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VARIATIONAL EFFECT IN SUBSTITUTED CALCIUM HEXAFERRITE

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Abstract- Twelve samples with the general formula $CaMe_xFe_{12-x}O_{19}$ (Me=Al, Cr and Co) with x=3, 4, 8 and 9 are synthesized and characterized. All these samples are found to have hexagonal crystal structure with magnetoplumbite (M) type structure. Temperature variation of inverse molar susceptibility and electrical conductivity are studied and reported here.

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Introduction

In the recent past a renewal of interest in hexaferrites has been induced by the possibility of application of these oxides in millimetre wave frequency devices. In order to improve the magnetic characteristics, several attempts have been made (1-3). For example, Al substituted Barium ferrite ($BaAl_xFe_{12-x}O_{19}$) may be used to control the saturation current in the circuit where the soft ferrites are used as the coils (4). Several applications like recording media etc have been reported using the Barium ferrite with several substitutions (5-8). In the M-type structure it is well known that the basic structure is hexagonal and all the 38 oxygen ions occupy the interstitial sites forming a close packed hexagonal structure. The 24 ferric ions occupy at five different locations in the unit cell structure such as 2a, 2b, $4f_1$, $4f_2$ and 12k. Of these, 2a, $4f_2$ and 12k are octahedral, $4f_1$ is tetrahedral and 12k is called bipyramidal site. The magnetic nature of the magnetoplumbites is determined by the substituted ions for the ferric ions which occupy different places in the structure (9-12).

With a view to understand the structural, magnetic and electrical properties, three series of four samples each have been prepared with the general formula $CaMe_xFe_{12-x}O_{19}$, where Me stands for Al, Cr and Co and x= 3, 4, 8 and 9. Systematic observations of lattice parameters, magnetic susceptibility and electrical conductivity of these samples have been carried out in the present work and reported as in the table below.

Experimental

Sample Preparation: The entire twelve samples have been prepared in the polycrystalline form using the oxide method. The samples were found to have single phase M-Type structure and was confirmed with the help of the XRD technique.

Measurements: Magnetic susceptibility of the series of samples was measures by Guoy's method by using Mercury Tetracynato cobaltate ($HgCo(CNS)_4$) as calibrant. Eight samples containing Al and Cr were found to be paramagnetic at room temperature. The other four samples containing the Co were found to be highly ferromagnetic and could not find the Curie temperature even upto 1073 K. The paramagnetic behaviour of the first eight samples studied and the Curie Molar constant of these samples experimentally and theoretically were found to be well in agreement with each other.

The AC susceptibility measurements of all the samples were taken at the room temperature and are as reported in the tabular column.

The DC electrical resistivity measurements were also made found the activation energy from these studies and all the samples were found to be semiconductors as expected.

Results and Discussion

All the samples were characterized structurally by XRD and are found to have single phase M-type structure. The variation in the lattice parameters and cell volume is found to be linearly decreasing with the increase in the concentration of Cr or Co in the two series containing Cr and Co. Whereas in the case of Al series the same is found to be increasing with the increase of Al content. The increase in lattice parameters is attributed as due to the creation of an additional sub lattice (12k') as observed in the $SrAl_xFe_{12-x}O_{19}$ (13), which reduces the interaction energy in the crystal lattice. The prominent places for the ferric ions in the M-type structure namely 2a, 2b, 4f1, 4f2 and 12k when replaced by the substituted ions, changes the magnetic structure of the samples (14-15). In the case $SrAl_xFe_{12-x}O_{19}$ the increase in cell volume and lattice parameters were attributed as due to the occupancy of the prominent place of Fe by the Al ions.

The paramagnetic nature of the Al and Cr series of samples were studied and Curie molar constant were matching both experimentally and theoretically.

The AC susceptibility measurements support that the magnetic behaviour of various samples is depending strongly on the type of substation made for the Fe ions in the original sample. For when Fe is replaced by Al or Cr the magnetic moment greatly reduced due to the reduced exchange interaction in the samples. Whereas in the case Co ferrite the exchange interactions lead to greater values of the magnetic moment thereby increasing the Curie temperature to a greater value.

The temperature variation of DC electrical resistivity is linear with increase in concentration of the dopant in all the cases. The activation energy for all the samples was found and is as reported in the tabular column.

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Table - Properties of the samples studied

Sample	Lattice Parametes a(Å)	c(Å)	Cell Vol (Å)^3	Mol. Wt.	X-Ray Density gm/cc	AC susceptibility at R.T (x10^{-3}emu/Oe)	Resistivity ohm-cm (x10^6)	Activation Energy (ΔE) eV
$CaFe_9Al_3O_{19}$	5.806	22.040	643.40	927.67	4.784	0.950	120	0.75
$CaFe_8Al_4O_{19}$	5.830	22.140	651.68	898.8	4.576	0.800	580	0.86
$CaFe_4Al_8O_{19}$	5.877	22.470	672.10	783.32	3.867	0.275	1200	0.90
$CaFe_3Al_9O_{19}$	5.908	22.508	680.36	754.45	3.679	0.000	5900	0.99
$CaFe_9Cr_3O_{19}$	5.795	22.070	641.84	1002.73	5.183	0.490	45	0.53
$CaFe_8Cr_4O_{19}$	5.789	22.020	639.06	998.88	5.186	0.450	0.57	0.43
$CaFe_4Cr_8O_{19}$	5.758	21.888	628.44	983.48	5.192	0.280	0.48	0.34
$CaFe_3Cr_9O_{19}$	5.750	21.845	625.69	979.63	5.195	0.215	0.13	0.32
$CaFe_9Co_3O_{19}$	5.877	22.277	666.32	1023.52	5.096	130	40	0.79
$CaFe_8Co_4O_{19}$	5.840	21.970	648.89	1026.60	5.249	125	32	0.74
$CaFe_4Co_8O_{19}$	5.828	21.840	642.41	1038.92	5.366	40.2	20	0.69
$CaFe_3Co_9O_{19}$	5.802	21.820	636.10	1042.00	5.435	10.4	6.1	0.60