

2. The discovery, composition and characteristics of the hexagonal ferrites

The magnetic mineral magnetoplumbite was first described in 1925 [2], and in 1938 the crystal structure was deduced as being hexagonal with the composition $\text{PbFe}_{7.5}\text{Mn}_{3.5}\text{Al}_{0.5}\text{Ti}_{0.5}\text{O}_{19}$ [3]. The synthetic form of magnetoplumbite was found to be $\text{PbFe}_{12}\text{O}_{19}$, or pure PbM, and a number of isomorphous compounds were suggested including $\text{BaFe}_{12}\text{O}_{19}$, although this material was not structurally investigated until after the Second World War, when Philips Laboratories led the way in developing ferrites under the direction of Snoek. $\text{BaFe}_{12}\text{O}_{19}$ is known by many names, including barium ferrite, hexaferrite, barium hexaferrite, ferroxdure, M ferrite and BaM, and was also shown to consist of a hexagonal structure by Went et al. [4]. Investigations of the $\text{BaO-Fe}_2\text{O}_3$ system by Wijn and Braun then produced more complex hexagonal compounds, in which there were both divalent and trivalent iron species ($\text{BaFe}_{18}\text{O}_{27}$) [5,6], and further compounds were also discovered by Jonker, Wijn and Braun when the ternary $\text{BaO-Fe}_2\text{O}_3\text{-MeO}$ system was heated at 1200–1400 °C, where Me = a small divalent cation [7]. Detailed reports of all the main hexaferrite phases were published by Philips Laboratories in the 1950s, culminating in Smit and Wijn's excellent book "Ferrites", published in 1959 [8]. BaM and the cubic MeFe_2O_4 spinel appear as the end members of this system, with zero populations of Me and Ba respectively. The physical characteristics of M ferrites and the cobalt-hexagonal ferrites, as categorised by their discoverers, are shown in Table 1.

All of these compounds were found to have a hexagonal crystal structure, with two crystalline lattice parameters: a , the width of the hexagonal plane, and c , the height of the crystal (Fig. 3). All had a

Table 1
The physical characteristics of the main hexagonal ferrites at room temperature [8].

Ferrite	Formula	Molecular mass (g)	ρ (g cm^{-3})	c (Å)	Magnetisation at room temp
BaM	$\text{BaFe}_{12}\text{O}_{19}$	1112	5.28	23.18	uniaxial
SrM	$\text{SrFe}_{12}\text{O}_{19}$	1062	5.11	23.03	uniaxial
Co_2Y	$\text{Ba}_2\text{Co}_2\text{Fe}_{12}\text{O}_{22}$	1410	5.40	43.56	in plane
Co_2Z	$\text{Ba}_3\text{Co}_2\text{Fe}_{24}\text{O}_{41}$	2522	5.35	52.30	in plane
Co_2W	$\text{BaCo}_2\text{Fe}_{16}\text{O}_{27}$	1577	5.31	32.84	in cone
Co_2X	$\text{Ba}_2\text{Co}_2\text{Fe}_{28}\text{O}_{46}$	2688	5.29	84.11	in cone
Co_2U	$\text{Ba}_4\text{Co}_2\text{Fe}_{36}\text{O}_{60}$	3624	5.31	38.16 ^a	in plane

^a Note that here the c parameter of Co_2U is given for a unit cell that consists of only one molecular unit, as it was described in the past when Ref. [8] was written. These days it is more typically taken to be three molecular units, with a c value three-times greater.

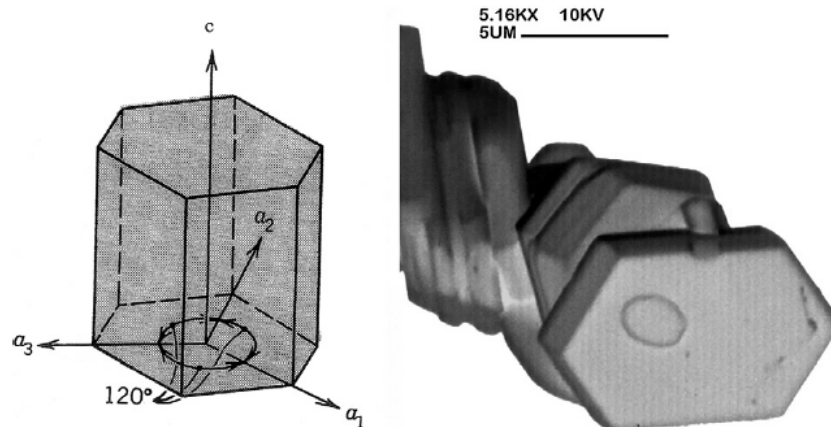


Fig. 3. A hexagonal crystal, showing the two lattice parameters a and c , and a SEM image by the author of a Co_2Z hexaferrite grain.

preferred direction of magnetisation when placed in a magnetic field, giving them an MCA, which was often parallel to the c -axis, coming out of the basal plane of the hexagonal crystal. This uniaxial anisotropy in effect fixes the magnetisation in the direction of the c -axis, and the magnetisation can only be moved out of this direction at the expense of the high anisotropic energy.

However, some compounds containing a divalent cation, especially those containing cobalt, were found to have a plane of spontaneous magnetisation in the basal plane, perpendicular to the c -axis. These compounds were named the ferroplana ferrites, and are now known also to include compounds which have a cone of magnetisation at an angle $0 < \theta < 90^\circ$ to the c -axis. While the direction of magnetisation can easily rotate within the plane or cone through an angle of 360° , the magnetisation is still locked in this plane or cone by a high magnetic anisotropy energy.

2.1. The M ferrites

The compound BaM, $\text{BaFe}_{12}\text{O}_{19}$, was known to exist for many years, with a melting point of 1390°C confirmed in 1936 [9]. However, the structure was not confirmed as being isomorphous with the hexagonal magnetoplumbite until it was first studied and characterised magnetically in the early 1950s by Philips [4]. BaM was initially named ferroxdure, to distinguish it from the spinel ferrite which was named ferroxcube [10]. At the time it was considered an unusual ferrite as it contained no cobalt or nickel, yet it was magnetically hard, with a coercivity of $160\text{--}255\text{ kA m}^{-1}$. Although it had a lower saturation magnetisation than the existing alloy magnets, it was much cheaper to produce, had a high electrical resistivity of $10^8\ \Omega\text{ cm}$ and the high magnetic uniaxial anisotropy along the c -axis [8]. The molecular mass of BaM is 1112 g and the maximum density is 5.295 g cm^{-3} [11], although in reality the ceramic material often has a density as low as 90% of theoretical density. The hardness of BaM in the c -axis has been calculated to be 5.9 GPa [12], and measured as 6.0 GPa [13].

SrM, in which the barium has been replaced by the smaller strontium atom, has a density of 5.101 g cm^{-3} [11] and molecular mass of 1062 g , but resembles BaM in most other physical properties [14]. The Pb^{2+} ion is sized in between Ba and Sr, but lead is a much heavier atom than barium, and so PbM has a molecular mass of 1181 g and a density of 5.708 g cm^{-3} [11]. Undoped CaM has never been seen as a pure phase, but it has been formed in glass by the glass crystallisation method [15]. A detailed study of the thermal properties of polycrystalline M ferrites has been made [16], and the values are shown in Table 2. The T_c values are lower than those published for single crystal ferrites, and were taken from peaks in the standard molar heat capacity plots.

Table 2

Some physical and thermal values and properties for polycrystalline M ferrites. δ = density in g cm^{-3} [11]. T_m = melting point in K, α_a , α_c and α_v = average thermal expansion coefficients for a axis, c axis and volume, in 10^6 K^{-1} . a and c = lattice parameters in \AA , and v = cell volume in \AA^3 , from RT XRD. T_c = Curie temperature, in K, from standard molar heat capacity plots.

	δ	T_m	α_a	α_c	α_v	a	c	V	T_c
SrM	5.101	1692	8.62	16.08	33.50	5.8844	23.0632	691.6	732
BaM	5.295	1611	10.74	16.29	38.16	5.8876	23.1885	696.2	725
PbM	5.708	1538	10.80	18.34	40.46	5.8941	23.0984	694.9	718

2.2. The W ferrites

W ferrites have the formula $\text{BaMe}_2\text{Fe}_{16}\text{O}_{27}$, where Me is usually a first row transition metal or some other divalent cation, and the barium can be substituted by another group two metal. The first reported W ferrite was Fe_2W ($\text{BaFe}_2\text{Fe}_{16}\text{O}_{27}$) [4], but it was initially only made as a mixed phase with M and X ferrites. Single phase Fe_2W was found to have an easy axis of magnetisation in the c -axis of the hexagonal crystal structure, but had a much higher electrical conductivity than BaM due to the Fe^{2+} ions. It has a calculated hardness of 5.5 GPa in the c -axis [12].

All of the W ferrites have uniaxial anisotropy, except Co_2W ferrite ($\text{BaCo}_2\text{Fe}_{16}\text{O}_{27}$) [7], which has a molecular mass of 1581 g and a density of 5.31 g cm^{-3} [8]. This has a cone of easy magnetisation at a constant angle of 70° to the c -axis from -273°C to 180°C , at which point this anisotropy rotates towards the c -axis with increasing temperature until it becomes uniaxial at 280°C , and the magnetisation remains in the c -axis with a further rise in temperature [17].

2.3. The X ferrites

The X ferrites were first reported in 1952 as a mixed phase with M or W ferrite, and have the chemical formula $Ba_2Me_2Fe_{28}O_{46}$, where Me is a divalent first row transition metal or some other divalent cation. The first reported X ferrite was Fe_2X , in which $Me = Fe^{2+}$ [18], and this was also found to have a uniaxial magnetic anisotropy along the c -axis and density of 5.29 g cm^{-3} [8]. All the X ferrites have this uniaxial anisotropy at room temperature, except for Co_2X (molecular mass = 2688 g), which has a cone of magnetisation at an angle of 74° to the c -axis [19]. Like the W ferrite it resembles, this cone changes to adopt an orientation parallel to the c -axis at a higher temperature, in this case 143°C [20].

2.4. The Y ferrites

The Y ferrites were the first ferroplana ferrites to be discovered, and it is now known that nearly all Y ferrites have a preferred plane of magnetisation perpendicular to the c -axis at room temperature [7]. The formula of the Y ferrites is $Ba_2Me_2Fe_{12}O_{22}$, where Me is a small divalent cation, and the first two to be made were Zn_2Y and Co_2Y . The molecular mass of Co_2Y is 1410 g, and it has a density of 5.40 g cm^{-3} [8].

Co_2Y has a planar magnetic anisotropy at room temperature, but this changes to a cone of magnetisation below -58°C . From this temperature to the Curie point the anisotropy remains in the preferred plane [7]. Cu_2Y is the only Y ferrite that has been found to have a preferred uniaxial direction of magnetisation [21].

2.5. The Z ferrites

The Z ferrites have the composition $Ba_3Me_2Fe_{24}O_{41}$, and they were discovered at the same time as the ferroplana Y ferrites [7]. Co_2Z has a molecular mass of = 2522 g and a maximum density of 5.35 g cm^{-3} [8]. The Z ferrites all have a uniaxial anisotropy parallel to the c -axis, except for Co_2Z , which is planar at room temperature but has a complex magnetic anisotropy, with at least four different anisotropic states.

At low temperatures Co_2Z has an easy cone of magnetisation, at an angle of 65° to the c -axis, and this remains constant up to -103°C . Between this temperature and -53°C the angle increases to 90° , and the preferred magnetisation remains in the basal plane until it switches to the c -axis at some temperature between 207 and 242°C [8,22].

2.6. The U ferrites

The U ferrites, $Ba_4Me_2Fe_{36}O_{60}$, although identified at the same time as the other hexagonal ferrites mentioned here, were not characterised much either structurally or magnetically until recently. The densities of Co_2U and Zn_2U have been calculated as 5.44 and 5.31 g cm^{-3} . They all have uniaxial anisotropy except Co_2U , which has planar anisotropy at room temperature [23], and a molecular mass of 3622 g.

2.7. Other hexagonal ferrites

Over 70 distinctive members of the hexagonal ferrites family have been discovered, related to either the W or Z ferrites. Most of these are extremely large and complex compounds, and the largest so far discovered has the formula $Ba_{70}Me_{86}Fe_{444}O_{802}$ and a molecular mass of 52 450 g (52.45 kg) [24].