

Structural and magnetic properties of $\text{CaMg}_2\text{Fe}_{16}\text{O}_{27}$

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Abstract. A new compound, $\text{CaMg}_2\text{Fe}_{16}\text{O}_{27}$, is synthesized for the first time, in polycrystalline form, using stoichiometric mixture of oxides with standard ceramic technique and characterized by X-ray diffraction. It is found to have a hexagonal W-type structure with lattice parameters $a = 5.850 \text{ \AA}$ and $c = 33.156 \text{ \AA}$. Electrical studies show that the compound is a semiconductor with energy of activation, $\Delta E = 0.56 \text{ eV}$. Electrical conductivity results show a transition in the conductivity vs temperature plot near the Curie temperature. The activation energy value obtained for the paramagnetic phase is found to be higher than that of the ferrimagnetic phase. The molar magnetic susceptibility was measured in the temperature range 300–850 K and the results show that the compound is ferrimagnetic at room temperature. The compound also shows hysteresis at 300 K. Paramagnetic nature of the sample above Curie temperature is also studied. The Curie molar constant C_M calculated from the plot of $1/C_M$ vs $T(K)$ is found to be nearly in agreement with the expected value.

Keywords. W-type ferrite; electrical conductivity; paramagnetic susceptibility; Curie molar constant.

1. Introduction

Calcium hexaferrite $\text{CaMg}_2\text{-W}$ belongs to the family of W-type ferrites like $\text{BaFe}_{18}\text{O}_{27}$ and $\text{SrFe}_{18}\text{O}_{27}$ (Smit and Wijn 1959; Lotgering *et al* 1980). The crystal structure and the chemistry of W-type hexaferrites are closely related to $\text{BaFe}_{12}\text{O}_{19}$ (M-type). The crystal structure of M- and W-type hexaferrite can be described as an alternating stacking of spinel and R blocks (figure 1) in the direction of the hexagonal C axis. The spinel blocks in the W-type structure are twice as thick as the M-structure (Braun 1957). Substituted hexaferrites are interesting due to their specific magnetic behaviour and electronic conduction (Graetsch *et al* 1984; Deschizeaux *et al* 1985). In the W hexaferrites the magnetic properties can be varied in wide range by a suitable choice of the additionally occurring divalent cations, without changing the iron content. Besides different types of substitutions, in the present paper, structure and magnetic properties of magnesium substituted $\text{CaMg}_2\text{-W}$ ferrite are reported with a view to study the effect of nonmagnetic substitution on the structural, electrical and magnetic behaviour of ferrites.

2. Experimental

Polycrystalline samples were prepared by the standard ceramic technique. High purity oxides of CaO, MgO, and Fe_2O_3 were carefully dehydrated and mixed in proper molar ratio under AR grade acetone in an agate mortar.

The samples were fired at 1200°C for more than 100 h in an electrical furnace. The temperature of the furnace was then cooled down at the rate 60°C/h . The phase of the final sample was verified by X-ray diffraction with copper radiation.

The d.c. resistivity of the sample was measured using a LCR meter. The end faces of the pellet were coated with a thin layer of conducting silver paste and the resistivity was measured from room temperature to 850 K. The magnetic hystereses at 300 K and 150 K for the compound were recorded using vibrating sample magnetometer. Curie temperature and paramagnetic behaviour above T_c were studied using a Guoy balance.

3. Results and discussion

The polycrystalline $\text{CaMg}_2\text{-W}$ sample has been studied by the X-ray diffraction powder method and found to exhibit a hexagonal W-type symmetry (space group $P6_3/mmc$) with lattice parameters $a = 5.850 \text{ \AA}$ and $c = 33.156 \text{ \AA}$. Typical X-ray diffraction pattern of the compound is shown in figure 2. The structural data, viz. d_{hkl} observed and calculated, and intensities observed with reflection indices are included in table 1.

The temperature dependence of magnetic susceptibility measurements showed that the Curie temperature of the compound $\text{CaMg}_2\text{-W}$ was 713 K. The compound also showed hysteresis at 300 K (figure 3) with $H_c = 20.76 \text{ Oe}$, $B_r = 0.048 \text{ emu}$ and $M = 6.857 \text{ emu/g}$. Generally a diamagnetic substitution leads to a decrease of the Curie temperature and of the saturation magnetization. But sub-

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stitution of Zn^{2+} shows opposite tendency for saturation magnetization in some W ferrites (Albanese *et al* 1976; Sawadh and Kulkarni 2000). The same is observed by Mg^{2+} substitution in $CaMg^{2+}Fe_{16}O_{27}$. The magnetization is found to be greater than the substitution of magnetic ions

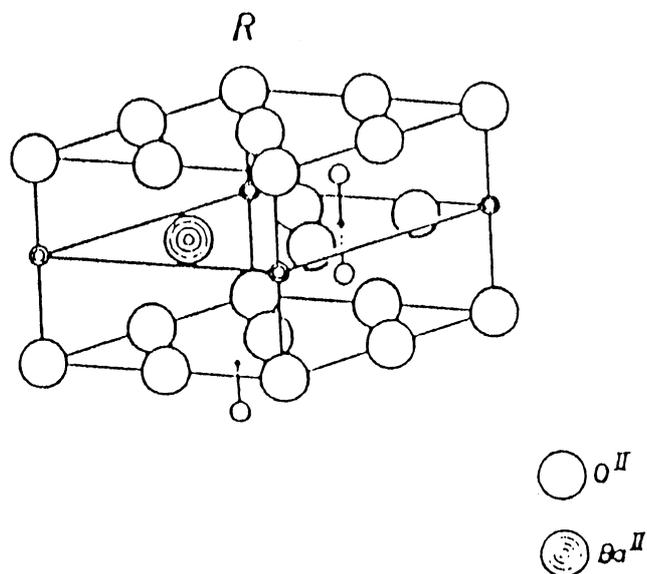


Figure 1. Perspective drawing of the R block.

like Cu^{2+} and Co^{2+} . This can be explained by the preference of the Mg^{2+} ions for tetrahedral coordination. As it has been pointed out by Albanese and Asti (1970) the only available tetrahedral sites ($4e$ and $4fiv$) belongs to the spin down oriented sublattice. The diamagnetic substitution with Mg^{2+} ions lowers the magnetic moment of this minority sublattice and increases the total magnetic moment. The value of H_c is found to be low ($\cong 20$ Oe) which may be due to formation of the W ferrite occurring at high temperature ($T \geq 1200^\circ C$) which implies a large grain growth and results in a very low coercive value (Leccabue *et al* 1986).

The value of Curie molar constant (C_M) was calculated from the plot of inverse molar magnetic susceptibility vs T shown in figure 4. The C_M determined from magnetically sensitive ions shows that all the iron ions are in trivalent state and the variation is linear indicating that no electron transfer has occurred during the reaction or against the temperature range of study. The theoretical value of C_M is calculated for high spin state of Fe^{3+} ions along with orbital quenching and is found to be 70 which is in fair agreement with experimentally observed value (62.50) indicating occurrence of no change in valency distribution.

The variation of $\ln S$ vs $10^3/T$ is shown in figure 5. The resistivity of the sample at room temperature is found to

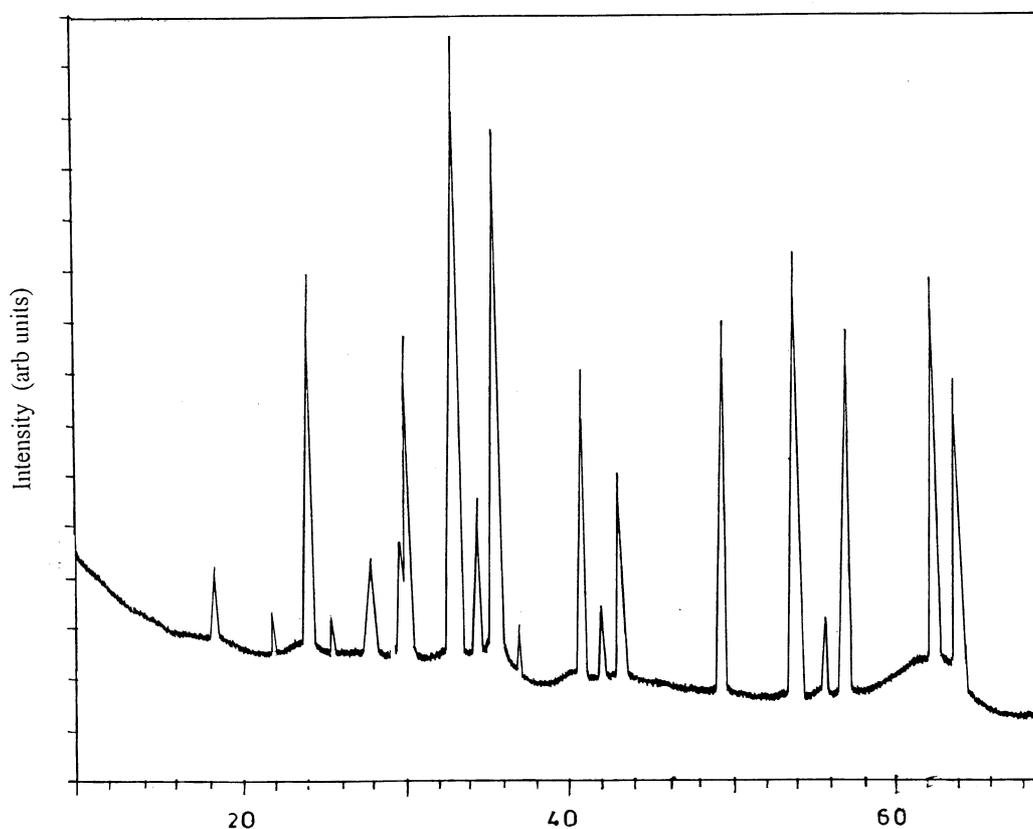


Figure 2. X-ray diffraction pattern of $CaMg_2Fe_{16}O_{27}$.

be of the order of $10^6 \Omega \text{ cm}$ which is much larger than magnetic double substitution of Me_2 by Cu and Fe jointly viz. $[\text{Ba}(\text{CuFe})\text{W} \cong 5000 \Omega \text{ cm}]$ (Mignot *et al* 1986). High activation energy of $\text{CaMg}_2\text{-W}$ (0.56 eV) may be due to higher room temperature resistivity as compared to $\text{Ba}(\text{CuFe})\text{W}$ ferrite (0.28 eV) and is also due to tight bonding of carriers in Mg^{2+} ions. The variation of resistivity and activation energy was explained on the basis of hopping mechanism for charge carriers between cations which are close to each other. The electrical resistivity temperature behaviour obey the relation,

$$S = S_0 \exp(-\Delta E/kT),$$

indicating the semiconducting nature of the compound. The dip observed is in the vicinity of the Curie temperature, contributed to the change in spin arrangement in

Table 1. X-ray diffraction data of $\text{CaMg}_2\text{Fe}_{16}\text{O}_{27}$.

d_{obs} (Å)	d_{cal} (Å)	I_{obs}	h	k	l
4.841	4.844	4.3	1	0	2
4.031	4.026	1.4	1	0	5
3.684	3.684	38.9	0	0	9
3.495	3.460	1.5	1	0	7
3.200	3.208	5.5	1	0	8
2.970	2.979	25.7	1	0	9
2.703	2.680	100.0	1	1	5
2.606	2.600	10.5	1	0	11
2.533	2.533	73.5	2	0	0
2.424	2.426	1.9	1	0	12
2.206	2.210	24.4	0	0	15
2.146	2.145	2.4	1	0	14
2.098	2.099	11.4	1	1	11
1.842	1.841	34.2	1	1	14
1.695	1.691	52.0	1	1	16
1.613	1.616	88.7	2	1	11
1.486	1.489	38.1	2	0	18
1.454	1.456	22.5	2	2	2

Lattice parameters: $a = 5.850 \text{ \AA}$; $c = 33.156 \text{ \AA}$.

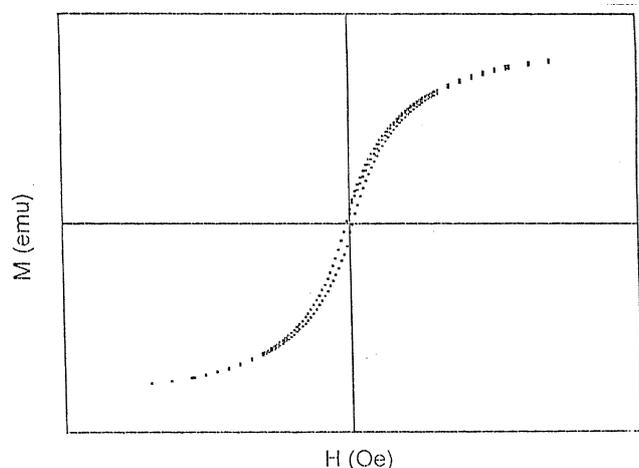


Figure 3. Typical hysteresis loop for $\text{CaMg}_2\text{Fe}_{16}\text{O}_{27}$ at 300 K.

ferrimagnetic compound at the Curie temperature below which magnetic ordering sets in.

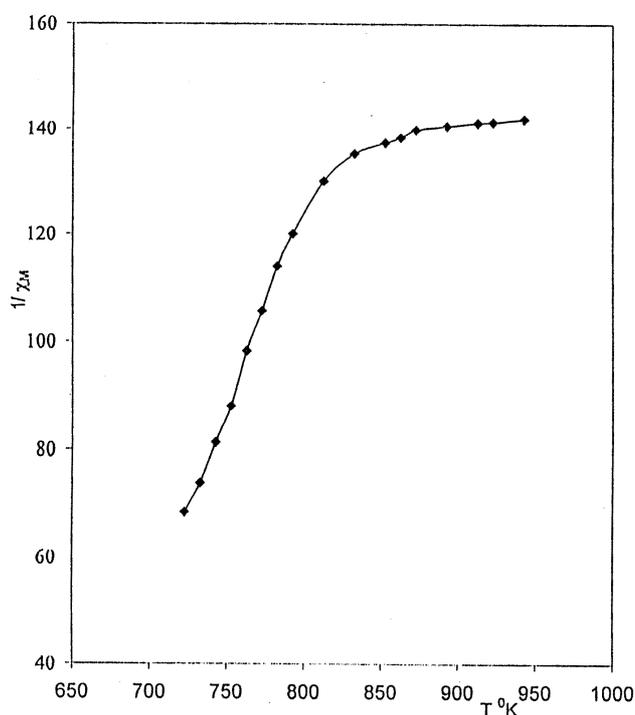


Figure 4. Magnetic susceptibility ($1/C_M$) vs $T^\circ\text{K}$ for $\text{CaMg}_2\text{Fe}_{16}\text{O}_{27}$.

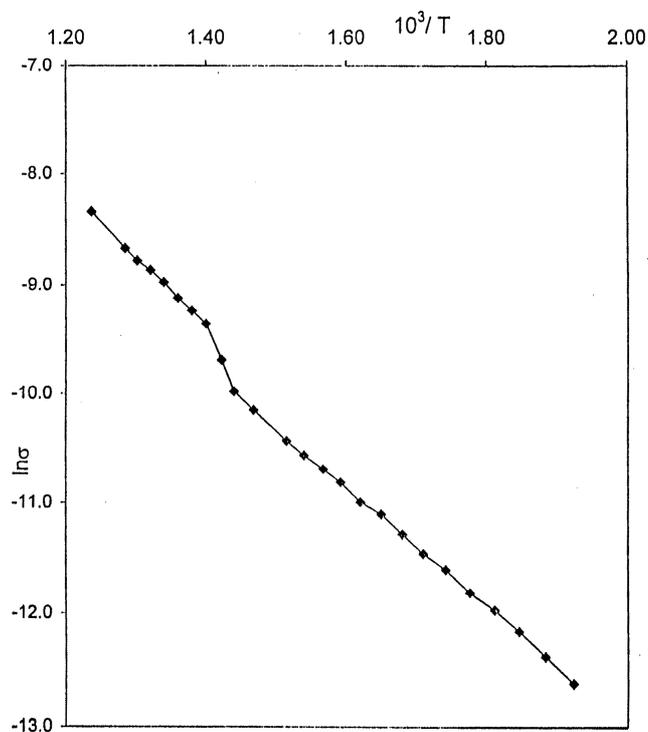


Figure 5. Conductivity ($\ln \sigma$) vs temperature for $\text{CaMg}_2\text{Fe}_{16}\text{O}_{27}$.

4. Conclusions

The standard ceramic technique which is used for preparing soft ferrites can equally be applied to W-type ferrites to yield the requisite properties. The experimental results show that improved magnetic properties can be achieved by adjusting the amount of the nonmagnetic substitution. The substitution of appropriate amounts of Mg^{2+} ions into the tetrahedral sites in the W-type structure enhances the magnetization and coercive force can be reduced. The paramagnetic studies above Curie temperature indicates no change to have occurred in valency distribution. Because of high value of Curie temperature, resistivity and magnetization, $CaMg_2Fe_{16}O_{27}$ can have large potential applications. We conclude that appropriate amount of Mg^{2+} substitution is important for the best magnetic properties.

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