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SYNTHESIS AND CHARACTERIZATION OF COBALT SUBSTITUTED W TYPE HEXAGONAL FERRITES

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In this work W type hexagonal ferrites with chemical composition $Sr_{1-x}Cr_xCo_2Fe_{16}O_{27}$(x= 0.0, 0.02, 0.04, 0.06, 0.08, 0.1) were synthesized by sol gel auto combustion method. Annealing of the samples was done at 1200 C for 8 hours. Structural and optical properties and grain morphology of the synthesized samples were studies through X-Ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), Ultraviolet visible spectroscopy techniques and scanning electron microscope (SEM). XRD analysis confirmed that all samples exhibited hexagonal W-type single phase crystalline structure at temperature range of 1200°C with no impurity phase. The estimated grain size from SEM images is in the range of 76-139 nm that confirms nanocrystalline structure of samples with hexagonal structure. The FT-IR spectral analysis exhibited that absorption band occurred in ranging from 450 cm^{-1} to 650 cm^{-1}. Evidence of successful formation of hexaferrites was revealed by FTIR spectra of prepared samples. The existence of metal oxygen bond at octahedral site and tetrahedral site confirms that all fabricated samples exhibit W-type hexagonal ferrites. Optical characteristic of $Sr_{1-x}Cr_xCo_2Fe_{16}O_{27}$ analyzed by UV-Visible spectroscopy. The absorption spectra of synthesized nanoparticles of W-type recorded in range of wavelength 300 to 800 nm. This spectroscopy is significant in exploration of materials electronic properties. W-type hexagonal ferrites are suitable for high frequency application such as microwave devices.

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1. Introduction

Ferrites have attracted more and more attention since their discovery. These are considered best magnetic materials due to lower cost, fabrication and resistivity characteristics [1, 2] Ferrites are widely utilized in microwave devices, satellite communication, computer memory cores, bubble devices, digital recording, permanent magnet, audio video recording radar and electrical devices[3, 4]. Ferrites has immense implication from microwave device to radio frequency[5]. It is utilized for insulator, phase shift moderators, ultrasonic generator, mechanical filter, antenna cores of radio receiver[5]. In these days ferrite is utilized in control equipment, telephone exchange and computers [2, 6]. There are many ferrites which form crystallize shape in hexagonal arrangement, and few have attained appreciable technological importance. These hexagonal ferrites can be classified into U, W, X, Y, M and Z-type compounds. They have different although related structures[7].

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W type hexagonal ferrites are promising candidates due to their interesting magnetic properties and have wide range of applications in different fields of life. W-type hexaferrites have common formula of $BaMe_2Fe_{16}O_{27}$ where Me represents generally transition metal or any divalent cation. The first presented W-type Fe_2W but at structure of hexagonal of single phases. It was observed that the c-axis is the easy axis in W type hexaferrites[8-10]. All W-type hexaferrites show uniaxial anisotropy out of ferrites of Co_2W having molecular mass 158g density 5.31g/cm^3 from $273\,℃-180℃$ exhibit anisotropy move to c-axis rise of temperature 280℃ and become unixial. In the crystal structure of W type hexaferrites there is alternate stacking of spinel and R blocks in the hexagonal C axis direction. Hexagonal ferrites have two S blocks and one R block and is quite similar to M-type configuration, however actually not same. In research laboratories of Philips in 1980 W-type hexaferrites $MBaMe_2Fe_{16}O_{27}$ (Me_2W) were investigated magnetic moderate characteristics, high coercivity, high magnetic product and anisotropy [11]. The spinel block in W type hexaferrite is two times thick as compared to M type Along the c axis these blocks are arranged as $RSSR^*S^*S^*$. Physical properties depend on many factors for example quantity of substitution, sintering temperature synthesis technique and composition[12] . Magnetic properties of the hexaferrites can be improved by the suitable substitution of different divalent cations. Several techniques have been used for the preparation of W type Sr hexaferrite, the most frequently used method on industrial level is ceramic method. But material is inhomogeneous at microlevel by the ceramic method. Other techniques are as coprecipitation method, solid state reaction method sol gel method. Out of these sol gel method is a best technique, Sol-Gel method have many advantages involving control of stoichiometry of precursor solution tailor able microstructure, relatively low annealing temperature, coating deposition on large area substrates and inexpensive and simple equipment.

2. Experimental procedures

2.1. Sol-gel Method

Sol-gel process is a flexible solution method for making sophisticated material involving organic, inorganic and ceramics materials. In last few years progress was formed with commercialization and development of this technology and it is one of most optimistic production technique in nanotechnology[13]. The sol-gel method includes the transformation of solution from liquid sol into solid gel phase. The obstacle of commercialization of sol-gel technology is lack of standardization. Sol-Gel method have many advantages involving control of stoichiometry of precursor solution tailor able microstructure, relatively low annealing temperature, coating deposition on large area substrates and inexpensive and simple equipment[14].

2.2. Preparation of the material by sol gel auto combustion method

W type hexagonal ferrites with composition $Sr_{1-x}Cr_xCo_2Fe_{16}O_{27}$ were prepared by the sol gel auto combustion method. First of all stoichometric amounts of metal nitrates and chlorides were weighted and dissolved in distilled water then mixed with each other to get a homogeneous solution. Citric acid was used as chelating agent[15]. In order to keep the solution neutral ammonia solution were also added. The molar ratio of the metal ions to citric acid was 1:1. The solution was evaporated at a temperature of about 70-80 C for 3-4 hours under constant stirring to form a gel type and the solution appeared to be brownish gel. Gel is heated to convert into fluffy loose powder. Samples were grinded in mortar and pestle for 20 minutes to form fine powder. To avoid the any chances of contamination mortar pestle was washed with the help of detergent and ethanol and then dried in oven. After grinding samples were annealed at 1200℃ for 8 hours.

3. Results and discussions

The structure of the prepared samples was identified by X ray diffraction measurements by using the Cu-K_α radiation source. FTIR were carried out using FTIR spectrometer in the range of $4000cm^{-1}$ to $400cm^{-1}$. Surface morphology was exhibited by scanning electron microscope (SEM). Optical properties were done by UV-Visible spectroscopy.

3.1. X-ray diffraction (XRD) analysis

X-ray diffraction technique is utilized to identify and inspect the samples state what hexagonal type either it crystalline, semi crystalline or amorphous in nature. The purity phase is recognized by XRD. The X-ray diffraction patterns of pure and Substituted W-type hexagonal ferrite samples of chemical composition $S_{1-x}Cr_xCo_2Fe_{16}O_{27}$ (x = 0.0, 0.02, 0.04, 0.06, 0.08, 0.1) are shown in Fig. 1.

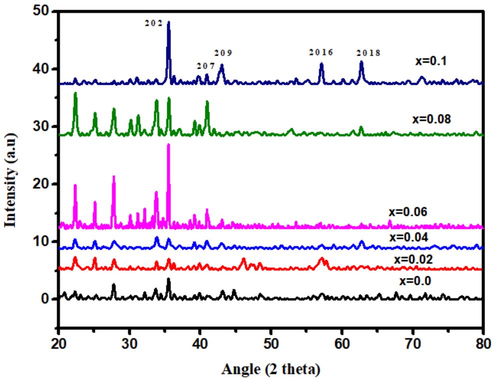

Fig. 1. XRD pattern of W type $Sr_{1-x}Cr_xCo_2Fe_{16}O_{27}$*(x= 0.0, 0.02, 0.04, 0.06, 0.08, 0.1) hexaferrites.*

It is investigated that all samples show single phase hexagonal W-type structure. The diffraction peaks which are observed are matched to the standard patterns. Any characteristics peak because of impurities is not detected in X-ray diffraction patterns of samples. So it shows that single phase samples are formed. Lattice parameters were measured by following equation (1),

$$1/d^2 = 4/3(h^2+hk+k^2) + (l^2/c^2) \tag{1}$$

Here a, c are lattice constants, d is interplaner spacing, hkl are miller indices. Debye scherer formula is used to calculate crystallite size by equation (2),

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{2}$$

D is the average size of crystallites, lambda is radiation wavelength, β is the peak width. Cell volume is calculated from values of (a) and (c) using following relation by equation (3),

$$V = a^2 c \sin 120° \tag{3}$$

It is observed that lattice parameters calculated values for unsubstantiated sample 32.89A° and 5.91A° that are in agreement with similar structure [16]. With increasing of dopants lattice parameters were altered, while lattice type unaltered. Peak intensity varies with the doping element. It is because of lattice sites occupation with substituted ions of varying ionic radius. By adding cations into crystal structure haxaferrite strontium shrinks the crystal lattice and decrease lattice parameters. So the distance among crystal planes decrease, then according to the Bragg's equation diffraction move to the higher angle [1]. It is evident that both lattice parameters decrease with the increase of Cr^{3+} contents (x). The decrease in lattice contents with increase of Cr^{3+} is because of higher ionic radii of with Cr^{+2} than Sr^{+2} [17]. The crystalline size is found in the range of 22nm to 38nm as shown in Table.1. And Fig. 2.

Table 1. Lattice constant, c/a ratio, cell volume V_{cell}, crystallite size of the hexaferrites.

X	**a(A^0)**	**c(A^0)**	**c/a**	**V_{cell} (A^0)^3**	**D(nm)**
0.0	5.91	32.89	5.56	994	23.70
0.02	5.90	33.36	5.65	1005	38.79
0.04	5.85	32.94	5.63	976	25.57
0.06	5.92	32.86	5.55	997	24.76
0.08	5.87	33.01	5.62	985	35.24
0.1	5.78	32.84	5.68	950	22.36

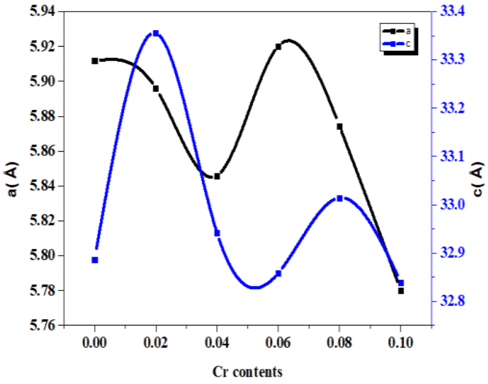

Fig. 2. Lattice constant a and c of the $Sr_{1-x}Cr_xCo_2Fe_{16}O_{27}$(x= 0.0, 0.02, 0.04, 0.06, 0.08, 0.1) hexaferrite magnetic powders.

3.2. Fourier transform infrared spectroscopy (FTIR) spectroscopy

The fourier transform infrared spectra of W-type hexagonal ferrites $Sr_{1-x}Cr_xCo_2Fe_{16}O_{27}$ (x=0.0,0.02,0.04,0.06,0.08,0.1) of sintered sample shown in following Fig. 3, the range of the wave number is from 400cm^{-1} to 4000cm^{-1}. After sintering the samples at 950℃ for 8 hours, absorption bands are investigated, however all the other characteristics peaks by substance were disappeared. The undoped sample exhibits absorption bands appearing at about 468cm^{-1} and 557cm^{-1} that is differentiated as respectively high frequency and low frequency band. The sample of composition x = 0.04 showing absorption band at about 455cm^{-1} and 570 cm^{-1}. The sample of composition x=0.08 exhibiting absorption band at about 473cm and Absorption bands from wave number 450cm^{-1} to 600cm^{-1} are the characteristic behaviour of all of the ferrites. The unsintered sample spectrum exhibits absorption bands peaks at 3450cm^{-1}. These peaks appears because of O-H stretching vibration as water exist in sample during fabrication, carbonates anti-symmetrical vibration at 1576cm^{-1}, stretching vibration of N-O of nitrates is at 1378cm^{-1}, stretching vibrations of metal oxygen at about 574cm^{-1} due to existence of α-Fe_2O_3 of as prepared sample. It is observed that sintered sample exhibits no absorption bands of nitrates, carbonates and O-H in sample. When powder is the sintered at temperature of 950℃, only absorption bands which are well resolved at about 430cm^{-1} and 582cm^{-1} are investigated. These bands appear due to tetrahedral complex and octahedral complex exist in hexagonal lattice [16].

The three well strong signals are appearing at about 430cm^{-1} to 590cm^{-1} which are corresponds to characteristic bands of $SrZn_2Fe_{16}O_{27}$. The bands are attributed to different ions vibration in crystal lattice. Two absorption bands appeared at about 430cm^{-1} can be categorized as higher frequency band and at 590cm^{-1} is lower frequency band. These two bands are tetrahedral complex group which is due to Fe^{3+}, O^{2-} band vibration and octahedral complex group due to Fe^{3+},

O^{2-} vibration exist in hexagonal ferrite. The third band of is at about 545cm^{-1} because of hexahedral group stretching vibration of the strontium bond along oxygen and all the W-type ferrites are known with this bond [1]. The IR spectrum was recorded was recorded using Fourier transform infrared spectrometer exhibiting absorption bands. The unsintered sample exhibits absorption bands around 546, 1387, 1624, 3449 cm^{-1}. The absorption bands around 1624cm^{-1} and 3449cm^{-1}peaks are because of O-H stretching vibrations of water mode. The band around 1387cm^{-1} exhibits stretching vibrations of N-O of nitrates ions, and the band around 546cm^{-1} because of iron oxygen bonds. The sintered sample at about 950℃exhibits absorption bands around 432cm^{-1} and 593cm^{-1} identified as stretching vibrations of metal oxygen of hexaferrites.

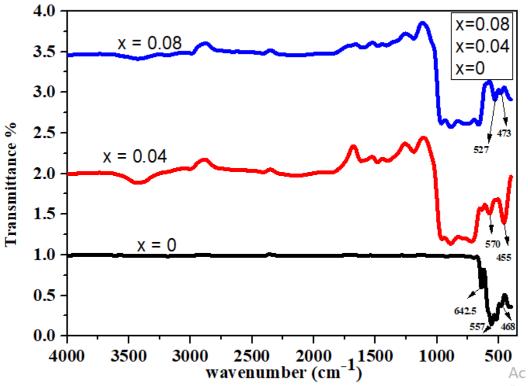

Fig. 3. FT-IR Analysis of $Sr_{1-x}Cr_xCo_2Fe_{16}O_{27}$ hexagonal ferrite at x=0, x=0.04, x=0.08.

3.3. UV-VIS Spectroscopy

UV-VIS spectroscopy is measurement of attenuation of light beam as it passes by sample or reflection from the surface of sample. Spectral range is approximately from 190nm to 900nm. This spectroscopy specifically attractive for the quantitative measurements. UV-Vis photons are the energetic for transition of electrons of to high energy states of materials and molecules. This spectroscopy is significant in exploration of materials electronic properties. This spectroscopy is divided in two categories, in characterization of electronic and optical properties of material and angle quantitative measurements in solid, liquid or gases.(Brain M. Tissue).Optical characteristic of $Sr_{1-x}Cr_xCo_2Fe_{16}O_{27}$ are analyzed by UV-Visible spectroscopy. The absorption spectra of synthesized nanoparticles of W-type recorded in range of wavelength 300 to 800 nm. It is observed from spectra that undoped hexagonal ferrite absorbs light below 650 nm. The samples with doping elements exhibit spectral red-shift up to nearly about 680 nm. As the concentration increases absorption spectra moves to higher wavelength. Energy of band gap can be measured from Tauc relation,

$$Ah\nu = B(h\nu\text{-}Eg)^n$$

Absorption spectrum is divided into three regions. (1) Weak absorption region is due to the impurities in samples. (2) Absorption edge appears due to lattice disorder. (3) strong absorption region give rise material band gap [18].

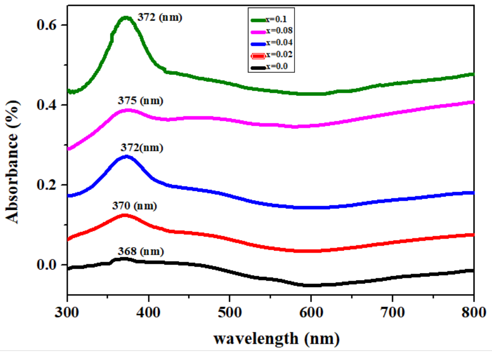

Fig. 4. UV-VIS Analysis of $Sr_{1-x}Cr_xCo_2Fe_{16}O_{27}$ hexagonal ferrite at x=0, x=0.02, x=0.04, 0.08, x=0.1.

3.4. Morphological analysis

Microstructure plays significant role in acquiring desired magnetic and dielectric characteristics of W-type hexagonal ferrites for microwave absorption implications. Fig. 5 exhibits morphology of hexagonal W-type ferrite samples. It can be investigated that morphologies changed from platelet like irregular structures of pure samples pyramidal, hexagonal platelet and irregular structures of substituted samples. Nanoparticles of strontium hexaferrite with the hexagonal platelet like and the hexagonal pyramidal structure are the potential materials used as radar absorption implications [1]. The estimated grain size from images of scanning electron microscope is in order of 139nm to 76nm that is considered in nanosized range. The outcomes exhibits that grain size was decreased of strontium based hexagonal ferrites after substitution of gallium (Ga^{3+}) ions. The decrease in the size of grain of gallium substitution is related with decrease in cell parameter [17-19]. The image of SEM of undoped specimen exhibiting crystallites of large size. Some nanoparticles of rice shaped were investigated of sample with composition having lower substitution, the size of the particle become smaller. The materials shape is most important for different applications and it is reported that rice shaped hexagonal ferrite is used in information storage, Raman scattering , catalysis and sensing [20-22]. The structure of platelet- like can be investigated in all samples. SEM micrographs exhibit that size of grain decreases by Cr^{3+} substitution. This is because of the fact Cr^{3+} ionic radius is less as compared to Sr^{2+} ionic radius. The size of the grain decrease with the increase in concentration of Cr^{3+} is due to that grain growth abnormality suppressed by lattice distortion.

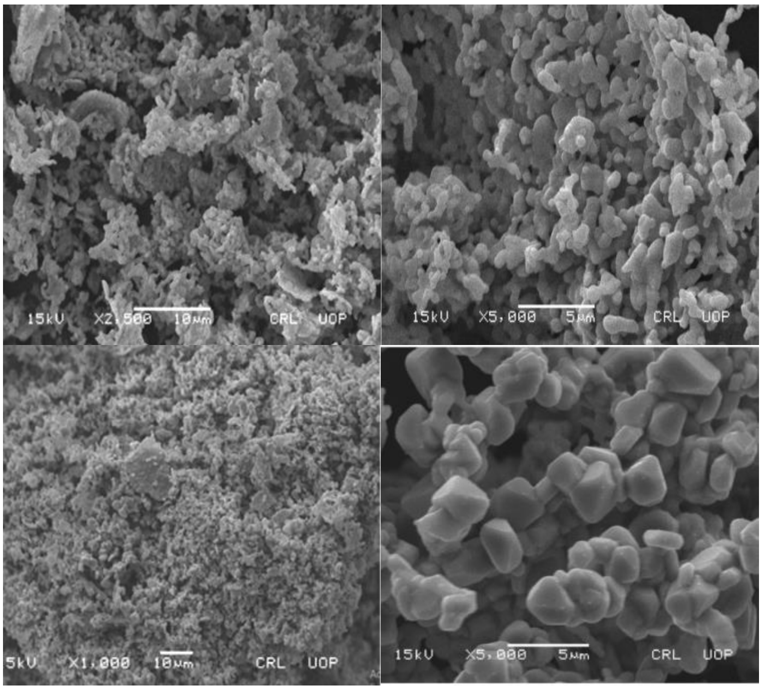

Fig.5. FESEM images of the w type hexaferrites $Sr_{1-x}Cr_xCo_2Fe_{16}O_{27}$ with (x=0.4,0.6,0.8,1.00).

4. Conclusions

Nanoparticles of hexagonal ferrites with chemical formula $Sr_{1-x}Cr_xCo_2Fe_{16}O_{27}$ (x= 0.0, 0.02, 0.04, 0.06, 0.08, 0.1) were synthesized by sol gel auto combustion method. Annealing of the samples was done at 1200°C for 8 hours. Structural and optical properties and grain morphology of the synthesized samples were interrogated through Fourier transform infrared spectroscopy (FTIR) and Ultraviolet visible spectroscopy and X-Ray diffraction (XRD) techniques. The FT-IR spectral analysis exhibited that absorption band occurred in range from 450 cm^{-1} to 650 cm^{-1}. Optical characteristic of $Sr_{1-x}Cr_xCo_2Fe_{16}O_{27}$ are analysed by UV-Visible spectroscopy. The absorption spectra of synthesized nanoparticles of W-type recorded in range of wavelength 300 to 800 nm.

This spectroscopy is significant in exploration of materials electronic properties. XRD analysis confirmed that all samples exhibited hexagonal W-type single phase crystalline structure with no impurity phase. Lattice parameters values have good agreement with reported earlier which confirm synthesis of W-type hexagonal ferrites. Evidence of successful formation of hexaferrites was revealed by FTIR spectra of prepared samples. The estimated grain size from SEM images is in the range of 139-76 nm that confirms nanocrystalline structure of samples. W-type hexagonal ferrites are suitable for synthesis of high frequency applications such as microwave devices.

References

[1] G. R. Gordani et al., Materials Research Bulletin **76**, 187 (2016).
[2] M. A. Iqbal et al., Ceramics International **38**(5), 3757 (2012).
[3] M. N. Ashiq et al., Journal of Magnetism and Magnetic Materials **324**(1), 15 (2012).
[4] M. Ahmad et al., Ceramics International **37**(8), 3691 (2011).
[5] M. Ahmad et al., Journal of Magnetism and Magnetic Materials **332**, 137 (2013).
[6] C. Stergiou, G. Litsardakis, Journal of Magnetism and Magnetic Materials **323**(18), 2362 (2011).

[7] F. Lv et al., Materials Letters **157**, 277 (2015).
[8] Y. Q. Li et al., Journal of Magnetism and Magnetic Materials **323**(16), 2224 (2011).
[9] M. Ahmad et al., Journal of Alloys and Compounds **577**, 382 (2013).
[10] L. Deng et al., Journal of Magnetism and Magnetic Materials **323**(14), 1895 (2011).
[11] X. Niu et al., Optik **126**(24), 5513 (2015).
[12] H.-S. Cho, S.-S. Kim, Ceramics International **45**(7, Part B), 9406 (2019).
[13] I. Sadiq et al., Physica B: Condensed Matter **407**(8), 1256 (2012).
[14] S. E. M. Ghahfarokhi, N. A. Varnosfaderani, M. Z. Shoushtari, Ceramics International **44**(15), 17592 (2018).
[15] M. Ahmad et al., Journal of Alloys and Compounds **579**, 57 (2013).
[16] F. Aen et al., Ceramics International **42**(14), 16077 (2016).
[17] F. Aen, M. Ahmad, M. U. Rana, Current Applied Physics **13**(1), 41 (2013).
[18] T. T. Carol et al., Physica B: Condensed Matter **575**, 411681 (2019).
[19] I. Khan et al., Journal of Alloys and Compounds **509**(31), 8042 (2011).
[20] H. M. KHAN , et al, Journal of Ovonic Research, **16**(05), 281(2020).
[21] S. ALTAF, et al, Digest Journal of Nanomaterials and Biostructures **14**(03) 727 (2019).
[22] Hasan M. Khan et al, Journal of Alloys and Compounds, **589** (15) 258(2014).