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Sabrina Arcaro
Janio Venturini

Modern Ferrites in Engineering

Synthesis, Processing and Cutting-Edge Applications

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Sabrina Arcaro
Universidade do Extremo Sul Catarinense
Criciúma, Santa Catarina, Brazil

Janio Venturini
Federal University of Rio Grande do Sul
Porto Alegre, Rio Grande do Sul, Brazil

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Chapter 1
A Brief History of Ferrites

Magnetic ceramic materials composed mainly of iron (III) oxide are commonly known as “ferrites.” The first of these materials known to men was lodestone, a mineral form of magnetite (Fe_3O_4) that is naturally magnetized. One of the earliest reports of the unique properties of this ore comes from Thales of Miletus. In the sixth century BC, the philosopher described the attraction of lodestone to iron and other lodestones. Ores from the region around the Greek town of Magnesia, in Asia Minor, are usually considered as the source of the term “magnet.” The attraction phenomenon was also known to the Chinese by the late Warring States period (fourth century BC), as referenced in the *Guiguzi*. By the first centuries of the current era, Chinese divinators reportedly used compass-like devices made of lodestone for their esoteric rituals.

William Gilbert gave us one of the earliest modern scientific descriptions of the properties of lodestones in his “*De Magnete, Magneticisque Corporibus, et de Magno Magnete Tellure*,” published in 1600. In this treatise, Gilbert proposed that the planet behaved like a giant magnet instead of a single region in the poles. He studied these properties via a scale model of the planet (*terrella*, Latin for “small Earth”) made of lodestone. The scientist also claimed that magnetism was the force holding the moon in orbit around Earth. Albeit erroneous, this was one of the first attempts at a scientific explanation for the motion of heavenly bodies as a counterpoint to Aristotelian astronomy.

The work of Takei and Kato kickstarted the utilization of ferrites in electrical appliances. In 1930, the Tokyo Institute of Technology scientists discovered that oxides containing iron and divalent cations had distinctive magnetic properties. Their discovery of these “ferrites” was presented at the Annual Meeting of the American Electrochemical in St Louis [1]. Although initially unsure whether these materials would find a commercial application, their work led to the creation of the TDK Corporation in 1935. Ferrite cores were produced and massively applied for the first time in 1937, mostly in wireless communication devices. By the end of World War II, the company had already produced 5 million ferrite cores, primarily to aid the Japanese war effort.

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In 1948, Neel gave his theoretical description of ferrimagnetism. His work successfully explained the magnetic properties of the zinc ferrites developed by Takei and Kato. The French scientist proposed a sublattice model in which the spins in each crystalline subunit interact with one another, leading to the intriguing magnetic behavior of ferrites. These developments created the conditions for the massive industrial application of ferrite-based electronic devices.

Studies conducted at the Philips laboratories in the Netherlands in the 1940s and 1950s also contributed decisively toward the advancement of ferrites. Snoeck and Verwey are some of the famous researchers from this era that helped create materials with high electrical resistivity and low relaxation losses. Their discoveries led to the quick development and adoption of ferrite cores. The laboratory also created several of the most utilized hexaferrites. In 1950, they created barium ferrite ($BaFe_{12}O_{19}$), a low-cost hexaferrite with elevated coercivity. A decade later, Philips developed strontium hexaferrite, a similar material with improved properties. Both hexaferrites now dominate the worldwide market for these materials.

In the year since, ferrites have become ubiquitous in most electronic devices. Antennas, ferrite cores, and EMI suppressors are examples of applied ferrites that one will undoubtedly interact with in our modern daily life. Nevertheless, the field of application of these materials has been broadening ever since their embryonic stages. Nowadays, the application of ferrites encompasses a wide range of commercial purposes, from the medical field to quantum computing. Given their low cost and unusual properties, it is no surprise that these materials have attracted the industry's interest.

Researchers worldwide are striving to find novel properties and applications for ferrites. Figure 1.1 shows the number of publications indexed in the ScienceDirect portal containing the terms "spinel" and "ferrite." As can be seen in the graph, there is growing interest from researchers worldwide in the development of these extraordinary materials. The number of scientific articles on these ceramics has grown almost ten times in the period between 2000 and 2020.

A bibliometric network of the publications from the same period (Fig. 1.2) gives us insight into the varied research areas focusing on ferrites. This network was created from co-citations, defined as the frequency with which two documents are cited simultaneously by other documents. The manuscripts were extracted from the Scopus database, and the minimum number of co-citations was 10. In general, much effort is still directed at improving their electrical and magnetic properties. However, ferrites are also considered promising materials for application in very disparate fields, such as in biomedicine and lithium-ion batteries, as seen in the network. Undoubtedly, many works focus on studying the structures of ferrites since the structure strongly influences the properties. The synthesis of pure ferrites and their composites is also given great attention. Another focal point for research groups worldwide is the utilization of these materials as magnetic catalysts in organic reactions, as the ease of magnetic separation allows their utilization as unsupported catalysts in industrial reactors.

The 15 countries that have published the most articles with the keywords "ferrite" and "spinel" in the last 20 years are shown in Fig. 1.3. A significant share of research

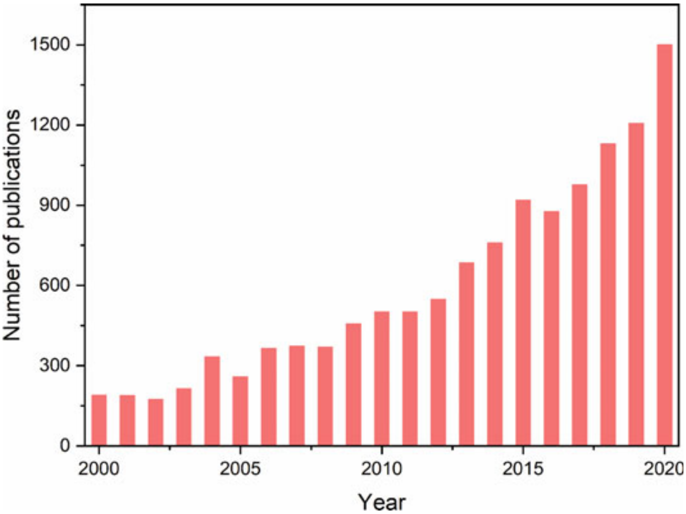

Fig. 1.1 Number of publications in the last twenty years containing the terms “spinel” and “ferrite” indexed in the ScienceDirect database

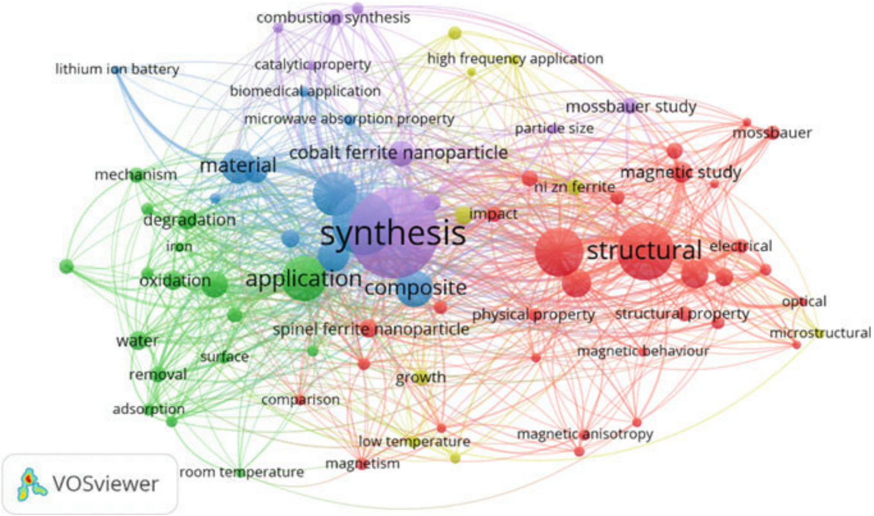

Fig. 1.2 Bibliometric network of publications containing the term “spinel ferrites” in the period between 2000 and 2020. Larger circles indicate a larger prevalence of the terms in the title or abstract of the article. Produced with the aid of the VOSviewer software

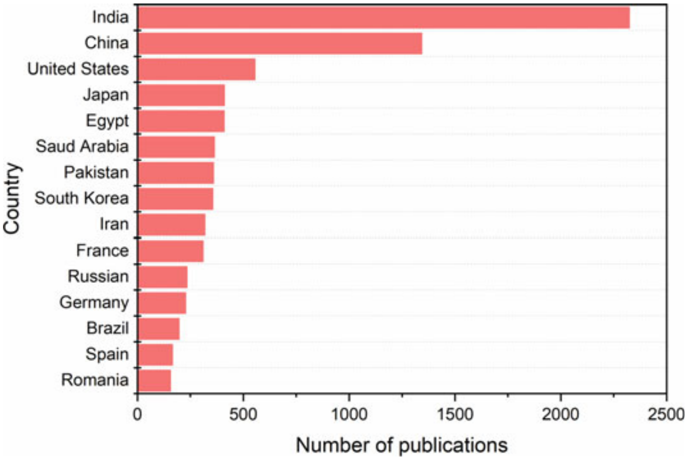

Fig. 1.3 Top 15 countries with the most publications containing the terms "spinel" and "ferrite" indexed in the ScienceDirect database in the last twenty years

in the field of ferrites is carried out in India and China, followed closely by the United States. Other countries such as Japan, France, and South Korea also have prominent publications in this area.

In summary, ferrites are an essential tool in the industrial arsenal ever since they were first mass-produced in the 1930s. This book aims to discuss several of the most relevant properties of these ceramics, as well as their production methods. Selected applications of ferrites will also be addressed.

Reference

1. Kato, Y, Takei, T (1930) Studies on zinc ferrite. Its formation, composition, and chemical and magnetic properties. J Electrochem Soc 57:297–312. https://doi.org/10.1149/1.3492161

Chapter 2
Structure of Ferrites

This chapter discusses the main families of ferrites, spinel, and hexaferrites, as well as some of the other possible crystal structures displayed by these materials. The structure of spinel ferrites and the magnetic consequences of this arrangement are thoroughly covered, along with a discussion on the methods utilized in the modification of the inversion degrees of these ferrimagnets. The structural units of hexaferrites and their main subclassifications are presented. Finally, the crystal structure of perovskite and garnet ferrites is discussed, along with the presentation of their most illustrious members.

2.1 Introduction

Ferrites are a group of materials that are composed of iron (III) oxide (Fe_2O_3) and another transition metal oxide. Their composition can thus be said to be $MeO_x.Fe_2O_3$, where Me is a d-block metal. In general, the material is said to be a ferrite based not only on its composition but also by their display of pronounced magnetic properties.

The family of the ferrites encompasses a wide range of ceramic compositions. Nevertheless, the majority of these materials can be categorized into one of the main ferrites subsets. The first one contains those materials displaying cubic symmetry, the *spinel ferrite*s. Many of the remaining ferrites exhibit hexagonal symmetry and are therefore aptly named *hexaferrites*. A few other crystal arrangements are also widely considered as ferrites and, as such, will likewise be discussed in this chapter.

2.2 Spinel Ferrites

The spinel ferrites are the most readily recognizable ferrites. The most familiar member of this group, magnetite (Fe_3O_4), is not only the archetypal ferrite but indeed

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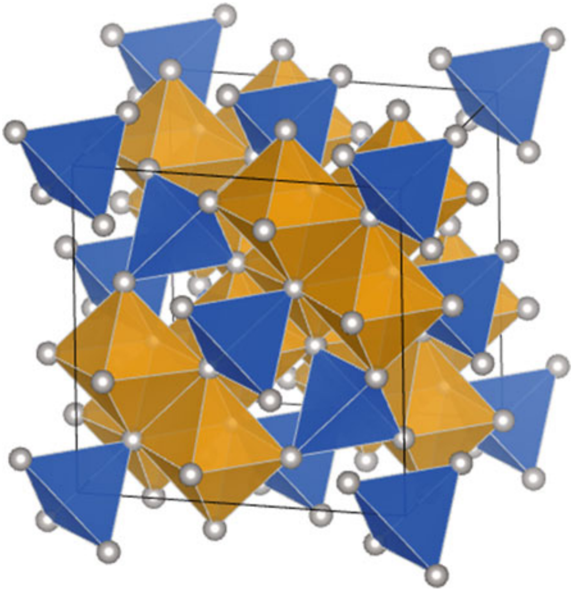

Fig. 2.1 Crystalline structure of spinel ferrites

the earliest material recognized to be magnetic, giving birth to the term “magnetism” itself.

Spinel ferrites can be described by the formula MFe_2O_4, where M is usually a divalent cation, such as cobalt or zinc, or a mixture of cations with an average charge of two (i.e., Li^+ and Fe^{3+}). These materials can display a structural configuration analogous to that of spinel ($MgAl_2O_4$), hence the name of this group. In this AB_2O_4 atomic arrangement, a face-centered cubic lattice of O^{2-} ions is partially filled by the metallic cations. More specifically, one-sixteenth of the tetrahedral positions (site A) is filled by the divalent cations, while one-eighth of the octahedral B sites is populated by trivalent metals—Fe^{3+} in the case of spinel ferrites. The crystal symmetry of this structure can be seen in Fig. 2.1.

Another very common configuration of ferrites is the inverse spinel arrangement. In this case, the tetrahedral positions are all filled by the trivalent iron atoms (Fe^{3+}), while the octahedral voids are populated by the remaining iron atoms and the divalent cation. Such configuration is widespread in some usual ferrites, such as $CoFe_2O_4$ and Fe_3O_4 in their bulk forms.

In reality, most ferrites are neither completely normal nor inverse spinels. In most cases, ferrites adopt a mixed configuration, i.e., an intermediate structure between those two extremes. Their crystalline arrangement can thus be characterized by its degree of inversion x. This parameter ranges from zero (normal spinel) to one, in the case of a wholly inverted spinel. Ferrites that are commonly considered as normal spinels tend to display values that are not precisely zero, given that slight deviations from this value incur a considerable increase in configurational entropy, thus stabilizing the structure. The same can be said of inverse spinels.

The inversion degree of spinel ferrites is of particular importance due to the ferrimagnetic nature of these materials. The major contributor toward the spontaneous spin alignment comes from AB interactions. In other words, the exchange interaction between the tetrahedral and the octahedral sites is the primary driver of the net magnetic alignment in spinel ferrites. These AB interactions are the closest to an ideal angle of 180° and have short Me-O distances, both of which work toward favoring this exchange geometry. BB exchange interactions are much weaker, and the AA situation is even worse, with an A-O-A angle of approximately 80°, thus decreasing the contribution of this exchange integral. The geometries of all possible interactions are depicted in Fig. 2.2. Néel himself explained the ferrimagnetism of most spinel ferrites in terms of the antiparallel alignment arising from the AB interaction. For the magnetism of the ferrites to be consistent throughout the crystal, the entire A (tetrahedral) sublattice arranges its spins antiparallel to those of the B (octahedral) sites. Therefore, in a perfect crystal, each of the sublattices behaves as a separate block with a self-consistent alignment. Consequently, in materials where cations with unpaired spins populate both A and B sublattices, as is the case of most spinel ferrites, the material displays ferrimagnetism. This term derives its name itself from the word "ferrite," the materials which were first observed to possess this form of magnetic alignment.

Given the prominence of the AB interaction toward the overall magnetism of spinel ferrites, the importance of the inversion degree of the structure becomes evident. In the case of only one of the positions being occupied by a magnetic cation, as is the case for zinc ferrite, no net alignment is observed. In this material, an inversion of zero is commonly observed; that is, the structure is a normal spinel. The tetrahedral A position is occupied by non-magnetic Zn^{2+}, which leaves the remaining magnetic Fe^{3+} ions in the octahedral sites. In this structure, no AB interaction is possible, and the remaining BB exchange (Fe^{3+}-Fe^{3+}) is not strong enough for the material to display any magnetism at standard conditions.

Even in ordinarily magnetic ferrites, such as cobalt ferrite ($CoFe_2O_4$), the inversion degree largely dictates the strength of the magnetism displayed by the sample.

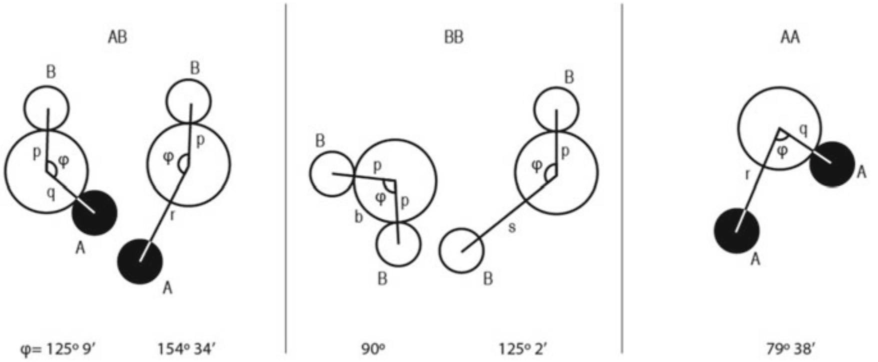

Fig. 2.2 Geometries of the possible interactions in the spinel structure

Table 2.1 Magnetic substructure in selected spinel ferrites

Ferrite	Tetrahedral lattice	Octahedral Lattice	Approximate net magnetic moment per unit formula (μ_B)
$ZnFe_2O_4$	Zn^{2+}	Fe^{3+} Fe^{3+}	0
$CoFe_2O_4$ (inverse)	Co^{2+} Fe^{3+}	Fe^{3+}	3
$CoFe_2O_4$ (normal)	Co^{2+}	Fe^{3+} Fe^{3+}	7

In a normal configuration, the much more substantial contribution of octahedral Fe^{3+} (5 unpaired spins each) is offset by the unpaired spins of Co^{2+} (3 μ_B per ion), which should result in an approximate net magnetic moment of 7 μ_B per unit formula. On the other hand, in an inverse arrangement, the magnetic contribution of the iron ions in the antiparallel octahedral and tetrahedral sublattices should cancel each other out, with the net magnetism being a function solely of the divalent component, resulting in a net magnetism of 3 μ_B per unit formula. A scheme depicting the summation of the antiparallel spins in each lattice can be seen in Table 2.1.

The preference of each cation toward each of the spinel sites was usually explained in terms of the CFSE (crystal field stabilization energy) theory. Some cations show a marked tendency toward populating either the octahedral or tetrahedral sites depending on the structure of their d-bands. If the divalent cation is much more stable in an octahedral environment, it should displace half of the B^{3+} ions, creating an inverse spinel. A similar situation would be created if the B ions have a low octahedral site stabilization energy, expelling the A^{2+} ions from the tetrahedral positions. Nevertheless, such explanations are nowadays taken with a pinch of salt; there is a plethora of examples of spinel arrangements that cannot be explained by the CFSE theory alone.

Size effects have also been utilized in explaining the site preference of different cations. Larger ions have a tendency toward occupying the octahedral site of the spinel lattice (0.414R, with R being the radius of the anion) while the smallest cation should be forced to fill the smaller tetrahedral void (0.225R). Charge effects can also account for the population of the sublattices; the trivalent ion would be better stabilized in an octahedral position, where it would be surrounded by six anions, than in the tetrahedral environment, with only four oxygen ions around it. The opposite could be said of the divalent cation, which would be forced into a tetrahedral configuration. In practice, a sum of these effects should dictate the inversion degree of the ferrites.

Nevertheless, kinetic effects show a much stronger influence than the expected thermodynamic factors. Quenching from high temperatures, for instance, is one of the strategies utilized in "freezing" different cation configurations in place. When rapidly cooled, the crystalline framework of the ferrites does not have enough time to relax toward its most thermodynamically stable state. The cations hold the positions that they would occupy at the higher temperature, therefore presenting an inversion degree that would not normally be expected under the studied conditions. For instance,

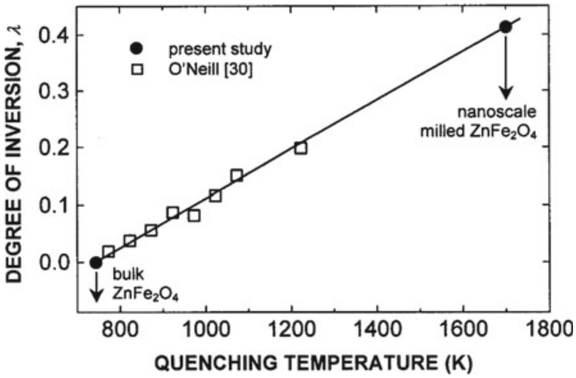

Fig. 2.3 Dependence of the inversion degree on the quenching temperature for $ZnFe_2O_4$. Data was obtained from the work of [2] (Reprinted from [3] with permission from Elsevier)

Faller and Birchenall [1] published a fascinating study on the effect of quenching on the cation distribution of magnesium and nickel ferrite and the relation of the inversion parameter with the temperature. A comparison of their results with the Boltzmann relation according to Néel can be seen in their manuscript. A relation between quenching temperature and degree of inversion for $ZnFe_2O_4$ is shown in Fig. 2.3.

Mechanical stresses have also been shown to lead to metastable inversion degrees. Sepelák and collaborators [4] have demonstrated the effect of high-energy milling on the cationic distribution inside magnesium ferrites. The mechanical stresses induced by the process led to a pronounced decrease in the inversion of the studied ferrites. The effect was comparable to that obtained by quenching from 900 °C. The thermal stability of the induced effect was also analyzed. The authors report recrystallization of the powders occurs above 600 K, above which the system relaxes toward thermodynamic equilibrium.

The synthesis method chosen in the preparation of ferrites is also widely regarded as crucial in the definition of the inversion degree. Dolcet et al. [5] have recently presented a very interesting work on different wet chemical approaches toward the production of $ZnFe_2O_4$ nanoparticles. The researchers have shown, for instance, that a combined microemulsion and hydrothermal approach favors the transfer of Zn^{2+} atoms to the octahedral sites. On the other hand, when using a microwave method, the different crystallization mechanisms lead to the production of frameworks with a stronger normal character. Furthermore, the article also shows that the inversion degree can also be tuned to a certain extent by varying the duration of the thermal step applied during the synthesis. The extraction of the inversion degrees relied on the Raman spectra of the produced materials, which are reproduced in Fig. 2.4.

Despite seeming to be a rather straightforward property, the determination of the inversion degrees of spinel ferrites poses quite a serious challenge. Several techniques are utilized in this determination, to varying degrees of success. X-ray diffractometry is often reported in the literature as one of the simplest methods for the estimation of the inversion degree of ferrites. Podwórny [6] recently published a fascinating study on the determination of the site occupancy in related spinels based on several