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Synthesis, Characterization and Magnetic Properties of Mn^{2+} Doped $Cdga_{2-2x}o_4$ Oxide Spinels

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Abstract: ***Mn^{2+} doped $CdGa_{2-2x}O_4$ oxide spinels with 'x' values ranging from 0.15, 0.30, 0.45, and 0.60 were synthesized by sol – gel method via nitrate citrate route. X-ray powder diffraction analysis confirms the presence of cubic structure with lattice parameters 8.5856, 8.6200, 8.6266 and 8.6469 Å for respective values of 'x', having space group Pm-3m. Average crystallite size values are determined by Scherrer's relation, which are found to be in the range of ~ 26 to 59 nm. Cell volume increases with increase in Mn^{2+} concentration which confirms the successful incorporation of bigger size Mn^{2+} in the host Ga^{3+} ion. VSM results confirm weak ferromagnetic behaviour of prepared samples with low values of coercivity, retentivity and magnetic saturation at room temperature. TGA-DSC results reveal no phase transition in the range 100 – 800˚C. Absorption spectroscopy plays an important role in determining the optical property of spinels. Optical properties of synthesized oxide are studied by using UV–Vis absorption spectroscopy. FT-IR spectra of the sample are recorded at room temperature in the range 4000 – 400 cm^{-1} which show characteristic absorption at 604 cm^{-1} and 473 cm^{-1}. Morphology of the samples shows particles are agglomerated having void space. Elemental analysis by EDX confirms the presence of individual element in the expected range. EPR spectra were recorded in X- band spectrometer at room temperature and 5 K, 94 K which are found to be isotropic in nature.***

Keywords: Spinels, EPR, SEM, EDX, VSM and sol – gel synthesis.

I. INTRODUCTION

Transition metal oxide gain importance because of their remarkable magnetic, electrical and optical property [1]. These properties depend on type of magnetic ion reside at tetrahedral and octahedral sites of cubic lattice and relative strength of intra- and inter-sub lattice interactions. Half filled *3d* transition metal attracts great interest and their resultant orbital angular momentum is zero [2]. Mn^{2+} with d^5 system acts as an efficient paramagnetic impurity in an octahedral site in which one can study the local environment about the paramagnetic ion and other structural factors. Substitution of Mn^{2+} ion strongly improves the ferromagnetic behavior of metal oxides. Mn^{2+} in oxide form has significant attention and posses application in different areas such as catalysis, battery technologies, electrode, energy storage, ion exchange, biomedical imaging, and drug delivery applications [3–7]. In this paper we discuss about synthesis, structure, electrical and magnetic property of $CdMn_{3x}Ga_{2-2x}O_4$ spinel oxides by sol-gel [8] method via nitrate - citrate route. Sol- gel combustion method is one of the best methods for preparing inorganic composite materials containing highly dispersed homogenous particle.

II. EXPERIMENTAL

$CdMn_{3x}Ga_{2-2x}O_4$ with 'x' values ranging from 0.15, 0.30, 0.45, 0.60 samples (B1 to B4) were prepared by sol-gel method via nitrate-citrate route and labelled with their 'x' values. The precursor oxides $Cd(CH_3COO)_2O$, $Mn(CH_3COO)_2O$ and Ga_2O_3 are taken in a stoichiometric ratio and mixed with acidified (HNO_3) deionised water to prepare 0.1 M solution of pH ~ 2. About 30 ml of 1.5 M citric acid is added to make it into transparent sol and the samples are kept in magnetic stirrer continuously at 50˚C for four days. After four days of stirring, a gel like substance is formed which is then decomposed at 120˚C. Then it is finally sintered at 400˚C for 2 hours and 800˚C for 4 hours in a muffle furnace. Loose powder obtained by sintering is grinded in an agate mortar and utilized for characterization.

III. RESULTS AND DISCUSSION

A. Phase structure from XRD

X-ray powder diffraction was recorded in a X'pert powder X-ray diffractometer (Make: PAN Analytical) with a scan rate 2˚ / minute in range 5˚ – 75˚ in 2θ. Monochromatic Cu K_α radiation (λ ~ 1.54060 Å) was used as an X ray source with power 40 kV/30 mA. Average crystallite size was calculated by using Scherrer formula. Full Prof Suite software package was used to analyze the

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powder X – ray diffraction data and to determine the unit cell parameters. Rietveld refinement method was used for the refinement of unit cell structure. Density measurements were done by using liquid displacement method using Carbon tetrachloride as an immersion liquid (density 1.596 g/cc at 300K)

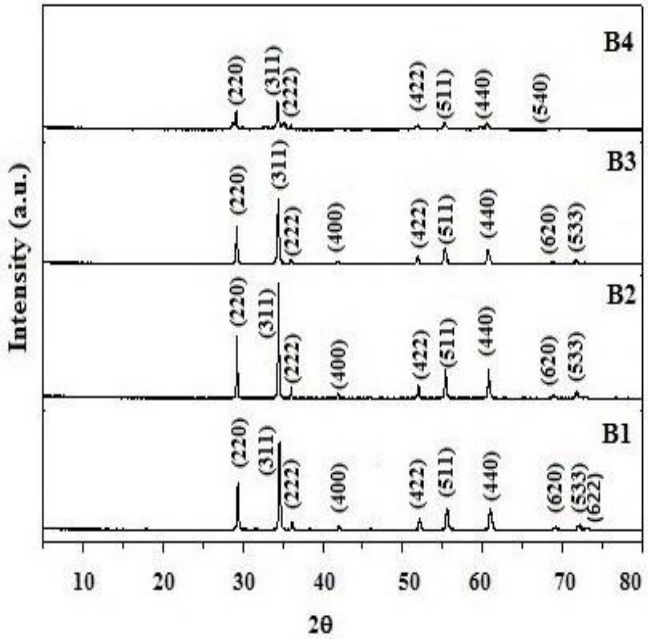

Fig. 1. Powder X-ray diffraction patterns of Mn^{2+} substituted $CdGa_{2-2x}O_4$ with from B1 to B4

Figure-1 shows the XRD pattern of Mn^{2+} substituted $CdGa_2O_4$ oxide prepared at different composition. Powder XRD analysis of the entire four samples exhibit a perfect cubic structure with lattice constant of 8.5856Å without any secondary phase. It can be mentioned that Mn^{2+} ion has a radius of (0.89 Å) which is bigger than Ga^{3+} (0.62 Å) and as a result cell volume increase with increase in concentration of Mn^{2+} ion. Average crystallite size of the sample are found to be 35, 59, 32, 26 nm respectively for the corresponding 'x' values. Depending upon the crystallite size, intensity of peak varies for B3 and B4. From the figure-1 one can infer that peaks in the spectra indicate spinel structure without any other inflections. (h k l) values shown in figure-1 agree well with the (h k l) values reported earlier [9-13]. Rietveld refinement of the unit cell structure composite oxides were carried out. The unit cell dimension, a (Å), and the agreement factors for the sample B1 i.e. $CdMn_{0.45}Ga_{1.7}O_4$ are given in table-1.

Agreement Factors

Sample Code	a (Å)	R_p (%)	R_{wp}(%)	R_{exp} (%)
B1	8.5856	55.33	60.36	0.12

Table. 1. Rietveld refinement of sample B1

B. Morphological studies

Surface structure and particle morphology was performed using SEM JSM – 5410. Hitachi S – 3400 instrument was used for elemental analysis. SEM images of the sample shows particles are highly dispersed and agglomerated. Agglomeration of the particle increases with the increase in concentration of manganese. Agglomeration of particles indicates that prepared samples are highly reacted by heat treatment or due to the exchange interaction between particles. Fig.4c shows the EDX measurement graph which

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confirms the presence of Mn, O, Ga and Cd signatures in the expected range. From the quantitative EDX measurement one can see that the weight percent of manganese is 7.1% which is in the expected range and increases proportionally as the concentration of manganese increases.

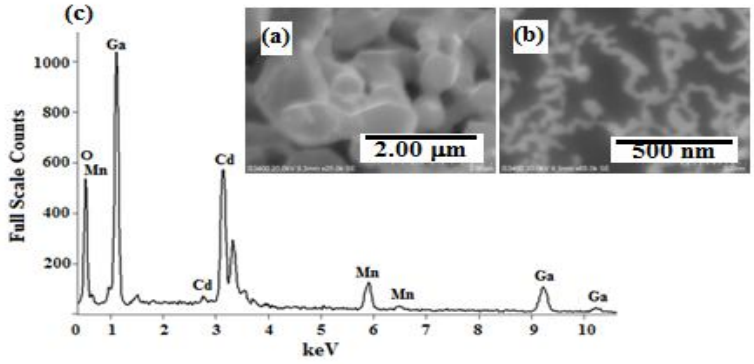

Fig. 2. (a) SEM images of B1 (b) B2 at different magnification and (c) EDX profile of B1

C. Thermal studies

TGA measurements were recorded using TA instruments (Model: Q600 and Q20 DSC). TG curve shows significant weight loss in the range 100 to 400°C which is due to removal of trapped water molecule. From TG curve we can conclude that prepared samples are thermally stable up to 800°C without any phase transition (Fig. 3.). Apart from weight loss of water no other anomalies were reported.

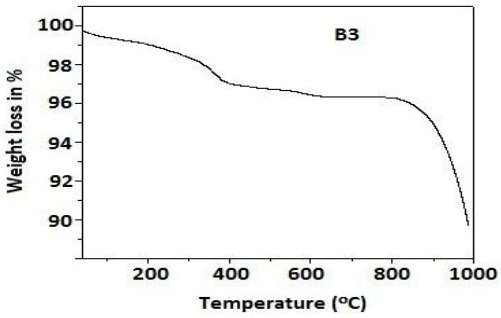

Fig. 3. TG curve of the prepared sample B3

D. UV –Vis absorption spectra

Optical absorption spectrum of the sample is recorded in UV-vis region in the range 200 – 800 nm using UV 2450 (Make: Shimadzu). Optical absorption band of Mn^{2+} doped samples are observed in UV region. From the figure-4 one can see optical absorption in the range 347-350 nm which agrees with the reported values [14-15]. This absorption is due to ligand to metal transition from 2p orbital of oxygen atom to 3d orbital of manganese. Optical band gap of the samples are determined from the plot of optical absorption coefficient vs photon energy. Intercept of this plot on photon energy axis gives energy band gap of samples. Observed band gap energy values are for B1-B4 are 2.39, 2.74, 2.15 and 2.16 eV respectively.

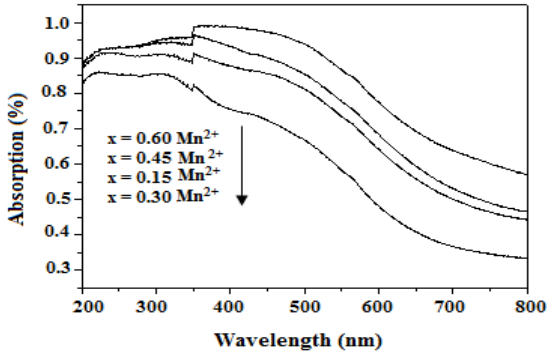

Fig. 4. (a) UV – Visible absorption spectrum of samples B1, B2, B3 and B4

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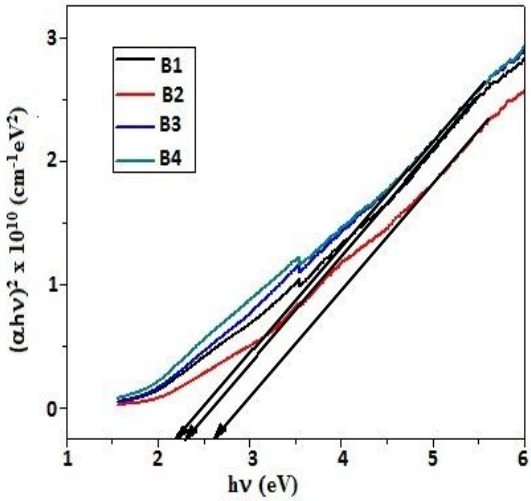

Fig. 4. (b) Band gap energy plot of samples B1, B2, B3 and B4

E. FT-IR Spectroscopy

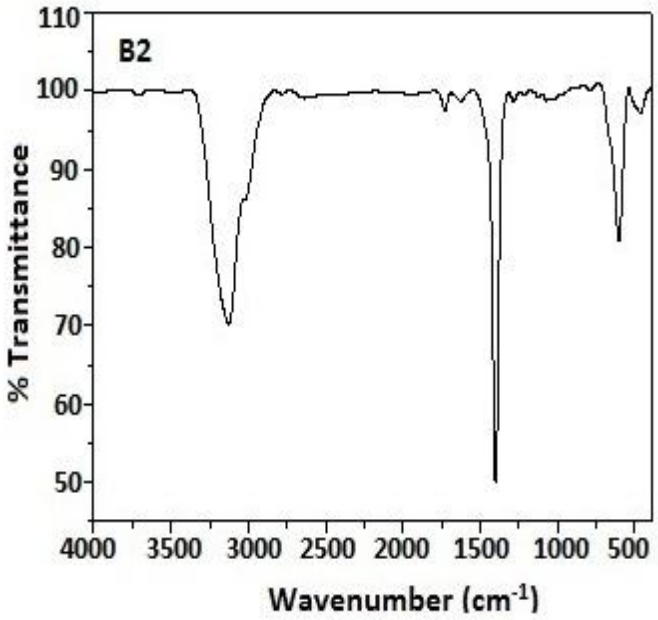

Fig.5. FT-IR spectra of B2 at room temperature

The Fourier transforms Infrared spectra are recorded using Thermo Scientific FT-IR spectrometer in the range 4000 – 450 cm^{-1}. FT-IR spectra of Mn^{2+} doped B2 are shown in figure-5. From FT-IR spectra one can identify the structure of spinel oxides. Generally metal-oxygen absorptions occur below in the range 1000 cm^{-1}. Absorption in the range 473 cm^{-1} assigned to symmetric bending mode of $[MnO_{6/2}]$ / $[GaO_{6/2}]$ units in octahedral sites [16] and absorption in the range 604 cm^{-1} attributed to stretching mode of Ga-O bond [17]. Broad band in the range 3125 cm^{-1} is assigned to stretching mode of OH group and absorption in the range 1630 cm^{-1} [18] is assigned to bending mode of OH group. Absorption in the range 1402 cm^{-1} and 1730 cm^{-1} is due to corresponding vibration in nitrate groups.

F. EPR studies

Electron Paramagnetic Resonance (EPR) spectra of powdered samples were recorded at room temperature and Liquid helium temperature. EPR spectra at 5 K were recorded using a Bruker spectrometer in X- Band with resonance frequency 9.0 GHz and

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modulation frequency of 500 KHz. The magnetic field was scanned from 2500 to 4000 T with a scan speed of 500 T. EPR spectra at room temperature using Bruker spectrometer operating at X- Band microwave frequency with resonance frequency 9.0 GHz and modulation frequency of 100 MHz also recorded.

Investigation of EPR spectra of Mn^{2+} ion in $CdGa_{2-2x}O_4$ oxides have shown that spectra consist of clear six line hyperfine pattern which have been characterized by intense resonance signal at g ~ 2.0. The Mn^{2+} ion has half filled outer shell $3d^5$ with electron spin S=5/2 and nuclear spin I = 5/2. Resonance signal at g ~ 2.0 is due to interaction of electron spin of manganese ion with its nuclear spin I = 5/2 [16, 19-23]. From the room temperature EPR spectra (Fig.6a) one can see that intensity of resonance signal increases with increase in manganese ion except for x = 0.30. The evaluated g values at room temperature spectra are 2.01, 2.02, 2.00 and 2.00 which are found to be isotropic in nature and close to free ion value. Figure-6b shows the EPR spectra of Mn^{2+} ion doped (x = 0.15) $CdGa_{2-2x}O_4$ oxide observed at 5 K. The spectra shows sharp six line hyperfine pattern with broad resonance at g ~ 2.0 which is due to Mn^{2+} centre in octahedral symmetry.

Thus the EPR spectrum at room temperature and 5 K shows characteristic six line hyperfine splitting for the samples B1 to B4 with transition ranging from -5/2 to +5/2 [21-23]. All the Mn^{2+} doped $CdGa_{2-2x}O_4$ shows a broad resonance at g ~ 2 with a sextet which indicate that Mn^{2+} ion reside in an highly ionic environment.

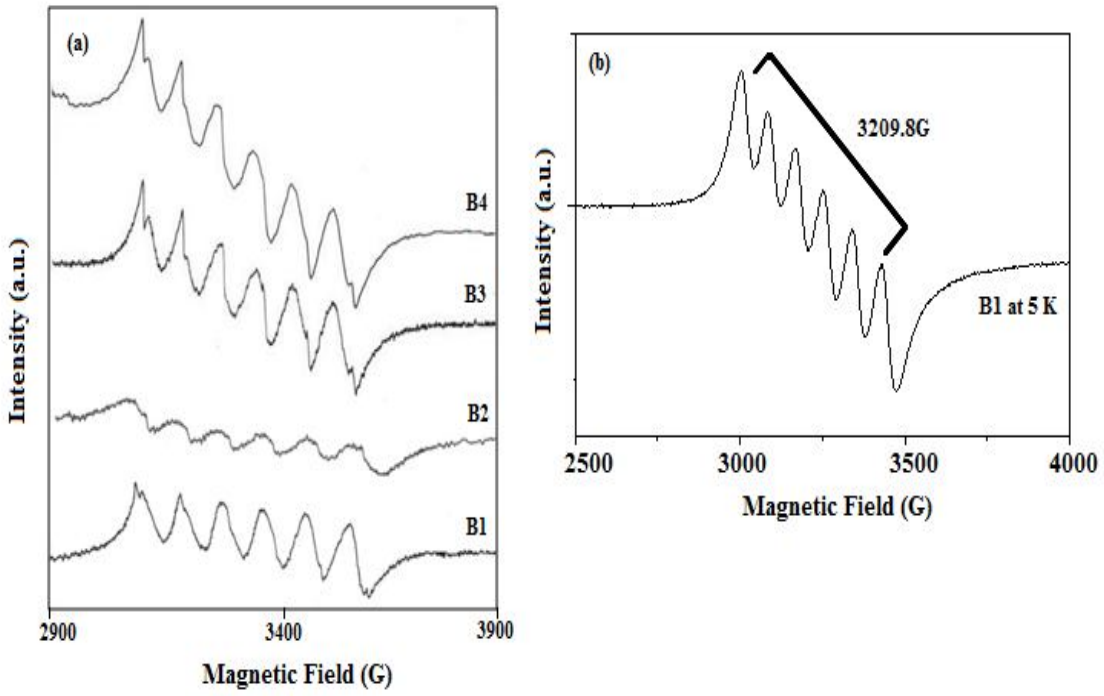

Fig.6. (a) EPR spectra of Mn^{2+} doped $CdGa_{2-2x}O_4$ with different Mn^{2+} concentration recorded at room temperature and (b) EPR spectra of Mn^{2+} doped $CdGa_{2-2x}O_4$ (B1, x = 0.15) recorded at 5K

G. Magnetic studies

Magnetic hysteresis measurements were made by using Vibrating Sample Magnetometer (VSM) at room temperature (Model: 7404, Make: Lake Shore). Variation of saturation magnetization and magnetic remanence were studied with different composition of manganese ion. M_s and M_r values show the insignificant change with increase in Mn^{2+} concentration (Fig. 7). This is can be attributed to the decrease in average crystallite size values which is influenced by increasing the manganese concentration. Decrease in average crystallite size value is due to Mn^{2+} ion which inhibits the growth of crystal structure [24-28].

From the table we can see that Magnetic coercivity value varies with different composition of Mn^{2+} concentration. Coercivity value is influenced by factor such as anisotropy, magnetic particle morphology, magnetic domain size and size distribution. Variation in magnetic coercivity values may be attributed to porosity. Since pores work as a generator for demagnetizing field which effects magnetization process. Variation in magnetic coercivity value is due to unquenched orbital angular momentum of manganese and to an anisotropy value.

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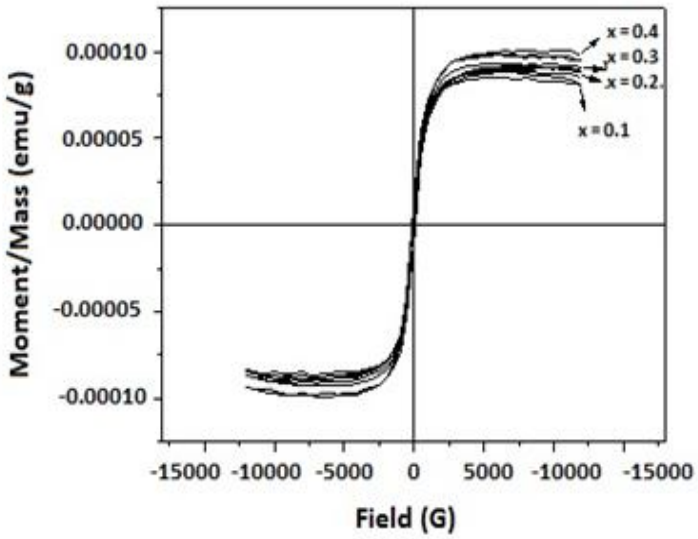

Mn^{2+} Substitution Molar Ratio	Magnetic Properties		
	Ms (emu/g)	Mr (emu/g)	Hc (G)
0.1	9.289 x 10^{-5}	0.907 x 10^{-5}	82.886
0.2	9.981 x 10^{-5}	1.133 x 10^{-5}	101.220
0.3	8.977 x 10^{-5}	1.028 x 10^{-5}	99.417
0.4	9.108 x 10^{-5}	0.927 x 10^{-5}	92.421

Fig. 7. Hysteresis loop of $CdMn_{3x}Ga_{2-2x}O_4$ oxides with corresponding magnetization values

IV. CONCLUSION

The Mn^{2+} substituted $CdGa_{2-2x}O_4$ spinel oxides were synthesised by sol-gel method. The XRD analysis confirms the presence of cubic structure with increased cell volume. FT-IR spectra confirms the formation of spinel structure having two significant metal oxygen absorption band in the range 604 and 473 cm^{-1}. The observed EPR spectrum of Mn^{2+} ion at different temperature shows the spectrum is isotropic in nature with hyperfine pattern of sextet. Optical absorption studies reveal that absorption in the range 347 – 350 nm is due to ligand to metal transition. EDX analysis confirms the doping of manganese ion with the presence of Cd, Ga, Mn and oxygen. SEM images of the sample reveals particles are agglomerated with non uniform particle size. TGA – DSC results reveal no phase transition in which the compound is thermally stable up to 800°C. Magnetic behaviour of Mn^{2+} doped $CdGa_{2-2x}O_4$ oxide shows soft ferromagnetic behaviour in the order of 10^{-5} emu/g.

REFERENCES

[1] J. Smit and H.P.J Wijn, Ferrites : Physical properties of ferrimagnetic oxides in relation to their technical applications, New York : Wiley, 1984.
[2] J. Lakshmana Rao, B. Deva Prasad Raju, N.O. Gopal, K.V. Narasimhulu, “Electron paramagnetic resonance and optical absorption studies on Mn^{2+} ions doped in $KZnClSO_4 \cdot 3H_2O$ single crystals” Physica B: Condensed Matter, vol.355, pp. 207–215, 2005.
[3] J.M. Trascon, M. Armard, “Issues and challenges facing rechargeable lithium batteries”, Nature, vol. 414, pp. 359-367, 2001.
[4] K. Terakura, T. Oguchi, A.R. Williams, J. Kubler, “Band theory of insulating transition-metal monoxides: Band-structure calculations”, Physical Review B, vol. 30, pp. 4734–4747, 1984.
[5] S. Massidda, A. Continenza, M. Posternak, A. Baldereschi, “Band-Structure Picture for MnO Reexplored: A Model GW Calculation”, Physical Review Letters, vol. 74, pp. 2323–2326, 1995.

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[6] A.R. Armstrong, P.G. Bruce, "Synthesis of layered $LiMnO_2$ as an electrode for rechargeable lithium batteries", Nature, vol. 381, pp. 499–500, 1996.
[7] W.S. Seo, H.H. Jo, K. Lee, B. Kim, S.J. Oh, J.T. Park, "Size-dependent magnetic properties of colloidal Mn_3O_4 and MnO nanoparticles", Angewandte Chemie - International Edition, vol. 43(9), pp. 1115–1117, 2004.
[8] M. Veith, S. Mathur, N. Lecerf, V. Huch, T. Decker, "Sol-Gel Synthesis of Nano-Scaled BaTiO3, BaZrO3 and BaTi0.5Zr0.5O3 Oxides via Single-Source Alkoxide Precursors and Semi-Alkoxide Routes", Journal of Sol-Gel Science and Technology, vol. 17, pp. 145–158, 2000
[9] V.K. Sharma, M. Najim, A.K.Srivastava, G.D. Varma, "Structural and magnetic studies on transition metal (Mn, Co) doped ZnO nanoparticles", Journal of Magnetism and Magnetic Materials, vol. 324, pp. 683–689, 2012.
[10] W. Ari Adi and A. Manaf, "Structural and Absorption Characteristics of Mn-Ti Substituted Ba-Sr Hexaferrite synthesized by mechanical alloying route", Journal of Basic and Applied Scientific Research, vol. 2, pp.7826-7834, 2012.
[11] I. Usman, R.S. Rawat, , Y. Wanga, T.L. Tan, P. Lee, R. Chen, H.D. Sunc, Li Fengji, Zhang Sam, "Alteration of Mn exchange coupling by oxygen interstitials in ZnO:Mn thin films", Applied Surface Science, vol. 258, pp. 6373– 6378, 2012.
[12] M.K. Shobana, and S. Sankar, "Structural, thermal and magnetic properties of $Ni_{1-x}Mn_xFe_2O_4$ nanoferrites", Journal of Magnetism and Magnetic Materials, vol. 321, pp. 2125–2128, 2009.
[13] B. Aktaş, S. Güner, F. Yıldız, A. Nateprov, A. Siminel, L. Kulyuk, "ESR study on Cr^{3+} and Mn^{2+} doped $ZnAl_2S_4$ single crystal", Journal of Magnetism and Magnetic Materials, vol. 258–259, pp. 409–412, 2003.
[14] S. Senthilkumaar, K. Rajendran, S. Banerjee, T.K. Chini, V. Sengodan, "Influence of Mn doping on the microstructure and optical property of ZnO", Journal of Materials Science in Semiconductor Processing, vol. 11, pp. 6-12, 2008.
[15] K. Omri, J. El Ghoul, O.M. Lemine, M. Bououdina, B. Zhang, L. El Mir, "Magnetic and optical properties of manganese doped ZnO nanoparticles synthesized by sol–gel technique", Superlattices and Microstructures, vol. 60, pp. 139–147, 2013.
[16] P.K. Sharma and M.S. Whittingham, "The role of tetraethyl ammonium hydroxide on the phase determination and electrical properties of γ-MnOOH synthesized by hydrothermal", Materials Letters, vol. 48, pp. 319-323, 2001.
[17] Y. Quan, D. Fang, X. Zhang, S. Liu, K. Huang, "Synthesis and characterization of gallium oxide nanowires via a hydrothermal method", Materials Chemistry and Physics, vol. 121, pp. 142–146, 2010.
[18] X. Ma, G. Lu, B. Yang, "Study of the luminescence characteristics of cadmium sulfide quantum dots in a sulfonic group polyaniline (SPAn) film", Applied Surface Science, vol. 187, pp. 235–238, 2002.
[19] G. Giridhar, M. Rangacharyulu, R.V.S.S.N.P. Ravikumar, P. Sambasiva Rao, "EPR and optical absorption studies on manganese ion doped in mixed alkali cadmium phosphate glasses", Materials Science and Engineering, vol. 2**,** pp. 1-5, 2009.
[20] A. Nag, S. Sapra, C. Nagamani, A. Sharma, N. Pradhan, S.V. Bhat, D.D. Sarma, "A Study of Mn^{2+} Doping in CdS Nanocrystals", Chemistry of Materials, vol. 19, pp. 3252-3259, 2007.
[21] T. Satyanarayana, M.A. Valente, G. Nagarjuna, N. Veeraiah, "Spectroscopic features of manganese doped tellurite borate glass ceramics", Journal of Physics and Chemistry of Solids, vol. 74, pp. 229–235, 2013.
[22] R.P. Sreekanth Chakradhar, G. Sivaramaiah, J. Lakshmana Rao, N.O. Gopal, "EPR and optical investigations of manganese ions in alkali lead tetraborate glasses", Spectrochimica Acta Part A, vol. 62, pp. 761–768, 2005.
[23] B. Sudhakar Reddy, N.O. Gopal, K.V. Narasimhulu, Ch. Linga Raju, J.L. Rao, B.C.V. Reddy, "EPR and optical absorption spectral studies on Mn^{2+} ions doped in potassium thiourea bromide single crystals", Journal of Molecular Structure, vol. 751, pp. 161–167, 2005.
[24] L. Zhuang, W. Zhang, Y. Zhao, D. Li, W. Wu, H. Shen, "Temperature sensitive ferrofluid composed of $Mn_{1-x}Zn_xFe_2O_4$ nanoparticles prepared by a modified hydrothermal process", Powder Technology, vol. 217, pp. 46–49, 2012.
[25] S.E. Shirsath, B.G. Toksha, R.H. Kadam, S.M. Patange, D.R. Mane, G.S. Jangam, A. Ghasemi, "Doping effect of Mn^{2+} on the magnetic behavior in Ni–Zn ferrite nanoparticles prepared by sol–gel auto-combustion", Journal of Physics and Chemistry of Solids, vol. 71, pp.1669–1675, 2010.
[26] R. Fathi and S. Sanjabi, "Electrodeposition of nanostructured $Ni_{(1-x)}Mn_x$ alloys films from chloride bath", Current Applied Physics, vol. 12, pp. 89-92, 2012.
[27] O. Caltun, G.S.N. Rao, K.H. Rao, B. Parvatheeswara Rao, I. Dumitru, C. Kim, C. Kim, "The influence of Mn doping level on magnetostriction coefficient of cobalt ferrite", Journal of Magnetism and Magnetic Materials, vol. 316, pp. 618–620, 2007.
[28] S.E. Shirsath, B.G. Toksha, R.H. Kadam, S.M. Patange, D.R. Mane, G.S. Jangam, A. Ghasemi, "Doping effect of Mn^{2+} on the magnetic behavior in Ni–Zn ferrite nanoparticles prepared by sol–gel auto-combustion", Journal of Physics and Chemistry of Solids, vol. 71, pp. 1669–1675, 2010.

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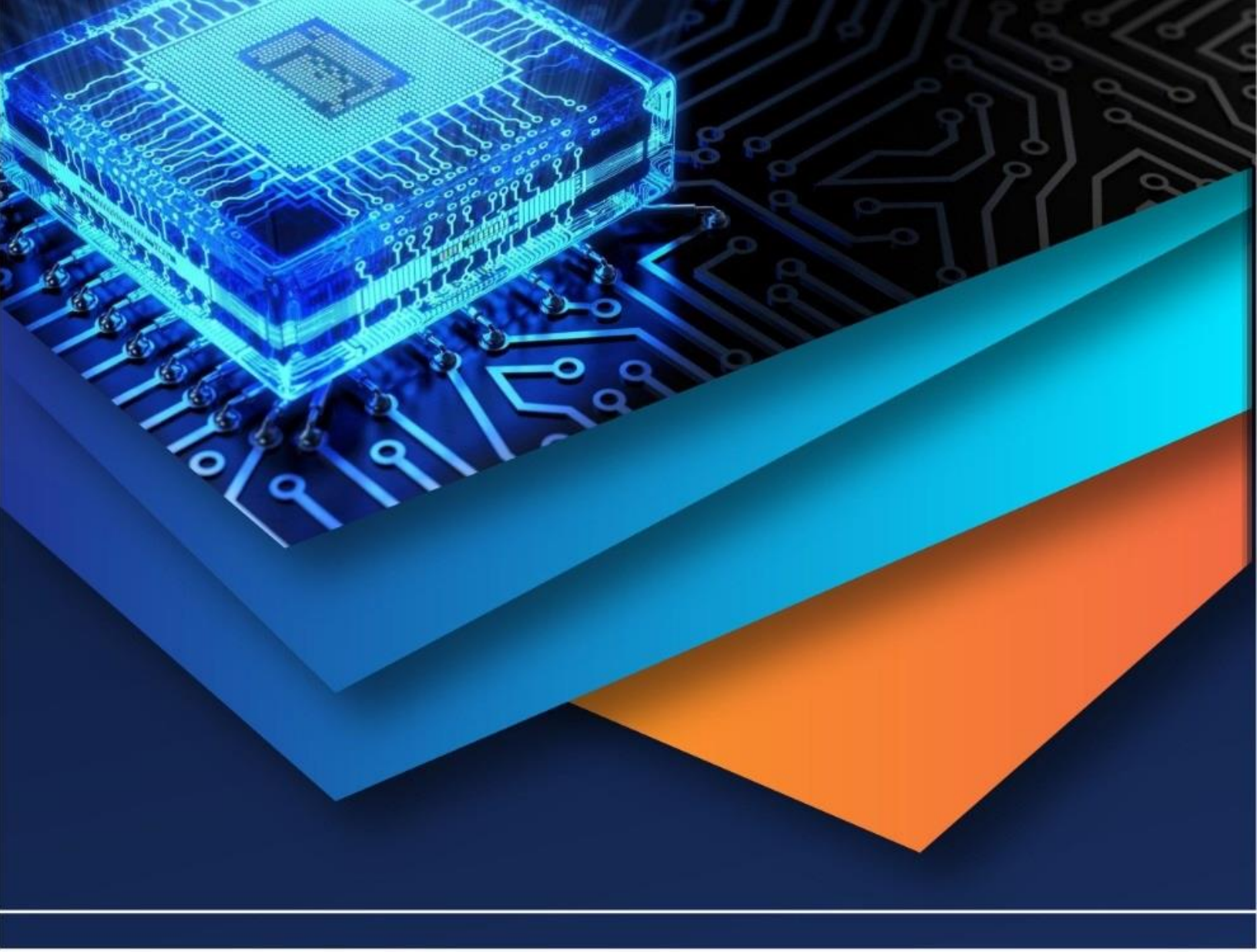

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