Synthesis, X-Ray, Neutron and Magnetic Studies of New In-Plane Anisotropy M-Hexaferrites $\text{BaFe}_{12-2x}\text{A}_x\text{Me}_x\text{O}_{19}$ (A = Ru, Ir; Me = Co, Zn)

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Abstract. Ti-Co substituted M-hexaferrites have been extensively investigated as promising materials for magnetic recording or microwave devices. Doping BaM hexaferrite with Ru-Me or Ir-Me (Me = Zn, Co), compounds are obtained with much higher Tc and Ms values than with Ti-Co elements. Powders and single crystals of $\text{BaFe}_{12-2x}\text{A}_x\text{Me}_x\text{O}_{19}$ have been prepared. Magnetization measurements have been performed on single crystals at room and liquid helium temperatures, and magnetic anisotropy constants K_1 and K_2 calculated. Precise crystal structures of substituted compounds have been determined by X-ray diffraction, and cation distribution on all crystallographic sites refined. Magnetic structures of $(\text{Ru-Co})_x$ and $(\text{Ir-Zn})_x$ substituted hexaferrites with $x = 0.3$ and 0.8 have been determined by using neutron diffraction. According to these studies, magnetic anisotropy change is correlated with the substitution of A for Fe cations on bipyramidal and octahedral sites in the R block, and Me for Fe cations on tetrahedral and bipyramidal sites. Magnetic moments rotate progressively with x from the c-axis to the (a, b) plane.

1. INTRODUCTION

The M-type hexaferrite $\text{BaFe}_{12}\text{O}_{19}$ has a very strong uniaxial anisotropy. Substituting x (Ti^{4+} - Co^{2+}) cations for $2x$ Fe cations changes the magnetic anisotropy that becomes in-plane from about $x = 1.3$. For this ratio the substituted material is magnetically soft but its Ms and Tc values have strongly decreased. In the 60's TAUBER [1] showed new BaM(Ir-Zn) substituted hexaferrites, with in-plane magnetic anisotropy, possess high Ms and H_{a0} values from a weak substitution ratio. To our knowledge no work had been published on this subject since TAUBER's paper. We have begun a systematic study of new BaM (A-Me) substituted hexaferrites and showed that with A = Ru, Ir and Me = Co, Zn, the same anisotropy change is obtained as with Ti and Co elements but for much smaller substitution ratios [2, 3, 4, 5]. In this paper we report the magnetic and structural studies we have performed on the substituted BaM ferrites by means of X-ray and neutron diffraction, and static magnetic measurements.

2. PREPARATION AND CHEMICAL CHARACTERIZATION.

For precise structural studies and magnetic measurements, we have first prepared single crystals with a flux method. Substituted single crystals were grown from Bi_2O_3 flux in platinum crucibles heated to 1250°C under air and slowly cooled at -2°C/h to 1000°C . The molar ratio $\text{Bi}_2\text{O}_3 / \text{Fe}_2\text{O}_3$ was about 2 which allows to reach the dissolution of the different raw materials (BaCO_3 , $\alpha\text{-Fe}_2\text{O}_3$, RuO_2 or IrO_2 , ZnO or CoC_2O_4) between 1100°C and 1200°C . Note BaCO_3 was always introduced in excess to prevent from the octahedral spinel crystal growth. Hexagonal platelets up to 3 mm across and 0.5 mm thick were obtained. As a first control of the crystal structure and to determine precisely their chemical composition, single crystals were analysed by Castaing microprobe. We often noticed Bi ions present in the analysed crystals, about 0.05 atoms by formula unit. Crystal chemical formulae have been normalized to obtain the theoretical 19 oxygen anions by formula unit.

In a second stage, polycrystalline hexaferrites with composition $\text{BaFe}_{12-2x}\text{A}_x\text{Me}_x\text{O}_{19}$ (A = Ru, Ir; Me = Co, Zn) were elaborated by high temperature solid state reaction from metallic oxides. Stoichiometric amounts of dried BaCO_3 , $\alpha\text{-Fe}_2\text{O}_3$, RuO_2 or IrO_2 , ZnO or CoC_2O_4 raw materials were mixed, grinded in a ball mill, then compressed into pellets to improve the solid state reaction, and finally annealed at 1150°C for 6 hours. In the case of Ir-Me substitutions the high temperature reaction was performed under O_2 atmosphere to prevent from the IrO_2 reduction. Powders were characterized by microprobe, X-ray diffraction and static magnetic measurements. Pure powders of doped hexaferrites, with single Curie temperatures, were obtained for $x \leq 0.8$. Increasing the substitution ratio x , synthesis of these substituted compounds is more and more difficult. X-ray diffraction analysis has showed the cell parameter a increases with x regularly, while the c parameter decreases slightly with Me = Co and is about constant with Me = Zn.

3. MAGNETIC MEASUREMENTS

Both order temperatures and hysteresis loops have been performed on powders and crystals by using a Faraday torque balance and a Foner magnetometer. We have found a good agreement between the T_c and M_s values obtained on powders and crystals [2]. Here we report some measurements on single crystals. As far as powders are concerned, we will only point out that the coercivity force of these samples strongly decrease from $x \approx 0.1$ in the case of (Ru-Me) doping elements and from $x \approx 0.2$ in the case of (Ir-Me) elements [2, 3]. Anisotropy constants have been calculated precisely from single crystal hysteresis loops by using the Sucksmith and Thomson method modified by Neel et al. [6]. In this purpose, magnetization loops have been measured at room and liquid helium temperatures on numerous doped crystals with various substitution ratios ($0 \leq x \leq 2$). For instance figure 1 shows hysteresis loops of a M(Ru-Zn) doped crystal with $x \approx 0.3$ both in the case of a magnetic field applied along the c-axis and perpendicular to the c-axis. These loops have been corrected of the demagnetizing field contribution. They are similar in the both directions. It proves the anisotropy change occurs for $x \approx 0.3$ and the magnetization lies along a direction situated between the c-axis and the (a, b) plane. Furthermore the magnetocrystalline anisotropy is weak and only an easy "magnetization rotation process" is sufficient to reach the saturation magnetization along the c-axis, or in the (a, b) plane.

Figure 1 : Hysteresis loops at room temperature of a M(Ru-Zn) doped single crystal with $x \approx 0.3$

Table 1 gives results concerning three M(Ru-Zn) doped crystals with $x = 0.25, 0.30$ and 0.35 , and a non doped crystal. The c-axis is an easy magnetization direction for $x = 0.25$, and an hard magnetization direction for $x = 0.35$. As seen above the magnetic anisotropy changes for $x \approx 0.3$ and the magnetocrystalline anisotropy reaches a minimum. For these ratios, the order temperatures and the saturation magnetization, which decrease steadily with x , are still close to those of the non substituted M hexaferrite while the H_{a0} anisotropy field has strongly decreased.

Table 1 : Magnetic characteristics of M(Ru-Zn) substituted crystals

Crystal	T_c (°C)	M_s (emu/g) (at 300 K)	Anisotropy constants (10^5 erg/g)			Anisotropy field (Oe) H_{a0}
			K1	K2	K3	
BaFe ₁₂ O ₁₉ $x = 0$	450	71	5.40	0.10	≈ 0	15100
(Ru-Zn) $x = 0.25$	415	67.5	1.15	0.20	0.05	3450
(Ru-Zn) $x = 0.30$	407	66	weak	weak	-	weak
(Ru-Zn) $x = 0.35$	400	65	- 1.75	1.45	- 0.60	1750

From the whole magnetic measurements on polycrystalline and single crystal (A-Me) doped M-hexaferrites, the following conclusions can be drawn :

- Curie temperature and magnetization decrease with x steadily. For the same ratio x , M_s and T_c values are higher than those of M(Ti-Co) doped hexaferrites ; with $x = 0.6$ for instance :

(i) $T_c = 350^\circ\text{C}$ and 390°C respectively for (Ti-Co) and (Ir-Co) substitutions.

(ii) $M_s \approx 60$ emu/g and 64 emu/g respectively for the same compounds .

- magnetocrystalline anisotropy becomes in-plane from only $x \approx 0.3, 0.4-0.5$ and 0.6 in the case of (Ru-Me), (Ir-Zn) and (Ir-Co) substitutions respectively, while doping with (Ti-Co) cations this ratio is about 1.3. After reaching a minimum, as magnetic anisotropy becomes in-plane, the anisotropy field H_{a0} increases again with x .

- the measured saturation magnetizations are well consistent with Gorter's collinear spin arrangement considering magnetic moments of $5 \mu\text{B}$ on Fe^{3+} cations, $3.7 \mu\text{B}$ on Co^{2+} cations, and zero or negligible on Zn^{2+} , Ru^{4+} and Ir^{4+} cations located in the R and S blocks as described in §4.

4. CATIONIC DISTRIBUTION

In order to correlate the anisotropy change with the substitution of A and Me cations on the five crystallographic sites of the substituted hexaferrites, precise crystal structure refinements have been performed from X-ray diffraction data collected from single crystals. Five refinements corresponding to five different substitutions have been done : (Ru-Zn)_x with $x = 0.3$ and 1.6, (Ru-Co)_{0.2}, (Ir-Zn)_{0.5} and (Ir-Co)_{0.8}. Details about the two last compound refinements are given in ref. 4 paper.

Cubic fragments of about 0.2 mm side was extracted from large crystals and mounted on a 4-circles diffractometer. About 6300 reflections with $\theta \leq 35^\circ$ were collected in half the Ewald sphere. At the early stages of refinement, atomic position coordinates, isotropic thermal parameters and atom population parameters of the Fe sites were refined. All the Fe population parameters except for the tetrahedral Fe3 and, in the case of moderate substitution, for the octahedral Fe1 sites of the S block, were higher than the theoretical population ones, indicating Ru (or Ir) cation presence on all these sites. Therefore, we positioned both Ru (or Ir) and Fe cations on each Fe site, constraining the sum of the atom population parameters to be equal to the theoretical one, and refined again. Microprobe analysis showed the presence of Bi atom (0.05 - 0.1 atom by formula unit) in the studied crystals. The Ba multiplicity on site 2d does not increase when this parameter is refined ; thus Bi atoms are not located on this site, but on Fe octahedral sites with Ru (or Ir) atoms. Bi cations (either as Bi³⁺ (7) or as Bi⁵⁺ cations like in Ba₂LaBiO₆ (8)) have been roughly distributed in proportion to the position multiplicities on Fe4 and Fe5 positions and fixed, while Ir population were refined on each Fe site. After refining with anisotropic thermal factors, the conventional agreement factors R and R_w were, in each case, close to 0.03.

The sites occupied by Co²⁺ or Zn²⁺ cations cannot directly be revealed by the structure refinement because of the scattering factor vicinity of Fe, Co and Zn atoms. However, the effective valency of each Fe site can be calculated using bond length - bond strength relations on basis of observed metal - oxygen interatomic distances. Bond strengths and then effective valencies have been calculated using Brown and al. relation (9) :

$$s_{ij} = \exp \left(\frac{r_0 - d_{ij}}{0.37} \right)$$

where s_{ij} is the bond strength between bonded atoms i and j , d_{ij} the bond length and r_0 a characteristic length ; for Fe³⁺ $r_0 = 1.759$ Å in oxides. The effective valency of the cation i is obtained by summing s_{ij} over the j first neighbours of the i atom. According this calculation, valencies of all Fe sites are found close to 3.0 except for those of the bipyramidal Fe2 site (about 2.7) and tetrahedral Fe3 site (from 2.8 to 2.5 according to the substitution ratio). Presence of Co or Zn atoms has been assumed at these positions. Co (or Zn) atoms were introduced on Fe2 and Fe3 sites proportionally to the populations estimated from calculated valencies and their occupation ratio refined ; Ru (or Ir) populations were fixed as previously determined on each position. The final R and R_w factors are unchanged. As an example, cationic distributions of (Ru-Zn)_x hexaferrites with $x = 0.3$ and 1.6, are given in tables 2 and 3 ; error on site population is smaller than 2%. Corresponding chemical formulas agree very well with those determined by microprobe analysis. As can be seen, Ru atoms are found in the two ferrites principally on the bipyramidal site Fe2 (10%) and, when the substitution ratio increases, on the octahedral sites Fe4 and Fe5, 20% and 19% respectively in the (Ru-Zn)_{1.6} substituted ferrite. All these sites are neighbouring sites. The Fe4 and Fe2 sites belong to the R block and the Fe5 site is located at the R/S block boundary.

Table 2 : Cationic distribution in (Ru-Zn)_{0.3} substituted hexaferrite.

Site	Position	Fe ³⁺		Zn ²⁺		Ru ⁴⁺ / Bi ⁵⁺		Spin
Fe1	2a	1.00(2)	100%	-	-	-	-	"up"
Fe2	4e (1/2)	0.80(1)	80%	0.10(1)	10%	0.10(1)	10%	"up"
Fe3	4f1	1.70(2)	84%	0.25(2)	13%	0.05(2)	3%	"down"
Fe4	4f2	1.92(2)	96%	-	-	0.06(2)	3%	"down"
Fe5	12k	5.85(3)	97%	-	-	0.09(3)	2%	"up"

All these results agree well with those obtained in Zn-Ti, Co-Ti or Co-Sn substituted M-hexagonal ferrites. According to Mössbauer spectroscopy studies the sites substituted by Ti atoms are principally the Fe5, Fe4 and Fe2 sites. The same sites are usually assumed to be substituted by Co atoms. However in a recent study by neutron diffraction of substituted Ti-Co M hexaferrites, Co atoms have been found principally on the Fe3 tetrahedral site and then on the Fe2 bipyramidal site like in this work (10). In fact that is not surprising, since large bivalent cations ($r_{Co^{2+}} = 0.58$ Å compared to $r_{Fe^{3+}} = 0.49$ Å in tetrahedral coordination) stabilize the spinel block structure and are often found on the spinel tetrahedral site (11). On the other hand, Zn atoms are considered as occupying tetrahedral sites in all the Zn-Ti substituted hexaferrites because of the very well known preference of Zn²⁺ cations for this site. The bipyramidal site which is preferentially occupied by Co or Zn cations, can be seen too as a pseudo-tetrahedral site because of the off-mirror position of the Fe2 atoms. Our results are therefore consistent.

The bipyramidal site Fe2 is considered to play a key role for the axial magneto-crystalline anisotropy of hexaferrites. Preferential substitution of Ir for Fe on octahedral sites Fe4 and Fe5 which are near neighbours of the bipyramidal site and

above all the preferential substitution both of Co (or Zn) and Ru (or Ir) for Fe atoms on the Fe2 site, lead naturally to a drastic change of the magnetic anisotropy. The Ti-Co substituted M-hexaferrite becomes planar for substitution ratio $x \approx 1.3$ and the Ru-Zn one for $x \approx 0.3$. Unlike Ru^{4+} (or Ir^{4+}) cations, Ti^{4+} never occupy the Fe2 site (10). This is certainly the origin of the much faster change of magnetic anisotropy in Ru (or Ir) substituted hexaferrites than in Ti substituted ones.

Table 3 : Cationic distribution in $(\text{Ru-Zn})_{1.6}$ substituted hexaferrite.

Site	Position	Fe^{3+}		Zn^{2+}		Ru^{4+}		Bi^{5+}		Spin
Fe1	2a	0.85 (2)	85%	-	-	0.15(2)	15%	-	-	"up"
Fe2	4e (1/2)	0.50(2)	50%	0.40(2)	40%	0.10(2)	10%	-	-	"up"
Fe3	4f1	0.80(9)	40%	1.20(9)	60%	-	-	-	-	"down"
Fe4	4f2	1.60(3)	80%	-	-	0.39(3)	20%	/	0.01(3)	"down"
Fe5	12k	4.85(5)	81%	-	-	1.13(5)	19%	/	0.02(5)	"up"

5. NEUTRON DIFFRACTION

In order to determine the magnetic arrangement in M(A-Me) doped hexaferrites, neutron diffraction patterns on polycrystalline M(Ru-Co) and M(Ir-Zn) doped samples with $x = 0.3$ and 0.8 have been collected on two-axis diffractometers DN5 (C.E.N. Grenoble) and G4-1 (L.L.B. Saclay) at room and low temperatures. In these patterns all magnetic contributions are consistent with the crystalline symmetry which indicates magnetic structures do not present any antiferromagnetic mode. As starting models for refinement with the Rietveld method we have applied crystal structures found from X-ray diffraction (84) whose cationic distributions have been extrapolated to $x = 0.3$ and 0.8 . Then every pattern refinement has led to magnetic parameters (magnetic moments and orientations on every crystallographic site) with correct agreements ($R_p \leq 0.1$). Best agreements have been found with a non collinear ferrimagnetic model where each cationic site shows spin canting. As an example table 4 gives the spin orientation on all crystallographic sites of M(Ru-Co) doped compounds.

Table 4 : Spin arrangement in M(Ru-Co) doped hexaferrites at 80 K, a) $x = 0.3$, b) $x = 0.8$

Mag. moment	Fe1 (2a)	Fe2 (4e 1/2)	Fe3 (4f1)	Fe4 (4f2)	Fe5 (12k)
a) μ_B , θ° / c	3.5, 45	3.7, 55	-3.5, 45	-3.5, 45	3.5, 55
b) μ_B , θ° / c	3.9, 50	3.2, 70	-3.4, 100	-4.0, 90	3.3, 80

Neutron diffraction pattern refinements show the magnetic structure of M substituted hexaferrites is not strictly collinear, and also confirm the magnetization direction rotates steadily with x between the c-axis and the basal plane. The largest spin cantings occur as the magnetocrystalline anisotropy reaches a minimum. Refined magnetic moments are found a little lower than theoretical ones calculated from the cationic distribution due to the fact only the coherent spin components have a contribution. Nevertheless relative values of magnetic moments on each site are about consistent with the cationic distribution of magnetic Co cations, and non (or weak) magnetic Zn, Ru and Ir cations.

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