



SUBSTITUTION OF TRANSITION METAL ION ON MAGNETIC BEHAVIOR OF $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Me}_x\text{Fe}_{12-2x}\text{O}_{19}$ BY SOLID STATE DIFFUSION PROCESS

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Abstract:

Ca-Sr hexaferrite samples with chemical composition $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Me}_x\text{Fe}_{12-2x}\text{O}_{19}$ where ($x = 0, 0.5, 1$) and ($\text{Me} = \text{CoTi}$) synthesized using proper stoichiometric proportions by solid state reaction at 1040°C for 105 hr. The chemical phase analysis has been carried out by X-ray powder diffraction (XRD) method, which confirms the formation of the ferrite structure. It shows hexagonal magnetoplumbite (M) type structure having unit cell dimension 'a' and 'c' varies between 5-6 Å and 21-23 Å. Coercivity (H_c), saturation magnetization (M_s), Retentivity (M_r) and Bohr magneton (η_B) measurements were carried out on a vibrating sample magnetometer (VSM) with an applied field up to 10 KOe. The results were explained in the light of Gorter's (1957) spin model. The magnetization results indicate that the Al³⁺ ions preferentially occupy the 2a, 12k, and 4f₂ sites. This confirms the use of samples in the various applications of digital data storage devices.

Keywords: X-ray density, porosity, magnetization, coercivity, retentivity etc.

Introduction:

Ca/Sr Ferrite, iso-structural with magnetoplumbite ferrites are widely used in permanent magnet market because of their low price combined with reasonable magnetic performances and wide availability of raw materials. Permanent magnets are characterized by high remanance, coercivity etc. [1]. Another advantage is the great chemical stability of these oxides, which makes in such a context a little improvement of their magnetic properties of great importance. Ferrite are technologically important materials because of their interesting physical and chemical properties that have attractive microwave device application i.e. micro strip antennas, radio frequency coil, high density recording media, computer memory chip, transformer coil, etc.[2-4].

The magnetic properties of hexagonal ferrites depend on the intrinsic magnetic properties of the M-type phase. The M-type ferrite crystallizes in a hexagonal structure with 64 ions per unit cell on 11 different symmetry sites. The 24 Fe³⁺ atoms are distributed over five distinct sites: three octahedral sites (12k, 2a and 4f₂), one tetrahedral (4f₁) site and one bipyramidal site (2b). The magnetic structure given by the Gorter model in the ferrimagnetic with five different sub-lattices, three parallel (12k, 2a and 2b) and two anti-parallel (4f₁ and 4f₂) which are coupled by super-exchange interactions through the O²⁻ ions [5-6].

To understand the lattice behavior of M-type ferrite, in the present work, a significant improvement of the intrinsic magnetic

properties of compounds can be obtained by the partial substitution of CoAl and CoTi. It has recently been shown that La-Co substitute $\text{SrFe}_{12}\text{O}_{19}$ ferrite have improved magnetic properties [2, 4, 7-8]. This improvement is largely associated with the increase of coercivity and underlying magneto-crystalline anisotropy. On the other hand, the complete substitution of Sr by La induces an increase of the anisotropy field [2]. In this way, a rare earth ion may contribute to a change of new magnetic interactions, thus improving the magnetic properties.

In this paper, we have investigated the structural analysis of M-type calcium hexaferrite with composition of Sr or (CoAl / CoTi) in $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Me}_x\text{Fe}_{12-2x}\text{O}_{19}$ prepared and observed the variation in the magnetic properties.

Experimental:

The powdered samples of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Me}_x\text{Fe}_{12-2x}\text{O}_{19}$ have been synthesized by using standard solid state reaction technique. The stoichiometric proportions of weighted oxides were mixed thoroughly in acetone medium for 5 h and pre-sintered at 500°C for 10 h to homogenize & calcinations. The calcinated powder were pressed into pellet and sintered at 1040°C in air atmosphere for about 96 h and slowly cooled to room temperature at the rate of $2^\circ\text{C}/\text{min}$ using a microprocessor controlled furnace.

The X-Ray diffractograms were obtained using Cu-K α radiation on a Philips X-ray diffractometer (model PW1732). The XRD pattern shows a single crystalline phase without

traces of impurities. The pattern were indexed to hexagonal magnetoplumbite structure pertaining to the space group $P6_3/mmc$ (No.194). The X-ray powder diffraction pattern of $Ca_{0.5}Sr_{0.5}Fe_{12}O_{19}$ is shown in **Figure.1** and X-ray diffraction data are enumerated in tables 1.

The lattice parameters, X-ray density, bulk density, porosity and grain size were calculated for each sample. The magnetic properties of polycrystalline sample have been measured by using a vibrating sample magnetometer in the applied field upto 10 KG at room temperature **Figure. 2**. In order to avoid rotation of the powder grain, pressed samples were used. The transition temperature (T_c) has been measure by using a Gouy's balance.

Result and discussions:

The recorded X-ray diffraction pattern of all the samples shows that all these lines belongs to hexagonal structure. The reflection from the planes (006), (113), (200), (0012), (220), (304) appears for all the samples. The appearance of these planes proved that the samples are M-type ferrite depicted in table 2.

The interplaner distance $d(\text{\AA})$ was calculated using Bragg's law and the value of lattice constant 'a' (\AA) were determined with an accuracy of 0.002\AA . The observed and calculated values of the interplaner distances for the sample $Ca_{0.5}Sr_{0.5}Fe_{12}O_{19}$ are depicted in

table-1. Thus obeying the Regard's law which may be attributed to the replacement of smaller Fe^{3+} ions (0.64\AA) by larger ionic radii of the combinations of (CoAl / CoTi) ions in $Ca_{0.5}Sr_{0.5}Me_xFe_{12-2x}O_{19}$ system.

The X-ray density is given in the Table-2, the variation of X-ray density with the concentration of CoAl, CoTi with Sr, which may be due to the ionic difference between Al^{+3} (0.50\AA) and Ti^{+3} (0.95\AA) as reported in the literature [7-8] or due to specific gravity of cations.

The porosity of all samples was found in the range of 39-42 %. The bulk density is determined and value as a function of concentration is given in table-3, it is observed that the bulk density increases with concentration (CoAl / CoTi). At sintering temperature of $1040 \text{ }^\circ\text{C}$, the number of pores is reduced, as a result of which individual grains come closer to each other and the effective area of grain to grain contact increases as also described [8].

The particle morphology of the samples was observed using a SEM the photographs were shown in fig- 3. The sample comprises hexagonal particles with their average grain size between $0.29 \mu\text{m}$ to $0.87 \mu\text{m}$, indicating improved homogeneity and grain size reduction of the starting powders.

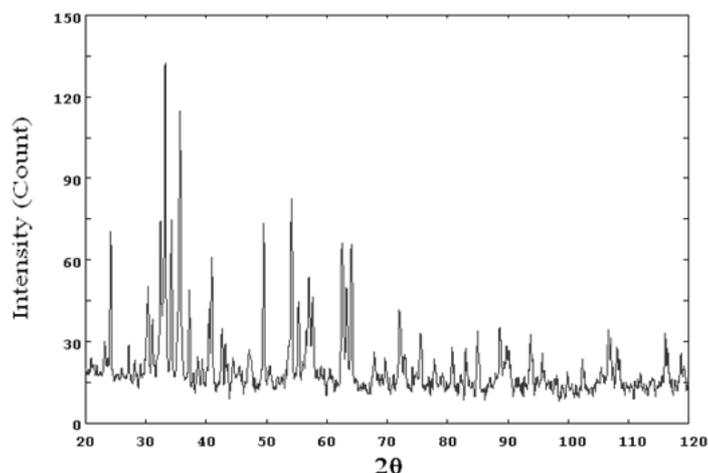
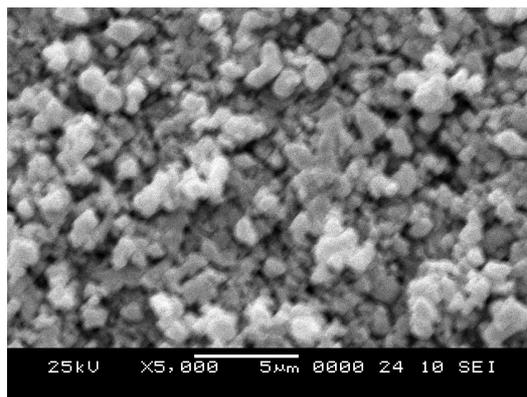
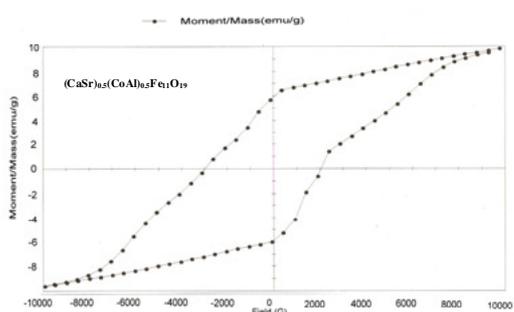
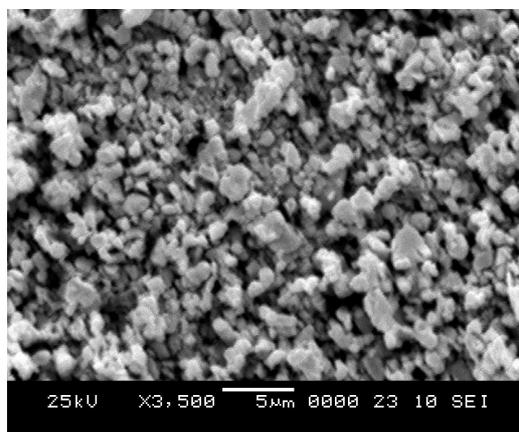
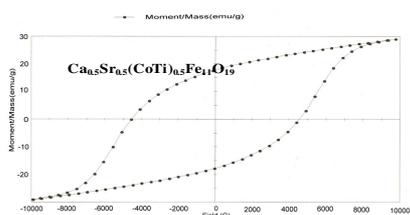


Figure. 1. XRD of compound $Ca_{0.5}Sr_{0.5}Fe_{12}O_{19}$



(a) $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Fe}_{12}\text{O}_{19}$



(b) $\text{Ca}_{0.5}\text{Sr}_{0.5}(\text{CoTi})_{0.5}\text{Fe}_{11}\text{O}_{19}$

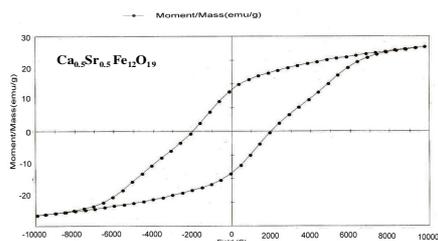


Figure. 3 SEM micrographs of the compounds

Figure. 2 BH curve of compounds

- (a) $\text{Ca}_{0.5}\text{Sr}_{0.5}(\text{CoAl})_{0.5}\text{Fe}_{11}\text{O}_{19}$
- (b) $\text{Ca}_{0.5}\text{Sr}_{0.5}(\text{CoTi})_{0.5}\text{Fe}_{11}\text{O}_{19}$ (c) $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Fe}_{12}\text{O}_{19}$

In table 4. we have summarized the crystallographic characteristics of five different sublattice together with the spin alignments corresponding to the collinear magnetic structure proposed [9]. The value of saturation magnetization per formula unit in Bohr magnetron (η_B) at 300 K for all the samples obtained from field dependence of magnetization is given in table-5. The variation of saturation magnetization M_s and η_B per formula unit with concentration of CoTi, CoAl are shown in table-4. It is seen that the value of (η_B) gradually increases with retentivity and saturation magnetization.

The results for compounds $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Fe}_{12}\text{O}_{19}$ here after abbreviated as [sample (c)] are compared with $\text{Ca}_{0.5}\text{Sr}_{0.5}(\text{CoAl})_{0.5}\text{Fe}_{11}\text{O}_{19}$ [sample (a)] and $\text{Ca}_{0.5}\text{Sr}_{0.5}(\text{CoTi})_{0.5}\text{Fe}_{11}\text{O}_{19}$ [sample (b)] then it is found that, saturation magnetization, magnetic moment, and retentivity values are larger for sample (c) than sample (a) and sample (b) compound. But coercivity declines for sample (b) than sample (a). This is due to the decrease of Fe content; the contribution towards saturation magnetization due to Fe-O-Fe exchange interaction gets reduced. The behaviour is in good agreement to that observe by [10-12] etc., when Fe is substituted by Al, Ga and Cr in M-

ferrites, affect the lattice dimensions, site distribution, Curie temperature and saturation magnetization. It is observed that saturation magnetization decreases when Fe is substituted by Co^{+2} and Ti^{+4} with increasing concentration. In compound $\text{Ca}_{0.5}\text{Sr}_{0.5}(\text{CoTi})_{0.5}\text{Fe}_{11}\text{O}_{19}$, the magnetic moment from the octahedrally surrounded ferric ions in the spinel blocks and those in the trigonal bipyramidal sites are opposed by a minority of ferric ions in tetrahedral sites of the spinel block along with octahedral sites. Which in case of compound $\text{Ca}_{0.5}\text{Sr}_{0.5}(\text{CoTi})_{0.5}\text{Fe}_{11}\text{O}_{19}$ larger value of saturation magnetization is observed which is obvious as substitution of ferrimagnetic ions such as CoTi in spinel blocks of the M-structure occupying the octahedral sites (12k), the interaction energy increase so high, which in turn increases the saturation magnetization [13].

The BH curve measurements were carried out at room temperature. The observed results are explained on the basis of site distribution. The saturation magnetization, coercivity, magnetic moment and retentivity decreased with CoAl and CoTi substitution. It is evident from the fact that Al and Ti ions are non magnetic in nature. In this compound the magnetic moment from octahedrally surrounded ferric ions in the spinel blocks and those in the trigonal bipyramidal sites are opposed by a minority of ferric ions in tetrahedral sites of the spinel block along with octahedral sites.

The large value of M_s , H_c , η_B is attributed to the fact that the interaction energy is so high, which in turn increases the saturation magnetization [14] have shown that the interaction 2a-12k is of immense importance and determines the magnetic behaviour of the compounds. The Fe^{+3} ions have high magnitude of super exchange and interactions, particularly when all the 24 sites (2a, 2b, 4f₁, 4f₂ and 12k) are filled in by magnets and ferromagnetic ions alone Fe (12k) sublattice making the link along octahedral R-S structural blocks is subjected to very strong competitive exchange interaction table 5.

A plot of inverse molar magnetic susceptibility versus temperature (T) is linear for the samples containing CoTi and CoAl ions, resembles ferromagnetic behaviour. The temperature dependence of magnetic susceptibility measurement showed that the Curie temperature of sample (a), (b) and (c) are 599, 516 and 547 K respectively. The variation in magnetic ordering temperature has variation amongst the compounds, as the magnetic moment of Co^{+3} and Fe^{+3} ions are different a

ferromagnetic is formed. The canting is not worked out in this case the canting of A-B interaction play a complex role such that almost a feeble magnetic anti-ferrimagnetic exchange is involved and hence a lesser degree of curvature is observed in the present case. The high value of T_c (599 K) demonstrates that some inter-substitute exchange interaction between two close sites, are decisive for strong magnetic characters. [15-17] while the low value of T_c (516 K) sample (B) means that the cations of the additive substitute for the Fe^{+3} of the 2b or the 12 k sites will weaken the total distance or angle due to the superexchange interaction Fe-O-Fe [18].

The interaction between close site such as 2a -2k, 2a – 4f₁, and 4f₁-12k are decisive for strong magnetic character. Whenever magnets ions are present in these sites, strengthening of super exchange interaction produces an increase in the magnetic characteristics such as Curie temperature, magnetization. In case of M-structure, the orientations of the magnetic moments of the ferric ions in the crystals are generally aligned along the c-axis in antiparallel with each other.

The neutron diffraction and NMR studies in BaM- ferrites [19] shows that the Ti^{+4} ions are mainly distributed with 4f₂ and 12k sites Co^{+2} ions occupy mainly 4f₁ and 12 k sites [20], because of 4f₁ and 4f₂ with down spin have larger value of magnetic moment can be obtained according the cationic distribution deduced from the neutron & NMR studies using the Gorter collinear spin model.

A mean field analysis of the exchange interaction in M-type hexaferrite has been carried out by [20-22]. The result shows that the Fe (12k) sublattice making link among R-S structural blocks is subject to very strong competitive exchange interaction. So when Fe^{+3} ions in the 12k sublattice are subjected to non magnets viz. Ti^{+4} or Al^{+3} ions weakening of super-exchange interaction between magnetic ions results in a fairly inclined ferrimagnetism [23-24].

Table - 1 X- Ray diffraction Result of $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Fe}_{12}\text{O}_{19}$ with lattice parameter $a = 5.8130 \pm 0.0008 \text{ \AA}$, $c = 22.0398 \pm 0.0009 \text{ \AA}$

d_{obs} (\AA)	d_{cal} (\AA)	I_{obs} (%)	h	k	l
3.6733	3.6732	32.7	0	0	6
2.6970	2.7026	100.0	1	1	3
2.5171	2.5171	67.2	2	0	0
2.4153	2.4159	31.0	1	0	8
2.2055	2.2049	27.7	0	0	10
1.8418	1.8418	35.3	2	1	3

1.8366	1.8366	21.0	0	0	12	
h k l	1.6954	55.4	0	0	13	
	1.6476	5.4	1	1	11	
	1.6330	15.9	3	0	3	
	1.6022	13.6	3	0	4	
	1.4876	24.6	2	0	12	
	1.4542	38.9	2	2	0	
0 0 6	1.3838	6.9	1	1	14	
1 1 3	1.3128	10.9	1	1	15	
2 0 0	1.2984	7.7	0	0	17	
0 0	1.2594	3.3	1	0	17	
	1.1916	3.8	3	0	13	
12	1.1435	6.2	3	1	11	
3 0 4	1.1049	4.1	0	0	20	
2 2 0	1.6954	1.0575	5.8	2	0	19
	1.6459	1.0435	3.5	3	1	14
	1.6301	0.9626	5.8	2	0	21
	1.6010	0.9536	7.3	2	1	20
	1.4871					
	1.4547					
	1.3833					
	1.3130					
	1.2999					
	1.2594					
	1.1914					
	1.1428					

1.1040			
1.0574			
1.0410			
0.9624			
0.9535			

Table. 2. Comparative d- values of various samples of the series $\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Me}_x\text{Fe}_{12-2x}\text{O}_{19}$

Table-3. X-ray diffraction analysis data

Compound	a (Å)	c (Å)	X-ray density (gm/cm ³)	Bulk density (gm/cm ³)	Porosity (%)	Particle size (Å)
$\text{Ca}_{0.5}\text{Sr}_{0.5}(\text{CoAl})_{0.5}\text{Fe}_{11}\text{O}_{19}$	5.8234	22.0986	5.24548	3.09244	41.045	36
$\text{Ca}_{0.5}\text{Sr}_{0.5}(\text{CoTi})_{0.5}\text{Fe}_{11}\text{O}_{19}$	5.8257	22.1298	5.28735	3.18611	39.746	24
$\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Fe}_{12}\text{O}_{19}$	5.8130	22.0398	5.34468	3.22206	39.714	24

Table 4 Five iron lattice sites, their spin direction, type, point symmetry, number of Fe ions per formula, and block situation in M-type ferrite.

Sublattice	Type	Point symmetry	Ions	Spin (5μ _B)	Block
12k	Octahedral	$\uparrow\bar{m}$	6	Up	S – R
4f ₁	Tetrahedral	$\downarrow\beta\bar{m}$	2	Down	S
4f ₂	Octahedral	$\downarrow\bar{3}m$	2	Down	R
2a	Octahedral	$\uparrow\bar{3}m$	1	Up	S
2b	Five Fold	$\uparrow\bar{6}m2$	1	Up	R

Table-5. Various magnetic parameters

Compound	Ms Magnetization	Retentivity emu/g	Hci Coercivity	η _B	Tc (K)

	emu/g		(G)		
$\text{Ca}_{0.5}\text{Sr}_{0.5}(\text{CoAl})_{0.5}\text{Fe}_{11}\text{O}_{19}$	9.7155	5.8900	2498.2	1.7832	599
$\text{Ca}_{0.5}\text{Sr}_{0.5}(\text{CoTi})_{0.5}\text{Fe}_{11}\text{O}_{19}$	17.740	8.7701	1986.7	3.2893	516
$\text{Ca}_{0.5}\text{Sr}_{0.5}\text{Fe}_{12}\text{O}_{19}$	29.052	17.773	4562.3	5.3994	547

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