Magnetic Properties of Sintered Ferrites of a MnO-ZnO-Fe₂O₃ Ternary System*

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An investigation of magnetic properties of a MnO-ZnO-Fe₂O₃ ternary system, crystallized in various atmospheric conditions is reported in this paper. The initial permeability, maximum permeability, saturation magnetization, Curie temperature and hysteresis loop were measured for these ceramic ferrites. Also, the crystal structure of these specimens were examined by X-ray diffraction. It has been found that a high permeability region in the ternary system is markedly wider in the case of sintering in nitrogen than in air, because the excess hematite is reduced to magnetite in the region where the Fe₂O₃ content is more than 50 mol %. It has also been found that the line connecting the maxima of the initial permeability agrees with the lines of zero magnetostriction and minimum magnetic anisotropy and that manganese-rich ferrites sintered in nitrogen, exhibit a square hysteresis loop.

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I. Introduction

Since Snoek⁽¹⁾ found that manganese zinc ferrites are useful in practice because of their high permeability and low loss over a frequency range of several hundred kc/sec, magnetic properties of some manganese zinc ferrites having some particular compositions have been studied in detail⁽¹⁾⁻⁽⁷⁾. But the general relation between magnetic properties and composition of the MnO-ZnO-Fe₂O₃ ternary system still remains unknown, owing to the fact that the properties of the sintered products are strongly dependent upon the conditions of the sintering treatment and ions of various valence states, especially Fe²⁺ and Mn³⁺ which are formed by oxidation and reduction during the sintering treatment⁽⁸⁻¹¹⁾. In the case of ferrites containing zinc, the preferential volatilization of Zn⁽¹²⁾⁻⁽¹⁴⁾ causes loss of Zn and often makes it difficult to prepare polycrystalline ceramics having definite compositions. In the present study, a systematic investigation was made of the magnetic characteristics of polycrystalline ceramics of the MnO-ZnO-Fe₂O₃ system. All sintering was done either in the atmosphere or in an atmosphere of nitrogen.

II. Experimental Procedure

1. Preparation of specimens

For the present work, a series of manganese-zinc ferrite specimens whose compositions are shown in Fig. 1 were prepared by standard ceramic techniques.

Fig. 1 Compositions of the manganese-zinc ferrites specimens used. Squares show the specimens having a square hysteresis loop.

For the initial metal oxides, α -Fe₂O₃ was prepared by heating ferrous oxalate, obtained from ferrous sulfate, in air at 450°C, Mn₂O₃ was prepared by heating MnCO₃ in air at 1000°C for 2 hours. To prepare zinc oxide, reagent grade ZnO was used. These reagents were weighed out in pre-determined proportions, mixed and ground in a steel ball-mill for 8 hours. Next the mixture was dried and pre-calcined at 800°C for 2 hours in air. The mixture was then ground in a steel mortar to a fine powder and pressed in dies to form rings or rods. Final sintering was made by either of two ways; (a) Molded samples were heated in air for 2 hours at 1400°C and cooled to 800°C at a cooling rate of 400°C per hour and then quenched in air from 800°C; (b) Samples were heated in nitrogen gas in the same way as in (a) except the specimens were slowly cooled in the furnace to room temperature. In the case of (a), the quenching treatment was carried out to prevent marked oxidation which occurs during the cooling process, of ferrites which have compositions near Mn_{0.5}Zn_{0.5}Fe₂O₄⁽⁴⁾.

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2. Method of measurement

The initial and maximum permeabilities, saturation magnetization, saturation magnetostriction, and the Curie temperature were measured for all of the ferrite specimens, for the purpose of phase identification in relation to the firing cycles, also X-ray diffraction patterns were taken of each specimen.

A ring-shaped specimen, outer diameter: 28 mm, inner diameter: 20 mm, height: 6 mm, having a square cross section, area of 4mm × 6mm was used for the measurement of permeabilities and the B-H curve. For the initial permeability, μ_0 , the effective permeability value was measured with an impedance bridge at a frequency of 1000 cycles. Maximum permeability, μ_m , was obtained from B-H curves which were obtained with an automatically recording fluxmeter⁽¹⁵⁾. The saturation magnetization was measured in the homogeneous field of an electromagnet on disk shaped specimens, about 0.5 mm thick and about 10 mm in diameter. The disk specimens were sliced from rod shaped specimens.

The saturation magnetostriction was measured by the resistance wire strain-gauge method. The strain-gauge was cemented on a disk, 1 to 2 mm thick and

tion of the gauge wire on the surface of the disk. Since the saturation magnetization, $4\pi I_s$, of this system is about 5,000 G maximum for the specimens. Therefore, the specimens can be saturated sufficiently at this field strength, even when the effect of the demagnetizing field cannot be neglected. Magnetostriction of the order of 10^{-6} could be measured by the use of a ballistic galvanometer having a sensitivity of the order of 10^{-9} amperes connected to a bridge consisting of two variable resistances and two gauges, i.e., the active gauge attached to the surface of the ferrite specimen and the dummy gauge attached to the Al_2O_3 plate.

The oxides formed by sintering in air or in nitrogen were examined by X-ray analysis to determine the crystal structure. The lattice constants were thus determined, and the presence of multivalency ions was confirmed by X-ray and chemical analysis. An X-ray diffractometer "Geigerflex" with iron target made by the Rigaku Electric Co. was used for the X-ray studies. The K_β line is eliminated with a Mn filter.

III. Experimental Results

1. Initial and maximum permeabilities

Contours of the initial permeability, μ_0 , and the

Fig. 2 Contours of the initial permeability (μ_0). The solid lines represents the data for the specimens sintered in nitrogen and the broken lines the data for the specimens sintered in air.

Fig. 3 Contours of the maximum permeability (μ_m). The solid lines represents the data for the specimens sintered in nitrogen and the broken lines the data for the specimens sintered in air.

about 10 mm in diameter, which had been sliced from a rod shaped specimen. External magnetic fields ranging up to 10,000 Oe were applied parallel to the direc-

maximum permeability μ_m , are obtained as shown in Figs. 2 and 3 respectively. Solid lines represent the data for specimens sintered in nitrogen and broken lines those for specimens sintered in air. In Fig. 2, the air sintered specimens containing 70 mol % MnO and 30

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mol % Fe₂O₃, show the highest μ_0 of the MnO-Fe₂O₃ binary system. In the ternary system, the highest μ_0 was observed with an air sintered specimen containing 50 mol % Fe₂O₃, 25 mol % MnO and 25 mol % ZnO, as is well known. The μ_0 value almost reached 3,000. The region where μ_0 is larger than 1,000 is a narrow zone extending toward the MnO side, as shown in Fig. 2. For specimens sintered in nitrogen, the contours of μ_0 were considerably different from those mentioned above. In the MnO-Fe₂O₃ system, the maximum μ_0 appears at 40 mol % MnO and 60 mol % Fe₂O₃. In the ternary system, the contours are almost the same as those of the samples sintered in air when the Fe₂O₃ content is less than 50 %, but the region of high μ_0

sintered in nitrogen. It may be accepted that the value of μ_0 will increase further if the nitrogen treatment is correctly done.

Equi μ curves of the maximum permeability are almost similar to those of μ_0 as shown in Fig. 3. The region of high μ_m extends toward the Fe₂O₃ rich side by nitrogen treatment. The composition which shows the maximum μ_m value is also the same as that in the case of μ_0 .

2. Saturation magnetization

Fig. 4 shows the relation between the saturation magnetization $4\pi I_s$ and the mixture composition. In the case of nitrogen treatment, the value of saturation

Fig. 4 Contours of the saturation flux density ($4\pi I_s$). The solid lines represents the data for the specimens sintered in nitrogen and the broken lines the data for the specimens sintered in air.

Fig. 5 Contours of Curie temperature in degrees Centigrade.

values extends much wider when the Fe₂O₃ content is more than 50 %. In the case of specimens sintered in air, the precipitation of α -Fe₂O₃ increases in specimens containing more than 50 mol % of Fe₂O₃ and the magnetic properties deteriorate. On the other hand in the case of specimens sintered in nitrogen, part of the excess Fe₂O₃ is reduced to magnetite and this forms a single phase structure of spinel in which magnetite exists as a solid solution in the region which contains up to 75 % Fe₂O₃. So the extension of the region of high μ_0 may be attributed to the extension of the spinel structure region. The maximum value of μ_0 obtained in the present study was 5,800 with those specimens

magnetization gradually rises with increasing Fe₂O₃ content, but in the case of treatment in air, the curve shows a smooth maximum at about 60 mol % Fe₂O₃ and then decreases with the increase of the Fe₂O₃ content. These results show that saturation was affected by precipitated hematite.

The rapid decrease of saturation magnetization in the ZnO side is quite the same as in permeability. Fig. 5 shows the relation between the Curie point and the mixture composition in the case of air-sintered specimens.

3. Magnetostriction

Fig. 6 shows the relation between the saturation

magnetostriction and the mixture composition. The value of saturation magnetostriction is positive in the Fe_2O_3 rich region and is negative in the Fe_2O_3 poor region for specimens treated either in air or in nitrogen. Therefore, there exists a region where the magnetostriction is zero between the two regions. Such a region is approximately in the region for 53 mol % Fe_2O_3 and there is no large difference between the specimens sintered in air and sintered in nitrogen. But, the maximum position of permeability appears in this region only when the sample is treated in nitrogen. As mentioned above, this is because the magnetic properties deteriorate markedly by the precipitation of $\alpha\text{-Fe}_2\text{O}_3$ when the specimens are sintered in air.

ture of the hysteresis curve on a specimen containing 35 mol % Fe_2O_3 , 60 mol % MnO and 5 mol % ZnO . These specimens contain ZnO and so they are characterized by a lower coercive force than the well-known manganese magnesium ferrites⁽¹⁶⁾. The coercive force decreased with the increasing ZnO content, but the rectangular hysteresis characteristics disappeared when the ZnO content becomes more than 15 mol %. Fig. 8 shows the effect of the ZnO content on the hysteresis characteristics and coercive force when the specimens are sintered in nitrogen. In this figure the content of Fe_2O_3 was fixed at 35 mol % and only the ZnO content was varied. (Here the hysteresis characteristics are expressed by the ratio B_r/B_s . B_r is the residual flux

Fig. 6 Contours of the magnetostriction (λ_s). The solid lines represents the data for the specimens sintered in nitrogen and the broken lines the data for the specimens sintered in air.

4. Rectangular hysteresis loop

It was found that the samples treated in nitrogen show excellent rectangular hysteresis loops when the

density and B_s is the flux density at a magnetic field of 5 Oe.)

It has also been reported that a similar tendency can be observed when Zn is substituted for Mg in manganese-magnesium ferrites⁽¹⁷⁾.

Fig. 7 Rectangular hysteresis loop at various temperatures.

composition corresponds to those denoted by squares in Fig. 1. A typical example is shown in Fig. 7 which shows the results of measurements at various tempera-

IV. Discussion

1. The effect of sintering treatment on the mixture composition

The magnetic property results obtained depend largely upon the amount of hematite which is formed during the firing cycle. When manganese ferrite was fired and cooled slowly in air, the Mn_2O_3 and the Fe_2O_3 phase appears in the ferrite phase at temperatures between 1,050 and 500°C⁽¹⁰⁾. In the present study the specimens were cooled comparatively rapidly (400°C/hour) in the furnace until 800°C is reached and then quenched from 800°C in air. So the above two phases are more or less present depending upon the composition. Especially, in the

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region where the Fe₂O₃ content is more than 50 mol %, the excess iron ion, which exists as Fe²⁺ at the sintering temperature, oxidizes to Fe³⁺ during the cooling process and the precipitation of α -Fe₂O₃ occurs to a

Fig. 8 Squareness and coercive force of square loop hysteresis ferrites containing 35 mol % MnO as dependent on the ZnO content.

considerable extent. In fact, the precipitation of α -Fe₂O₃ is significant in all of the Fe₂O₃ rich composition region in the ternary diagram, according to results obtained by X-ray analysis. The amount of α -Fe₂O₃ in each specimen

Table 1 X-ray intensities of α -Fe₂O₃ for specimen sintered in air.

Composition			Intensity of α -Fe ₂ O ₃ (104)	Composition			Intensity of α -Fe ₂ O ₃ (104)
Fe ₂ O ₃	MnO	ZnO		Fe ₂ O ₃	MnO	ZnO	
mol %	mol %	mol %		mol %	mol %	mol %	
100	0	0	100	60	30	10	11
90	10	0	100		20	20	33
	0	10	87		10	30	15
80	20	0	80		0	40	—
	10	10	54	50	50	0	18
	0	20	74		40	10	0
70	30	0	23		30	20	0
	20	10	17		20	30	5
	10	20	28		10	40	0
	0	30	54		0	50	0
60	40	0	18	40	60	0	0

Fig. 9. Contours of the lattice constants in Angstrom. The solid lines represents the data for the specimens sintered in nitrogen and the broken lines data for the specimens sintered in air.

is estimated as shown in Table 1, from the intensity of the (104) line of α -Fe₂O₃. In this table, the intensity of the (104) line of a specimen consisting of 100 mol % Fe₂O₃ was taken as 100. According to this result, α -Fe₂O₃ could not be detected when the Fe₂O₃ content was less than 50 mol %. In the region of 50 to 30 mol

% Fe₂O₃, 60 to 10 mol % MnO, and 0 to 50 mol % ZnO, the specimen consists of a single phase of cubic spinel. The lattice constant is 8.45 to 8.50 Å, as shown in Fig. 9. On the other hand, in the case of treatment in nitrogen, the precipitation of α -Fe₂O₃ is not detectable at all in the region of 30 to 70 mol % Fe₂O₃. But, when the Fe₂O₃ content was more than 80 %, the presence of a small amount of α -Fe₂O₃ as a 2nd phase was noticed. Consequently, the excess Fe ion forms magnetite in specimens treated in nitrogen and the spinel phase will consist of a solid solution of manganese zinc ferrite and magnetite, corresponding to the composition. Actually, according to the result of chemical analysis (Fig. 10), about 40 mol % FeO is contained in a specimen of 100 mol % Fe₂O₃ treated in nitrogen. As the Fe₂O₃ content decreases the amount of FeO formed decreases linearly.

According to the results obtained by X-ray analysis, both the intensity and the lattice constant were almost the same for specimens consisting of a single spinel phase, in treatment either in air or nitrogen.

In specimens containing an excess of more than 50 % MnO, μ_0 largely decreases by treatment either in nitrogen or in air. This may be attributed to the appearance of a small amount of Mn₂O₃⁽¹⁸⁾, as will be mentioned later.

2. The origin of the high permeability

Harvey *et al.*⁽¹⁹⁾ reported that the composition which shows the highest permeability lies near that of zero magnetostriction, in the sintered oxide of the NiO-ZnO-Fe₂O₃ system. The same results were obtained by measurement of the magnetostriction of the MnO-ZnO-Fe₂O₃ system (Fig. 2'6). The composition which gives the highest initial permeability is 50 mol % Fe₂O₃, 25 mol % MnO, and 25 mol % ZnO. The magnetostriction is almost equal to zero at this composition. It was also mentioned above that the line of the highest per-

meability appears near the line of composition where the magnetostriction is zero, only in the case of specimens sintered in nitrogen.

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On the initial permeability of sintered, polycrystalline ferrite, it cannot be simply determined whether the permeability originates by wall displacement or by spin rotation because the permeability is affected by the size

Fig. 10 Results of chemical analysis for the MnO-Fe₂O₃ system.

of the crystallites and by the size and the distribution of the pores. Since any appreciable increase in μ_0 occurs by wall displacement, the crystalline magnetic anisotropy constant K_1 can be roughly estimated for several compositions of the ternary system, assuming μ_0 is only due to the spin rotation in a region where μ_0 is comparatively low.

The initial permeability due to rotation in the anisotropy field is given by the following general equation

$$\mu_0 - 1 = kI_s^2/K_1$$

where I_s is the saturation magnetization and k is a constant variously given. Weisz⁽²⁰⁾ found the value of k to be 21 from the value of K_1 , magnetic anisotropy constant, of a single magnetite crystal⁽²¹⁾, which is -1.1×10^5 ergs/cm³. Now taking this value for k , K_1 was calculated for several compositions which give comparatively low μ , i.e., for the compositions on the line of 20, 50, and 70 mol % MnO, and the variation of K_1 was examined

Fig. 11 Estimated anisotropy constants for different compositions.

with respect to the composition. Fig. 11 shows the results obtained. According to the calculation, the value of $|K_1|$ is 1.8×10^4 ergs/cm³, and 1.4×10^3 ergs/cm³ for specimens containing 50 mol % MnO and 50 mol % Fe₂O₃, and 20 mol % MnO, 30 mol % ZnO, and 50 mol % Fe₂O₃, respectively. Known values of K_1 are -2.8×10^4 ergs/cm³ for MnFe₂O₄⁽²²⁾ (from torque experiments) and -3.8×10^3 for Mn_{0.45}Zn_{0.55}Fe₂O₄⁽²³⁾ (from microwave measurements). When the value obtained by the authors are compared with those already known, it is noticed that the author's values are quite reasonable, if we consider the difference in composition. It is known from Fig. 11 that $|K_1|$ rapidly decreases with the increase of the ZnO content and the decrease of the Fe₂O₃ content, if the MnO content is constant. This fact is obviously due to the effect of the addition of ZnO and is also deduced from the decrease of Curie temperature with increase of the ZnO content. It is noticed that the region of small $|K_1|$ almost agrees with the narrow zone of high initial permeability shown in Fig. 2. As shown in Fig. 12, the Curie temperature is below 0°C for the specimens on the high ZnO side of the high initial permeability zone, and the initial permeability of such a specimen is more than 1,000 at temperatures below 0°C.

Fig. 12 Initial permeability of some specimens as a function of temperature.

3. Squareness in the hysteresis loop

It was mentioned before that the specimens showing a rectangular hysteresis loop are obtained when they are sintered in nitrogen and have compositions of 30 to 45 mol % Fe₂O₃, 40 to 70 mol % MnO, and 0 to 15 mol % ZnO. From the results obtained by X-ray analysis the lattice constant is 8.52 to 8.60 in this region and are shown in Fig. 9. These values are comparatively larger than that of other compositions but the axial

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ratio a/c is the same (0.708*) as that of the other compositions. Also the specimens sintered in air have the same lattice constant and the same axial ratio but the hysteresis loop is not rectangular.

Since the presence of the Mn^{3+} ion has been considered to be necessary for the square hysteresis loop⁽²⁴⁾ of manganese magnesium ferrites, this was examined from the amount of Mn_2O_3 precipitated. In Fig. 10, the amount of Mn_2O_3 in the region of the square loop is more than those in the Fe_2O_3 rich region, but no difference was found between the specimens sintered under different atmospheric conditions. Therefore, further investigation is required before the cause of the squareness of this material is clearly understood.

The ferrites with rectangular hysteresis, developed in our laboratory, has been used for double frequency memory cores⁽²⁵⁾. Especially those with 2 to 5 wt. % MgO added have excellent characteristics in high speed correspondence and low watt consumption.

V. Summary

We have studied the relation between the magnetic

*Here the index of the diffraction line of spinels is treated as a tetragonal system, so the axial ratio of the cubic spinel is 0.708.

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properties and the compositions of a polycrystalline ferrite $MnO-ZnO-Fe_2O_3$ ternary system, sintered in air or in nitrogen, and determined the region of composition which gives high permeability. Sintering in nitrogen gas gives preparations of high permeability in a wider region of composition than that in air. This may be attributed to the fact that, in the case of nitrogen treatment, the precipitation of $\alpha-Fe_2O_3$ does not occur at all but solid solution of the magnetite and manganese zinc ferrite exists in a wide range below 70 mol % Fe_2O_3 whereas in the case of air treatment, the single cubic spinel phase can only exist within a narrow region between 30 to 50 mol % Fe_2O_3 . It was also confirmed that the highest permeability occurs along the line of minimum $|K_1|$ and the line of zero magnetostriction.

Furthermore in the Mn-rich ferrite region, it was found that the hysteresis loop becomes rectangular. These materials are characterized by a low coercive force compared with manganese magnesium ferrites.

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