Effect of sintering on the magnetization behaviour of $\text{Mg}_x\text{Zn}_{(1-x)}\text{Fe}_2\text{O}_4$ system

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Abstract. Magnesium zinc ferrites with the general formula $\text{Mg}_x\text{Zn}_{(1-x)}\text{Fe}_2\text{O}_4$ were prepared by the standard ceramic technology route involving double sintering. X-ray analysis was carried out to confirm the single-phase formation as well as to calculate the lattice parameters. Two sets of samples were prepared by sintering the samples at 1100°C for 15 and 30 h respectively. The high-field loop tracer was used to measure the hysteresis parameters. It is observed that the sintering conditions effectively modify the magnetization characteristics of these ferrites.

Keywords. Magnetization; Mg-Zn ferrites; sintering.

1. Introduction

Recent trends in ferrite technology have shifted towards the study of ferrites in relation to their microstructure and modification of their properties through microstructure control (Jonker and Stuijts 1971). It has been well established that the properties of ferrites depend greatly on the intrinsic parameters like grain size and porosity and the latter in turn is determined by sintering time and temperature (Rodrigue 1977). The relation between magnetism, microstructure and crystal chemistry has been treated by Broese van Groenou *et al* (1968/69). Naik and Powar (1985) reported the effect of porosity on electrical properties of Ni-Zn ferrites. The effect of pentavalent additions on the microstructure and grain growth characteristics of Ni-Zn ferrites has been presented by Jain *et al* (1983). Igarasi and Okazaki (1977) studied the effect of porosity and grain size on the magnetic properties of Ni-Zn ferrites. Rikukawa (1982) established a semi-empirical relation between permeability, anisotropy and average grain size. The effect of intergranular porosity on the initial permeability and coercive force in a manganese zinc ferrite was reported by Jain *et al* (1976).

The zinc-containing ferrites are a class of very important magnetic materials because of their wide variety of applications in microwaves. Magnetic hysteresis studies on slow-cooled and quenched Cu-Zn ferrites were discussed by Sawant and Patil (1981). Rezelescu and Cuciureanu (1969) correlated the curie point with cation distribution in Cu-Zn ferrites. Evans *et al* (1968) and Patil and Kulkarni (1979) studied these ferrites using Mössbauer spectroscopy. The Mössbauer spectra of some Mg-Zn ferrites have been reported by Kulkarni and Joshi (1985). Similar results on $\text{Mg}_{0.25}\text{Zn}_{0.75}\text{Fe}_2\text{O}_4$ were discussed by Josyulu *et al* (1982).

Not much data on magnetization of Mg-Zn ferrites is available in the literature in relation to their microstructure. The present communication reports the magnetization behaviour of Mg-Zn ferrites for varying concentrations of zinc and the effect of sintering conditions.

2. Experimental

The Mg-Zn ferrite samples ($\text{Mg}_x\text{Zn}_{(1-x)}\text{Fe}_2\text{O}_4$) with varying Zn contents ($x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0) were prepared by double-sintering method starting with AR grade component chemicals MgO, ZnO and Fe_2O_3 . The samples were presintered at 800°C for 15 h in clean platinum crucibles in air. The samples were finally sintered at 1100°C for 15 and 30 h respectively. Lattice constants calculated from X-ray data using computerized X-ray diffractometer (APD 1700 automated powder diffractometer, Philips, Holland) are in good agreement with the previously reported values (Smith and Wijn 1959). The microstructure was studied using a scanning electron microscope (Cambridge Stereoscan 250 MK3). The hysteresis characteristics were measured using a high-field loop tracer at liquid N_2 temperature (Likhite *et al* 1965).

3. Results and discussion

The experimental values of saturation magnetization (M_s) and magnetic moment (nB) as a function of sintering time are given in table 1 along with the data on Curie temperatures and Yafet-Kittle (Y-K) angles. The Y-K angles and nB values were calculated using the formulae

$$nB = (6 + x) \cos YK - 5(1 - x), \quad (1)$$

$$nB = (\text{molecular weight} \cdot M_s) / 5585 \cdot \text{density}. \quad (2)$$

The values of nB for copper ferrite samples sintered at 1100°C for 30 h agree well with the values reported earlier (Sawant and Patil 1981). A typical hysteresis pattern is shown in figure 1 and the electron micrographs in figure 2. Figures 3 and 4 show the graphical variation of M_s and nB values as a function of zinc content in the samples. It can be clearly observed that as the zinc content in the samples increases the M_s value increases along with the nB value until they become maximum for a sample with $\text{Zn} = 0.2$ and then fall to zero for zinc-rich samples viz. $\text{Mg}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$ and ZnFe_2O_4 . In general, it is observed that M_s and nB curves (figures 3 and 4) for samples sintered for 30 h lie above similar curves for samples sintered at 15 h at the same temperature. The Curie values show a continuous decrease as the Zn content increases, it being zero for zinc ferrite.

Table 1. Values of porosity, M_s , nB , Y-K angles and Curie temperatures for samples sintered at 1100°C for 15 h (I) and 30 h (II).

Composition	Porosity		M_s (emu/g)		Magnetic moment nB		Y-K angles		Curie temperature	
					(Bhor magneton)		(deg)			
	I	II	I	II	I	II	I	II	I	II
MgFe_2O_4	0.31	0.27	29.67	36.34	1.058	1.296	0.0	0.0	441	426
$\text{Mg}_{0.8}\text{Zn}_{0.2}\text{Fe}_2\text{O}_4$	0.35	0.34	41.25	67.64	1.532	2.513	0.0	0.0	368	352
$\text{Mg}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$	0.35	0.31	32.41	46.28	1.252	1.787	48.37	41.58	198	181
$\text{Mg}_{0.4}\text{Zn}_{0.6}\text{Fe}_2\text{O}_4$	0.36	0.34	16.61	22.57	0.666	0.905	66.17	63.88	—	—
$\text{Mg}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$	0.35	0.31	5.93	7.85	0.247	0.326	79.43	78.75	—	—
ZnFe_2O_4	0.28	0.25	—	—	—	—	90.0	90.0	—	—

$$(\text{Zn}_x\text{Fe}_{1-x})^A(\text{Mg}_{1-x}\text{Fe}_{1+x})^B\text{O}_4.$$

The values of M_s and hence nB for the zinc-rich ferrites are zero. The Curie points are also not observed for these samples. For the zinc ferrite A - B interaction does not exist, the B - B interaction lines up half the magnetic ions in one direction and the other half in the opposite direction so that alternate planes of the B sublattice are magnetized in opposite direction rendering zinc ferrite antiferromagnetic.

Figure 2. Scanning electron micrograph of $\text{Mg}_{0.6}\text{Zn}_{0.4}\text{Fe}_2\text{O}_4$ sintered at 1100 °C for 15 h (a) and 30 h (b).

The values of Y - K angles for samples with $x=0.8$ and 1.0 ($\text{Zn}=0.2$ and 0) are zero indicating clearly that their magnetization can be explained on the basis of Néel two sub-lattice model. Further the Y - K angles increase as the content of zinc increases. It suggests that the magnetization in these two particular samples cannot be explained on the basis of two sub-lattice models. However, the same can be explained on the basis of canted spin model. The rise of Y - K angles with the content of zinc is indicative of the fact that the triangular spin is favoured in the B site leading to the reduction in A - B interaction. Though the B - B interactions are antiferromagnetic, the overall effect of A - B interaction prevails over that of B - B interaction causing the spins on the B sites to become parallel to each other.

Figure 3. Variation of n_B (Bohr magneton) with Zn content.

Figure 4. Variation of M_s with Zn content.

Similarly, the presence of canted spins have been confirmed both experimentally and theoretically in the case of Cu-Zn ferrites (Kulkarni and Patil 1972).

In general, it can be observed that magnetization values for samples sintered for longer duration are higher than samples sintered for shorter duration. As has been established in ceramic samples, the increase in grain size and decrease in porosity occur as a function of sintering time, the sintering temperature being sufficiently high and constant. The results have been confirmed in our case (figure 2) and have been discussed in detail earlier with scanning electron microscope studies (Patil 1988). As a result, saturation magnetization increases for samples sintered for longer durations. Apart from the increase in grain size, the rise in magnetization may be attributed to a number of other microstructural changes that take place during sintering.

Each grain possesses a certain resultant magnetic moment. Since the rate of grain growth depends on sintering time (Smith 1986), the porosity is high for specimens sintered for lower sintering times. A pore is a sort of void or a gap and this will break up the magnetic circuit between grain to grain. If the number of pores is large this may lead to the net reduction of magnetization in the bulk. The grain boundary acts as an obstacle for the domain wall motion or rotation. Due to the large

number of grains per cc, the net area of the grain boundary increases and thus greater resistance for the process of magnetization is observed. When the material is sintered for longer sintering time, the net area decreases due to densification of grains and the magnetization gets intensified more easily.

Besides, when there are more pores the probability of occurrence of closed pore chains increases leading to reduction of magnetization. This view is supported by the work of Rikukawa (1982). According to the model proposed by him, the demagnetizing field is caused by closed pores and closed grain boundaries. Rikukawa proposed an expression connecting permeability, porosity, average grain size and effective thickness of grain boundaries. It appears that at a high sintering temperature the pores are reduced and the effect of formation of closed chains is decreased. For a further understanding a detailed microstructure analysis of the samples is required to be carried out to find out the relation between magnetization and grain size at different sintering temperatures and durations.

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References

- Broese van Groenou A, Bongers P F and Stuijts A L 1968/69 *Mater. Sci. Engg.* **3** 317
Evans B J and Hafnes S S 1969 *J. Phys. Chem. Solids* **29** 1573
Gorter E W 1954 *Philips Res. Rep.* **9** 321
Igarasi H and Okazaki K 1977 *J. Am. Ceram. Soc. (USA)* **60** 51
Jain G C, Das B K, Khanduja R S and Gupta G C 1976 *J. Mater. Sci.* **11** 4335
Jain G C, Das B K, Tripathi R B and Narayan R 1983 *J. Mater. Sci.* **18** 1583
Jonker G H and Stuijts A L 1971 *Philips Tech. Rev.* **32** 79
Josyulu O S, Sobhanadri J, Narayanaswamy A and Nagarajan T 1982 *Indian J. Pure Appl. Phys.* **20** 404
Kulkarni R G and Joshi H H 1985 *Solid State Commun.* **53** 1005
Kulkarni R G and Patil V U 1972 *J. Mater. Sci.* **17** 843
Likhite S D, Murthy C R K and Sahsrabudhe P W 1965 *Rev. Sci. Instrum.* **36** 1558
Naik A B and Powar J I 1985 *Indian J. Pure and Appl. Phys.* **23** 436
Patil S R 1988 *Studies on the physical properties of some magnesium-zinc ferrites*, M. Phil. Thesis, Shivaji University, Kolhapur, 149
Patil V U and Kulkarni R G 1979 *Solid State Commun.* **31** 551
Rezlescu N 1970 *C. R. Acad. Sci. Ser. B (France)* **270** 18, 1134
Rezlescu N and Cuciureanu 1969 *C. R. Acad. Sci. B (France)*, **269** 19, 952
Rikukawa H 1982 *IEEE Trans. Magn. (USA)* **18** 1535
Rodrigue G P 1977 in *Treatise on materials science* (ed.) R K MacCrown (New York: Academic Press)
Sawant S R and Patil R N 1981 *Solid State Commun.* **40** 391
Smith W F 1986 in *Principles of materials science and engineering*, (New York: MacGraw-Hill) pp. 527
Smith J and Wijn H P J 1959 *Ferrites: Philips Technical Reports* 144
Yafet Y and Kittle C 1954 *Phys. Rev.* **9** 295