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EFFECT OF Mg DOPING ON DIELECTRIC AND MAGNETIC PROPERTIES OF Co-Zn NANO FERRITES

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In this paper, we report on the preparation and study of Mg doped Co-Zn Nano-ferrites. Properties of nano ferrites strongly depend upon synthesis methods and conditions. To get better properties of prepared samples, Co-Zn ferrite nano particles having composition $Co_{0.5}Zn_{0.5-x}Mg_xFe_2O_4$ (with x= 0.1, 0.2, 0.3, 0.4, 0.5) were prepared by using simplified sol-gel process. The cations in synthesized composition of spinel ferrites occupy appropriate lattice sites and results in exchange coupling. The crystallite size of the specimen increased by sintering the samples at 700 ^oC for 3 hours. The dielectric loss and dielectric constant of sintered samples were increased with the Mg doping concentration. Saturation magnetization was decreased while coercivity increased with Mg doping concentration.

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1. Introduction

Ferrites are complex oxides that are derived from the magnetite by replacing divalent iron atom with another transition metal atom. The magnetite formula is $Fe^{+2}OFe_2^{+3}O_3$ (Here +2 and +3 indicates valency). The formula for ferrites is; ($M^{+2}O$, $Fe_2^{+3}O_3$) or in simple form it is (MO, Fe_2O_3) where M can be selected from list of transition metals i.e. (Cromium, manganese, cobalt, nickel, copper, zinc, etc) [1]. The metals we used were cobalt, zinc and magnesium to get the optimum properties for microwaves absorption application. The properties of resulting material depend upon the nature of replaced metal ion and its proportions. When divalent iron is replaced completely by cadmium or zinc, the obtained ferrite is non-magnetic, but when it is replaced by magnetic ions like cobalt, manganese, nickel or chromium, the material obtained is magnetic, with high values of magnetic permeability [2]. It is also possible to obtain complex ferrites when the iron atoms are replaced by two or more divalent metals at the same time, for example nickel-zinc, cobalt –zinc, nickel cobalt, nickel-aluminum ferrites. The chemical formula thus becomes for nickel-zinc ferrites, αNiO, βZnO, Fe_2O_3, with $\alpha+\beta=1$. It is also possible to replace trivalent iron atom in Fe_2O_3 by the trivalent metal atom for example aluminum. So, nickel-zinc-aluminum ferrites formula is written as, αNiO, βZnO, $Fe_{(2-x)}Al_xO_3$ [3].

Nano materials have large surface to volume ratio that exhibit amazing properties differing from bulk materials. The magnetic and structural properties of nano materials are affected by various factors which include cation distribution, sintering temperature, chemical composition, grain size voids and doping [4]. One of the important factors for dielectric properties of materials is measure of dissipation factor. Dielectric losses in materials are due to some crystal defects i.e.,

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porosity, micro cracks and impurities. Previous studies show that losses in the sintered materials are gradually affected by these extrinsic factors [5].

Ferrite nano particles are very important materials. They have better magnetic properties and high values of D.C. resistivity. Applications of ferrites are in several technological fields such as information storage devices, permanent magnets and magnetic drug delivery [6]. All properties of polycrystalline ferrites are sensitive to microstructure. The microstructure is determined by grain (bulk) and grain boundaries [7]. The physical properties of nanomaterials tend to be exceptionally closely dependent on size and morphology of particles. So, material scientists focus their efforts in developing effective method for the development of nanomaterials [8]. Magnetic properties of ferrites are greatly affected by size of particles and cation distribution[9, 10]. Spinel ferrite nanoparticles have been studied in recent years for high frequency applications. High frequency devices like converters, inductors and microwave absorbers require high initial value of permeability at radio frequency range. Now a days, there is interest in Mg-Zn ferrite for device applications instead of Ni-Zn ferrites because nickel and their compounds produce carcinogenic effects and environmental toxicity. There are number of reports on Ni-Cu-Zn ferrites having good electromagnetic characteristics at low sintering temperature but these materials are sensitive to stress which affects the inductance and so magnetic properties of the ferrite material. To avoid domain formation, the diameter of nanoparticles is kept smaller than critical diameter during synthesis. For single domain, the only contribution to magnetization is from rotation of spin thus improving the operating frequency for the material; the spin rotation frequency is in GHz range [11].

Magnesium spinel ferrites offer desirable properties at elevated and ambient temperatures. But these materials are not popular commercially because their sintering process is difficult. Formation of spinel from its oxides is a counter diffusion process of Mg^{+2} [12]. The materials doped with Mg can improve the electromagnetic properties of Ni-Cu-Zn ferrites [13].

The magnetization of ferrite particles also depends upon particle size which is influenced by sintering temperature [14]. Recently a lot of research is devoted to development of materials for microwave absorption. For microwaves absorption, magnetic materials with high dielectric constant and dielectric loss tangent, high saturation magnetization and coercivity are desired. High dielectric constant and dielectric loss results in dielectric loss while high saturation magnetization and coercivity results in higher magnetic losses. Microwaves incident on such materials are absorbed and converted into heat. Among spinel ferrites, Co-Zn ferrites have relatively high dielectric constant, high coercivity and saturation magnetization [15] that makes it suitable for variety of applications such as magnetic drug delivery, high density storage devices and ferro fluids [16]. To further improve these properties of Co-Zn ferrites, Mg is doped. Dielectric constant, dielectric loss and coercivity of these materials increased with Mg doping. From dielectric and magnetic data, we conclude that these materials will perform well for microwave absorption applications [17]. Also by increment of Co in the samples, the magnetic properties are enhanced [18]. Mg doped Co-Zn ferrites have a spinel structure in which Co^{+2} and Mg^{+2}ions occupy octahedral locals, Zn^{+2} occupy tetrahedral locals and Fe^{+3} ions are conveyed amongst tetrahedral and octahedral sites. The interaction between Fe^{+3}, Zn^{+2} and Co^{+2} ions as well as their substituted metal cations dopants allows the changes in magnetic and electric properties of nano ferrite [19].

2. Experimental procedure

2.1 preparation of materials

For the preparation of ferrites nano-particles, firstly stoichiometric amount of zinc nitrate hydrated ($Zn(NO_3)_2.6H_2O$), iron nitrate hydrated ($Fe(NO_3)_3.9H_2O$), cobalt nitrate hydrated ($Co(NO_3)_2.6H_2O$) and magnesium nitrate hydrated ($Mg(NO_3)_2.6H_2O$) were dissolved in ethylene-glycol with continuous stirring for 30 minutes at room temperature to get uniform solution. Molar ratio of ethylene-glycol to precursor salts was kept at 56:1. Then the temperature of the solution was raised to 80 ^oC with continuous stirring until a thick gel was formed. Temperature of the gel was then raised to 350 ^oC such that the gel burns slowly and changes into fine powder [1]. The powder was grinded by mortar and pestle. Some of the powder was compacted into pallets. These pallets were used for different characterizations. The pallets are formed by hydraulic press. The resulting powder and pallets are then annealed at 700 ^{o}C for 3 hours and again characterized to compare the results of as prepared samples and annealed samples.

2.2 Structural properties

The structural properties of the synthesized samples were studied by using X-ray diffraction techniques (XRD). XRD plots of an un-sintered sample and samples sintered at 700 ^{o}C are given in figure 1. XRD pattern of un-sintered sample shows broader peaks with less intensity depicting smaller crystallite size with poor crystallinity. After sintering the samples, XRD patterns become sharper and narrower showing improved crystalinity and increased crystallite size. All the XRD peaks are indexed with standard patterns for Co-Zn ferrites confirming single spinal phase for the prepared samples.

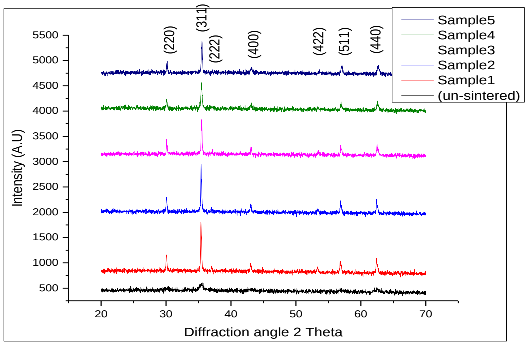

Fig. 1. XRD plots of prepared samples.

Table 1. Crystallite size and lattice constant of the samples.

Sample	Crystallite size (nm)	Lattice constant a(Å)
$Co_{0.5}Zn_{0.5}Fe_2O_4$	20.67	7.097
$Co_{0.5}Zn_{0.4}Mg_{0.1}Fe_2O_4$	11.24	7.136
$Co_{0.5}Zn_{0.3}Mg_{0.2}Fe_2O_4$	6.35	7.129
$Co_{0.5}Zn_{0.2}Mg_{0.3}Fe_2O_4$	6.35	7.127
$Co_{0.5}Zn_{0.1}Mg_{0.4}Fe_2O_4$	12.46	7.112

The crystallite size was calculated from XRD data using most intense peak (3 1 1) using Deby-scherrer formula. Lattice constant and crystallite size calculated from XRD data is given in Table 1.

The particle size was investigated by using Scanning Electron Microscope. A characteristic SEM micrograph of a sample is shown below in Fig. 2.

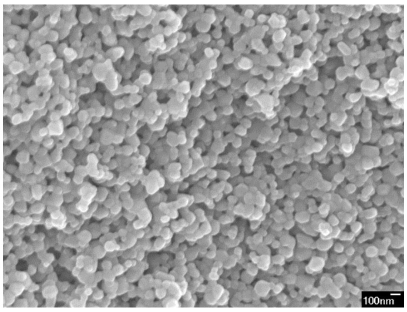

Fig. 2. Characteristic SEM image of the sample $Co_{0.5}Zn_{0.1}Mg_{0.4}Fe_2O_4$ sintered powders.

The average particle size found by using SEM is around 100 nm. SEM image show narrow size distribution of the particles.

2.3 dielectric properties

The dielectric constant of different Mg doped Co-Zn nanoferrite samples were determined using LCR meter having frequency ranges from 20 Hz to 3MHz at room temperature. Variation of dielectric constant at low frequency is shown in figure 3(a). It is observed that dielectric constant decreases by increasing frequency and at further high frequency it becomes almost constant. This decrease in dielectric constant is due to decrease in interfacial polarization.

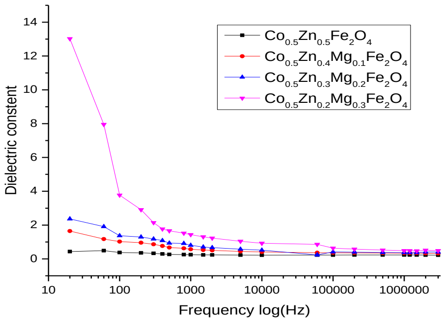

Fig. 3(a) : Dielectric constant at low frequency (MHz).

The variation of dielectric constant is explained on the base of space charge polarization. The exchange of electrons between $Fe^{+2} \leftrightarrow Fe^{+3}$ results into the local electrons displacement within the direction of applied electric field. The polarization decreased by increasing frequency and then reached a smaller value. This is due to the reason that above specific frequency of applied field, the electronic exchange between $Fe^{+2} \leftrightarrow Fe^{+3}$ cannot follow alternating field which results in the decrease of dielectric constant. Space-charge polarization is observed only at low frequency ranging (few Hz-KHz). Dielectric constant of the prepared samples increased with Mg doing. Also, with high values of dielectric constant, dielectric loss increases and penetration depth of electromagnetic waves decreases which are due to skin effect. After freeze out of space charge polarizations, next dominant contribution to dielectric constant is from ionic polarization.

Dielectric constant of different Mg doped Co-Zn nanoferrite samples was also determined in the frequency range from 1 MHz to 3 GHz using network analyzer and is shown below in the figure 3(b) & 3(c). Different polarization mechanisms are involved at high frequency of applied electric field, i.e, dipolar polarization, ionic polarization and electronic polarization. Orientation or dipolar polarization is seen due to orientation of dipoles under the application of electric field. Applied electric field aligns the dipoles and these dipoles results in the polarization of material. The dielectric constant of many dielectric materials depends on temperature. Debye explained dielectric constant of materials having permanent dipole moment.

Ionic polarization is due to the displacement of nucleus of ions which forms molecules. When molecules are formed by different atoms there is a polar bond. The distance between negative and positive ions changes due to applied field. This type of polarization involves changing in bond angle, bond length and bending of polar molecules with each other. Another contribution to dielectric polarization is from electronic polarization. Electronic polarization is due to the shift of electron cloud with respect to nucleus with the application of electric field. This field displaces center of electron cloud relative to nucleus and dipole moment is induced. Electronic charge is assumed to be distributed in the form of spherical cloud and is coincided with central nucleus. Under applied field charges experience electric force, this force cause negative charge cloud to displace relative to nucleus and so atom is said to be polarized. Each polarization mechanism has characteristic frequency called resonance frequency and when the frequency of the applied field increases beyond the resonance frequency, response of that particular polarization to the applied field freezes out and contribution of that particular polarization to dielectric constant vanishes [1].

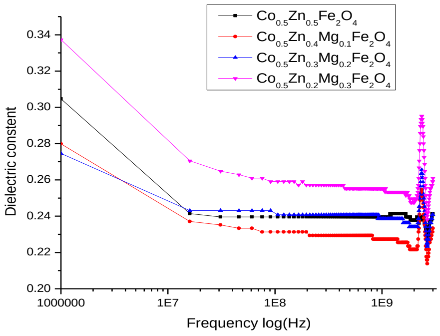

Fig. 3(b). Dielectric constant at high frequency (GHz).

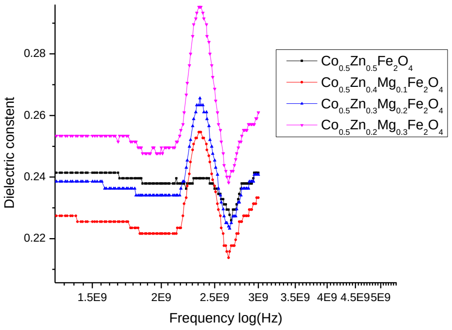

Fig. 3(c). Fluctuation of dielectric constant at high frequency.

Dielectric constant of the prepared samples increased with the Mg content. This may be due to the reason that Mg is more electropositive as compared to Zn ions therefore has stronger response of ionic and electronic polarization to the applied electric field. Also ionic radii of Mg^{+2} is larger than Fe^{+3} that is replaced at B- site. Larger ionic radii mean greater ionic polarizabilty. Greater electro positivity and larger ionic radii of Mg ions may be responsible for the increase in dielectric constant of these samples. Above resonance frequency there is a fluctuation in dielectric constant. Fig. 1(c) shows fluctuation of dielectric constant above resonance frequency. Because at resonance frequency the loss increases so peak grows upward. By adding Mg into the material, the dielectric constant fluctuates. Electrical conduction in these materials can also be explained by hoping electron model of Jhonstan and Heikes. From this model electron transfer in the adjacent octahedral sites in spinel structure. The displacement of electrons is in the direction of applied electric field. This displacement of electrons determines the polarization of the sample. Due to this polarization field inside the material reduced. So, the dielectric constant of material decreases by increasing frequency.

Dielectric constant for prepared samples at different frequency is given below in the Table 2.

Table 2. Dielectric constant for prepared samples at different frequency.

Frequency	$Co_{0.5}Zn_{0.5}Fe_2O_4$	$Co_{0.5}Zn_{0.4}Mg_{0.1}Fe_2O_4$	$Co_{0.5}Zn_{0.3}Mg_{0.2}Fe_2O_4$	$Co_{0.5}Zn_{0.2}Mg_{0.3}Fe_2O_4$
20 KHz	0.4331	1.6447	2.3662	3.0256
3MHz	0.2191	0.3227	0.4007	0.4878
1MHz	0.3047	0.2313	0.2408	0.2591
3GHz	0.2414	0.2333	0.2408	0.2610

2.4 Dielectric loss tangent (D)

Plot of dielectric loss tangent (D) for Mg doped Co-Zn nano-ferrites as a function of frequency at room temperature is shown in Fig. 4(a). The plot shows that ‘D’ decreases continuously by increasing frequency for all samples. It is expected that dielectric loss decreases inversely with frequency because space-charge polarization freezes out and only contribution to dielectric loss is due to ionic and electronic polarizations. Dielectric loss increased with the Mg concentration because of increase in dielectric constant with Mg concentration. When microwaves are incident on high dielectric loss materials, microwaves are lost as heat in the material therefore higher dielectric loss is desired for such applications.

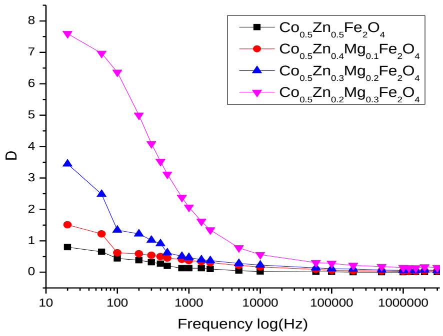

Fig. 4(a). Dielectric loss tangent at low frequency (MHz).

Dielectric loss tangent at frequency range of 1 MHz to 1.5GHz was studied as a function of frequency. Also Mg doping increases crystal field which results in dielectric loss.

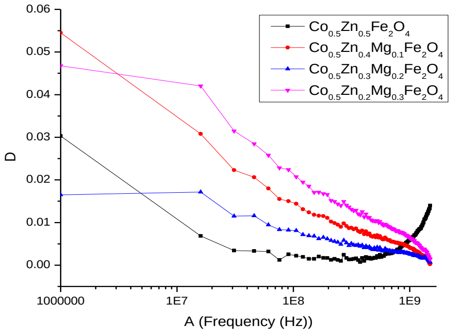

Fig. 4(b). Dielectric loss tangent at high frequency (GHz).

Dielectric loss tangent for prepared samples at different frequency is given below in the table.

Table 3. Dielectric loss tangent for prepared samples at different frequency.

Frequency	$Co_{0.5}Zn_{0.5}Fe_2O_4$	$Co_{0.5}Zn_{0.4}Mg_{0.1}Fe_2O_4$	$Co_{0.5}Zn_{0.3}Mg_{0.2}Fe_2O_4$	$Co_{0.5}Zn_{0.2}Mg_{0.3}Fe_2O_4$
20 KHz	0.8000	1.5100	3.4500	7.6000
3MHz	0.0080	0.0370	0.0600	0.1500
1Mhz	0.3047	0.2799	0.2746	0.3373
1.5GHz	0.2414	0.2255	0.2356	0.2534

3.5 Magnetic properties

The magnetic measurements of prepared samples are determined by using vibrating sample magnetometer having applied field range of -10 to +10 KOe. Hysteresis loops shows the variation of saturation magnetization M_s with applied magnetic field H of synthesized nano-crystalline samples. The obtained hysteresis plots are depicted in figure 5. Plot shows that the saturation magnetization decreased with Mg^{+2} concentrations. When Zn^{+2} is replaced by Mg^{+2}, the magnetic properties like saturation magnetization and coercivity changes. It is observed that the saturation magnetization of samples decreased by increasing Mg content in the material. These ferrites are ferrimagnetic in nature and net magnetization arises from the difference between the magnetic moments at B and A sites. Mg^{+2} and Zn^{+2} ions are both non-magnetic in nature [20] and Zn^{+2} ion prefer A site while Mg^{+2} ion prefer B site. When Zn^{+2} ion is replaced with Mg^{+2} ion, it force Fe^{+3} ion already present at B site to migrate to A site resulting in decrease of the net magnetic moment i.e., total magnetic moment at B site minus total magnetic moment at A site, hence saturation magnetization decreases. Hysteresis plot also shows that coercivity is increased by increasing Mg concentration in the samples due to larger magnetic moment at A site and hence stronger coupling between A and B sites [21]. Larger coercively means higher magnetic losses that make this material suitable for microwaves absorption.

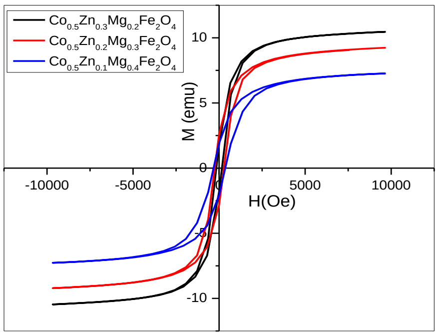

Fig. 5. Hysteresis curves for $Co_{0.5}Zn_{0.3}Mg_{0.2}Fe_2O_4$, $Co_{0.5}Zn_{0.2}Mg_{0.3}Fe_2O_4$ and $Co_{0.5}Zn_{0.1}Mg_{0.4}Fe_2O_4$ nano-crystalline samples.

Saturation magnetization, coercivity and retentivity for the synthesized samples are given below in the Table 5.

Table 4. Saturation magnetization, coercivity and retentivity.

	$Co_{0.5}Zn_{0.3}Mg_{0.2}Fe_2O_4$	$Co_{0.5}Zn_{0.2}Mg_{0.3}Fe_2O_4$	$Co_{0.5}Zn_{0.1}Mg_{0.4}Fe_2O_4$
Saturation magnetization (emu)	10.465	9.2268	7.2717
Coercivity (Oe)	160.97	255.94	322.27
Retentivity (emu)	1.7821	2.5862	1.8814

4. Conclusions

The samples synthesized by sol-gel method have single phase spinal structure and all the XRD peaks of cubic crystal system corresponding to space group Fd-3m were indexed with the standard pattern for $ZnFe_2O_4$ reported in ICDD PDF card # 00-023-1119. The dielectric constant and dielectric loss tangent of the prepared samples increased with the increase of Mg doing. Saturation magnetization decreased while coercivity increased with the Mg concentration. It is observed that with the Mg doping, the desired dielectric and magnetic properties of the prepared samples improved for microwave absorption applications.

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References

[1] S. Nasir, G. Asghar, Muhammad, Ali Malik, M. Anis-ur-Rehman, J. Sol-Gel Sci. Technol. **59**, 111 (2011).
[2] S. Nasir, A. S. Saleemi, Fatima-tuz-Zahra, M. Anis-ur-Rehman, Journal of Alloys and Compounds **572**, 170 (2013).
[3] L. Thourel, Translated By J. B. Arthur, 1964, Pergamon Press Oxford, London.
[4] R. M. Rosnan, Z. Othaman, R. Hussin, Ali A. Ati, Alireza Samavati, Shadab Dabagh, Samad Zare. Chin. Phys. B **25**, 047501 (2016).
[5] Mamilla Lakshmi, Katrapally Vijaya Kumar, Krishnan Thyagarajan, Advances in Materials Physics and Chemistry **6**, 141 (2016).
[6] Ritu Rani, Sangeeta Thakur and M.Singh, AIP Conf. Proc. **1349**, 287 (2010)
[7] M. H. Abdullah, A. N. Yusoff, Journal of Alloys and Compounds **233**, 129 (1996).
[8] S. Daliya Methew, Ruey-Shing Jaung, Chemical Engineering Journal **129**, 51 (2007).
[9] Ritu Rani, S. K. Sharma, K. R. Pirota, M. Knobal, Sangeeta Thakur, M. Singh, Ceramics International **38**, 2389 (2012).
[10] P. B. Rao, K. H. Rao, Journal of Materials Science Letters **22**, 1607 (2003).
[11] C. Sujatha, K. V. Reddy, K. S. Babu, A. R. C. Reddy, K. H. Rao. Ceramics International **38**, 5813 (2012).
[12] A. Ghosh, Retwik Sarkar, B. Mukharjee, S. K. Dass. Journal of European ceramic society **24**, 2079 (2004).
[13] Biju Thangjam, Ibetombi Soibam, International Journal of Applied Engineering Research ISSN 0973-4562, 13201 (2017).
[14] K. M. Shobana, S. Sankar, Journal of Magnetism and Magnetic Materials **321**, 599 (2009).
[15] D. Visinescu, C. Paraschiv, A. Lanculescu, B. Jurca, B. Vasila, O. Carp, Dyes and Pigments **87**, 125 (2010).
[16] Vithal Vinayak, Pankaj P. Khirade, Shankar D. Birajdar, P. K. Gaikwad, N. D. Shinde, K. M. Jadhav, International Advanced Research Journal in Science, Engineering and Technology **2**, 2015.
[17] V. G. Patil, S. E. Shirsath, S. D. More, S. J. Shukla, K. M. Jadhav, J. Alloys and Compds. **488**, 199 (2009).
[18] M. T. Jamila, J. Ahmad, S. H. Bukharia, T. Sultan, M. Y. Akhter, H. Ahmadd, G. Murtaza, Journal of Ovonic Research **13**, 45 (2017).
[19] S. Bhukal, S. Bansal, S. Singhal. Solid State Phenomena **232**, 197 (2015).
[20] S. F. Mansour, Egypt. J. solids **28**(2), 2005.
[21] A. Manikandan, J. J. Vijaya, M. Sundararajan, C. Meganathan, L. J. Kennedy, M. Bououdina, Super lattices and Microstructures **64**, 118 (2013).