

Structural and magnetic properties of $\text{CaAl}_4\text{Fe}_8\text{O}_{19}$

D K KULKARNI and C S PRAKASH

Department of Physics, Institute of Science, Nagpur 440 001, India

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Abstract. A new compound, $\text{CaAl}_4\text{Fe}_8\text{O}_{19}$, was synthesized for the first time and characterized by X-ray diffraction. It was found to have a hexagonal magnetoplumbite structure with lattice parameters $a = 5.83 \text{ \AA}$ and $c = 22.14 \text{ \AA}$. The electrical studies showed that the compound was a semiconductor with energy of activation $q = 0.86 \text{ eV}$. The magnetic susceptibility was studied in the temperature range 300 K to 850 K, in which the compound was paramagnetic with a Curie molar constant of 31.03.

Keywords. Magnetoplumbite; electrical conductivity; paramagnetic susceptibility; curie molar constant.

1. Introduction

Magnetoplumbites (M) have attracted much attention as they have wide application in industry (Di Marcello *et al* 1988; Twafik and Bakarar 1988; Bahadur and Chakravorthy 1989; Kotnala 1992), e.g. as magnetic recording media. The systems $\text{BaO-MeO-Fe}_2\text{O}_3$ and $\text{SrO-MeO-Fe}_2\text{O}_3$ have gained popularity due to their high-quality magnetic behaviour (Rathenau 1953; Cochart 1963; Sauer *et al* 1978; Ram 1989; Sato *et al* 1990). In addition to these, M-type compounds of the systems $\text{MO-Fe}_2\text{O}_3\text{-B}_2\text{O}_3$ ($\text{M} = \text{Ba, Sr, Ca and Pb}$) are used in developing glass ceramics (Bahadur and Chakravorthy 1989). Thus magnetoplumbites have more and more applications in present-day industries.

Substituted magnetoplumbites with Ca^{2+} for Ba^{2+} , trivalent metallic ions for Fe^{3+} , and a combination of divalent and tetravalent ions for Fe^{3+} have been reported (Summargard and Banks 1957; Van Uitert 1957; Mulay and Sinha 1970; Haneda and Kojima 1971, 1973; Asti *et al* 1980; Batlle *et al* 1988; Nedkov *et al* 1988). Asti *et al* (1980) even suggested a substitution of Ca^{2+} up to 70% for Ba^{2+} in BaM, where one can get magnetoplumbites without appreciable change in lattice dimensions. Total replacement has been made, as in $\text{CaAl}_{12}\text{O}_{19}$ (Wisnyi 1967) and $\text{CaFe}_{12}\text{O}_{19}$ (Ichinose and Kurihara 1963; MacChesnyi *et al* 1971; Borkar 1987), which have been found to exist in magnetoplumbite structure.

Glasser *et al* (1972) reported samples in the series $\text{CaAl}_{12-x}\text{Fe}_x\text{O}_{19}$, with $x = 6.0, 4.8, 2, 1.2, 0.5, 0.1$, forming solid solutions of the end members. Considering barium ferrite ($\text{BaFe}_{12}\text{O}_{19}$), the unit cell contains 38 oxygen ions, 24 ferric ions and two barium ions. Oxygen ions occupy the interstitial sites forming a close-packed hexagonal structure. Ferric ions occupy five different crystallographic sites, viz. 2a, 2b, 4f₁, 4f₂, and 12k. Of these 2a, 4f₂ and 12k are octahedral, 4f₁ is the tetrahedral site, and 2b the trigonal bipyramidal site. The unit cell contains two spinel blocks, in which aside from slight differences in lattice parameters the ionic positions are identical with those in the spinel structure, with the c axis of the hexagonal unit cell oriented along the (111) axis of the spinel structure (Summargard and Banks 1957).

The magnetic nature of the magnetoplumbites is determined by the magnetic ions occupying the different sites and by the superexchange interactions. It is observed in $\text{BaFe}_{10}\text{CoTiO}_{19}$ hexaferrite that nonmagnetic ions (Ti^{4+}) occupy the 12k sites which reduce the superexchange interactions and hence Curie temperature and magnetic moment (Gu *et al* 1992). In the case of $\text{CaFe}_{12}\text{O}_{19}$ a high Curie temperature (718 K) was observed (Ichinose and Kurihara 1963), and the other end member $\text{CaAl}_{12}\text{O}_{19}$ is a nonmagnetic compound (Borkar 1987).

With a view to understand the structural properties, a compound with chemical formula $\text{CaAl}_4\text{Fe}_8\text{O}_{19}$, intermediate between $\text{CaFe}_{12}\text{O}_{19}$ and $\text{CaAl}_{12}\text{O}_{19}$, was prepared by ceramic technique and characterized by X-ray diffraction (XRD). The XRD pattern showed a single phase with hexagonal structure of M-type ferrite. Interestingly, as expected the lattice parameters of $\text{CaAl}_4\text{Fe}_8\text{O}_{19}$ were found to be in the range of those of $\text{CaAl}_{12}\text{O}_{19}$ and $\text{CaFe}_{12}\text{O}_{19}$ and hence may be considered as a solid solution of the end members in appropriate proportions. Further characterization was carried out using electrical and magnetic studies.

2. Experimental

2.1 Preparation

The sample was prepared by standard ceramic technique (Economos 1955). AR grade oxides of (99.9% purity) CaO , Al_2O_3 and Fe_2O_3 were used. The oxides were mixed in the molar ratio 1:2:4::($\text{CaO}:\text{Al}_2\text{O}_3:\text{Fe}_2\text{O}_3$) and ground using AR grade acetone in an agate mortar. Then the powder was heated in air at 1000°C for 120 h in an electric furnace, which was then cooled at the rate of $100^\circ\text{C}/\text{h}$ up to 500°C and further cooled naturally to room temperature. The hard sample thus formed was then ground for about 30 min (Standley 1972) for experimental investigations.

2.2 XRD

The sample was analysed using a Philips X-ray diffractometer and Cu-K_α radiation with wavelength 1.542 \AA . The X-ray pattern showed a single crystalline phase without any impurity and unreacted oxidic reflections. The XRD pattern was indexed as hexagonal magnetoplumbite structure (Henry *et al* 1953). By the isomorphism of the M compounds the space group is presumed to be D_{6h}^4 or $P6_3/\text{mmc}$ (Smit and Wijn 1959). The structural data, viz. d_{hkl} observed and calculated, and intensities observed with reflection indices are included in table 1.

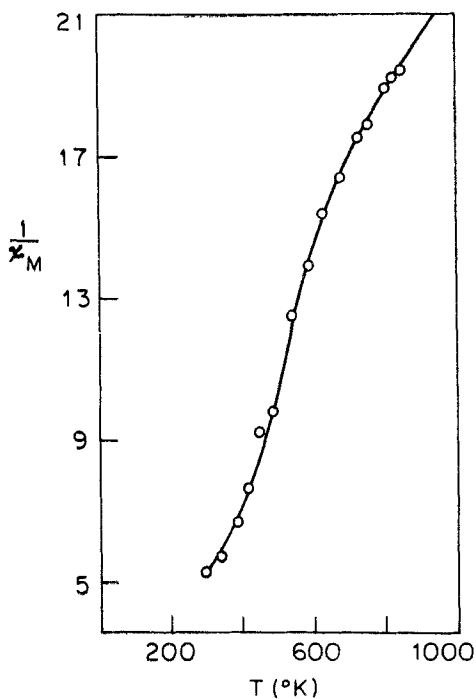
2.3 Magnetic properties

Magnetic susceptibility of the powdered sample was studied by Guoy's method (Bates 1939). The sample was found to be paramagnetic at room temperature. The variation of inverse molar susceptibility vs absolute temperature (K) is shown in figure 1. From the paramagnetic behaviour of the sample, the Curie molar constant C_M was calculated and matched with the theoretically expected value of C_M , with spin only states of magnetic ions (Fe^{3+}). The asymptotic Curie temperature was found to be 100 K from the graph.

Table 1. Crystallographic data of $\text{CaAl}_4\text{Fe}_8\text{O}_{19}$.

d_{obs} (Å)	d_{cal} (Å)	I_{obs}	hkl
3.6897	3.6898	32.8	0006
3.4864	3.3290	11.6	10 $\bar{1}$ 5
2.6750	2.6803	100.0	10 $\bar{1}$ 7
2.5246	2.5246	62.8	20 $\bar{2}$ 0
2.3873	2.3886	8.7	20 $\bar{2}$ 3
2.2925	2.2969	3.8	20 $\bar{2}$ 4
2.2116	2.2114	20.9	10 $\bar{1}$ 9
2.0886	2.0836	18.4	20 $\bar{2}$ 6
1.8435	1.8476	30.9	21 $\bar{3}$ 3
1.6981	1.6951	40.4	21 $\bar{3}$ 6
1.4882	1.4858	24.2	30 $\bar{3}$ 7
1.4568	1.4576	21.3	22 $\bar{4}$ 0
1.4079	1.4095	7.7	22 $\bar{4}$ 4
1.3786	1.3758	9.7	31 $\bar{4}$ 3
1.3122	1.3093	9.7	31 $\bar{4}$ 6
1.2606	1.2622	4.8	40 $\bar{4}$ 0

Lattice parameters: $a = 5.83 \text{ \AA}$, $c = 22.14 \text{ \AA}$.

**Figure 1.** Plot of temperature (K) vs $1/\chi_M$.

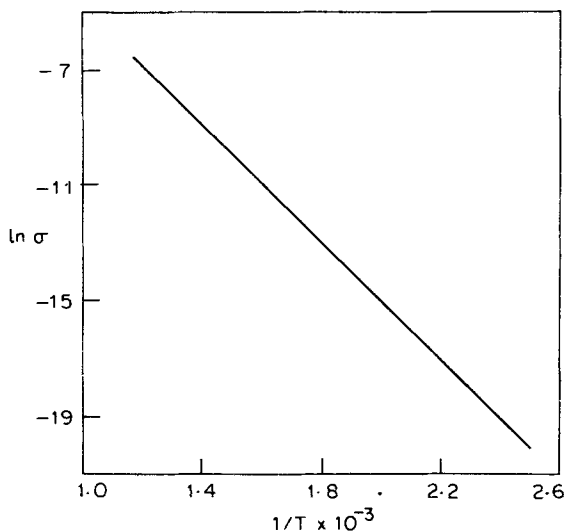


Figure 2. Plot of $\ln \sigma$ vs $1/T$.

2.4 Electrical properties

Electrical conductivity of the sample was measured by two-terminal method. Pellets were prepared by mixing 4% polyvinyl acetate (PVA) as a binder under 2 tonnes/cm pressure. Initially, the pellet was heated at 300°C for 3 h and then at 1000°C by gradual rise in temperature. The final sintering was made for 3 h and the sample was furnace-cooled. A thin layer of silver paste was applied over the crack-free pellet for good electrical contacts. Measurements were made from room temperature (300 K) to 800 K. A graph plotted for $\ln \sigma$ vs $1/T$ shows a linear behaviour (figure 2).

3. Results and discussion

The crystallographic analysis of the data shows that the compound is hexagonal with cell dimensions $a = 5.83 \text{ \AA}$ and $c = 22.14 \text{ \AA}$. The compound $\text{CaAl}_4\text{Fe}_8\text{O}_{19}$ may be thought to be solid solution of two known compounds, viz. $\text{CaAl}_{12}\text{O}_{19}$ and $\text{CaFe}_{12}\text{O}_{19}$, in definite proportions of 1:2. It is interesting to note here that the lattice constants of these compounds are $a_1 = 5.56 \text{ \AA}$, $c_1 = 21.98 \text{ \AA}$ and $a_2 = 5.877 \text{ \AA}$, $c_2 = 22.91 \text{ \AA}$ respectively. The observed parameter a is close to that of $\text{CaFe}_{12}\text{O}_{19}$, which is obvious as Fe^{3+} ions have larger ionic radii than Al^{3+} and hence a is predominantly governed by the larger Fe^{3+} ions. A perusal of the structure shows that c is more susceptible to stoichiometric changes than a . The plot of $1/\chi_M$ vs T (figure 1) is nearly linear, indicative of paramagnetic behaviour of the compound. The compound is found to be paramagnetic even at room temperature. This may be attributed to the substitution of Al^{3+} (up to 23%), replacing the magnetic ions occupying the sites in the five-fold position, which contributes to the dominant magnetic moment to the material. The plot of $\ln \sigma$ vs $1/T$ is shown in figure 2. The activation energy is found to be 0.86 eV.

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