Synthesis and Magnetic Properties of Partially Exchanged Nonstoichiometric Hexaferrites

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Nonstoichiometric hexaferrite particles containing both Ba and K, with typical composition $K_{0.8}Ba_{0.6}Fe_{10.5}Co_{0.25}O_{17}$, have been prepared by partial ion exchange in an aqueous solution of $Ba(NO_3)_2$ at 40–80°C, from β'' ferrite precursor phase $K_2Fe_{10.5}Co_{0.25}O_{17}$. The β'' structure is maintained after the exchange reaction and the hexaferrite structure is formed by heating at $T > 600$°C. Exchange of K^+ by H_3O^+ also takes place in the aqueous solution, resulting in the formation of Fe_2O_3 during annealing. The crystal structure is described as an M-type hexaferrite structure with intergrown β-type cells. Saturation magnetization in a field of 20 kOe at room temperature is 35–38 emu/g; coercive field $H_c \approx 2.0$ kOe and $T_c = 460$°C. Low magnetization values have been related to the low percentage (66%) of M-type cells in the structure. © 1996 Academic Press, Inc.

1. INTRODUCTION

Ba hexaferrite is a magnetic material with high anisotropy. In fine particle form it is suitable for magnetic recording applications. Actually, the very high coercivity of $BaFe_{12}O_{19}$ needs to be reduced in order to conform with current recording system/heads. This is usually accomplished by partial substitution of Fe^{3+} by Co^{2+}–Ti^{4+} ions (1), but in this case, the introduction of diamagnetic cations also reduces the saturation magnetization and Curie temperature.

The formation of nonstoichiometric Ba hexaferrites containing Co, Zn, Mg, or Ni has been examined in previous works (2, 3) and proposed as an alternative way of producing Ba ferrite fine particles with modified characteristics. Nonstoichiometric hexaferrites are synthesized from β ($KFe_{11}O_{17}$) or β'' ($K_2Fe_{10.5}Co_{0.25}O_{17}$) ferrites by ion exchange. Complete exchange of K by Ba takes place in $BaCl_2$–KCl melt, at $T = 750$–800°C. The exchange product is nonstoichiometric M-type hexagonal ferrite particles with the approximate chemical formula $BaFe_{10.5}Co_{0.25}O_{17}$. Compared to Co–Ti substituted hexaferrites, they have improved magnetic properties, and their overall characteristics, morphological and magnetic, are suitable for use as magnetic recording media.

The investigation of exchange reactions producing nonstoichiometric hexaferrites has led to the elaboration of a novel method of ion exchange. It consists of performing the exchange reaction not in a melt but in aqueous solution, yielding a magnetic hexaferrite that has been partially exchanged and contains both Ba and K. In order to acquire a better understanding of the underlying processes in the formation of nonstoichiometric hexagonal ferrites, the synthesis procedure and the magnetic characteristics of the new hexaferrite have been studied and they are discussed in the present work.

Formation of mixed K–Ba and K–Sr M-type hexaferrites has also been reported by Ito *et al.* (4). They are obtained from K–β-ferrites, partially exchanged in nitrate melt and present magnetization that reaches 33 emu/g at room temperature at 10 kOe. A mixed but nonmagnetic K–Ba hexaferrite, synthesized by the ceramic method, has been reported as well (5).

2. EXPERIMENTAL

Ionic exchange is performed on β'' ferrites, stabilized by divalent cations such as Co^{2+}, Mg^{2+}, or Zn^{2+}. The β'' ferrites are prepared by the organometallic method (6): K and Fe ions in stoichiometric proportion are precipitated in a solution of KCl and $FeCl_3$ with ammonia. The precipitate is then dissolved in citric acid solution, in which small amounts of Co^{2+}, Mg^{2+}, or Zn^{2+} ions in oxide form are introduced. Then ethylene glycol is added and the mixture is slowly evaporated and heated at 300°C. The organic constituents of the powder are burned away at 450°C, and finally, by heating at $T > 700$°C the β'' ferrite with typical chemical formula $K_2Fe_{10.5}Co_{0.25}O_{17}$ is produced.

The exchange of K ions of the β'' ferrite by Ba takes place in an aqueous solution of $Ba(NO_3)_2$, at $T = 40, 60$, or 80°C, for 2 h. The exchange product is then subject to successive annealings at $T = 400$–1000°C for 20 h each. X-ray diffraction patterns have been used for the examina-

68

TABLE 1
Chemical Analysis Results for the Precursor, Washed, and Exchanged in Aqueous Solution β'' Ferrites

	K	Ba	Fe	Co
Precursor β'' ferrite	1.8	—	10.5	0.17
→ After washing	0.9	—	≫	≫
→ After exchange at 40°C	0.75	0.38	≫	≫
60°C	0.65	0.44	≫	≫
80°C	0.65	0.48	≫	≫

tion of purity of the obtained phases. Plasma and atomic absorption methods of chemical analysis have been employed. The dehydration process has been monitored by differential thermogravimetry (DTG). Magnetization and hysteresis curves have been traced at room temperature and in fields up to 20 kOe, by means of a fluxmeter and a data acquisition and processing system. The Curie temperature is determined by tracing magnetization versus temperature curves in constant field (500 Oe).
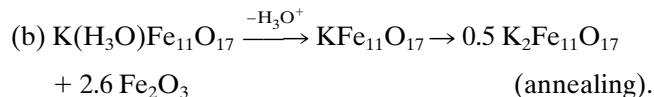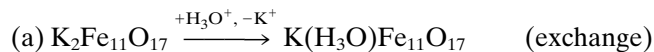
3. RESULTS AND DISCUSSION

3.a. Exchange in Water

Before discussing the results of the solution exchange, we shall deal with the influence of water on the β'' ferrite phase. According to chemical analysis results (Table 1), the composition of the β'' precursor ferrite, produced by the organometallic method, is $K_{1.8}Fe_{10.5}Co_{0.2}O_{16.8}$. If the β'' precursor ferrite is washed with water, the structure remains β'' type. However, the chemical analysis reveals that the washed β'' phase contains only half of the K ions of the original phase, 0.9 compared to 1.8 per formula unit, respectively (Table 1). The amount of K detected and the corresponding charge are too low for a β''-type structure. In β'' aluminas for example, typical values of nontransition metal cations and their charges are close to 1.65 and 1.8, respectively (7). Therefore it may be concluded that an exchange of K^+ by H_3O^+ ions has taken place so that the missing K^+ ions are substituted by H_3O^+. The exchange of K^+ by H_3O^+ has been studied in β and β'' aluminas (8), while in β and β'' ferrites it has been reported to take place in concentrated H_2SO_4 (9, 10). The exchange has been confirmed by DTG analysis (Fig. 1). During the DTG process, up to $T = 350°C$, a total weight loss of $\approx 2\%$ is observed. This is attributed to the removal of exchanged H_3O^+ as the temperature increases. As a matter of fact, this weight difference corresponds to the percentage of H_3O in the molecular weight of β'' ferrite $K(H_3O)Fe_{10.5}Co_{0.2}O_{17}$, that is 19 units in 929.

On annealing, the β'' structure is maintained while Fe_2O_3 is formed at $T \geq 600°C$. The Fe_2O_3 amount increases with

temperature. The β'' phase $KFe_{10.5}Co_{0.25}O_{17}$ that exists at higher temperature after the removal of H_3O^+ contains only one K^+ per conduction plane and therefore is unstable. It is interesting to notice that this loose β'' phase $KFe_{11}O_{17}$ does not convert to β structure, for which this chemical formula, with one K^+, is typical. Instead, as the temperature rises, Fe_2O_3 is rejected from the β'' structure, so that K proportion is increased and the phase transforms to stable β'' ferrite $K_2Fe_{10.5}Co_{0.25}O_{17}$, with two K^+ ions per f.u. The whole process may be described by the following schematic reactions, in which the atomic proportions have been rounded to nominal values:

(a) $K_2Fe_{11}O_{17} \xrightarrow{+H_3O^+, -K^+} K(H_3O)Fe_{11}O_{17}$ (exchange)

(b) $K(H_3O)Fe_{11}O_{17} \xrightarrow{-H_3O^+} KFe_{11}O_{17} \rightarrow 0.5\,K_2Fe_{11}O_{17}$
$+ 2.6\,Fe_2O_3$ (annealing).

3.b. Exchange in Aqueous Solution

The β'' precursor ferrite $K_{1.8}Fe_{10.5}Co_{0.2}O_{16.8}$ is immersed in a $Ba(NO_3)_2$ aqueous solution where exchange is performed under the conditions described in the previous section. After the exchange, there are 0.4 to 0.5 Ba ions per formula unit, depending on the temperature of the exchange solution (Table 1). The exchange is not complete since there still remain 0.7 to 0.6 K ions per f.u. The diffraction diagrams before and after the exchange are similar; both are β'' patterns. Therefore, in the aqueous solution K^+ ions are only partially exchanged by Ba^{2+}, while the β'' structure is not altered.

By heating at $T > 600°C$, the exchanged β'' ferrite is transformed into M-type hexaferrite, which contains both K and Ba. At $T = 700°C$ Fe_2O_3 is evidenced in the diffraction diagrams. The amount of Fe_2O_3 impurity increases with the annealing temperature. Similarly to the case of
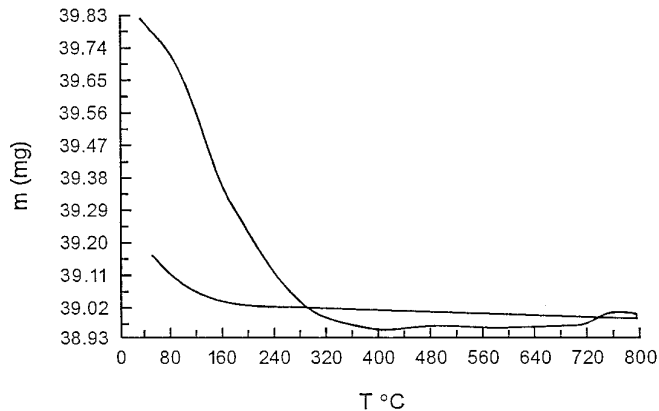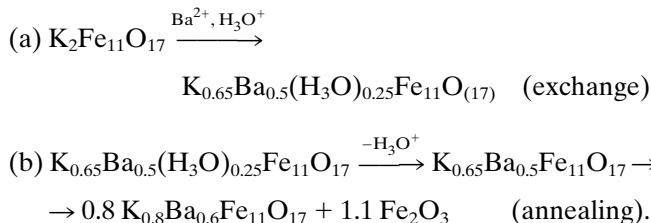

FIG. 1. DTG plot of washed β'' precursor ferrite.

the washed β'' ferrite, the sum of K + Ba ions in the exchanged β'' phase is too low, 1.1 per f.u.; the sum of their charges as well is 1.6, lower thabn expected for a β''-type structure. The apparent cation deficit may be explained if we assume that, due to the presence of water in the exchange bath, K^+ ions have also been exchanged by H_3O^+, as it has been concluded earlier for the washed β'' ferrite. In the present case the deficit is lower, indicating that a smaller amount of H_3O^+ has entered the structure.

Although the presence of H_3O^+ has not been evidenced by DTG, we may estimate the proportion of H_3O^+ that substitutes for K^+ by the exchange reaction to be about 0.25 per f.u. This amount leads to a possible chemical formula for the exchanged β'' ferrite:

$$K_{0.6}Ba_{0.5}(H_3O)_{0.25}Fe_{10.5}Co_{0.25}O_{17}.$$
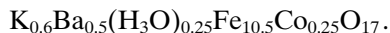
In this formula the sum of cations in the conduction plane is 1.4 and their charge is 1.9, values that are more reasonable for a β''-type structure. The amount of H_3O^+ is indeed too small to be evidenced by DTG, since a weight loss lower than 5‰ should be detected. A schematic diagram of the hexaferrite formation process is

(a) $K_2Fe_{11}O_{17} \xrightarrow{Ba^{2+},\ H_3O^+}$

$\qquad K_{0.65}Ba_{0.5}(H_3O)_{0.25}Fe_{11}O_{(17)}$ (exchange)

(b) $K_{0.65}Ba_{0.5}(H_3O)_{0.25}Fe_{11}O_{17} \xrightarrow{-H_3O^+} K_{0.65}Ba_{0.5}Fe_{11}O_{17} \rightarrow$

$\qquad \rightarrow 0.8\ K_{0.8}Ba_{0.6}Fe_{11}O_{17} + 1.1\ Fe_2O_3$ (annealing).

The assumption of exchange of K^+ by H_3O^+ can also explain the formation of Fe_2O_3 by a mechanism similar to that suggested in the annealing of the washed precursor phase. The above mechanism relates directly the amount of Fe_2O_3 formed to the H_3O^+ content of the β'' phase. According to the schematic reactions, by which we have described the transformations during annealing, the proportion of Fe_2O_3 in the case of the exchange β'' ferrite is $1.1 \div 0.8, \approx 20$ wt%, while it is $2.6 \div 0.5, \approx 45$ wt%, in the case of the washed β'' ferrite. The experimental results confirm that Fe_2O_3 impurity in the exchanged β'' ferrite is much lower than in the washed ferrite. This is evidenced by the comparison of the relative intensities of Fe_2O_3 peaks in the diffraction diagrams of a washed β'' ferrite sample compared to a solution exchanged M-phase sample, both annealed at $T = 1000°C$ (Fig. 2).

Formation of Fe_2O_3 is an inevitable effect, related to the presence of water in the exchange bath. In fact, it is a characteristic of ion exchange in aqueous solution, since no Fe_2O_3 is formed when the exchange is performed in a melt and one takes care that no washing with water takes place before or after the exchange as in Refs. (2, 3).
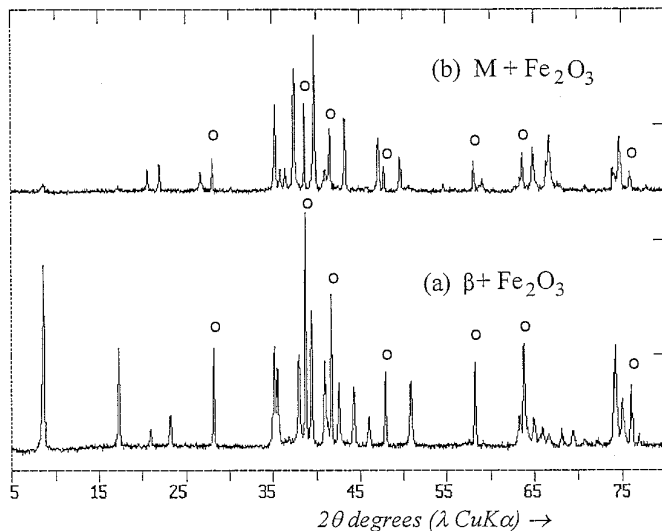

FIG. 2. Diffraction diagrams of (a) washed β'' precursor ferrite and (b) exchanged hexaferrite, both annealed at $T = 1000°C$, showing Fe_2O_3 peaks (°).

3.c. Description of Crystal Structure

Due to the nonstoichiometric composition, a pure M-type structure is hard to imagine. For the mixed K–Ba hexaferrite prepared by ceramic method (5), a sodium–lanthanum–aluminate (SLnA) structure model, with ordered K and Ba ions has been proposed, based on powder diffraction diagrams, while problems of nonstoichiometry have not been examined. In order to perform a study of the crystal structure, a partially exchanged nonstoichiometric hexaferrite has been prepared in single crystal form, with chemical formula

$$K_{0.31}Na_{0.64}Ba_{0.71}Fe_{10.55}Mg_{0.29}O_{17.3}.$$
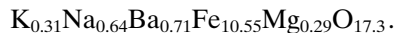
The detailed structure analysis is to be published elsewhere (11); here the main results of this study are presented. The resolution of the crystal structure has been helpful in the explanation of magnetization values, which will be discussed in the next section. The starting material is a K–Na β'' ferrite single crystal with the chemical formula $K_{1.2}Na_{0.8}Fe_{10.55}Mg_{0.29}O_{17.5}$. The β'' ferrite single crystals have been exchanged in a eutectic $Ba(NO_3)_2$–KNO_3 melt at moderate temperature, $T = 650°C$ for 15 min. According to chemical analysis results, the exchange is only partial. The β'' structure is maintained after the exchange and is transformed, by heating at $1000°C$ for 24 h, into nonstoichiometric M-type hexaferrite with the above mentioned chemical composition.

The basis for the structure description is the magnetoplumbite structure of the M-type hexagonal ferrites. The position parameters are indeed very close to those of the

TABLE 2
Calculated Population of Fe Sites p(Fe) and Partition of Fe in the Three Cells Constituting the Structure

	p(Fe)	$BaFe_{12}O_{19}$ $x = 0.66$	β $y = 0.20$	β $z = 0.14$
Fe1 2a ↑	0.93	x	y	$z/2$
Fe2 2b ↑	0.66	x	y^a	—
Fe3 4f ↓	0.96	x	y	$3z/4$
Fe4 4f ↓	0.80	x	—	z
Fe5 12k ↑	0.86	x	y	—

[a] In this cell type Fe(2) site is occupied by (Ba + Na) ions.

M-type structure. However, due to the nonstoichiometric composition, there are significant deviations from the original magnetoplumbite structure. Apart from a decrease of the population parameters, there are two sites of the magnetoplumbite structure, namely Fe(2) and O(1), in which, besides the expected Fe or O atoms, respectively, there have been located Ba, Na, and K atoms as well.

The resolved structure can finally be described in the noncentrosymmetric space group $P\underline{6}$ as an intergrowth of an M-type cell in proportion 66% and two β-alumina cells in proportion 20% and 14%, respectively (Table 2). The M-type cell is characterized by the occupation by Fe atoms of site Fe(2) with bipyramidal coordination. The proportion of the first β-type cell is identified by the presence of Ba, Na in the place of Fe(2), which excludes, according to bond length considerations, the existence of O atoms in O(1) and O(3) sites. The other β-type cell is identified by the location of Ba, K, and Na atoms in site O(1), which is inconsistent with and excludes the occupation by Fe of the neighbor Fe(2) and Fe(5) sites. A similar description of intergrowth cells has been employed in the analysis of the crystal structure of the completely exchanged nonstoichiometric hexaferrite $Ba_{1.25}Fe_{10.55}Co_{0.25}O_{17.3}$ (12).

The Fe(2) site is not only important for the distinction of the cell types; it is also the significant site regarding the magnetic structure. It is the presence of Fe in this site, the characteristic bipyramid of M-type hexaferrites, that ensures the ferrimagnetic coupling of the adjacent spinel layers. Otherwise, as in β and β'' ferrites, the coupling between the spinel layers and consequently the whole magnetic structure is antiferromagnetic.

3.d. Magnetic Properties

The nonstoichiometric K–Ba hexaferrites, prepared by ion exchange in aqueous solution, are magnetic, with Curie temperature $T_c = 460°C$ ($\pm 5°C$). The T_c is, for all samples, the same, within standard deviation, and quite close to that of stoichiometric $BaFe_{12}O_{19}$ (470°C). The magnetization increases sharply for samples annealed at temperatures

$T = 550$–$650°C$, at which, according to diffraction diagrams, the hexaferrite phase is formed (Fig. 3). M_{20}, the magnetization at room temperature and a field of 20 kOe, reaches 35–38 emu/g, depending on the temperature of the exchange solution. The coercive field, measured on compacted samples, is 2.0–2.2 kOe.

We may comment on the magnetization values after a correction of the raw experimental values, because of the presence of Fe_2O_3 impurities. If, according to the proposed reaction scheme in Section 3.b, we assume that the proportion of Fe_2O_3 in the sample is 20 wt%, then the magnetization of pure K–Ba hexaferrite (at room temperature and a field of 20 kOe) would be $M_{20} = 44$–47 emu/g. This value is rather low, compared to the M_{20} values of completely exchanged nonstoichiometric hexaferrites: the experimental M_{20} of annealed powders (2, 3) and that of single crystals (13) are 55–64 emu/g. The saturation magnetization of stoichiometric $BaFe_{12}O_{19}$ is still higher, 72 emu/g at room temperature.

In order to compare with theoretical values, experimental values measured at room temperature are reported to $T = 0$ K, using the ratio $M(0)/M(rt)$ of $BaFe_{12}O_{19}$, where $M(0) = 100$ emu/g and $M(rt) = 72$ emu/g, since the T_c of the two compounds are almost equal. Furthermore, it is considered that the magnetization at 20 kOe is about 90% of the saturation value. The resulting $M(0)$ equals 70–78.5 emu/g or 12.4–14.2 μ_B per f.u.

The theoretical magnetization is calculated according to the Gorter model of spin orientation (14) with the magnetic moment of Fe^{3+} ions equal to 5 μ_B and using the site population p(Fe) (Table 2), determined by the single crystal structure analysis (11). The amount of Co or other transition metal cation, about 0.2 per f.u., is incorporated in Fe population, since the resulting difference in magnetization is negligible. If all Fe ions are presumed to contribute to the magnetization, we calculate
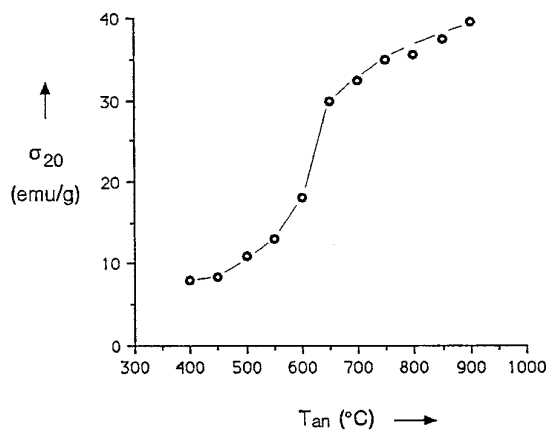

FIG. 3. Magnetization at 20 kOe vs annealing temperature of the final product.

$$M(0)_{th} = [p(Fe1) + p(Fe2) + 6p(Fe5) - 2p(Fe3) - 2p(Fe4)] \cdot 5 = 16.15 \ \mu_B \text{ per f.u.}$$

This is equivalent to $M(0)_{th} = 90$ emu/g and reported to room temperature, $M_{th20} = 57$ emu/g. These values exceed the experimental ones (44–47 emu/g) by at least 20%, indicating that not all Fe ions contribute to the magnetization. It should have been taken into account that site Fe(2) is occupied by Fe ions in only 66% of the cells, those that are M-type. The other 34% of cells are β-type, where the coupling of Fe ions is, in principle, antiferromagnetic. In this sense only those Fe ions that are located in M-type cells may contribute to the magnetization. Therefore the theoretical magnetization is 13.0 μ_B/f.u., resulting from 66% of Fe spins that present the ferrimagnetic ordering of $BaFe_{12}O_{19}$, whose magnetization is 20.0 μ_B/f.u. Then $M(0)_{th} = 74$ emu/g, from which we deduce that $M_{th20} = 48$ emu/g, values in agreement with the experimental ones. It is evident that the Fe ions of M-type cells are sufficient to account for the observed magnetization values.

A different approach that takes into account Fe ions besides those of M-type cells has been employed in (13), in order to explain the observed magnetization values in completely exchanged nonstoichiometric hexaferrites. In that case the proportion of M-type cells is higher, 75%. The theoretical magnetization resulting from this percentage (i.e., considering that only Fe ions in M-type cells are magnetically ordered) is 15 μ_B/f.u. or $M(0)_{th} = 80$ emu/g. On the other hand, when all Fe ions are taken into account, using Fe population, the theoretical magnetization is 17.5 μ_B/f.u. or $M(0)_{th} = 93$ emu/g. Experimental saturation magnetization of single crystals at 4.2 K is $M(0) = 85$ emu/g or 16 μ_B/f.u. Magnetization of powder samples at room temperature is $M_{20} = 55$–64 emu/g; the corresponding values at $T = 0$ K (calculated as previously by using $M(0)/M(rt) = 1.4$), are $M(0) = 78$–91 emu/g or 14.7–17.2 μ_B/f.u. The experimental values lie between the two theoretical limits; it is concluded that in this case Fe ions of β-type cells contribute, to some extent, to the observed magnetization. In Ref. (13) it has been suggested that since the β cell is intergrown with the M cell in a unique phase, it is submitted to the strong molecular field of the M-type magnetic structure. As a consequence, magnetic order may be induced in β-type intergrown cells. It should be mentioned that the theoretical magnetization value of 17.5 μ_B/f.u. calculated from all Fe ions, in the limit case of complete ferrimagnetic order in β-type cells, is close to, but not exceeded by, the highest value of magnetization attainable in completely exchanged nonstoichiometric hexaferrites, 64 emu/g at room temperature or 17.2 μ_B/f.u.

The two explanations are different but not incompatible. It is reasonable to assume that if the proportion of M cells is relatively low, then the induced ferrimagnetic order in β cells is not significant. This is the case of partially exchanged hexaferrites, where the proportion of M to β cells is $2 \div 1$. In contrast, in completely exchanged hexaferrites where the proportion is $3 \div 1$, β cells show induced ferrimagnetic order at a higher degree. Furthermore, the assumption of induced order explains the fact that the value of T_c in all nonstoichiometric hexaferrites is essentially equal to that of Ba–M, in spite of the different composition or different magnetization values they present.

4. CONCLUSION

Nonstoichiometric hexaferrites have been obtained by ion exchange in an aqueous solution. At the low temperature of the solution the exchange of K^+ by Ba^{2+} is partial and the crystal structure remains β''. The transformation from the β'' to the M phase is accomplished by heating at $T > 600°C$. Exchange of K^+ by H_3O^+ also takes place in the aqueous solution, resulting in the formation of Fe_2O_3 during annealing. This way the possible advantages of low exchange temperature are cancelled by the formation of a considerable amount of Fe_2O_3 impurity.

The crystal structure of partially exchanged nonstoichiometric hexaferrites is similar to that of completely exchanged hexaferrites: it is an M-type hexaferrite structure with intergrown β-type cells. In partially exchanged hexaferrites the proportion of M-type cells is lower.

Magnetization values are lower than those of completely exchanged hexaferrites. The comparison between calculated and experimental values in both cases suggests that in nonstoichiometric hexaferrites the magnetization is dictated by Fe ion content of the bipyramidal site Fe(2), characteristic of M-type cells. In contrast with completely exchanged compounds, induced ferrimagnetic order has not been assumed for partially exchanged compounds examined in the present work, the magnetization corresponding to the percentage (66%) of M-type cells in the structure. Besides Fe_2O_3 formation, which has been observed in compounds exchanged in aqueous environment, these seem to be the reasons of the comparatively low magnetization values observed.

The possibility of induced ferrimagnetic order in β-type cells has yet to be evidenced by magnetic measurements at high fields and low temperature. It is also related to the fundamental question of local crystal structure in nonstoichiometric hexaferrites, that is to the stacking sequence of M and β blocks. These issues constitute the objectives of further structural and magnetic characterization in this class of materials.

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