Synthesis and Characterizations of Group II-IV 0D Nanoferrites by Sol-Gel Method

Jayapriya J and Seenuvasakumaran P
PG department of Physics, Muthurangam Government Arts College (Aut),
Vellore 632 002, Tamil Nadu, India,
Corresponding Author: rpyeskay@gmail.com

Abstract:= **Recently, Nano material ferrites have applications in making cores of high frequency transformers, coils, chokes, permanent magnets, magneto optical displays, microwave absorbers, high density information storage, color imaging etc. In the present investigation CadmiumZincStrontium nanoferrites ($CdZnSrFe_2O_4$) and CadmiumZincBarium nanoferrites ($CdZnBaFe_2O_4$) are synthesized by Sol-Gel method. These synthesized ferrites are characterized by X-ray diffraction (XRD), FTIR, UV–VIS spectroscopic techniques and Scanning Electron Microscopy (SEM). The crystalline nature and the structure of the synthesized nanoferrites are confirmed from X-Ray diffraction analysis. The ferrite powders showed XRD line broadening peaks and the average particle size of the materials is calculated using Scherer formula. The strain (ε) and dislocation density (δ) of the materials are also calculated from XRD data. The optical band energy (E*g*) at the edge of absorption band has been determined by the Tauc relation using UV-VIS spectroscopic data. The magnetic properties are studied using Vibrating Sample Magnetometer at room temperature and it is found that this study shows a soft super paramagnetic behavior of the synthesized ferrites. This significant property allows this type of ferrites can be used in fabrication of magnetic and energy storage media.**

Key words: Sol-Gel, nanoferrites, Tauc relation, strain, dislocation density.

I. INTRODUCTION

Ferrite materials have significant importance because of their large number of technological applications. Ferrites are superior magnetic materials which are widely used in microwave and electrical industries. The most significant and popular usage of ferrites are in optics, electronics, mechanics and other technical fields [1], also used in chlorine gas sensors (2), high density information storage (3), color imaging (4), bioprocess (5), medical diagnosis (6), electromagnetic wave absorption, (7) etc. Some interesting applications of these materials include small permanent magnets, magnetic media used in computers, recording devices, magnetic cards etc [8]. Recently, one of the challenges is to improve the magnetic properties of soft ferrites such as saturation magnetization, magnetic hysteresis, demagnetizing force and anisotropic energy [9].

These applications depend on selection of materials to form nanomaterials mostly from group II elements and IV semiconductors such as Cd, Zn, Ba, Fe, Sr, S, can be used. Nano-cadmium ferrite ($CdFe_2O_4$) is a normal spinel ferrite that can be applied in various fields [10, 11, 12]. In this paper, $CdZnBaFe_2O_4$ and $CdZnSrFe_2O_4$ are synthesized using the sol-gel technique. This method gives enhanced homogeneity, better control for size, shape, and degree of agglomeration of the resulting nanocrystals, simple compositional control and low processing temperature. These characteristics, along with the chemical composition, are found to influence significantly the magnetic properties of nanoferrites. [13]

$CdFe_2O_4$ compounds were synthesized by the sol–gel method which has been already reported. Here we dope Zinc, Barium and Strontium elements to $CdFe_2O_4$ [10, 11]. So, the aim of this present work is to obtain CadmiumZincStrontium ferrites ($CdZnSrFe_2O_4$) and CadmiumZincBarium ferrites ($CdZnBaFe_2O_4$) Nanopowders by Sol-Gel method and compare their characteristics. The prepared nonmagnetic materials are characterized by using X-ray diffraction (XRD), Fourier transform infrared spectra (FTIR) and UV–VIS spectroscopic techniques. The magnetic properties are studied using Vibrating Sample Magnetometer and surface morphology is studied by using Scanning Electron Microscopy (SEM) techniques.

2.EXPERIMENTAL DETAILS

A. Synthesis of $CdZnBaFe_2O_4$ and $CdZnSrFe_2O_4$

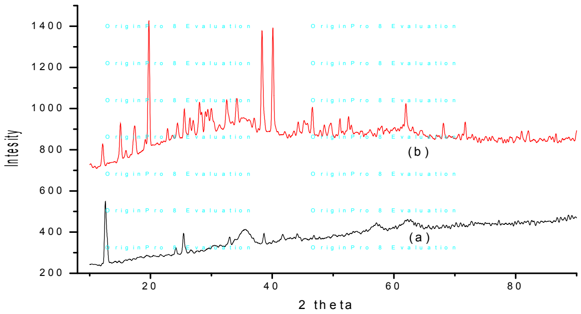
The analytical grade Fe $(NO_3)_3 \cdot 9H_2O$, Cd $(NO_3)_2 \cdot 4H_2O$, Zinc acetate [Zn $(CH_3COO)_2 .2H_2O$], Barium nitrate [Ba $(NO_3)_2$], isopropanol and acetic acid were used as precursor materials. In 1:2 stoichiometric ratios these precursors' are first dissolved in 100 ml of distilled water by continuous stirring for 3 hours to form a clear solution. 20 ml of isopropanol and acetic acid are added to the resulting clear solution, the stirring is continued for two hours. When these capping agents are added. They hooks on to the metal nano particles of certain size, they reach solubility limit, since the net charge on the metal particle is now controlled by the hooked up capping agent.

The solution was evaporated by intensive stirring and heating for 2 hours at 80 °C and kept at this temperature until the sol turned into a transparent gel. The gel was then heated at 80°C for 48 hours for auto-combustion to takes place. The resulting powder is crushed in an agate mortar to obtain the nanoferrites.

3.RESULTS AND DISCUSSION

A.XRD ANALYSIS

The crystalline phase of the $CdZnBaFe_2O_4$ and $CdZnSrFe_2O_4$ are conformed from the peaks obtained in the X-Ray diffraction with the wavelength λ=1.5406 A^0 as shown in figure 1.



.

Figure 1. XRD analysis of (a) $CdZnBaFe_2O_4$ and (b) $CdZnSrFe_2O_4$

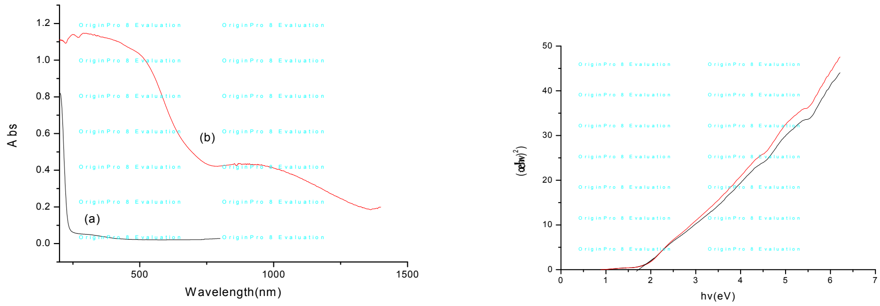
The broadened diffraction peaks in XRD indicates that the synthesized nanomaterial has very small size crystallites with poly crystalline nature. Using XRD, UV-Visible Spectroscopy data the following values of crystal size [14], Strain [15], Dislocation density [16] and Energy band gap [20] are found, as shown in table 1.

TABLE I

S. No	**PROPERTIES**	**$CdZnBaFe_2O_4$**	**$CdZnSr\ Fe_2O_4$**
1	Crystal structure & lattice parameters	Tetragonal a=5.8676 A^0, c=7.1470 A^0 $\alpha=\beta=\gamma=90^0$	Tetragonal a=9.8124 A^0, c=6.1530 A^0 $\alpha=\beta=\gamma=90^0$
2	Crystal Size (D)	13.27 nm	3.07 nm
3	Strain (ε)	1.2307	0.0658
4	Dislocation Density (δ)	$5.706X10^{-15}m^{-2}$	$1.059X10^{-17}\ m^{-2}$
6	Energy band gap Eg)	1.75 eV	1.75 eV

B.UV-VISIBLE SPECTRAL STUDY

Using UV-Visible spectrometer of model FP-8500, absorption spectrum was studied in the region 200-1400 nm at room temperature to analyze the optical absorption of the grown particles. The cut of wave lengths are found to be in visible region. Tauc plots are as shown in figure 2 for $CdZnBaFe_2O_4$ and $CdZnSrFe_2O_4$. The extended absorption wavelength towards the visible region and the increased absorption intensity indicates the increased formation of electron–hole pairs. This indicates that synthesized particles can be used for wide variety of nonlinear optical devices, semiconductor, electroluminescence devices, industrial catalysts, solar energy conversion devices etc.

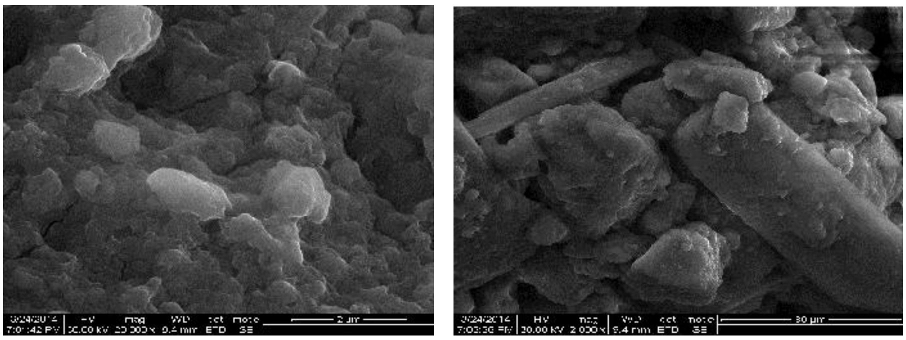


(a) **(b)**

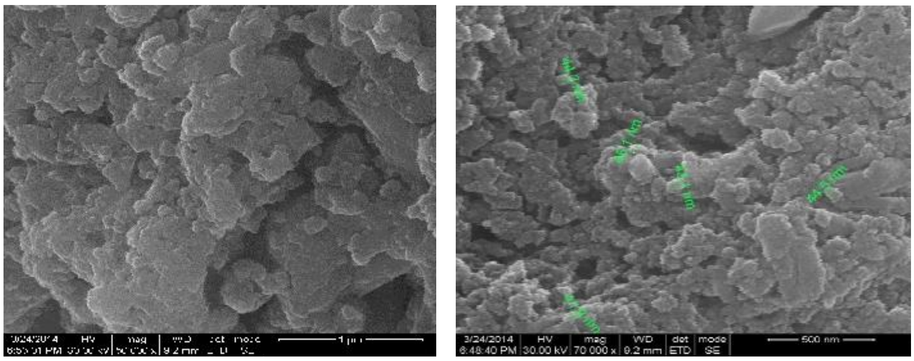
Figure 2.(a)Absorbance spectra of $CdZnBaFe_2O_4$ & $CdZnSrFe_2O_4$, (b) Plot of $(\alpha h\upsilon)^2$ vs $h\upsilon$ for $CdZnBaFe_2O_4$ and $CdZnSrFe_2O_4$

C.MORPHOLOGICAL STUDY:

The morphological studies of the nanomaterials have been carried out using scanning electron micrographs (SEM). Figure 3 shows the SEM images of $CdZnBaFe_2O_4$ and $CdZnSrFe_2O_4$ for different scale regions. The figure 3 (a) shows the SEM image of $CdZnBaFe_2O_4$ at 2µm and 30µm. The study of SEM micrographs reveals less number of pores with smaller lump size. Rod-like morphology is observed at 30 µm with discontinuous grain growth [21]. They have some Pinholes, cracks and spherical-like particles in 2 µm which aggregated to form larger rocky-stone like particles. The spherical particles are detected due to the surfactant effect. The figure 3(b) shows the SEM image of $CdZnSrFe_2O_4$ at 1µm & 5µm respectively. The surface morphology of the particles are Cauliflower like structure at 1 µm [22].Through the micrograph, we observe the formation of soft agglomerates with irregular morphology constituted the quite fine particles. The Sr doped specimens show a bi-phasic microstructure constituted of dark ferrite matrix grains and small whitish grain at the grain junction/boundary present in 500 µm respectively as, proposed by Sattar et, al [23,24]



(a)



(b)

Figure (3) SEM images of (a) $CdZnBaFe_2O_4$ for as 2 & 30 µm (b) $CdZnSrFe_2O_4$ for as 1 µm & 500nm

D. VIBRATING SAMPLE MAGNETOMETER – Study of Magnetic peroperties

The magnetic properties are studied using Vibrating Sample Magnetometer at room temperature is shown in figure. The various magnetic properties of them are listed in table II. Both the samples exhibit an excellent soft magnetic property with super paramagnetic behavior [25, 26].

Table II

S.NO	PROPERTIES	$CdZnBaFe_2O_4$	$CdZnSrFe_2O_4$
1	Coercivity	0.3317G	22.32G
2	Retentivity	$12.485X10^{-6}$ emu	$36.49X10^{-6}$ emu
3	Saturation magnetization	0.22765 emu	0.0214 emu.

The low coercive value indicates that particle can be easily magnetized without any flux loss but in $CdZnSrFe_2O_4$ has very few flux loss compared to $CdZnBaFe_2O_4$. This significant property allows this type of ferrites can be used in fabrication of magnetic storage media and also Ferrites, typically spinel ferrite and magnetoplumbite ferrite, can be used as recording materials, microwave devices, humidity sensors, pigments etc. Compared with spinel ferrite, magneto plum-bite ferrites, strontium ferrite have attracted more scientific research in recent years due to their high uniaxial magnetic anisotropy, high saturation magnetization and high coercivity. [25,26]

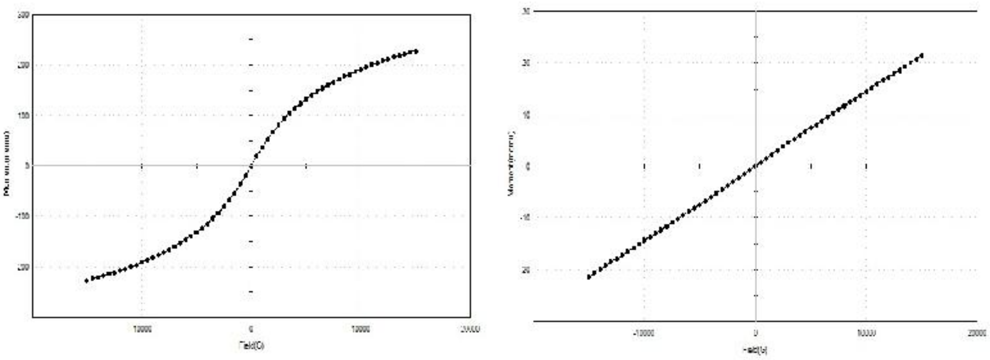


Figure 4. VSM study for (a) $CaZnBaFe_2O_4$, (b) $CdZnSrFe_2O_4$nanoferrites

4. Conclusions

$CdZnBaFe_2O_4$ and $CdZnSrFe_2O_4$ Nanoferrites have been synthesized successfully by sol-gel method. The crystalline nature of the ferrite is evident by the peaks obtained in X- Ray diffraction analysis and they are grouped under tetragonal crystal system. The average particle sizes are found to be 3.07 nm for $CdZnBaFe_2O_4$ and 13.27 nm for $CdZnSrFe_2O_4$ respectively using Scherer formula. The strain (ε) values are 1.2307 for $CdZnBaFe_2O_4$ and 0.0658 for $CdZnSrFe_2O_4$. The dislocation densities of CdZnBaferrite and CdZnSrferrites are found to be $5.706X10^{-15}$ and $1.059X10^{-17}$ m^{-2} respectively. The different functional groups are conformed by Fourier Transform Infra-Red Spectroscopy. The optical energy band gap (E*g*) for both ferrites at the edge of absorption band has been determined as 1.75 eV by the Tauc relation using UV-VIS spectroscopic data. This result indicates that these ferrites have semiconducting property. The surface morphology is studied from Scanning Electron Microscopy. The synthesized nanoferrites belong to the group of soft ferrites which is confirmed from VSM data. The low coercivity value from the hysteresis shows super paramagnetic behavior in the synthesized nanoferrites. The increased retentivity allows that they can be used in magnetic storage media.

REFERENCE

1. Xue B, Liu R., Xu Z D Zheng, Y F. 'Microwave Fabrication and Magnetic Property of Hierarchial Spherical Fe_2O_3 Nanostructures Chemistry Letters **37** (10) 2008 pp. 1058 – 1059.

2. Y L N Murthy, I V KasiViswanath, T. KondalaRao, Rajendrasingh Synthesis and characterization of Nickel Copper Ferrit*e*, **1** No 4 pp. 1308-1311 Oct-Dec 2009
3. Gopalreddy C V, Manorama S V, and Rao V J, Semiconducting gas sensor for chlorine based on inverse spinel Nickel ferrite. Sensors and Actuators B 1999 55(1**)** 90-95**.**
4. S.N. Dolia, Role of Particle Size on Structural and Magnetic Behavior of Nanocrystalline Cu-Ni Ferrite, Solid State Phenomena, 2011 **171** 79-91
5. Nixon L, Koval C A, Noble R D, SlaffG S, Preparation and characterization of novel magnetic coated ion exchange particles, Chem. Mater. **4** 1992 117
6. Mac Michael R.D, Shull R.D, SwartzendruberL J, Watson R.E, Magneto caloric effect in super paramagnets J. Magn. Mater. 1992 **111** 29-33.
7. Bulte J W M, Magneto ferritin, Characterization of novel super paramagnetic M R contrast agent J. Magn.Reson. Imaging. **4** 1994, 497-505.
8. R K Swarnkar, S C Singh and R Gopal Effect of aging on copper nanoparticles synthesized by pulsed laser ablation in water structural and optical characterizations Bull. Mater. Sci. **34** No. 7 December 2011, pp. 1363–1369. © Indian Academy of Sciences
9. D Carta, M F Casula, P Floris, A Falqui, G Mountjoy, A Boni, Y C Sangregorio and A Corrias, Synthesis and microstructure of manganese ferrite colloidal nanocrystals Chem. Phys **12** 2010 , 5074–5083
10. S M Ismail, Sh Labib, and S S Attallah Preparation and Characterization of Nano-Cadmium Ferrite Journal of Ceramics 2013 (2013) Article ID 526434 8 pages
11. P K Nayak, Synthesis and characterization of cadmium ferrite, Materials Chemistry and Physics **112** no. 1 pp. 24–26 2008.
12. Desai, R. V Mehta, R. V Upadhyay, A Gupta, A Praneet and K V Rao Bulk magnetic properties of CdFe2O4 in nano-regime, Bulletin of Materials Science, **30** no. 3 pp. 197–203, 2007.
13. Ismail Ab Rahman1 and Vejayakumaran, Synthesis of Silica Nanoparticles by Sol-Gel Size-Dependent Properties, Surface Modification, and Applications in Silica-Polymer nanocomposites Journal of Nanomaterials **2012** (2012) Article ID 132424, 15 pages.
14. K Manickathai, S Kasi Viswanathan and M Alagar Synthesis and Characterization of CdO and CdS nanoparticles. **46** 2008 pp.561-564
15. Wasi Khan, Z A Khan, A A Saad, S Shervani, A Saleem, A H Naqvi, Synthesis and Characterization Of Al Doped ZnO Nanoparticles. **22** (2013) 630–636.
16. TBanerjee M., Chongad L and Sharma A. Structural and Optical Properties of Pure and Copper Doped NiS Nanoparticles Research Journal of Recent Sciences **2** (ISC-2012) 326-329 (2013)
17. F A Lopez, A Lopez-Delgado, J L Martin de Vidales, E Vila, Analysis Of FTIR Spectra Of Nanoparticles J Alloys Compds. 1998, 265 291.
18. Harisingh Nalwa (Ed), Handbook of nanostructured materials and nanotechnology (Academic Press, NewYork), 2000.
19. Marykutty Thomas, K. C. George, Infrared and magnetic study of nanophase zinc ferrite Indian Journal of Pure & Applied Physics. **47** 2009, 81.
20. Wasi Khan, Z. A Khan, A A Saad, S Shervani, A Saleem, A H Naqvi, Synthesis and Characterization Of Al Doped Zno Nanoparticles**. 22** (2013) 630–636.
21. R M Sangshetti, V A Hiremath and V M Jali, Combustion synthesis and structural characterization of Li–Ti mixed nanoferrites Bull. Mater. Sci, **34**, No. 5 August 2011 pp. 1027–1031 Indian Academy of Sciences.
22. T Theivasanthi, N Kartheeswari and M Alagar**,** Chemical Precipitation Synthesis of Ferric Chloride Doped Zinc Sulphide Nanoparticles and Their Characterization Studies. Research gate, 03/2013, DOI 10, 7598/cst 2013.207.
23. A A Sattar et.al, Rare Earth Doping Effect on the Electrical Properties of Cu-Zn Ferrites, [J] J. Phys. IV France **7**. 1997
24. K Muthuraman, S Alagarsamy, M Ameena Banu, Vasant Naidu, Synthesis of Nano sized Ce-Co Doped Zinc Ferrite and their Permittivity and Hysteresis Studies. International Journal of Computer Applications (0975 – 8887) **32** No.3 October 2011 18.
25. Ilmārs Zālīte, Gundega Heidemane, Māris Kodols, Jānis Grabis, Mikhail Maiorov, The Synthesis, Characterization and Sintering of Nickel and Cobalt Ferrite Nanopowders. Materials Science **18** No. 1 2012.
26. Shama Rehman , A Mumtaz , S K Hasanain, Size effects on the magnetic and optical properties of CuO nanoparticles J Nanopart Res (2011) 13:2497–2507 DOI 10.1007/s11051-010-0143-8.