Current trends in applications of magnetic ceramic materials

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Abstract. Magnetic oxides, a major constituent of magnetic ceramic materials, are most extensively used in a variety of applications as soft, moderate and hard ferrites. I review here its applications with special emphasis on some recent developments in magnetic recording materials.

Keywords. Magnetic ceramic materials; their applications.

1. Introduction

Among the magnetic ceramics, magnetic oxides are the most important and rather the only relevant materials from the point of view of their applications. Magnetic oxides which are commonly known as ferrites are ferrimagnetic in structure as originally proposed by Neel (1948). The most common magnetic oxides which find wide applications as soft, hard or moderate ferrites are spinels, garnets and hexaferrites. Here I will limit this review to various applications of these oxides only. Comprehensive reviews on this subject are given by Standley (1972) and Wohlfarth (1982). The latest developments in the area of ferrites has been very well documented in the proceedings of ICF5 (Srivastava and Patni 1989). In this review, special emphasis will be given to magnetic recording materials and some typical results of the work in this area carried out in our laboratory will be presented.

2. Magnetic oxides—some relevant properties

The magnetic oxides (spinels, garnets and hexaferrites) by virtue of their structure can accommodate a variety of cations at different sites enabling a wide variation in properties. Further variation in synthetic methods can bring about large changes in some extrinsic properties. A majority of them are high resistivity materials making them more suitable for high frequency and low loss applications. Besides their resistance to oxidation, which is quite an advantage over metallic systems, they are also corrosion resistant. Spinels, $M^{2+}Fe_2^{3+}O_4$, which are cubic with 8 formula units possess two sublattices. If all the M^{2+} ions go at the tetrahedral and Fe^{3+} ions at the octahedral sites, normal spinel is formed. The typical examples are $ZnFe_2O_4$ and $CdFe_2O_4$. When half of the Fe^{3+} ions go to the tetrahedral site while the rest to the octahedral site with M^{2+} ions, the inverse spinel such as $NiFe_2O_4$ or $MnFe_2O_4$ is formed.

Garnets ($Y_3^{3+}Fe_5^{3+}O_{12}$) are bcc cubic structures with 8 formula units and three sublattices. While Fe^{3+} ions distribute between octahedral and tetrahedral sites in 2:3 ratio, Y^{3+} ions (or rare earth ions) go to dodecahedral site. Substituted garnets and ferrites as soft ferrites find numerous applications. γ-Fe_2O_3 (which is also a spinel structure) has been widely used as magnetic recording material. Among hexaferrites,

M-type ($BaFe_{12}O_{19}$) and W-type ($BaMe_2Fe_{16}O_{27}$) are the most common because of their easy formation and wide applications. Besides, X ($Ba_2Me_2Fe_{28}O_{46}$), Y ($Ba_2Me_2Fe_{12}O_{22}$) and Z ($Ba_3Me_2Fe_{24}O_{47}$) type hexaferrites are also known (Wohlfarth 1982). These are hexagonal crystal structures with a fairly large crystal anisotropy formed by superposition of R ($BaFe_6O_{11}$), S ($Me_2Fe_4O_8$) or T ($Ba_2Fe_8O_{14}$) blocks. For example, when successive R blocks are interspaced by S blocks, a M-type ferrite is formed, while when successive R blocks are interspaced by two S blocks, a W-type ferrite is formed. T blocks are required in the formation of Y or Z-type hexaferrites. Hexaferrites have been commonly applied as permanent magnets. Recently, they have also been exploited as recording materials which will be discussed later in this review.

3. Applications of ferrites

Ferrites are mainly classified into three categories based on their coercivity. Generally, most of the hard ferrites applications can be envisaged when the coercivity is > 1.5 K Oe. The H_c of moderate ferrites lie within the range of 100 Oe and 1.5 KOe when most of the recording applications are feasible. For the soft ferrites, H_c has to be very low (< 10 Oe). Soft ferrites can be further classified into two categories based on the low and high frequency applications. The growing applications of ferrites have been elucidated in figure 1 in the form of a tree after Hoshino (1980).

3.1 *Soft ferrites*

For the low and high frequency applications, the most important technical properties are M_s, H_c, μ_i and losses. It is generally not possible to obtain the best combination of these properties for any specific application. By varying the composition or adding additives or by varying the preparation technique, one can, to a large extent, control
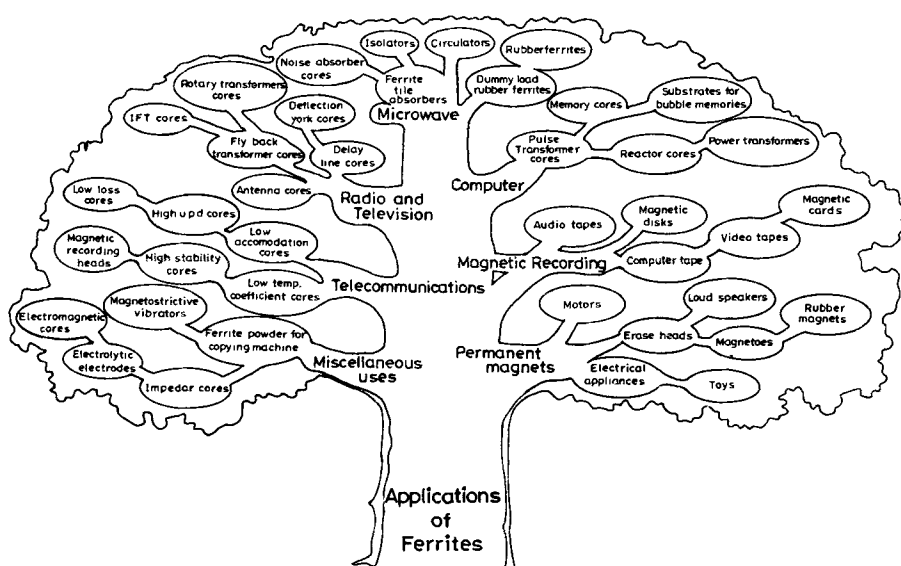

Figure 1.   Wide range of applications of ferrites (symbolised after Hoshino 1980).

most parameters required for any particular application. A comprehensive account of these are given by Das (1981). The largest consumption of soft ferrites is in television where almost half a kilogram is used for each set in the form of deflection yoke, UI core, U, L, E and I cores. Mn–Zn ferrite has the most appropriate parameters for this application. A typical data for a good quality Mn–Zn ferrite for the above application is as follows: $\mu_i = 900 \pm 25\%$, $B = 3500\,G$, $\rho = 10\,Ohm\,cm$, $T_c \sim 150°C$. Dimensional tolerances are quite critical. Because of low resistivity, Mn–Zn ferrites are generally used up to 500 kHz only.

Some of the other low frequency applications of soft ferrites include magnetic recording heads, inductor and transformer cores, filter cores, magnetostrictive vibrators and many other miscellaneous applications. However, each application warrants some different characteristics. Accordingly, the material has to be developed and tailor-made. For example, for magnetic recording head, besides low H_c, high μ, thermal stability, wear and corrosion resistance, one also requires low magnetostriction and high frequency response. Amongst the ferrites, hot pressed and single crystal Mn–Zn and Ni–Zn ferrites are found quite suitable for this purpose. As regards the high frequency applications of these soft ferrites, high resistivity and passive dielectric properties are a must and the variation of RF permeability is important. The most important parameters which need to be evaluated are $4\pi M_s$, T_c, g_{eff}, ΔH, spin wave linewidth ΔH_k, dielectric constant ε and dielectric loss tangent, $\tan \delta$. High frequency applications include large number of microwave components such as circulators, isolators, gyrators, phase shifters, YIG tuned filters, switches and substrates for microwave integrated circuits. The materials which are generally known to be suitable for the above applications are substituted yttrium iron garnets such as YAlIG, YGdIG, YAlGdIG and spinel ferrites such as Ni–Zn, Mg–Zn and Mg–Mn ferrites. Typical data for Al substituted hot pressed YIG is as follows: $4\pi M_s = 1200\,G$, $g_{eff} = 2\cdot00$, $\Delta H = 40\,Oe$, $\Delta H_{eff} = 4\,Oe$, $\Delta H_k = 3\cdot5$ and $\tan \delta = 2 \times 10^4$.

3.2 Hard ferrites

Magnetic hardness is due to fine particles having shape and crystalline anisotropy. A large crystalline anisotropy is characteristic of hexaferrites. Hence, a large coercivity is almost an inherent property of hexaferrite and other than that it is oxidation- and corrosion-resistant. Its temperature stability is good and cheapest among all the hard magnets. By virtue of its low cost and being suitable $(BH)_{max}$ for isotropic and anisotropic hexaferrites, it finds wide applications in motors, generators, loudspeakers, telephones, meter switches, magnetic separators, toys, flexible and rubber magnets, magnetic latch and magnetic levitation.

Among metallic systems, a number of alloys are superior property-wise. Still, due to reasons mentioned above, hexaferrites capture major portion of the hard magnet applications. To illustrate this, table 1 and figure 2 give the cost and percentage application comparison of hexaferrite magnets with other metallic magnets respectively. While table 1 shows that it is the cheapest among all the hard magnets, figure 2 exhibits the dominance of hard ferrites in the market. The projected growth in figure 2 for NdFeB is rather optimistic and according to experts, it could be even much lower. It is worth mentioning here that some of the unusual applications of ferrites include magnetic paints, vibration absorber, catalyser, artificial manure and several medical applications. Sugimoto (1984) discussed these applications in detail.

Table 1. Cost comparison (with respect to weight and energy-product) of hexaferrite with other known metallic magnet systems.

	Anisotropic ferrite	Alnico	$SmCo_5$	NdFeB
Energy product in MGOe	$3 \cdot 6 \sim 4 \cdot 3$	$\sim 5 \cdot 5$	$18 \sim 20$	35
in MJ/m^3	$28 \cdot 6 \sim 34 \cdot 4$	~ 44	$143 \sim 159$	275
Price ($/kg)	$2 \cdot 5 \sim 5$	$25 \sim 35$	~ 350	~ 570
Price ($ per Joule)	$\sim 0 \cdot 55$	$5 \cdot 07$	$\sim 19 \cdot 04$	$15 \cdot 1$
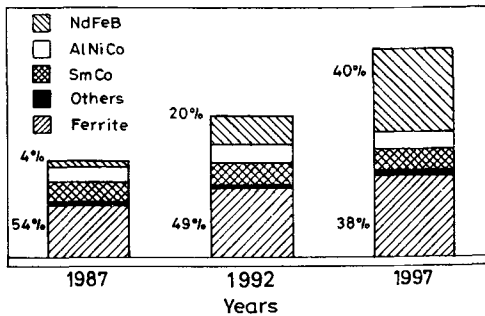
Figure 2. Projected applications of hexaferrite compared to other metallic alloy magnets.

4. The world and Indian scenario

Table 2 shows the estimated ferrite production in different parts of the world in 1990. The corresponding figure pertaining to 1979 is also shown for comparison. India's contribution is hardly 1% of the world's total output. Japan tops the list in the manufacture of both soft and hard ferrites. While in some countries, such as the US, UK etc. where labour is expensive, the production has decreased, in other countries such as South Korea and Taiwan (where labour is cheaper), the production has increased. Unfortunately, in India, there has been no increase in the production over these years. While only about 25% of our demand of soft ferrites for low frequency applications is being met by indigenous manufacture of hardly 600 metric tons per year, for high frequency applications, we are importing them.

As far as hard ferrite goes, the situation in the country is much better. In fact, the manufacturing of hard ferrites started in 1971 in this country. Now, there are a large number of manufacturers and the total capacity is about 6000 T per year. The world market for permanent magnet is very close to $2 billion and is expected to grow to $3 billion by 1997.

5. Magnetic recording materials

Amongst the recording materials, the most exploited commercial materials are the discrete particles of magnetic oxides such as γ-Fe_2O_3 or Co doped γ-Fe_2O_3 and CrO_2

Table 2. Estimated ferrite production (in tons) in different countries of the world in 1979 and in 1990 (after Ruthner 1989 in ref. 3).

Country	Hard ferrites		Soft ferrites	
	1979	1989	1979	1989
Canada	4000	4000	3000	300
USA	95000	75000	45000	10000
Mexico	3500	2500	2800	400
Venezuela	2500	1000	1500	200
Brasil	15000	10000	5000	3000
Argentina	3000	1500	2000	500
Chile	600	600	400	200
Scandinavia	1500	100	2000	300
Great Britain	10000	6000	7500	6000
Spain	3000	2500	2000	1000
France	13500	13500	8000	8000
Germany	12500	12500	9000	8000
Italy	20000	18000	1500	200
Netherlands	2500	200	3500	500
Yugoslavia	1600	1600	1000	1000
Bulgaria	1200	1500	600	800
Rumania	1500	1500	800	800
Hungary	1500	1500	1500	1000
CSSR	3000	2500	2000	2000
Poland	4000	2000	3000	1000
German Dem. Rep.	16000	12000	8000	7000
USSR	30000	30000	15000	15000
Egypt	1500	1000	1000	200
Algeria	1000	1000	1000	200
South Africa	1000	1000	0500	200
China	20000	25000	15000	12000
Japan	85000	140000	50000	40000
India	6000	6000	3000	3000
Indonesia	2500	2500	1200	1200
Singapore		6000		500
				500
Thailand		3000		
Malaysia				1000
Philippines	1500	1500	1000	500
Australia	1200	1000	600	500
Turkey	1000	1000	500	100
Israel	600	600	300	200
Iran	1500	1000	1000	500
South Korea	6000	20000	4000	18000
North Korea	2000	500	1500	200
Taiwan, China	6000	20000	4000	14000
Total	382200	431100	209700	159500

(Sharrock 1990). The latest and yet not exploited enough is the fine particles of hexaferrites which derives the required magnetic coercivity from its magnetocrystalline anisotropy while other oxides, as mentioned above, possess the requisite coercivity due to acicular nature. The coercivity, H_c, is perhaps the most important parameter to be controlled for a good magnetic recording material. Low H_c gives poorer wavelength

and frequency response whereas high H_c would require very high bias and erase currents. Therefore, a compromise is required between these two limits. The suitable range is anywhere between 300 Oe and 1·5 KOe depending upon the specific requirement.

Besides the appropriate coercivity, H_c, saturation magnetisation, M_s should be high enough to optimize the output and M_r/M_s, which determines the tape output, should be as close to 1 as possible. The other important basic property is the particle size which needs to be controlled. It should be large enough to provide adequate stability against time dependent magnetic effects. On the other hand, for high signal to noise ratio, narrow transitions, smooth tape and disc surface requires very small particles. Again, a compromised particle size is necessary. An excellent combination of the above mentioned properties should be accompanied by structural, wear and frictional characteristics which depend upon the organic components used for making dispersion.

As pointed out earlier, of late, barium hexaferrite is gaining popularity as a magnetic recording media (Speliotis 1987; Sharrock 1990). Already, high density flexible discs using barium hexaferrite is available commercially (Yamamovi *et al* 1986) and is the most likely candidate for contact duplication of digital audio tapes (Okazaki *et al* 1989). Barium hexaferrite has some obvious advantages over many other recording media. These are high density recording (with a possibility of perpendicular recording), lower cost, easier production, superior high frequency response and its stability and inertness. Besides, coercivity can be changed over a wide range without much reduction in M_s. A variety of synthetic methods have been developed to achieve a wide range of shapes, sizes and coercivities (Nagai *et al* 1985; Bahadur and Chakravorty 1989; Marcello *et al* 1989; Brahma *et al* 1990). One of the synthetic methods widely investigated in the last few years is through glass ceramic route whereby a large control of the above mentioned parameters is possible by small changes in composition, heat-treatment and using nucleating agents (Kubo *et al* 1982; Ram *et al* 1986a, b, c; Bahadur and Chakravorty 1989). In the next section, we discuss some of our own results on hexaferrites synthesized through glass ceramic route.

6. Hexaferrite through glass ceramic route

The glass ceramic route yields intimate mixing of ions at the atomic level with subsequent nucleation and growth at lower temperatures. It also prevents large scale grain growth which is rather common in conventional ceramic route. Apart from this, it yields high strength ceramics due to pore-free uniform microstructure. Also, a fine control of the grain size and shape and its magnetic properties is possible through the appropriate use of nucleating agent and heat-treatment. In the light of these advantages, we have investigated crystallization of hexaferrites in $Mo-Fe_2O_3-B_2O_3$ based glass system (M = Ba, Sr, Ca and Pb) (Ram *et al* 1986a, b, c, 1987, 1988). Also, in many cases up to 1 mol% of nucleating agents of Bi_2O_3, P_2O_5, Ag_2O, As_2O_3, Sb_2O_3 and TiO_2 were used which influence the reaction kinetics considerably. Hence, the resultant glass ceramics exhibit a large variation in magnetic and other relevant properties. Table 3 gives some typical results for Ba hexaferrite based glass ceramics with different nucleating agents.

A significant variation in magnetic properties and volume fraction is indicated with

Table 3. Some typical results of hexaferrite based glass ceramics with different nucleating agents in nominal composition $35\,MO-33\,Fe_2O_3-32\,B_2O_3$ (M = Ba, Ca).

NA used	Hexaferrite phase and its maximum volume fraction	Ms at 10 KOe	Coercivity range (Oe)
M = Ba			
Bi_2O_3	70% M phase	~40	650–3600
Ag_2O	65% M phase	~35	50–2000
P_2O_5	42% M phase	~25	800–1200
TiO_2	Completely inhibits the growth of M-phase	negli-gible	50
As_2O_3	44% M-phase	32	750–3600
$As_2O_3^*$	48% W-phase	~38	3500–5300
When M = Ca			
Ag_2O	25% M-phase	~17	1100–1300
Bi_2O_3	51% M-phase	41	1200–1900
P_2O_5	10% M-phase	45	180
$P_2O_5^{**}$	60% $Ca_3Fe_{15}O_{25}$	47	170–1100

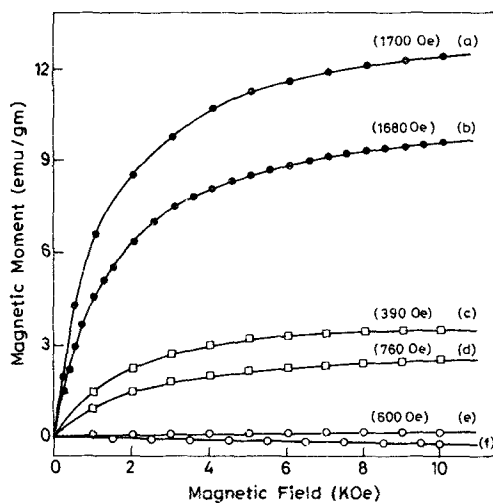NA = Nucleating agent used; * Very small change in nominal composition was done; ** also with $0.1\%\ As_2O_3$.

Figure 3. Plot of magnetisation vs magnetic field for composition $50\,PbO-$, $20\,Fe_2O_3-$, $30\,B_2O_3$ with different heat-temperature. Temperatures and duration are given in degree Kelvin and hours. (a) $725/2\,h + 765/25\,h$, (b) $980/2\,h + 1060/2\,h$, (c) $625/2\,h + 655/2\,h$, (d) $850/2\,h + 925/2\,h$, (e) $625/2\,h + 765/2\,h$ and (f) $850/2\,h + 970/2\,h$. Values of coercivities are given in parenthesis along with each magnetization curve (after Ram *et al* 1986c).

respect to different nucleating agents used. Similarly, there is also a large variation in magnetic properties as a function of variation in the heat-treatment schedule even though no nucleating agent is used (Ram *et al* 1986c). For example, for composition 50 $PbO-20\ Fe_2O_3-30\ B_2O_3$, the magnetization vs field data for different heat-treated samples is shown in figure 3. While sample *e* essentially shows a paramagnetic
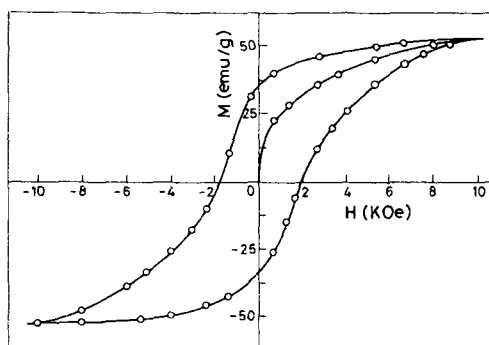
Figure 4. A typical hysteresis loop for a glass ceramic sample in composition $13\,CaO$–$48\,Fe_2O_3$–$39\,B_2O_3$ heat-treated at $1030\,K/2\,h + 1110\,K/2\,h$ (after Ram *et al* 1988).

behaviour with a very low moment, sample *f*, on the other hand, is diamagnetic. All the other glass ceramic samples exhibit a much larger magnetic moment. But, they do not show saturation up to a field of 10 KOe. However, most of them exhibit high coercivity. The coercivity is indicated in parenthesis along with their respective magnetization curves for comparison (figure 3). A typical hysteresis loop for glass ceramic sample obtained after ceramizing the glass composition $13\,CaO$-, $48\,Fe_2O_3$-, $39\,B_2O_3$ at $1030\,K/2\,h + 1110\,K/25\,h$ is shown in figure 4. It exhibits a coercivity of ~ 1800 Oe and a large remanence. This glass ceramic has M-type Ca $Fe_{12}O_{19}$ phase as much as $53\,vol\%$. It may be pointed out that M-type Ca-hexaferrite is not stable if synthesized through normal ceramic route. However, in the above mentioned composition, M-type hexaferrite could be stabilized through the glass ceramic route (Ram *et al* 1988).

Depending upon the nucleating agent used and heat-treatment given, the particle size could vary between hundreds of Angstroms to tens of microns (Ram *et al* 1986c, 1987, 1988). In many cases, acicular particles with aspect ratio up to 26 were obtained while in many other cases platelets were obtained. In some cases, a large value of M_r/M_s (> 0.8) was obtained (Ram *et al* 1986b, 1987), particularly in case of Sr and Ba hexaferrite based glass ceramics. This is another important parameter to be controlled for magnetic recording applications. Therefore, most of the characteristics warranted for a good magnetic recording material are available in glass ceramic based hexaferrites. Attempts are underway to leach out the glass portion with suitable etchant to obtain a fine powder with the required properties for the magnetic recording applications.

Acknowledgement

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