XXIst Century Ferrites

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Abstract. Ferrites have always been a subject of great interest from point of view of magnetic application, since the first compass to present date. In contrast, the scientific interest for iron based magnetic oxides decreased after Ørsted discovery as they where replaces by coil as magnetizing sources. Néel discovery of ferrimagnetism boosted again interest and leads to strong developments during two decades before being of less interest. Recently, the evolution of power electronics toward higher frequency, the downsizing of ceramics microstructure to nanometer scale, the increasing price of rare-earth elements and the development of magnetocaloric materials put light again on ferrite. Areview on three ferrite families is given herein: harder nanostructured Ba\textsuperscript{2+}Fe\textsubscript{12}O\textsubscript{19} magnet processes by spark plasma sintering, magnetocaloric effect associated to the spin transition reorientation of W-ferrite and low temperature spark plasma sintered Ni-Zn-Cu ferrites for high frequency power applications.

1. Introduction

Brief history of ferrites

Ferrite is the oldest magnetic material known, together with iron, but the only terrestrial native magnetic material, since natural metallic iron is from meteoritic origin. Furthermore, magnetic virtue of iron is observable only in presence of a appreciable magnetic field, i.e. a loadstone, or natural magnet, the only source of magnetic field known until Ørsted’s discovery in 1819. The load stone is mainly composed of magnetite, Fe\textsubscript{3}O\textsubscript{4} nowadays classified as a semi-hard ferromagnetic, which is formed by cooling of magma coming out from earth liquid coat, in atmosphere. Contrarily to common thinking, magnetite is not efficiently magnetized by the earth magnetic field, but thunders impacts that produce very strong currents do. Indeed, load stones are mostly found on the top of volcanoes and magnetized in circles. The attracting power of loadstone on iron was reported in 685 BC by Thales of Milletus, a Greek scientist leaving in Magnesia province (presently Turkey). During the early middle-age, Chinese made relatively inefficient compasses from spoon shaped magnetite stones, but the modern compass made out from a magnetized hard-steel needle pivoting on a brass pin was known about X\textsuperscript{th} century in China and Arabic word although is precise origin (Arabia or China) is still controversial. However, the real efficient navigation compass was invented in Genova, from an Arabic one, improved by putting it in a brass box, which damp oscillations by producing eddy currents. Improvement in understanding of magnetism was bring by a French military engineer, Pierre de Maricourt (known as Petrus Peregrinus, the vehicular language of science was Latin until the XVII\textsuperscript{th} century) in 1269: he defines north and south poles and shown that breaking a magnet creates new poles on the broken surfaces (one would say now $\text{div}\mathbf{B}=0$). Then it was not 1600, when the doctor of Queen Elisabeth the first, William Gilbert, observed the direction of a compass around magnetite bar and sphere, plotting for the first time what we call now a magnetic vector field. Until the 1820’s, the
loadstone was used mainly for magnetizing compass needles and scientific shows for aristocrats and bourgeois in the Europeans universities and curiosity cabinets. The most famous exception is the young uneducated bookbinder Michael Faraday, who used a magnetite bar to make the first prototype electrical motor in the aim of experimenting the reciprocal effect of Arago’s rotation. Faraday in his magnetic classification (ferro, para, diamagnetism) obviously ranked magnetite in the ferromagnetic bodies class from macroscopic observation. Then, magnetite disappeared from scientific preoccupations since coils feed by Volta stacks and soon after electrical machines, where better magnetic field sources and hard steels better permanent magnets. When Pierre Weiss (a French political refugee in Switzerland when Alsace was occupied by Prussians) established in mean field theory based on Langevin classical statistical paramagnetism, he discovered that magnetic metal poorly obey his theory as the Ms vs T slope in the low temperature range was too steep in his theory. However, he and other physicists had a great confidence on the mean field theory since it was describing very well the Ms vs T curve of magnetite. Ironically, the fact magnetite is not ferromagnetic was demonstrated by Weiss’ most famous student, Louis Néel in 1948. Interestingly, while most of magnetic alloys were known and used in industry (Fe-Si, Fe-Co, Fe-Ni, Cr-Co hard steels, AlNiCo), ferrites where still limited to iron ferrite, namely magnetite having the spinelle structure and formula $M^2Fe_3O_4$ (M=Fe). Néel’s theory and high frequency electronics development boosted ferrite research and created ferrite industry. Great efforts have been done in order improve ferrite properties by softening (M=Mg), hardening (M=Co), increasing magnetisation (M=Zn$_{0.5}$+Fe$_{0.5}$) or making them electrical insulators (M=Cu or Ni). With industrial development of radiocommunications and power electronics, two main families of cubic ferrites emerges in the 50’s, in one hand, the (Mn,Zn)Fe$_2$O$_4$ for LF-MF band having a high induction, high permeability and low losses and, in the over hand, (Ni,Zn) Fe$_2$O$_4$ for HF-VHF band showing high resistivity [2]. One should also mention Li-ferrites and Y-garnets used in UHF, the later being the only transparent magnetic material known. In parallel, a great advance in hard materials was realized in Japan in 1955 with the discovery of hexagonal ferrites, from which the common M type, BaFe$_{12}$O$_{19}$ showing the magnetoplumbite structure, and the less known Y, W and Z type, used in the UHF-SHF band having slightly different structures. Since the beginning of the 60’s, only gradual improvements have been obtained in ferrite industry: we are now trying to show three direction that can undergo strong evolution in the near future.

**Fig. 1:** Gilbert’s drawing of field around a spherical magnet  
**Fig.2:** Vortex image in a 70 nm permalloy particle obtained by electron holography  
**Fig.3:** Domain structure in a Fe-Si grain oriented steel sheet obtained by magneto-optical Kerr effect.

**Why nanostructured dense ferrites?**
Magnetism is mainly governed by three kind of energy:
- exchange energy, a quantum mechanical term originating from electrostatic interaction and depending on between outer shell electrons distance, represented by the exchange constant 50<A<200 pJm\(^{-1}\), which forces spins to be parallel or anti-parallel at atomic scale;
- magnetocrystalline energy, represented by the anisotropy constant 100<K<10\(^6\) Jm\(^{-3}\) linked to spin orbit coupling and lattice symmetry which forces spin to be aligned within an easy axis;
- magnetostatic energy, proportional to the squared saturation magnetisation 0.3<J<2.5 T, a classical term described by Maxwell equations acting at any distance from atomic to macroscopic scale, which tends to create a close structure of magnetic moments.

Minimisation of the total energy for a given particle as a function of its size, shows that in coarse grain materials, the magnetisation organizes itself in a so-called domain structure where spin are parallel inside the domains and anti-parallel from one domain to its neighbour (eventually perpendicular in cubic materials), these domain being separated by a region where spins turns helically, the Bloch's wall, which thickness is L\(\text{w}=\sqrt{(A/K)}\). In soft materials, where the magneto-cristalline energy is low compared to magnetostatic, a crystal is multi-domain when its size is roughly over 3L\(\text{w}\) typically about 100 nm. The single-domain (uniformly magnetized) configuration is energetically favourable when exchange dominates the magnetocrystalline energy, which corresponds to a particle more or less smaller than 8L\(\text{w}\), with L\(\text{w}=(2 \mu_0 A/\sqrt{J_s})\). In between, the favoured state is a vortex structure where the spins curls around an easy-axis [4,5]. As domain walls motion is always a dissipative phenomena, the single domain state in soft magnets is favourable to high frequency applications.

In hard materials, the magnetocrystalline terms is very strong (3L\(\text{w}\) is typically few nm) and the uniformly magnetized configuration is favoured for particles smaller than 36\(\mu_0(AK)^{1/2}/J_s\). Because the mechanism of magnetic switching involves mainly phenomena related to the walls (pinning of the wall on defects, nucleation of the walls), the single domain state in hard magnets increases the coercivity, in principle close to the limit given by the so called Stoner-Wohlfarth theory \(\mu_0H_K = 2K/M_s\) [5,6].

In this paper, we will show how these XXth century compounds should evolved with modern chemical and elaboration processes, dragged by the needs of innovative technological applications. In the first part, it will be shown how giant coercivity nanostructured Ba ferrites can be obtained. In the second part, magnetocaloric effect associated to the spin reorientation transition will be addressed, and the third one will describe the properties of Ni-Zn-Cu and the realisation of monolithic solid magnetic components.

| Elaboration conditions | Grain size (±10 nm) | Density (%) | \(M_s\) (Am\(^2\)/kg) | \(M_t/M_s\) | \(\mu_0H_C\) (T) |
|------------------------|---------------------|-------------|------------------------|-------------|-----------------|
| Conventional           | >1000               | >95         | 62                     | 0.51        | 0.26            |
| Calcinated 900°C       | 60                  | -           | 55                     | 0.51        | 0.56            |
| SPS 800°C/0min         | 70                  | 76          | 66                     | 0.57        | 0.51            |
| SPS 800°C/13min        | 84                  | 88          | 66                     | 0.57        | 0.49            |
| SPS 800°C/20min        | 77                  | 86          | 62                     | 0.58        | 0.49            |

2. Giant coercivity of nanostructured M-type Ba hexaferrite

Enhancement of the coercivity of M ferrite has been first obtained by replacement of Ba with Sr. However, this improvement is not spectacular and the coercivity remains below 0.3 T in isotropic magnets and 0.35 in anisotropic ones. Several authors have studied the effect of rare-earth elements (La substitution for Ba, and Co, Ni respectively [3]) and more recently in Sr ferrites, resulting in a coercivity enhancement by about 20% with a maximum value of 0.42 T for Sr\(_{10}\)La\(_{0.2}\)Fe\(_{11.8}\)Co\(_{0.2}\)O\(_{19}\) [4]. Our approach has been completely different: starting from the fact coercivity is inversely dependent on particle size, downsizing of grain down to nanometer range should increase noticeably that figure, a
well known fact observed in Ba ferrite powders. Indeed, according to Néel and Stoner, the upper limit of the coercivity is $\mu_0 H_K = 1.7$ T (these quantities being respectively the anisotropy constant and the magnetisation), for perfectly oriented particles and $0.48 H_K$ for an assembly of non-interacting uniaxial particles with isotropic distribution of easy axes. Several authors have succeed to produce Ba ferrite nanoparticles by soft chemical route and they have found coercivities as high as $0.58$ T for a mean grain size about 100 nm [7,8]. As the anisotropy field is $1.7$ T, the theoretical value for an isotropic magnet is $0.82$ T, so that they reached $70\%$ of the upper limit. However, applications requires solid materials with high density in order to maximize the magnetic induction. This densification is currently obtained by sintering the powder at temperatures about $1000^\circ$C and above, yielding grain growth and in turn a dramatic drop in coercive field.

In a previous work [9], sol-gel route was used to produce particles smaller than the single domain limit (about 200 nm). After calcination at $900^\circ$C, the coercivity for the powder is over 0.5 T. Then the problem to be solved is the grain growth, which was done by using the spark plasma sintering process (SPS). Basically, the technique consist in pulsing an electrical current in a powder closed in a die between to pistons, these part being made from conducting refractory material, usually graphite, under neutral atmosphere or vacuum. The process is capable to reduce the temperature by 100-200°C compared to standard sintering and to keep more or less the grain size of the powder. For metallic powders SPS is actually a Joule heating with locally high temperature at the grains contact points, which, with the help of pressure makes the process very fast. There was a controversial on the process involved in ceramics since there are usually insulating. Actually, even if the ferrites can have resistivity as high as $10^6$ $\Omega m$, this figure rapidly goes down with temperature because of the semi-conducting behavior and drops by several orders of magnitude above $500^\circ$C [2]. The result is that after sintering at $900^\circ$C (heating and cooling rates about $200^\circ$C/min) for different times, a more than 80% dense material can be obtained with a coercivity close to 0.5 T (see Table1 and Fig. 4), a value never reached before for a hexaferrite anisotropic magnet, which makes it very strong against demagnetisation. The B vs H curve in the second quadrant (see Fig. 4) is almost linear owing to the high coercivity, and the energy product $(BH)_{max}$ which is usually considered as the merit factor for magnets, reaches $90$ kJm$^{-3}$, a valuable enhancement compared to usual value arround 60.

![Graph](image_url)

Fig. 4 : Hystéresis loops of nanostructured hexaferrite magnets obtained by SPS (left) and second quadrant B vs. H loops (right). Lines are iso-BH curves from 60 Jm$^{-3}$ (bottom) to 100 Jm$^{-3}$.

3. Magnetocaloric effect associated to spin transition reorientation in W-type Ba hexaferrite

The magnetocaloric effect referrers to an exchange of heat between a magnetic material and a medium, upon magnetization or demagnetisation. In particular, when the temperature is close to an order/disorder magnetic transition (typically a Curie point), the application of magnetic field can drive the material from disorder (paramagnetic) to magnetic order by orienting spin towards the field,
producing heat release to the medium. Inversely, demagnetization drives back the material to magnetic disorder and heat is absorbed by the material. This thermodynamic cycle is quite similar to the vapour to liquid transition upon pressure exploited in classical cooling systems. As in the former, a latent heat can be associated to the transition to characterize the energy associated to the effect. The magnetocaloric effect at room temperature was first studied by Weiss on pure gadolinium [10], but can be experimented also on Cr substituted Fe-based amorphous ribbons [11] or any kind of alloys having a close to 300 K Curie point such as Fe-Ni-Cu alloys [12]. However, the magnetocaloric effect is not only associated to order/disorder transition (ferro to paramagnetic, i.e. Curie point) but to any change in order yielding a drastic change in the net magnetization. The term giant magnetocaloric effect usually refers to a first order magnetic transition produced by a crystallographic lattice symmetry change: this change can be either ferro to para like in LaFeSi [13] or ferro to antiferro like in CoMnSi [14] or CoMnGeP [15], both yielding a large entropy change due to the metamagnetic transition. Also, a much less known magnetocaloric effect is that associated to spin transition reorientation (STR). Indeed, it has been shown by Belov in 1978 that W-type hexaferrite can show temperature change [16].

W-type hexaferrite is a complex structure composed of M spinel sublattice having the composition BaCo$_{x}$Zn$_{1-x}$Fe$_{16}$O$_{27}$. In this particular compound, the Co contain, x, controls the first and second anisotropy constants and hence the type of anisotropy and its direction.

Fig. 5: the three states of the magnetization in W-ferrite as a function of the relative value of the anisotropy constants and the magnetization curves in the different states when temperature changes.

Measurements performed on single crystals of W-ferrite with x=0.7 shows the change of magnetisation curves across the SRT estimated around 200 K. The magnetocaloric effect is usually measured applying Maxwell relation to the M(T) curve as in [17], however this method is naturally inaccurate because the computation of dM/dT. A more complex but straightforward method is the direct measurement of entropy change. This has been done using a Peltier cell based calorimeter [18]. As seen in Fig.X, this material exhibits a maximum entropy change of $\Delta s = 0.2 \text{ Jkg}^{-1}\text{K}^{-1}$. This value is 20 times smaller than usual magnetocaloric materials but with an almost 4-fold reduced field. Thus the question is to determine whether or not these W-ferrite have practical interest compared to LaFeSi and to find a global criterion for comparison. Indeed, if LaFeSi exhibits high $\Delta s$, the field necessary to reach this value is above 1.5 T, a value that exceeds the residual magnetisation of stronger magnets. As a consequence, Halbach type magnets, 'magic ring' type, have to be used to produce that field. Let's consider a Halbach ring with inner and outer diameter a and b, respectively, and length L, which cavity is completely filled with the magnetocaloric material. The field in the cavity is given by $H=M_0 \ln(a/b)$. The total volume of the system is given by $V=nbL$ and the energy exchanged with the
fluid is \( E = \rho V_{MC} \Delta s(T_2 - T_1) \), with \( V_{MC} = \pi a^2 L \). From these simple equations, one can easily derive the energy per total volume of the system (including magnet) per kelvin:

\[
F = \frac{E}{V(T_2 - T_1)} = \rho \Delta s e^{-2H/M_S} \tag{1}
\]

On the same basis, if one takes the cooling power corresponding to a 1000 cm\(^3\) system (magnet+MC material) based on gadolinium as a reference, one can compute the volume of equivalent system based on other MC material and NdFeB magnets. In Table 2, systems based on different material are presented. These results shows clearly that refrigerators based on W-ferrite would be bigger compared to RE-based ones, they would need at least twice less RE elements.

| Material   | \( \Delta s \) (Jkg\(^{-1}\)K\(^{-1}\)) | \( M_s H \) (T) | \( F \) (Jm\(^3\)K\(^{-1}\)) | RE mass / 1000 cm\(^3\) | V (cm\(^3\)) | V\(_{MC}\) (cm\(^3\)) | RE mass (kg) |
|------------|---------------------------------|----------------|-----------------|---------------------|---------|----------------|------------|
| Gd         | 4                               | 1.6            | 3200            | 7.9                 | 1000    | 153            | 4.4        |
| LaFeSi     | 6                               | 1.6            | 4700            | 1.3                 | 670     | 102            | 2.3        |
| W-ferrite  | 0.2                             | 0.1            | 900             | 0                   | 2350    | 3050           | 1.1        |
| NdFeB      | -                               | 1.4            | -               | 2.4                 | -       | -              | -          |

Table 2: Comparison between MC materials and device dimensions.

Fig. Entropy change at different temperatures as a function of the applied field along c-axis.

Fig. 5: Permeability spectra of SPS Ni-Zn-Cu ferrites.

3. NiZn spinel ferrites for power integration.

Ni-Zn ferrite are well known and widely used for signal application in high frequency due to there high resistivity, but usually not for power applications. The reason is that losses in these materials are considered too high for this kind of applications. Copper substitution in Ni-Zn ferrite was introduced by Nomura in 1992 with the aim of reducing the sintering temperature [20]. Indeed, the high mobility of copper ions makes possible to reduce the sintering temperature significantly (1000°C or even less) that makes possible co-firing with silver instead of Ag-Pd, a more resistive and expensive alloy. Later on, it was proved that by cobalt doping, the material undergoes a spin transition reorientation near room temperature [22] around which the losses are minimized under inductions of several 10 mT above 1 MHz, allowing to use that material in high frequency power applications instead of Mn-Zn [23].
Properties of Ni₁₀₀₋₁₉₅Cu₁₀₀₋₂𝑍n₁₀₀₋₅ninCo₀₀₋₆Fe₂O₄ synthesized by the classical solid route (basic oxides mixing, calcination, milling) and sintered by means of SPS are reported in Table 3. All samples, even sintered at 650°C, are solid and show porosity of 7 to 3%. As SPS is done using graphite dies, the atmosphere must be neutral. As a consequence, heating oxides in contact with carbon produce carbon deposition on the surface of samples and possibly reduction. The carbon deposition is detected by XRD on as-sintered samples and evidenced by the low conductivity. A subsequent carbon burning step has been performed on all samples at 500°C in air for 20 min. The result is a dramatic increase in resistivity reaching values similar to standard annealing in air for the lowest temperatures. Above 700°C, the resistivity remains one or to orders of magnitude below, presumably because of reduction in the core of the sample, which can't be re-oxidized because the porosity is closed. The core reduction is indicated by the high permittivity which DC can be as high as 6000 for samples annealed at 800°C due to internal barrier layer capacitance (IBLC) phenomenon [24].

Table 3: Structural and magnetic properties of NiZnCu ferrite sintered at different temperatures (5 min heating/cooling plus 10 min plateau time).

| Sintering (°C) | Grain size (nm ±20) | Density (%) | Resistivity (Ωm) | ε_r (@1 MHz) | μ_R | f_R (MHz) |
|----------------|-------------------|-------------|------------------|---------------|-----|----------|
| 650            | 60                | 93          | 2.10^3           | 17            | 18  | 200      |
| 700            | 100               | 94          | 3.10^4           | 45            | 45  | 100      |
| 750            | 100               | 96          | 7.10^4           | 60            | 60  | 33       |
| 800            | 80                | 97          | 4.10^5           | 150           | 150 | 210      |

The permeability is increasing with sintering temperature and at the same time, the resonance frequency (i.e. the frequency at which the imaginary part of the permeability is maximum) is decreasing accordingly. The merit factor μ_R.f_R is between 3.6 and 5 GHz, the latter value being comparable to that obtained by classical process [22]. Usually, the increase of the permeability upon sintering temperature is explained by the increase in grain size. Indeed, the area of Bloch walls is enhanced accordingly leading to an uprise in permeability. However, in our case, the grains are small enough to prevent formation of Bloch walls in a grain. Part of the explanation lies to the effect of porosity according to Lorenz relation

\[ \chi_{\text{eff}} = \frac{(1-p)\chi}{1+pN\chi} \]  

As a computation can show, this effect is still not sufficient to explain the change in permeability. It is well known that due to its half-filled 3d shell, Fe³⁺ has a week spin-orbit coupling and thus gives almost no magnetocrystalline anisotropy and magnetostriction. Thus, in this material, anisotropy and magnetostriction are both due to Ni²⁺ only and negative. As we have shown, SPS produce reduction of Fe³⁺ into Fe²⁺ which not only results in increasing the conductivity but also give a positive contribution to both anisotropy and magnetostriction. As a results, there is a net reduction of the anisotropy of the lattice producing the observable enhancement of the permeability. As consequence, the reduction of Fe³⁺ is not only a drawback but also an advantage if it is well controlled in order to optimize the properties globally.

Conclusion

Although ferrites are known since long and can be seen as old materials, they have been in constant evolution in order to satisfy the the demand of industry in terms of properties. One of the main advantage of ferrites is their adaptability: indeed, because of the accommodation capacity of different sites (tétra, octa and eventually bipiramidal) substitutions with many different ions (divalent in general but also mixed-valence) is possible and due to the localized electron nature of their magnetism, the
effect of these substitutions is relatively predictable and usually show quite linear dependence on the substitution rate. For all these reasons, it is expected that ferrites will have a strong development in the XXIst century not only in the three directions explored herein, Ni-Zu-Cu spinels for high frequency, W and M-type hexaferrites for magnetocaloric refrigeration and hard magnets, but also Z and Y-type hexaferrites for microwave antennas and the multiferroic bismuth ferrite BiFeO \(_3\) that shows ferromagnetic as well as ferroelectric behaviours [25].

Fig. 7 : Realization of toroids directly by SPS. Left, mould geometry; centre picture of toroid (scale is cm); right, comparison between permeability spectra of a toroid directly made by SPS and another made by drill a SPS pellet made from the same powder in same conditions (750°C, 110 min)

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