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On the formation of manganese ferrite from MnO_2 and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ aqueous solutions through coprecipitation

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Abstract

The formation and evolution of MnFe_2O_4 ferrite phase coprecipitated with NaOH from MnO_2 and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in aqueous solution are discussed, grounded on X-ray diffraction and derivatographic data, IR spectra and magnetic measurements. The results concerning the nature of the initial coprecipitates, their structural changes during ageing in the original solutions at temperatures in the range 25–95°C as well as the structure of the resulting ferritic phases are presented.

Keywords: Manganese iron mixed oxides; Coprecipitation; Structure; Solid solutions; Ferrites

Introduction

According to the literature data [1], the procedures to obtain MnFe_2O_4 by coprecipitation in solution can be classified as follows:

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1. Methods in which salts of Fe^{3+} and of Mn^{2+} are coprecipitated. The obtained coprecipitate consists in a single phase of polycrystalline ferrite with crystallite sizes of 20 Å and superparamagnetic behaviour. The ageing of the coprecipitate without changes of crystalline phase, characterised by rather low values of the activation energy (25 kJ/mol) is most probably described by an Ostwald ripening process; the unstable thermodynamically crystallites with sizes below 20 Å from the initial coprecipitate, dissolve again into the alkaline solution generating Fe^{3+} and Mn^{2+} ions which reprecipitate in higher sizes ferritic particles which are more stable thermodynamically.

2. Methods in which salts of Fe^{2+} and Mn^{2+} are coprecipitated. In such conditions the initial coprecipitate contains either one or more phases formulated as $\text{Fe}_{3,6}^{2+}\text{Fe}_{0,9}^{3+}(\text{O},\text{OH},\text{Cl})_9$, $\text{Fe}_{3,6}^{2+}\text{Fe}_{0,9}^{3+}(\text{O},\text{OH},\text{Br})_9$, $\text{Fe}_{3,6}^{2+}\text{Fe}_{0,9}^{3+}(\text{O},\text{OH},\text{SO}_4)_9$, and called “green rust” [2,3]. Obviously in this case the MnFe_2O_4 phase is generated in the ageing period; the change of the hexagonal structure of the green rust into the spinel structure of MnFe_2O_4 (cubic with tetragonal distortions) occurs through the hexagonal structure of αFeOOH [4] and its dissolution followed by nucleation and growth of the ferritic phase.

According to our literature information, this investigation is dedicated to a new method (wet method) to obtain MnFe_2O_4 . The novelty of this method consists in the use as raw materials MnO_2 and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ which, when are simultaneously dissolved in an aqueous solution of H_2SO_4 , determine the oxidation $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$. Taking into account the standard potentials ($\varepsilon^\circ \text{Fe}^{2+}/\text{Fe}^{3+} = 0.77 \text{ V}$ [1], $\varepsilon^\circ \text{MnO}_2 + 4\text{H}^+/\text{Mn}^{2+} + 2\text{H}_2\text{O} = -(1.3 \pm 0.1) \text{ V}$ [5] and $\varepsilon^\circ 2\text{SO}_4^{2-} + 4\text{H}^+/\text{S}_2\text{O}_6^{2-} + 2\text{H}_2\text{O} = -0.2 \text{ V}$ [1]) one can state that the oxidation is almost total. On the other hand, the reduction of Mn^{4+} ions (from MnO_2) is due to $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ oxidation as well as to the $\text{O}^{2-} \rightarrow \text{O}^0(1/2\text{O}_2)$ oxidation, according to the chemical equation [6]:



Thus the solution submitted to coprecipitation contains mostly the Fe^{3+} and Mn^{2+} ions, the presence of Fe^{2+} and Mn^{3+} ions not been excluded.

This work aims to present the results concerning the nature of the initial coprecipitates obtained at temperatures in the range 25°C–95°C, their structural changes during ageing at constant temperature in the original solution, as well as the structure of the resulted ferritic phases.

Experimental

2N solutions of the cations obtained through simultaneous dissolution, in the presence of H_2SO_4 , of stoichiometric amounts of MnO_2 and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ have been used. The coprecipitation at a pH of 12 was performed by adding a 15% solution of NaOH (Merck) to the solution of the two cations which was kept at constant temperatures in the range 25°C–95°C.

Actually 5 series of isothermal measurements at 25°C, 55°C, 70°C, 80°C and 95°C, without adding NH_4NO_3 and without stirring or air bubbling during ageing, have been carried out.

Samples from the coprecipitate have been taken at the initial instant and at various ageing times. After washing and drying them in air at ambient temperature for 48 hours the samples have been analysed by X-ray diffraction, derivatography, IR-spectra and magnetic measurements.

The X-ray diffractograms have been recorded by help of a DRON-2 equipment using the Mo K_{α} radiation.

In order to record the IR spectra a PERKIN-ELMER 903 spectrometer in the range of wave number 200–4000 cm^{-1} has been used.

The thermal analysis curves have been obtained using a MOM Budapest type Paulik-Paulik-Erdey derivatograph in static air atmosphere at a heating rate of 5 K/min.

The Fe^{2+} ions in the coprecipitation solution have been determined using redox volumetry (bichromatometry) in the presence of NaF with diphenylamino-barium-sulphonate as indicator. As far as the determination of Fe^{2+} ions in coprecipitates is concerned, after dissolution in a reducing atmosphere, and bringing in solution, the same procedure was applied.

The hysteresis loops of the coprecipitates have been recorded at the ambient temperature by help of a FERRO-TESTER type 9801/A Hungary. Equal amounts of powdered samples introduced in glass tubes with $\Phi = 5$ mm and settled through vibration have been used.

The magnetic parameter H_c (coercitive field) has been calculated from the hysteresis loops using the relationship:

$$H_c(\text{Oe}) = K_1 V_H \quad (1)$$

where K_1 is the coil constant and V_H the signal (in volts) measured on the Ox axis.

The experimental value of the lattice parameter, a , for the spinel structure in the investigated samples has been calculated from the X-ray diffraction data using the formula:

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \quad (2)$$

where d is the interplanar distance and h, k, l are the corresponding Miller indexes.

The theoretical values of the lattice parameter for various oxidation states of manganese and iron ions and various fractions of them, x_A and x_B , in the tetrahedral (A) and octahedral (B) sites of the spinel structure have been calculated by help of Poix's method [7]. Using the values of the cation-oxygen distances given in Table 1, according to the mentioned method the lattice parameter of the spinel $M_A[M_B]_2O_4$ is given by the relationship:

$$a(\text{\AA}) = 2.0995 A + [5.8182 B^2 - 1.4107 A^2]^{1/2} \quad (3)$$

with: $A = \sum x_A (M_A - O)_4 = M_A - O$ mean distance metal-oxygen in tetrahedral sites; $2B = \sum x_B (M_B - O)_6 = M_B - O$ mean distance metal-oxygen in octahedral sites; x_A and x_B are the respective cations numbers of M_A and M_B per formula unit; $(M_A - O)_4$ and $(M_B - O)_6$ are the cation-oxygen distances in tetrahedral and octahedral sites respectively.

Table 1
The values of the cation-oxygen distances used to calculate the lattice parameter [7]

| Cation | Cation-oxygen distance (Å) | |
|------------------|----------------------------|---------------------|
| | tetrahedral (A) site | octahedral (B) site |
| Mn ²⁺ | 2.041 | 2.220 |
| Mn ³⁺ | – | 2.045 |
| Fe ²⁺ | 2.012 [8] | 2.138 [8] |
| Fe ³⁺ | 1.858 | 2.020 |

The crystallite sizes of the ferritic phases obtained at various temperatures and times of ageing have been calculated by help of Scherrer's formula [9] for the most intense diffraction line which corresponds to the plane (311).

The specific areas of the aged ferritic powders have been determined using BET method (N₂ adsorption at 77 K) with a MICROMETRICS 2100E equipment.

Results and discussion

The values of the Fe²⁺ content of the coprecipitation solutions as well as of the aged coprecipitates are listed in Table 2.

The IR spectra, X-ray diffractograms and derivatograms of the initial (non-aged) coprecipitates and corresponding to various ageing times are given respectively in Figures 1, 2–5 and 6.

The presented data lead us to the following considerations concerning the formation and evolution of the coprecipitated ferritic phase.

1. On the influence of the temperature on the nature of the initial coprecipitates

The temperature has a substantial influence on the nature of the coprecipitated phase.

Table 2
Fe²⁺ contents of the coprecipitation solution as well as of the aged coprecipitates

| Sample | Fe ²⁺ content (% weight) |
|---|-------------------------------------|
| Fresh prepared coprecipitation solution | 19.5** |
| Coprecipitate aged for 480 min. at 55°C | 8.5* |
| Coprecipitate aged for 330 min. at 70°C | 7.9* |
| Coprecipitate aged for 330 min. at 80°C | 5.20* |
| Coprecipitate aged for 330 min. at 95°C | 4.70* |

* reported to the total mass of the dried sample

** reported to the total mass of dissolved iron

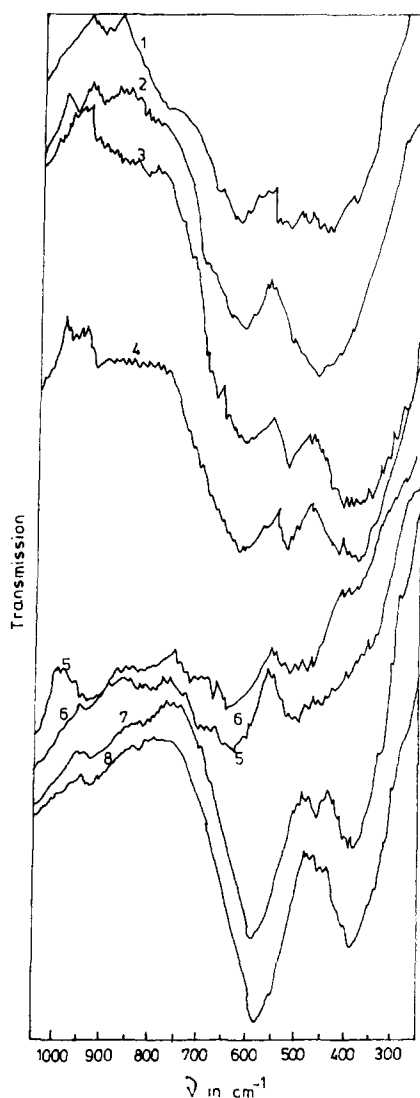


Fig. 1. IR spectra of coprecipitates obtained at : 25°C, 0 min.(1); 55°C, 0 min. (2); 55°C, 60 min. (3); 80°C, 0 min. (4); 95°C, 0 min. (5); 95°C, 5 min. (6); 95°C, 10 min. (7); 95°C, 330 min. (8)

The coprecipitate obtained at 25°C exhibits almost an amorphous state. However, the coherent diffraction zones corresponding to the interplanar distances $d = 2.49 \text{ \AA}$ and $d = 2.54 \text{ \AA}$ indicate a local (short range) ordering corresponding to Mn_3O_4 and probably $\delta\text{FeO}(\text{OH})$. The existence of some Mn_3O_4 nuclei is confirmed by the IR spectrum (Fig. 1, curve 1) which contains the bands at 680 cm^{-1} , 630 cm^{-1} and 530 cm^{-1} . The bands of the same spectrum at 940 cm^{-1} , 530 cm^{-1} , 470 cm^{-1} and

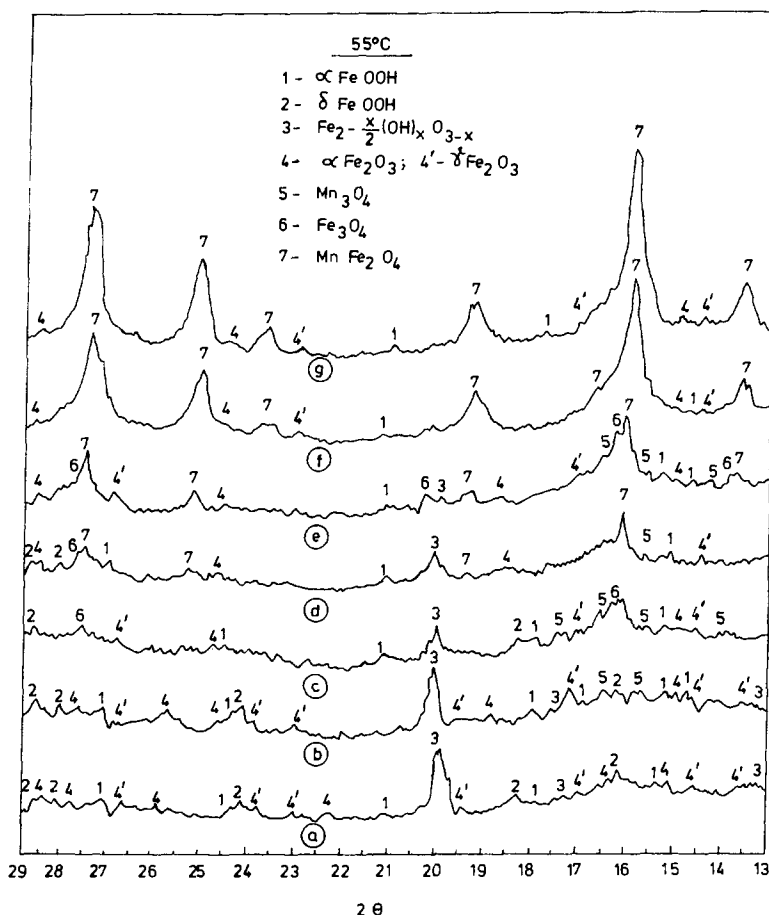


Fig. 2. X-ray diffractograms of the coprecipitates obtained at 55°C: nonaged sample (a) and samples after 10 minutes (b), 20 minutes (c), 60 minutes (d), 120 minutes (e), 330 minutes (f) and 480 minutes (g) of ageing in the original solution. All the samples have been dried in air at ambient temperature.

380cm^{-1} indicate the phase $\text{Fe}_{2-x/3}(\text{OH})_x\text{O}_{3-x}$ [10] called hydrohematite and the bands at 575cm^{-1} and 450cm^{-1} indicate the presence of $\alpha\text{FeO}(\text{OH})$ nuclei.

The coprecipitate obtained at 55°C contains beside nuclei of the hexagonal phases α , δFeOOH , $\text{Fe}(\text{OH})_2$, $\alpha\text{Fe}_2\text{O}_3$, of the tetragonal spinel Mn_3O_4 , a hexagonal crystalline phase of hydrohematite (Fig. 2, curve a). The presence of hydrohematite is confirmed by the IR absorption band at 470cm^{-1} (Fig. 1, curve 2).

The coprecipitates obtained at temperatures in the range 70°C – 95°C exhibit rather complex structures. In spite of broad and weak X-ray diffraction peaks, by help of the IR spectra, one can notice that these structure contain nuclei of cubic inverse spinel Fe_3O_4 , cubic with tetragonal distortions spinels MnFe_2O_4 [11] and $\text{Mn}_y\text{Fe}_{3-y}\text{O}_4$ [20], tetragonal spinel Mn_3O_4 , as well as $\text{Fe}_{2-x/3}(\text{OH})_x\text{O}_{3-x}$, $\alpha\text{FeO}(\text{OH})$, and $\alpha\text{Fe}_2\text{O}_3$ (Fig. 3–5, curves a).

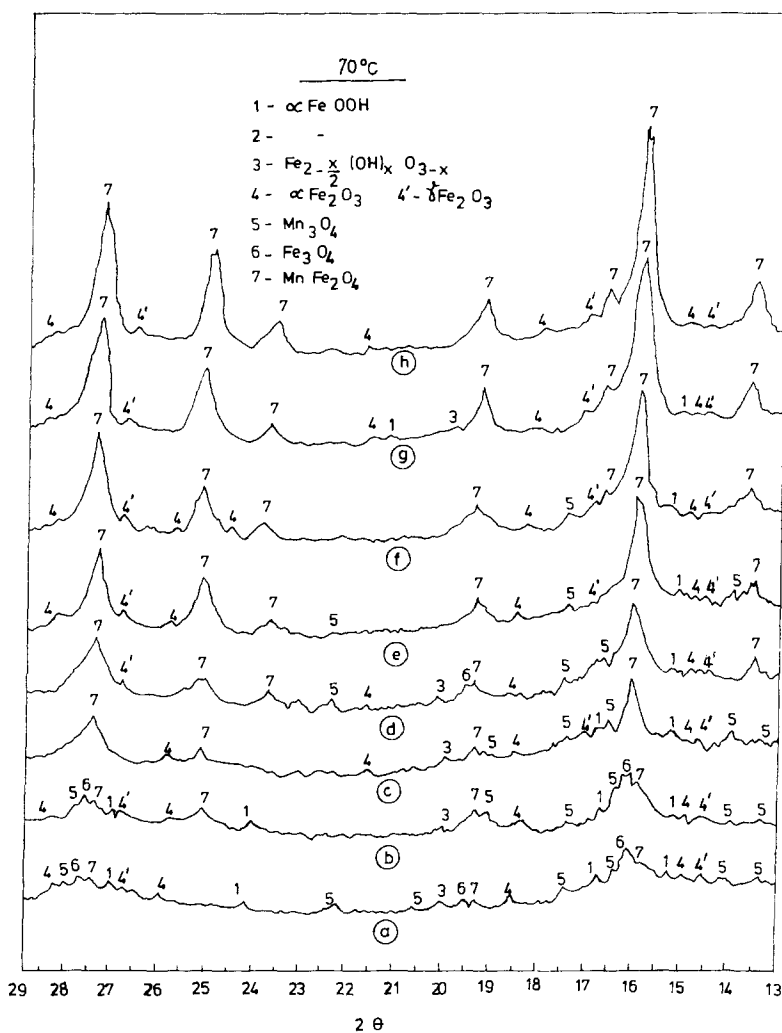


Fig. 3. X-ray diffractograms of the coprecipitates obtained at 70°C: nonaged sample (a) and samples after 5 minutes (b), 10 minutes (c), 20 minutes (d), 40 minutes (e), 60 minutes (f) and 120 minutes (g) and 330 minutes (h) of ageing in the original solution. All the samples have been dried in air at ambient temperature.

As shown by the X-ray diffractograms and the IR spectra, the coprecipitate obtained at 80°C exhibits the most well formed spinellic phases. As far as the weight of these phases is concerned the X-ray diffractogram (Fig. 4, curve) indicates that the most well formed crystalline phase is Fe_3O_4 , while the IR spectrum (Fig. 1, curve 4) indicates that the most ordered phases are Mn_3O_4 and MnFe_2O_4 [12]. Actually, the diffraction lines of Fe_3O_4 are shifted to higher values of 2θ and correspondingly lower values of d , thus indicating a substitution of iron with manganese in the tetrahedral site which leads to the formation of $\text{Mn}_y\text{Fe}_{3-y}\text{O}_4$; this substitution shifts the ν_1 band of Fe_3O_4 in IR

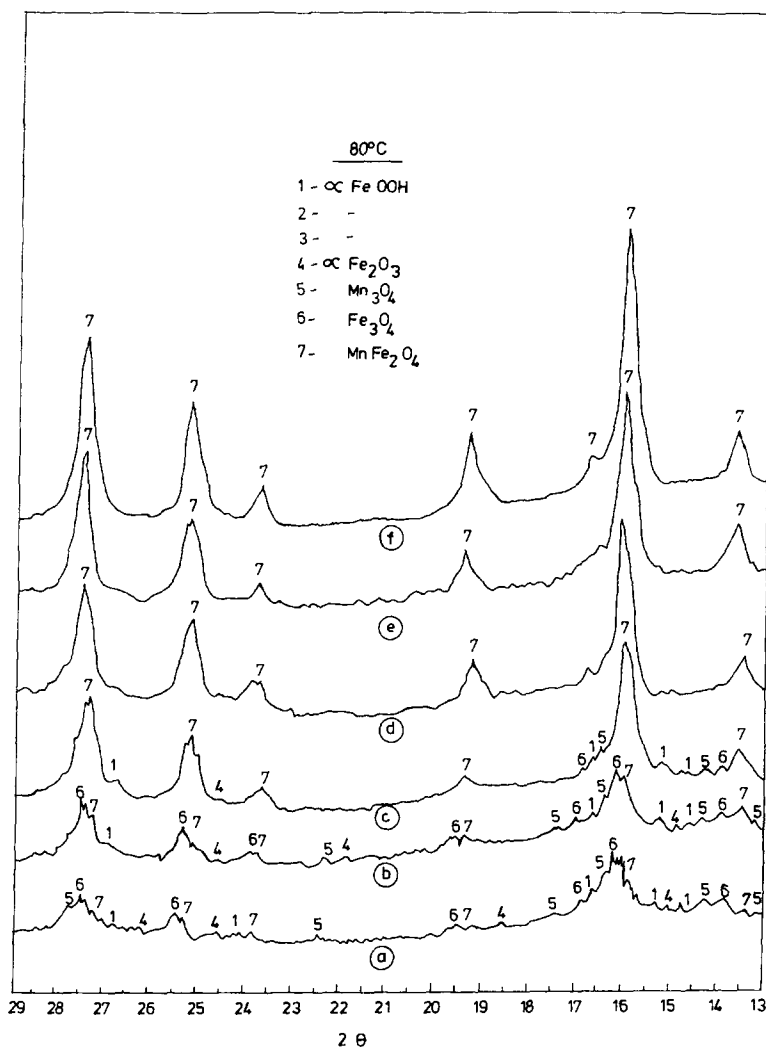


Fig. 4. X-ray diffractograms of the coprecipitates obtained at 80°C: nonaged sample (a) and samples after 5 minutes (b), 10 minutes (c), 40 minutes (d), 60 minutes (e), 330 minutes (f) of ageing in the original solution. All the samples have been dried in air at ambient temperature.

spectrum, from 570 cm^{-1} to 540 cm^{-1} [12]. The splitting of the ν_2 band (400 cm^{-1}) of the cubic spinel in $\nu_2(1)$ at 420 cm^{-1} and $\nu_2(2)$ at 380 cm^{-1} indicates the presence of the cubic spinel MnFe_2O_4 with tetragonal distortions [12].

The hysteresis loops show the existence of stable nuclei of the ferritic phases Fe_3O_4 , $\text{Mn}_y\text{Fe}_{3-y}\text{O}_4$, MnFe_2O_4 , which are magnetic single domain particles due to sizes below 1000 \AA [12,13,14] with superparamagnetic behaviour [1,12], only in the initial coprecipitates obtained at 80°C and 95°C. The values of H_c in the range 900 A/m –

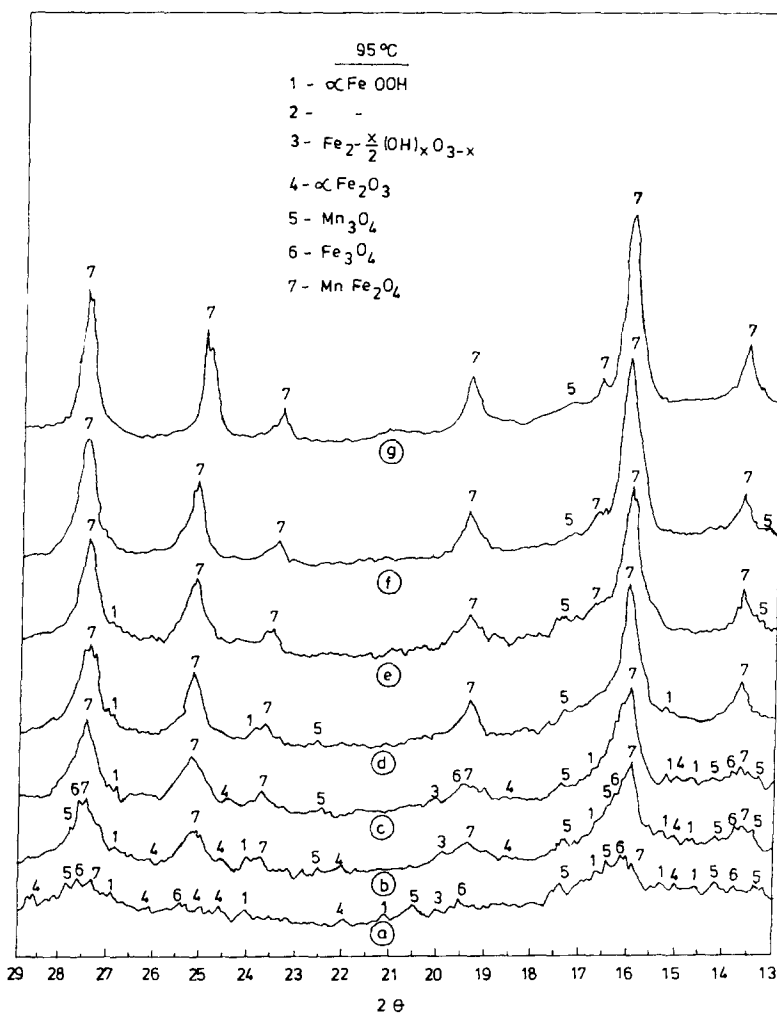


Fig. 5. X-ray diffractograms of the coprecipitates obtained at 95°C: nonaged sample (a) and samples after 5 minutes (b), 10 minutes (c), 20 minutes (d), 40 minutes (e), 60 minutes (f), 330 minutes (g) of ageing in the original solution. All the samples have been dried in air at ambient temperature.

1300A/m indicate a rotational magnetisation mechanism which is specific to the ferromagnetic dispersions [13].

As shown by the TG curves (Fig. 6, curves 1–4), all the initial coprecipitates exhibit important mass losses in the temperature range 20°C–200°C which correspond to the removal of different kinds of water [17]. The amount of water in coprecipitates diminishes with the increase of the temperature of precipitation, changing from 11% for the coprecipitate obtained at 95°C to 26% for that obtained at 55°C; the only exception is exhibited by the coprecipitate obtained at 80°C with the highest crystallinity and the lowest mass loss (8%).

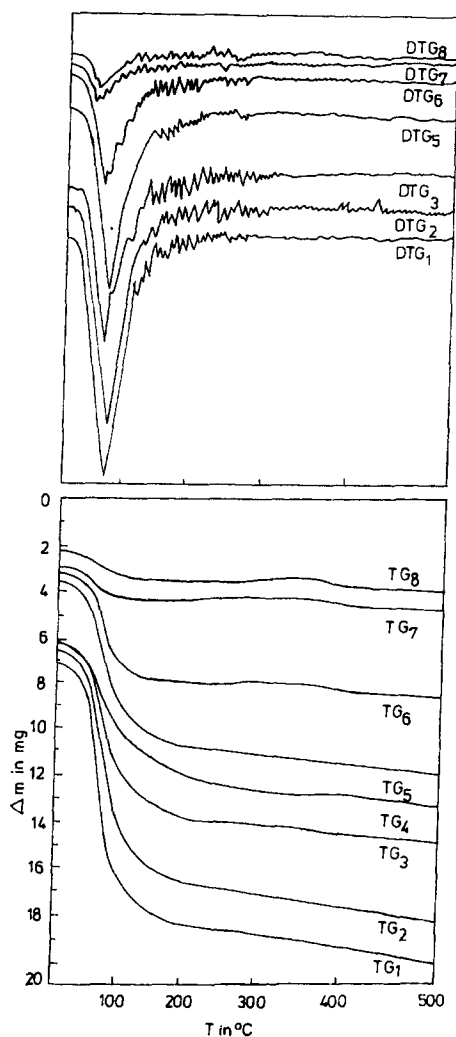


Fig. 6. The TG and DTG curves of the coprecipitates obtained at various temperatures and times of ageing in the original solution: 55° C, nonaged(1); 70° C, nonaged(2); 80° C, nonaged(3); 95° C, nonaged(4); 55° C, 60 minutes(5); 70° C, 60 minutes(6); 95° C, 60 minutes(8); 95° C, 330 minutes(9).

The DTG curves (Fig. 6, curves 1–3) show a shift towards a lower temperatures of the maximum dehydration rate with the increase of precipitation temperature.

The presence of OH^- groups and water in the coprecipitates is confirmed by the characteristic bands from 930 cm^{-1} , 800 cm^{-1} (Fig. 1), 1650 cm^{-1} and $\sim 3300\text{ cm}^{-1}$ in the IR spectrum. The shifts of these bands to higher values of the frequency with the increase of the coprecipitation temperature indicates a stronger bonding of the water molecules.

2. On the change of the coprecipitates during ageing in solution

The ageing at 25°C does not lead to neither phase changes, nor to an increase of the crystallinity of the initial phases. In the coprecipitate obtained at 25°C, after 24 hours ageing, filtering, washing and 12 hours drying at 95°C, only small amounts of nuclei belonging most probably to the Mn_3O_4 , α and $\delta\text{FeO}(\text{OH})$ and $\alpha\text{Fe}_2\text{O}_3$ phases can be detected.

The ageing at 55°C as shown by the X-ray diffractograms (Fig. 2), leads to important changes which consist in the dissolution of the hexagonal phases of oxyhydroxides, the formation of spinellic phases Fe_3O_4 , Mn_3O_4 , as intermediates, the formation and growth of $\text{Mn}_y\text{Fe}_{3-y}\text{O}_4$ and MnFe_2O_4 particles. After 10 minutes of ageing one has to notice the appearance of Fe_3O_4 and Mn_3O_4 nuclei (Fig. 2, curve b). After 20 minutes of ageing the phases Fe_3O_4 and $\text{Mn}_y\text{Fe}_{3-y}\text{O}_4$ prevail the phase Mn_3O_4 (Fig. 2, curve c). Thus Mn_3O_4 is dissolved and Mn^{2+} ions are incorporated in the cubic spinel Fe_3O_4 generating substituted magnetites [12]. The X-ray diffractograms (Fig. 2, curve d) of the coprecipitate aged for 60 minutes indicates a bimodal size distribution; higher sizes stable nuclei of ferritic phases coexist with lower sizes (thermodynamically unstable) ones. The IR spectra (Fig. 1, curve 3 and 4) show that during ageing for 60 minutes at 55°C, the same spinellic phases as in the initial coprecipitate at 80°C are generated, and one can conclude presently that stable nuclei of the ferritic phase are present. The increase of the amount of ferritic phase as well as of its particle sizes is accompanied by a continuous increase of the lattice parameter (Fig. 7), thus indicating a continuous increase of the substitution degree (y) of the iron with manganese in the cubic spinel structure of the solid solution $\text{Mn}_y\text{Fe}_{3-y}\text{O}_4$ (Fig. 9, paragraph 3).

The ageing at 70°C occurs also with some peculiarities. The nonaged coprecipitate contains various kinds of ferritic nuclei from Fe_3O_4 ($d_{311} = 2,530 \text{ \AA}$) to MnFe_2O_4 ($d_{311} = 2,563 \text{ \AA}$) as well as Mn_3O_4 (Fig. 3 curve a). In the first 5 minutes of ageing, an increase in amount of phases Fe_3O_4 , $\text{Mn}_y\text{Fe}_{3-y}\text{O}_4$, MnFe_2O_4 and Mn_3O_4 can be noticed (Fig. 3, curve b). After 10 minutes of ageing the most important ferritic phase is that with $d_{311} = 2,556 \text{ \AA}$ indicating a substituted magnetite phase $\text{Mn}_y\text{Fe}_{3-y}\text{O}_4$. Beginning with this ageing time, the formation of the ferritic phase is accompanied by a continuous increase of the lattice parameter (Fig. 7) indicating, like in case of ageing at 55°C, an increase of the degree of substitution with manganese in the spinel structure (Fig. 9). After 330 minutes of ageing the mean crystallite size was 400 Å.

The ageing at 80°C leads to a fast generation of the ferritic phase and growth of its particle sizes (Fig. 4). After 5 minutes of ageing, an increase of the amount of cubic ferritic phase ($d_{311} = 2,554 \text{ \AA}$) and simultaneously a decrease of the amount of the tetragonal phase of Mn_3O_4 can be noticed. After 10 minutes of ageing the coprecipitate consists from well formed crystallites of ferritic phase with $d_{311} = 2,576 \text{ \AA}$, $a = 8,517 \text{ \AA}$. The important increase of the lattice parameter correlated with the fast diminution of the amount of Mn_3O_4 phase can be assigned, taking into account the data from Fig. 9, to the formation of solid solutions $\text{MnFe}_2\text{O}_4 \cdot \text{Mn}_3\text{O}_4$ described by the general formula $\text{Fe}_{2y}\text{Mn}_{3-2y}\text{O}_4$ (paragraph 3C). Beginning with this ageing time, a decrease of the lattice parameter (Fig. 7) indicates the change of the solid solution into the cubic spinel MnFe_2O_4 with mean crystallite size of 480 Å after 330 minutes of ageing.

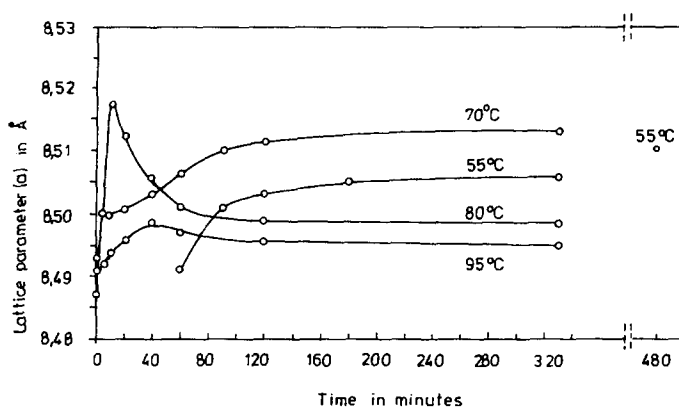


Fig. 7. The change of the lattice parameter as function of reaction time for various ageing temperatures

The ageing at 95°C occurs with the fast generation of the ferritic phase (Fig. 5). In the first 5 minutes of ageing a development of all MnFe_2O_4 , Fe_3O_4 , Mn_3O_4 and αFeOOH phases can be noticed. The decrease of the lattice parameter as function of reaction time (Fig. 7) is determined, according to the data from Fig. 9, by the change of the initial phases into the solid solution $\text{MnFe}_2\text{O}_4 \cdot \text{Fe}_3\text{O}_4$ ($\text{Mn}_y\text{Fe}_{3-y}\text{O}_4$) described by one of the formulae IV-VIII (paragraph 3B), with 440 Å for the mean crystallite size. The IR spectra (Fig. 1, curves 5–7) account also for the fast changes occurring in the first 10 minutes of ageing.

The generation of the ferritic phase and the increase of its crystallinity in time and with the ageing temperature results of a decrease of the amount of different types of bound water [17] from the coprecipitates (Fig. 6). The TG curves (Fig. 6, curves 7 and 8) show that through ageing in solution at 95°C the water which is evolved at temperatures in the range 100°C–200°C is removed. Thus the temperature exhibits an important influence of the structural changes of the initial coprecipitates in solutions. A detailed investigation on this subject is going to be presented in a next work.

3. On the influence of the ageing temperature on the structure of the resulted ferritic phases

The low values of the magnetic crystallite sizes in the range 400 Å–480 Å correspond to those (< 1000 Å) of magnetic single domains. These values account for the high value of the coercitive field H_C [14] in the range 1500A/m–2300A/m thus indicating a rotational mechanism of magnetisation characteristic for the fine ferromagnetic dispersions [13].

Fig. 7 shows an important change of the spinel lattice parameter with the temperature of formation thus indicating important microstructural differences. These are probably due to the differences in the ratio distribution and oxidation degree of manganese and iron ions in the octahedral (B) and tetrahedral (A) sites of the spinel structure.

Various references concerning the presence of Mn^{3+} ions on the manganese ferrites are given in literature [9,11,15,17–19]. Due to the preference of the Mn^{3+} and Fe^{2+} [18,19] ions for octahedral coordination as well as to the fact that the $\text{Mn}^{2+} \rightarrow \text{Mn}^{3+}$ oxidation (at the transition from A to B sites) occurs on account of the reduction of Fe^{3+} ions (from B sites) to Fe^{2+} ions which remain in B sites, one can consider that the MnFe_2O_4 spinel is a mixed one with various inversion degrees (x) and the general formula $\text{Mn}_{1-x}^{2+}\text{Fe}_x^{3+}[\text{Fe}_{2-2x}^{3+}\text{Fe}_x^{2+}\text{Mn}_x^{3+}]\text{O}_4$. Thus for the stoichiometric spinel, the Fe^{2+} contents can be correlated with the inversion degree and correspondingly with the lattice parameter. At the increase of the inversion degree, the concentration of Fe^{2+} ions increases and the lattice parameter decreases (due to the increase of the Mn^{2+} ions number which leave the tetrahedral site for the octahedral ones with larger volume). From this standpoint, the experimental results obtained by us are rather contradictory as the increase of Fe^{2+} contents (Table 2) is accompanied by an increase of the lattice parameter (Fig. 7) when the temperature decreases.

In order to account for the mentioned apparent contradiction, the theoretical values of the lattice parameter corresponding to various structural formulae have been calculated using Poix's method [7]. For these structural formulae, grounded on the literature data as well as on the experimental data presented in paragraphs 1 and 2, the following possibilities have been considered.

A. *The ferritic phase consists in the stoichiometric spinel MnFe_2O_4 .* In this case the following structures have to be taken into account:



The calculated values, according to [7], of the lattice parameter corresponding to the structures (I)–(III) as well as the calculated values of the Fe^{2+} ion concentrations corresponding to various inversion degrees (x) are given in Fig. 8; in relationship (3), $x_{\text{A}(\text{Mn}^{2+})} = 1 - x$, $x_{\text{A}(\text{Fe}^{2+})} = x_{\text{A}(\text{Fe}^{3+})} = x$, $x_{\text{B}(\text{Fe}^{2+})} = x_{\text{B}(\text{Mn}^{3+})} = x$, $x_{\text{B}(\text{Fe}^{3+})} = 2 - x$ for structures I and III, and $2 - 2x$ for structure II.

Taking into account the experimental values of the Fe^{2+} ions concentration (Table 2) and of the lattice parameter (Fig. 7), the experimental data can be correlated with the theoretical ones only for the ferrite obtained at 80°C : the experimental value of Fe^{2+} ions concentration equal to 5.2% leads (according to curve 4 from Fig. 8) to an inversion degree of 0.21 which corresponds (according to curve 2 from Fig. 8) to a calculated value of the lattice parameter of 8.498 Å, the same with the experimental one (Fig. 7).

Thus, only the ferrite obtained after minimum 2 hours of ageing at 80°C corresponds to the cubic stoichiometric spinel MnFe_2O_4 with an inversion degree (x) of 0.21, being described by the more exact formula $\text{Mn}_{0.79}^{2+}\text{Fe}_{0.21}^{3+}[\text{Mn}_{0.21}^{3+}\text{Fe}_{0.21}^{2+}\text{Fe}_{1.58}^{3+}]\text{O}_4$.

The experimental value of the lattice parameter $a = 8.498 \text{ \AA}$ is close to that given in literature for $x = 0.2$ which equals 8.499 Å [23]. This value is also close to the reported one for MnFe_2O_4 ($a = 8.497 \text{ \AA}$) obtained by coprecipitation of a aqueous solution of Mn^{2+} and Fe^{2+} ions with NaOH at 85°C [19]. In this last case, the authors indicate a value of the inversion degree which equals 0.38

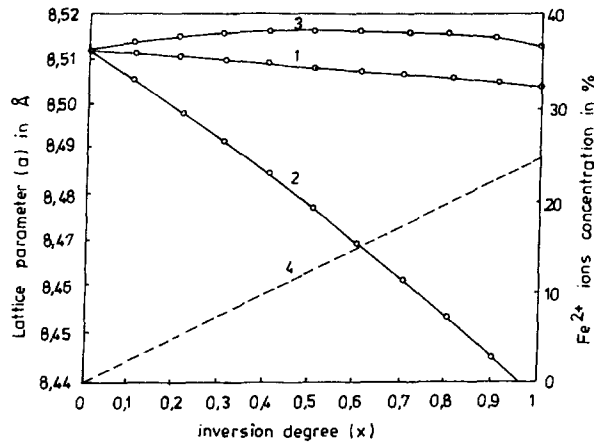
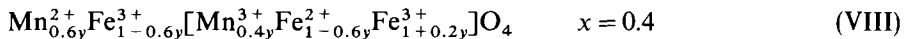
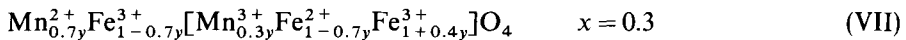
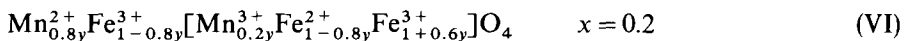
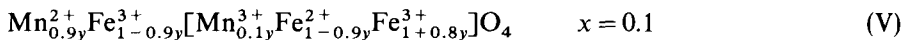


Fig. 8. Calculated values of the lattice parameter for various structural formulae of the spinel MnFe_2O_4 : 1 – $\text{Mn}_{1-x}^{2+}\text{Fe}_x^{2+}[\text{Mn}_x^{3+}\text{Fe}_{2-x}^{3+}]\text{O}_4$; 2 – $\text{Mn}_{1-x}^{2+}\text{Fe}_x^{2+}[\text{Mn}_x^{3+}\text{Fe}_x^{2+}\text{Fe}_{2-2x}^{3+}]\text{O}_4$; 3 – $\text{Mn}_{1-x}^{2+}\text{Fe}_x^{3+}[\text{Mn}_x^{2+}\text{Fe}_{2-x}^{3+}]\text{O}_4$ and 4- Fe^{2+} ions concentration versus the inversion degree of the spinel.

B. The ferritic phase consists in solid solutions between MnFe_2O_4 and Fe_3O_4 with the general formula $\text{Mn}_y\text{Fe}_{3-y}\text{O}_4$ (y is the degree of substitution of iron with manganese). These solid solutions are generated at the formation of ferritic phase through solid state reaction as well as through coprecipitation [13,15,19–23]. According to [15,20,23] the solid solutions are described by the formula $\text{Mn}_{0.8y}^{2+}\text{Fe}_{1-0.8y}^{3+}[\text{Fe}_{1-0.6y}^{3+}\text{Fe}_{1-0.8y}^{2+}\text{Mn}_{0.2y}^{3+}]\text{O}_4$ which for the value $y=1$ leads to the stoichiometric ferrite with an inversion degree of 0.2.

In the following we suggest structural formulae similar to the previous one; for $y=1$ these formulae should lead to MnFe_2O_4 with inversion degree (x) of 0.0; 0.1; 0.2; 0.3; 0.4:



The change of the calculated values of the lattice parameters corresponding to the structures (IV)–(VIII), using the method of Poix [7], with the substitution degree (y) are given in Fig. 9, curves 1–5.

As shown by these curves the increase of the degree of substitution of iron with manganese until $y=1$ leads to an increase of the lattice parameter until the value corresponding to MnFe_2O_4 with the considered inversion degree (x). The ordinate in the right side of the Fig. 9 (corresponding to $y=1$), evidences the change of the lattice parameter of stoichiometric MnFe_2O_4 with the inversion degree; this change should be the same with that given by the curve 2 from Fig. 8 corresponding to the structural formula (II).

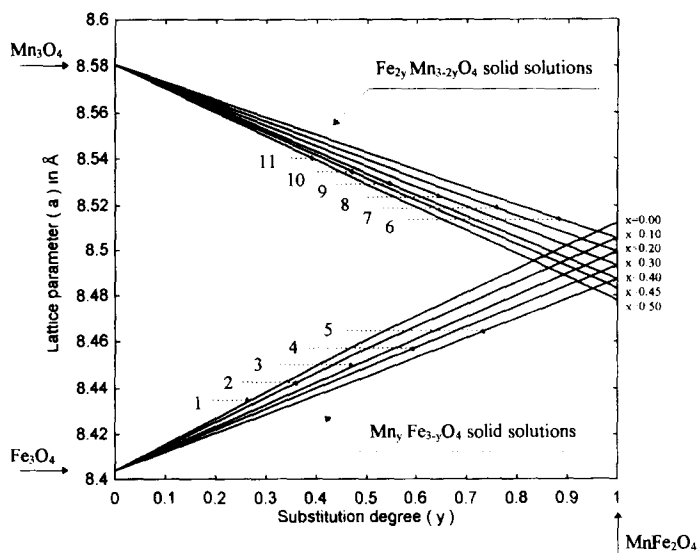


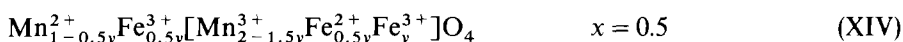
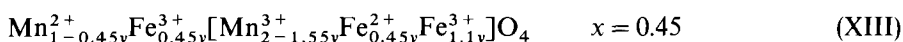
Fig. 9. Calculated values of the lattice parameter for solid solutions between Fe_3O_4 and Mn_3O_4 corresponding to the structural formulae: $\text{Mn}_y\text{Fe}_{3-y}\text{O}_4$ solid solution: IV (1), V (2), VI (3), VII (4), VIII (5) and $\text{Fe}_{2y}\text{Mn}_{3-2y}\text{O}_4$ solid solution: IX (6), X(7), XI (8), XII (9), XIII (10), XIV (11), versus the substitution degree (y). For $y = 1$, these formulae lead to the stoichiometric spinel. MnFe_2O_4 characterised by the structural formula $\text{Mn}_x^{2+}\text{Fe}_{1-x}^{3+}\text{Mn}_{2-x}^{3+}\text{Fe}_x^{2+}\text{Fe}_{2-x}^{3+}\text{O}_4$ with various inversion degrees (x): $x = 0.0$ for curve 1; $x = 0.1$ for curves 2 and 6; $x = 0.2$ for curves 3 and 7; $x = 0.3$ for curves 4 and 8; $x = 0.4$ for curves 5 and 9; $x = 0.45$ for curves 10 and $x = 0.5$ for curves 11.

Considering this type of solid solutions, only in the case of the ferrite obtained at 95°C the experimental results (Fe^{2+} content in Table 2 and lattice parameter in Fig. 7) can be correlated with the theoretical ones: experimental value $a = 8.495 \text{ \AA}$ (Fig. 7) leads, according to the curve 2 from Fig. 9, to a substitution degree $y = 0.90$ which leads, according to the structural formula (V), to the more exact structural formula $\text{Mn}_{0.81}^{2+}\text{Fe}_{0.19}^{3+}[\text{Mn}_{0.09}^{3+}\text{Fe}_{0.19}^{2+}\text{Fe}_{1.72}^{3+}]\text{O}_4$. This formula corresponds to the Fe^{2+} ions concentration of 4.61% which is in satisfactory agreement with the experimental one (Table 2).

The same experimental value $a = 8.495 \text{ \AA}$ (according to the curves 1 or 3 from Fig. 9) leads to $y = 0.835$ and $y = 0.965$ respectively. These values indicate, according to formulae (IV) and (VI) respectively that the Fe^{2+} ions concentrations are not in agreement with the experimental one (Table 2).

The character of a solid solution between MnFe_2O_4 and Fe_3O_4 of the coprecipitate aged in solution at 95°C is confirmed by the Mössbauer spectrum and by the IR spectrum (Fig. 1, curve 8). Indeed, the presence of magnetite shifts the ν_1 band from 530 cm^{-1} to $\sim 580 \text{ cm}^{-1}$ [12]. A band at 588 cm^{-1} for MnFe_2O_4 obtained through a wet method has been reported by other authors to [25].

C. The ferritic phases consists in solid solutions between MnFe_2O_4 and Mn_3O_4 with the general formula $\text{Fe}_{2y}\text{Mn}_{3-2y}\text{O}_4$. The results concerning the ferrite phase obtained at 70°C and 55°C (Table 2 and Fig. 7) cannot be explained in the framework of the models discussed at the points A and B. The literature data concerning the mixed oxides of iron and manganese [19,22,25] with the general formula $\text{Fe}_{2y}\text{Mn}_{3-2y}\text{O}_4$ do not mention any proposals for structural formulae. That is the reason which we suggest the following structural formulae which, for a substitution degree $y = 1$, lead to MnFe_2O_4 with inversion degree (x) of 0.1; 0.2; 0.3; 0.4; 0.45 and 0.5:



The change of the theoretical value of the lattice parameters of structures (IX) - (XIV) with the substitution degree (y) is shown in Fig. 9 curves 6–11.

From a discussion similar to that presented previously (point B), taking into account the experimental values of the lattice parameters (Fig. 7) and Fe^{2+} ions concentration (Table 2) results that the ferritic phases obtained at 55°C consists of solid solution with structural formula (XIV) for which $y = 0.68$. The ferritic phases obtained at 70°C consists of solid solution with structural formula (XIII) for which $y = 0.70$. Thus the experimental values $a = 8.510 \text{ \AA}$ and $a = 8.512 \text{ \AA}$ lead, according to the curves 11 and 10 from Fig. 9 to $y = 0.69$ and respectively $y = 0.70$. In such conditions the particular forms of the formulae (XIV) and (XIII) respectively are:



to which corresponds a Fe^{2+} ions concentration of 8.51% , and



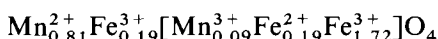
to which corresponds a Fe^{2+} ions concentration of 7.79%.

Conclusions

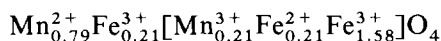
1. The coprecipitation at $\text{pH} \geq 12$ with NaOH of the solutions of MnO_2 and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ leads to initial coprecipitates which differ in their structures and crystallinities at different temperatures.

2. The ageing of the initial coprecipitates leads to ferritic phases as follows:

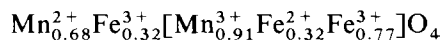
– at 95°C the ferritic phase consists in a solid solution $\text{MnFe}_2\text{O}_4 \cdot \text{Fe}_3\text{O}_4$ which corresponds to the structural formula:



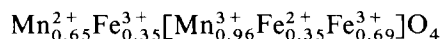
– at 80°C the ferritic phase consists in the stoichiometric spinel MnFe_2O_4 with the structural formula:



– at 70°C and 55°C the ferritic phases consist on solid solutions $\text{MnFe}_2\text{O}_4 \cdot \text{Mn}_3\text{O}_4$ characterised by the following structural formulae:



and respectively



3. Concerning the procedure to obtain MnFe_2O_4 applied in this work, one can state that it does not belong to the two groups of methods previously mentioned, the presented results ground an intermediate one.

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