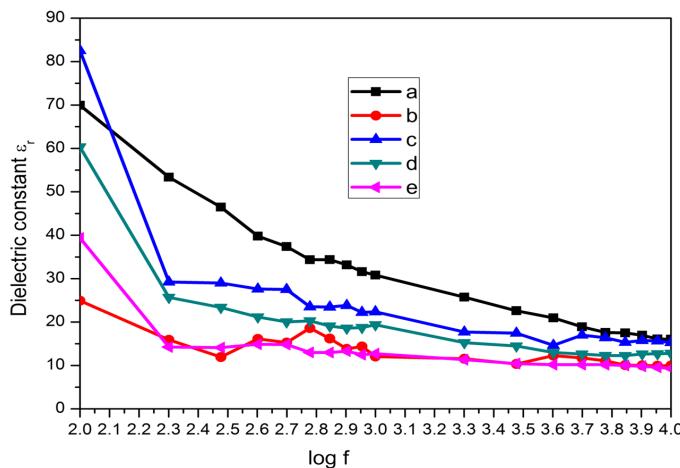


Figure 4. Figure of Dielectric constant vs log of the samples (a) pure ZnO (b) 0.3 wt% Er doped ZnO (c) 0.6 wt% Er doped ZnO (d) 0.9 wt% Er doped ZnO (e) 1.2 wt% Er doped ZnO.

Figure 5 as a function of concentration of erbium. The dielectric constant is found to be decreased first with small amount of erbium incorporation (0.3 wt%). It is striking to see that the dielectric constant increases dramatically while the concentration of erbium is increased to 0.6 wt%. Further increase in erbium concentration decreases the dielectric constant of ZnO. The incorporation of small amount of Erbium ions produces distortion and an abrupt instability in the crystal lattice of ZnO, which results in the decrease of dielectric constant of the material. But when the concentration is increased to an optimum concentration of 0.6 wt%, the system gets stabilized and results in the reduction of the number of oxygen vacancies [18]. This leads to an increase in the dielectric constant. Further increase of erbium content would result in the unit cell contraction and hence the free volume available for the displacement of ions gets reduced. This results in the decrease of dielectric polarization and dielectric constant.

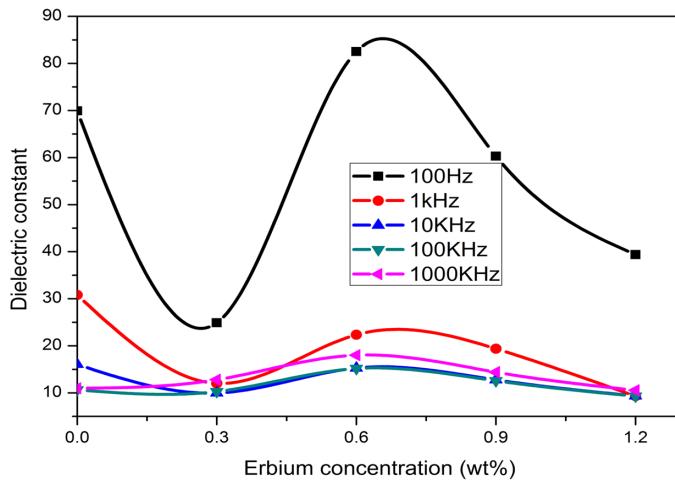


Figure 5. Dielectric constant of erbium doped ZnO at selected frequencies.

An important observation from **Figure 5** is the frequency dependence of the dielectric constant of the samples with erbium concentration 0.6 wt% and 0.9 wt% and the frequency independent behaviour of dielectric constant of samples with 0.3 wt% and 1.2 wt% erbium incorporation. This observation will be very useful in the practical applications of these materials. It is interesting to note that the sample with 0.6 wt% erbium incorporation appears to be the best dielectric material than the parent ZnO at 100 Hz, 10 KHz, 100 KHz and 1000 KHz. This helps us to optimize the concentration of erbium in ZnO for making good dielectric material.

Figure 6 shows the variation of ac conductivity of undoped and Erbium doped samples with frequency. The ac conductivity of all the samples gets increased with increase in frequency. But the maximum ac conductivity is seen for undoped ZnO sample and which decreases with the erbium incorporation. The production of defects like zinc interstitials in the ZnO host system by erbium ions can be considered as the reason for this reduction in ac conductivity. It is very relevant that the doping percentage plays important role in tuning the electrical property of the sample. Because the 0.6 wt% erbium incorporation show maximum ac conductivity as compared to other doped samples. After this optimum doping percentage the ac conductivity is found to be decreased with increase in doping percentage. This decrease may be due to the defects produced by erbium ions in ZnO host matrix. As doping concentration increases, the defect ions which facilitates the formation of grain boundary defect barrier, leading to blockage to the flow of charge carriers. This in turn decreases the conductivity of the system on doping.

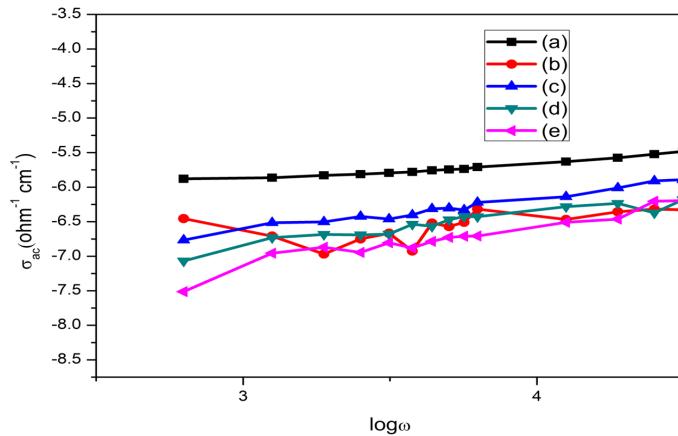


Figure 6. Figure of $\log \sigma_{ac}$ vs $\log \omega$ of the samples (a) pure ZnO (b) 0.3 wt% Er doped ZnO (c) 0.6 wt% Er doped ZnO (d) 0.9 wt% Er doped ZnO (e) 1.2 wt% Er doped ZnO.

Figure 7 shows the variation of dielectric loss values $\tan(\delta)$ with frequency of the un doped and erbium doped ZnO samples. Loss tangent i.e. $\tan(\delta)$ is the energy dissipation in the dielectric system. It is found to be maximum for undoped ZnO samples. As erbium doping increases, this loss factor is decreased to a large extend. The decrease of $\tan(\delta)$ with increase in frequency seen in erbium doped samples is due to the space charge polarization. This peculiar behaviour as well as the very low loss factor compared to the parent ZnO makes the prepared samples suitable for high frequency device applications.

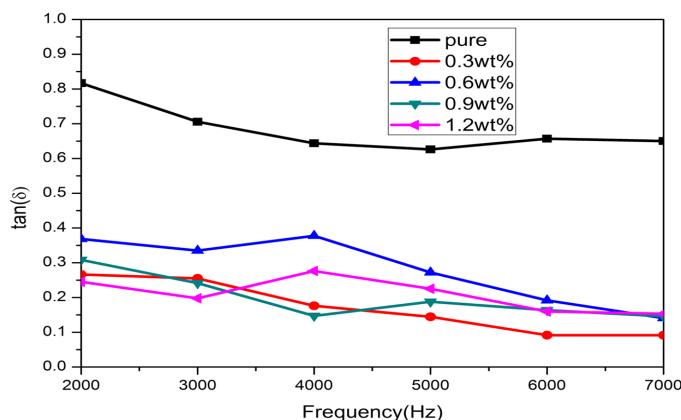


Figure 7. Plot of $\tan(\delta)$ Vs Frequency of the samples (a) pure ZnO (b) 0.3 wt% Er doped ZnO (c) 0.6 wt% Er doped ZnO (d) 0.9 wt% Er doped ZnO (e) 1.2 wt% Er doped ZnO.

4. Conclusion

The structural and dielectric studies of Erbium doped ZnO synthesised via simple solid state reaction route were investigated. Since rare earth elements have larger ionic radii compared with Zinc, the incorporation of trivalent erbium ions in ZnO host lattice can cause a significant distortion in ZnO crystal lattice. This is first time reporting the production of perfectly doped ZnO within the solubility limit of erbium in ZnO via solid state reaction method. Thus, this report opens a path for the production of RE doped ZnO with high dielectric constant. The crystallite size is calculated using Scherrer formula and is found to be decreased with erbium doping. The average crystallite size of pure ZnO nanoparticle was 57.71 nm. It is decreased to 45.26 nm with 1.2 wt% doping of erbium. The incorporation of Er^{3+} ion was confirmed using EDS. The AC conductivity of the erbium doped samples is found to be decreased with frequency. Dielectric constant of 0.6 wt% erbium incorporated ZnO is found to be maximum compared with other undoped and doped samples. The decrease in loss factor with erbium incorporation as well as its decrease with increase in frequency is very relevant results as far the application of material concerned. Sample with 0.6 wt% erbium incorporation is showing maximum dielectric constant and low loss compared with other samples. Thus it can be concluded that 0.6 wt% erbium doped ZnO is a very good dielectric material than the parent ZnO. These results make the prepared samples as promising candidates for high frequency device applications.

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References

- [1] Ishizum, Y. and Kanemitsu, I. (2005) Structural and Luminescence Properties of Eu-Doped ZnO Nanorods Fabricated by a Microemulsion Method. *Applied Physics Letters*, **86**, Article ID: 253106. <http://dx.doi.org/10.1063/1.1952576>
- [2] Zamiri, R., Kaushal, A., Rebelo, A. and Ferreira, J.M.F. (2014) Er-Doped ZnO Nanoplate: Synthesis, Optical and Dielectric Properties. *Ceramics International*, **40**, 1635-1639. <http://dx.doi.org/10.1016/j.ceramint.2013.07.054>
- [3] Omar, K., Jhohan Ooi, M.D. and Hassin, M.M. (2009) Investigation on Dielectric Constant of Zinc Oxide. *Modern Physics*, **3**, 110-116.
- [4] Jadwisienczak, W.M., Lozykowski, H.J., Xu, A. and Patel, B. (2002) Visible Emission from ZnO Doped with Rare-Earth Ions. *Journal of Electronic Materials*, **31**, 776-784. <http://dx.doi.org/10.1007/s11664-002-0235-z>
- [5] Chen, G.Y., LIU, H.C., Somesfalean, G., Sheng, Y.Q., Liang, H.J., Zhang, Z.G., Sun, Q. and Wang, F.P. (2008) Enhancement of the Upconversion Radiation in $\text{Y}_2\text{O}_3:\text{Er}^{3+}$ Nanocrystals by Codoping with Li^+ Ions. *Applied Physics Letters*, **92**, Article ID: 113114. <http://dx.doi.org/10.1063/1.2901039>
- [6] Rodnyi, P.A. and Khodyuk, I.V. (2011) Optical and Luminescence Properties of Zinc Oxide. *Optics and Spectroscopy*, **111**, 776-785. <http://dx.doi.org/10.1134/S0030400X11120216>
- [7] Willander, M., Nur, O., Sadaf, J.R., Qadir, M.I., Zaman, S., Zainelabdin, A., Bano, N. and Hussain, I. (2010) Luminescence from Zinc Oxide Nanostructures and Polymers and Their Hybrid Devices. *Materials*, **3**, 2643-2667.
- [8] Li, H.L., Zhang, Z., Huang, J.Z., Liu, R.X. and Wang, Q.B. (2013) Optical and Structural Analysis of Rare Earth and Li Co-Doped ZnO Nanoparticles. *Journal of Alloys and Compounds*, **550**, 526-530. <http://dx.doi.org/10.1016/j.jallcom.2012.10.080>
- [9] John, R. and Rajakumari, R. (2012) Synthesis and Characterization of Rare Earth Ion Doped Nano ZnO. *Nano-Micro Letters*, **4**, 65-72. <http://dx.doi.org/10.1007/BF03353694>
- [10] Kaid, M.A. and Ashour, A. (2007) Preparation of ZnO-Doped Al Films by Spray Pyrolysis Technique. *Applied Surface Science*, **253**, 3029-3033. <http://dx.doi.org/10.1016/j.apsusc.2006.06.045>
- [11] Binitha, M.P. and Pradyumnan, P.P. (2013) Structural, Thermal and Electrical Characterization on Gel Grown Copper Succinate Dihydrate Single Crystals. *Physica Scripta*, **87**, Article ID: 065603. <http://dx.doi.org/10.1088/0031-8949/87/06/065603>
- [12] Rahman, Md.T., Vargas, M. and Ramana, C.V. (2014) Structural Characteristics, Electrical Conduction and Dielectric Properties of Gadolinium Substituted Cobalt Ferrite. *Journal of Alloys and Compounds*, **617**, 547-562. <http://dx.doi.org/10.1016/j.jallcom.2014.07.182>
- [13] Li, J.-L., Chenn, G.-H. and Yuan, C.-L. (2013) Microstructure and Electrical Properties of Rare Earth Doped ZnO-

- Based Varistor Ceramics. *Ceramics International*, **39**, 2231-2237.
<http://dx.doi.org/10.1016/j.ceramint.2012.08.067>
- [14] Pathak, D., Wagner, T., Adhikari, T. and Nunzi, J.M. (2015) Photovoltaic Performance of AgInSe₂-Conjugated polymer Hybrid System Bulk Heterojunction Solar Cells. *Synthetic Metals*, **199**, 87-92.
<http://dx.doi.org/10.1016/j.synthmet.2014.11.015>
- [15] Pathak, D., Bedi, R.K. and Kaur, D. (2010) Growth of Heteroepitaxial AgInSe₂ Layers on Si (100) Substrates by Hot Wall Method. *Optoelectronics and Advanced Materials—Rapid Communications*, **4**, 657-661.
- [16] Pathak, D., Bedi, R.K., Kaur, D. and Kumar, R. (2011) 200 Mev Ag+ Ion Beam Induced Modifications In AgInSe₂ Films Deposited By Hot Wall Vacuum Evaporation Method. *Chalcogenide Letters*, **8**, 213-222.
- [17] Divya, N.K. and Pradyumnan, P.P. (2014) Variation in Morphology and Crystallinity of ZTO Ceramics. *Research Journal of Recent Sciences*, **3**, 71-74.
- [18] Chang, F.G., Song, G.L., Fang, K. and Zeng, Q.J. (2006) Effect of Gadolinium Sbstitution on Dielectric Properties of Bismuth Ferrite. *Journal of Rare Earths*, **24**, 273-276. [http://dx.doi.org/10.1016/S1002-0721\(07\)60379-2](http://dx.doi.org/10.1016/S1002-0721(07)60379-2)