Synthesis and magnetic study of Co–Al substituted calcium hexaferrite

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Abstract. A series of calcium substituted polycrystalline ferrite ceramics with magnetoplumbite structures were synthesized using perfect stoichiometric mixtures of oxides with chemical composition, $CaAl_xCo_xFe_{12-2x}O_{19}$ ($x = 2$–5), by standard ceramic technique. The variation in the values of H_c and M_s, which depends on the additive content and the temperature, was studied by means of a vibration magnetometer. The strong variation observed in coercivity, saturation magnetization and Curie temperature with chemical composition give rise to the possibility of controlling these properties and hence applying these compounds in the millimeter–micro-wave range.

Keywords. Polycrystalline ferrites; saturation magnetization; Curie temperature; coercivity; magnetoplumbite.

1. Introduction

Ba/Ca-ferrite particles media is considered a promising material for high density magnetic recording (Speliotis 1987) and many attempts have been devoted to improve their magnetic characteristics by substitution of Fe^{+3} cations with other diamagnetic or paramagnetic cations (Figgis and Nyholm 1958). Although single-domain Ba/Ca ferrite particles have an intrinsically large coercivity H_c, it is known that substitution with equimolar Co^{+3} ions may dramatically alter H_c without significantly affecting the magnetism (Kubo *et al* 1982). Structurally, *M*-type ferrites consist of spinel (*S*) block interspersed with five distinct lattice sites for the metallic cations (table 1). Each Fe^{+3} ion sublattice contributes differently to the overall character of the ferrite. In $CaFe_{12}O_{19}$ (CaM) the usual quasi-linear temperature dependence of the saturation magnetization, M_s, results from a rapid decrease in the contribution from the octahedral 12 K sublattice. This has been interpreted as indicating that the 12 K ions interact strongly with the bipyramidal 2b sublattice, in addition to the expected super-exchange interaction with the spin down $4f_{IV}$ and $4f_{VI}$ ions (Albanese 1977). Similarly the characteristic uniaxial anisotropy of CaM has been attributed to the dominating contributions from the single ion anisotropies of the 12 K and 2b sublattices (Asti and Rinaldi 1976). The magnetic behaviour of the compound has been explained in the light of interactions amongst the ions occupying these crystallographic sites. Various comparative magnetic interactions occurring in the lattice due to several site distributions, which in turn decide the magnetic behaviour. In the present study a series of four compounds with general formula, $CaAl_xCo_xFe_{12-2x}O_{19}$ with $x = 2$, 3, 4 and 5 are reported.

2. Experimental

The synthesis of polycrystalline $CaAl_xCo_xFe_{12-2x}O_{19}$ ($2 < x < 5$) samples were done by high temperature solid state reactions of stoichiometric mixtures of AR grade CaO, Fe_2O_3, Al_2O_3 and Co_2O_3 oxides. The synthesis was divided into two steps: (i) After calcinations at 800°C for 2 h in air. The mixture was grinded and dried, compressed into pellets, and (ii) finally subjected to a thermal treatment at 1200°C for 1250 h with intermediate grinding and were quenched in air. The preparational procedure was similar to that reported earlier (Kulkarni and Prakash 1994; Rewatkar *et al* 1998). The samples were analysed using an X-ray powder diffractometer with filtered CuK***a***-radiation with nickel as a filter. The magnetic susceptibility measurements were carried out on Gouy's balance in the temperature range 300–850 K, using mercury–cobaltate–tetrathiocynate [HgCo(CNS)₄] as calibrant (Lotgering *et al* 1980). The ferrites doped with high concentration of Co^{+3} possess high Curie temperature, the additive components were restricted within the interval of $2 \leq x \leq 5$.

The magnetic measurements on polycrystalline samples were carried out by using a vibrating sample magnetometer in the applied field up to 300 Oes at room temperature, which is indicative of substitution of Fe^{+3} with Co^{+3} and enhances the intensity of magnetization.

3. Results and discussion

Synthesis of polycrystalline samples were verified using

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Phillips X-ray diffractometer and Cu-Ka radiation with wavelength, $l = 1.542$ Å. The X-ray pattern showed a single crystalline phase without any trace of impurity indexed as hexagonal magnetoplumbite structure (Sharrock 1989). The structural data of compound, $CaAl_2Co_2Fe_8O_{19}$, is given in table 2. By isomorphism of the M compounds the space group is presumed to be D_{6th}^4 or $P6_3/mmc$ (Kojima 1982). The hexagonal lattice parameters of the compounds were deduced from XRD pattern. The replacement of Al^{+3} ions has been investigated because of resemblance of the ionic radii. It is seen that the former ions are very easily replaced at any substitution ratio without changing the crystal geometry. The lattice parameters 'a' and 'c' increase linearly with substitution of Fe^{+3} and Co^{+3} ions in Ca-ferrite.

It is obvious as Fe^{+3} and Co^{+3} ions have larger ionic radii (0.64 Å, 0.63 Å), respectively than Al^{+3} (0.50 Å) and hence 'a' is predominantly governed by large Fe^{+3} ions. A perusal of the structure shows that 'c' is more suscep-

tible to stoichiometric changes than 'a'. The lattice parameters and consolidated data on coercivity (H_c), saturation magnetization (M_s) and magnetic moment (μ) are enumerated in table 3. The magnetic moment, μ, per unit formula of the compounds were in the range of 13.01–16.12 μB/FU, this value is much smaller than 20 μB/FU for $BaFe_{12}O_{19}$ ferrite. This indicates that substitution of Fe^{+3} with Co^{+3} and Al^{+3} ions causes a strong decrease of the magnetic moment and occupation of spin up sites by Al^{+3} ions particularly.

The 12 K sublattice (spin up) is antiferromagnetically coupled with the 2b (spin up) and 2a as well as the 12 K intersublattice interactions and have only perturbing effect on the orientation of magnetic moment of 12 K ions. The neutron diffraction and NMR studies also reveal that Co^{+3} ions are mainly distributed within $4f_{IV}$ and 12 K sites (Henry *et al* 1953; Smit and Wijn 1959).

The strong increase in Curie temperature (T_c), saturation magnetization (M_s) and coercivity (H_c) demonstrates that

Table 1. Distribution of the cations and spin orientations for various sublattices of *M*-type hexaferrites.

Sublattice	Coordination	Block	Number of ion FU	Spin orientation
2a	Octahedral	*S*	1	up
2b	Pseudo-tetrahedral	*R*	1	up
$4f_{IV}$	Tetrahedral	*S*	2	down
$4f_{VI}$	Octahedral	*R*	2	down
12 K	Octahedral	*R–S*	6	up

Table 2. X-ray diffraction data of $CaAl_2Co_2Fe_8O_{19}$.

d_{obs} (Å)	d_{cal} (Å)	I/I_0	$h\,k\,l$
3.6154	3.6155	6.3	1 0 4
3.5438	3.5441	12.2	0 0 6
2.8789	2.8784	17.0	1 0 6
2.7964	2.7973	30.9	1 1 0
2.7055	2.7053	5.1	1 1 2
2.5863	2.5863	100	1 0 7
2.6020	2.6021	21.2	1 1 3
2.4754	2.4754	84.8	1 1 4
2.4400	2.4499	14.7	2 0 1
2.3386	2.3395	36.3	1 0 8
2.3206	2.3294	13.5	2 0 3
2.1960	2.1959	6.5	1 1 6
2.1312	2.1307	12.5	1 0 9
2.0223	2.0244	37.5	2 0 6
1.8312	1.8314	44.4	2 1 0
1.6428	1.6439	7.3	3 0 0
1.5713	1.5706	8.2	3 0 4
1.5333	1.5334	6.2	3 0 5
1.3988	1.3987	16.2	2 2 0
1.3723	1.3723	15.2	2 2 3
1.2711	1.2711	8.3	2 0 15
1.1739	1.1739	5.5	3 1 9
1.1560	1.1561	6.3	2 0 17
1.0573	1.0573	6.2	4 1 0

Table 3. Data on lattice parameters a and c, H_c, M_s, μ for $CaAl_xCo_xFe_{12-2x}O_{19}$.

Sl. no.	x	a (Å)	c (Å)	H_c (Oes)	M_s (emu/g)	μ	T_c (K)
1	2	5·6950	21·2620	115·0	10·71	13·01	634
2	3	5·7939	21·8075	168·0	26·37	14·01	725
3	4	5·8074	21·8410	198·5	39·11	15·81	798
4	5	5·8185	21·8798	215·0	51·63	16·12	823

some inter sublattice exchange interactions are dominant. It can be seen that the spin co-linearity appears mostly in the spin up sublattice, especially the 12 K sublattice has degree of frustration being in this way strongly affected by increase of 12 K–$4f_{IV}$ interaction. A mean field analysis of the exchange interaction in BaM hexaferrite has been carried out by Isalgue *et al* (1986). The result shows that the Fe (12 K) sublattice making a link among R and S structural block is subjected to very strong competitive exchange interaction. So, when the Fe^{+3} ions in the 12 K sublattice are substituted by non-magnetic ions, weakening of the super exchange interaction between magnetic ions results in a fairly inclined ferromagnetism.

The measurements of M_s, H_c and μ imply an increase with Fe^{+3} and Co^{+3} ion concentration in series, which are indicative of ferromagnetic nature of the compounds. The continuous increase in H_c and M_s with decrease of Al_2O_3 contents may be explained by assuming that Al^{+3} substitution is preferentially performed on the spin up magnetic sublattice, for the composition. Similar phenomenon has also been reported (Stepankova *et al* 1991) in $SrO_{(6-x)}Fe_2O_{3x}Al_2O_3(0 < x < 6)$ ferrite system.

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