# Synthesis of MnFe$_2$O$_4$ nanoparticles by mechano-chemical reaction

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The influence of long-term milling of a mixture of MnCO$_3$ and $\alpha$-Fe$_2$O$_3$, and of MnO$_2$ and $\alpha$-Fe$_2$O$_3$ powders in a planetary ball mill on the reaction synthesis of nanosized MnFe$_2$O$_4$ ferrites was studied. The mechano-chemical reaction leading to formation of the MnFe$_2$O$_4$ spinel phase was followed by X-ray diffraction. The spinel phase was first observed after 10 h of milling and its formation was completed after 20 h in case of the MnCO$_3$ - $\alpha$-Fe$_2$O$_3$ mixture. The synthesized MnFe$_2$O$_4$ ferrite has a nanocrystalline structure with a crystallite size of about 28 nm. The thermal treatment of the as-milled powder at 400$^o$C for 4 h led to formation of the MnFe$_2$O$_4$ crystalline phase in case of the mixture of MnCO$_3$ and $\alpha$-Fe$_2$O$_3$, but in MnO$_2$ - $\alpha$-Fe$_2$O$_3$ case thermal treatment at temperatures of 400 $^o$C and higher leads to formation of (Mn,Fe)$_2$O$_3$ and separation of Mn$_2$O$_3$ and Fe$_2$O$_3$.

## 1. Introduction

Developments in microelectronic devices have promoted the development of new methods for their preparation. An essential prerequisite for tailoring magnetic materials is the possibility of creating a broad range of microstructures, i.e. from amorphous to single crystals. Soft ferrites, owing to their simple preparation and good magnetic characteristics, are frequently applied in magnetic recording media, ferrofluids, permanent magnets, etc. [1,2].

Beside chemical composition, microstructure has a significant influence on magnetic properties. Therefore nanostructured materials exhibit unusual physical and chemical properties, significantly different from those of conventional bulk materials, due to their extremely small grain size or large specific surface area [3].

Fully dense bulk ferrites have been synthesized by several different methods: low-temperature sintering of fine or ultra fine powders, thermal decomposition of carbonates or nitrates and co-precipitation [4,5]. The advantages of preparation from ultra-fine powders are that the composition can be more easily controlled and the electrical and thermal properties are improved as a result of the reduced grain size [5].

In addition to the aforementioned methods, a relatively new solid-state process named mechano-chemical treatment may also be applied for the synthesis of electroceramics. In general, mechano-chemical treatment has been recognized as a powerful technique for synthesis of a wide range of materials. Thus, complex, multicomponent metallic and ceramic materials, which may otherwise be difficult to prepare by conventional high temperature treatment, have been successfully prepared by milling.

Mechano-chemical treatment is a non-equilibrium solid-state process in which the final product retains a very fine, typically nanocrystalline or amorphous structure [6]. Therefore, such powders may be used as a precursor for later solid-state reactions and, potentially, for the preparation of thin or thick solid films.

Manganese ferrite (MnFe$_2$O$_4$) is a well-known magnetic material. This property of MnFe$_2$O$_4$ is significantly affected by the particle size. In this study we demonstrate the synthesis of nanocrystalline MnFe$_2$O$_4$ by mechano-chemical treatment, starting from a mixture of 1) manganese carbonate (MnCO$_3$) and hematite ($\alpha$-Fe$_2$O$_3$) as reactant powders; and 2) manganese oxide (MnO$_2$) and hematite ($\alpha$-Fe$_2$O$_3$).

## 2. Experimental procedures

Two mixtures of crystalline powders, denoted by (A) and (B), were used as the starting material (A: $\alpha$-Fe$_2$O$_3$ (Merck), MnO$_2$ (Alfa Aesar), both of 99% purity; B: $\alpha$-Fe$_2$O$_3$ (Merck), MnCO$_3$ in equimolar ratio). Manganese(II)-carbonate was synthesized from sodium carbonate and manganese(II)-chloride. Mechano-chemical treatment was performed in a planetary ball mill (Fritsch Pulverisette 5). A hardened-steel vial of 500 cm$^3$ volume, filled with 40 hardened steel balls with a diameter of 13.4 mm, was used as the milling medium. The mass of the powder was 20 g and the balls-to-powder mass ratio was 20:1. The milling was done in air atmosphere without any additives. The angular velocity of the supporting disc and vial was 32.2 and 40.3 rad s$^{-1}$, respectively. The intensity of milling corresponded to an acceleration of about 10 times the gravitational acceleration. At the expiration of the selected milling times (5, 10 and 20 h) the mill was stopped and a small amount of powder was removed from

the vial for examination. X-ray diffraction analysis of the powders treated for various periods of time (milling times) was done by a Philips PH 1050 automatic diffractometer with CuK$\alpha$ graphite-monochromatised radiation ($\lambda$=0.1542 nm).

The pellet was also investigated by cyclic voltammetry method using Metrohm VA 797 Computrace with the Ag/AgCl electrode potential ranging from 0 to 1.5 V. Scan rate of 50 mV/S was used in order to determine the valence of manganese in the sample. The tablet was used as the working electrode while the reference electrode was a silver chloride one. Platinum electrode was the auxiliary electrode.

Thermal treatment of the mechano-chemically obtained mixture of powders (A) and (B) was performed under air atmosphere at temperatures of 400 $^o$C, 600 $^o$C and 800 $^o$C, followed by X-ray structural analysis using the same diffractometer.

## 3. Results and discussion

Mechanical milling of (A) $2MnO_2 + 2Fe_2O_3 \rightarrow 2MnFe_2O_4 + O_2$ and (B) $MnCO_3 + Fe_2O_3 \rightarrow MnFe_2O_4 + CO_2$ was also carried out under air atmosphere. Fig. 1a shows the X-ray diffraction patterns of powders (A) mechano-chemically milled for different milling times (5, 10 and 20 h). Before any mechanochemical treatment (milling time 0 h) only sharp peaks from the well-crystalized MnO$_2$ and $\alpha$-Fe$_2$O$_3$ are present in the XRPD pattern. It can be noticed that the major peaks for the hematite phase at 2$\theta$ = 35.6$^o$ and 33.15$^o$ were continuously reduced by increasing the milling time. After 20 h only the weak peak detectable in the XRPD pattern is visible. Alongside these two hematite peaks, peaks at 2$\theta$ = 29.7$^o$ and 56.2$^o$ can be seen in the XRPD pattern, which may indicate the trace presence of the spinel phase (Fig. 1a). MnO$_2$ peaks cannot be seen, which leads us to the conclusion that amorphization of manganese dioxide has occurred. Further mechano-chemical treatment (> 20 h) does not produce any significant structural changes. The course of the mechanochemical reaction in the other case (MnCO$_3$ - Fe$_2$O$_3$) is different. After 5 h of milling all the characteristic peaks of $\alpha$-Fe$_2$O$_3$ (ICPD 33-0664) and MnCO$_3$ (ICPD 07-0268) can be seen in the pattern, and apart from the relative decrease of peak heights and widths compared to the starting mixture, there are no peaks which would indicate the presence of a new phase. Broadening of the peaks is a consequence of the decrease in particle size and the appearance of tension in the crystal lattice. Further milling up to 10 h gives rise to the synthesis of a new phase. The appearance of a new peak at 2$\theta$ = 34.9$^o$, as well as of peaks at 2$\theta$ = 29.7$^o$, 42.52$^o$ and 61.96$^o$ clearly points to the formation of the new phase of MnFe$_2$O$_4$ (ICPD 10-0319) (Fig.1b). After prolonging the milling to 20 h the XRPD pattern shows all the characteristic peaks of the spectrum ( 2$\theta$ = 18.06$^o$, 29.7$^o$, 34.98$^o$, 42.52$^o$, 56.19$^o$ and 61.96$^o$) which unambiguously indicates that after 20 h of mechano-chemical treatment the reaction has been fully completed. Furthermore, the XRPD pattern (Fig.1b-20h) shows no other peaks or spectra of the starting components ($\alpha$-Fe$_2$O$_3$ and MnCO$_3$) so that we can claim with confidence that single-phase manganese ferrite compound was obtained.
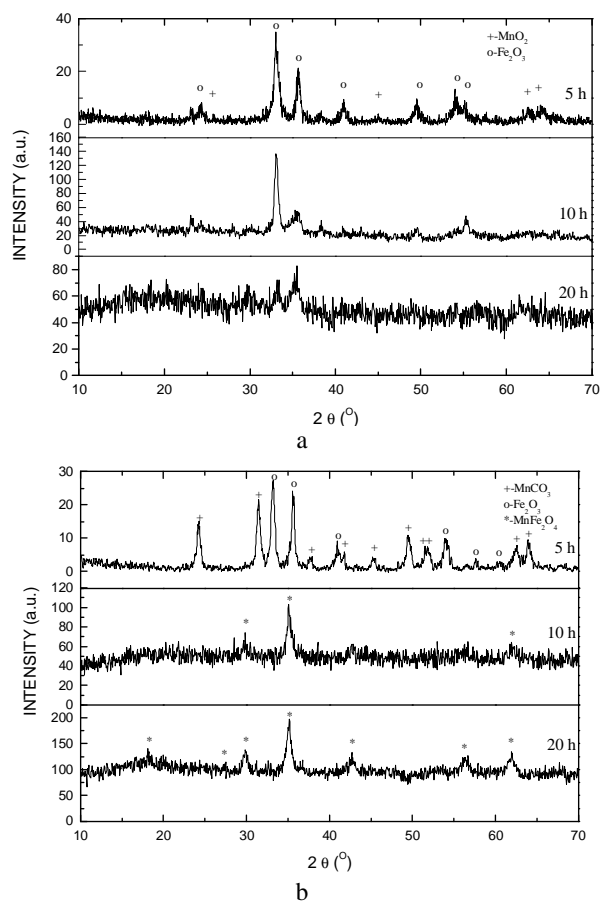


Fig. 1. XRPD patterns of a) MnO$_3$ and Fe$_2$O$_3$ and b) MnCO$_3$ and Fe$_2$O$_3$ powders after various milling times.
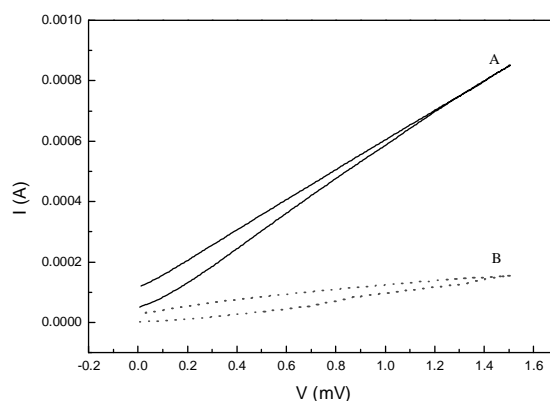


Fig. 2. C-V curve plot of sample A and B with scan rate of 50 mV/s.

In Fig. 2 the CV (cyclic voltamograms) of the mechanochemically treated samples (A) and (B) are presented. They were obtained with a scan rate of 50 mV/S in 0.01 M KCl under the same conditions and with the same area of the working electrode. Increase of the anode current for sample (B) can be seen in Fig. 2 It is a consequence of the oxidation of bivalent manganese.

The corresponding increase for sample (A) was negligible and it could be attributed to the residual current originating from the presence of impurities or traces of bivalent manganese in the sample. These results are in agreement with the results of X-ray diffraction analysis and they confirm that the compound synthesized is $MnFe_2O_4$ when starting with $MnCO_3$ and $Fe_2O_3$, while in case of the oxide, manganese stays in the $4^+$ valence state and no synthesis occurs.

A 20 hour thermal treatment of the mechanochemically treated samples yields entirely different results. In case of the sample (A), which is a mixture of the oxides $MnO_2$ and $Fe_2O_3$, formation of a two-phase mixture of the oxide $Fe_2O_3$ and the compound $(Mn_{0.983}Fe_{0.017})_2O_3$ occurs (ICPD 24-0507), irrespective of the temperature of thermal treatment (400 $^o$C, 600 $^o$C or 800 $^o$C) (Fig. 3a). On the other hand, thermal treatment of the sample (B) at 400 $^o$C leads to structural arrangements and crystallite growth in the mechano-chemically synthesized phase of $MnFe_2O_4$ (Fig. 3b). However, as in the previous case of the sample (A), the thermal treatment at higher temperatures leads to decomposition of the mechano-chemically synthesized compound and to formation of the mixture of $Fe_2O_3$ and $(Mn_{0.983}Fe_{0.017})_2O_3$.
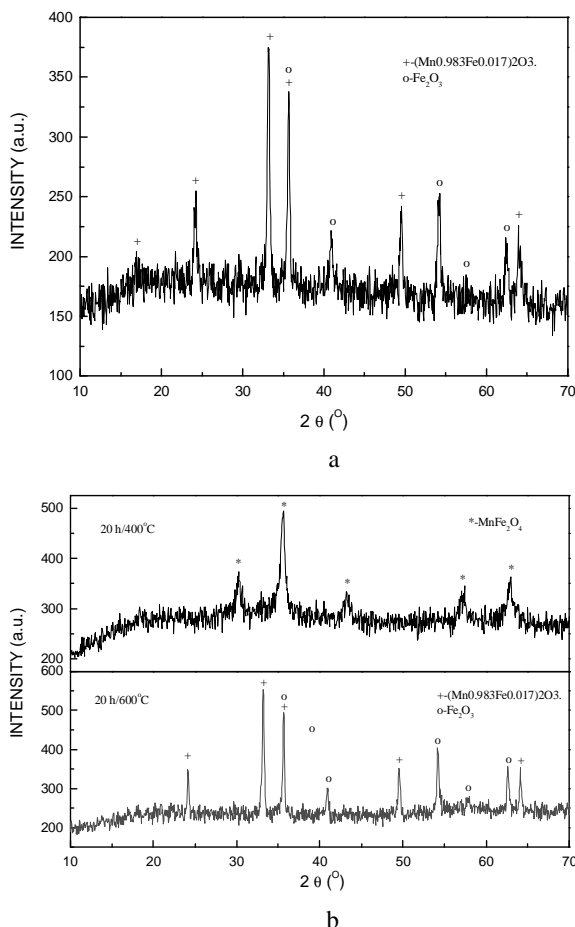


a



b

*Fig. 3. XRPD patterns of a sintered samples a) $MnO_2$ and $Fe_2O_3$ and b) $MnCO_3$ and $Fe_2O_3$ powders at various temperatures.*

Particle sizes of powders (B) treated mechanochemically for 20 h and thermally for 4 h at 400 $^o$C were determined using XRDP data as:

$$S = 0.9\lambda/(B cos\theta_B)$$

where $S$ is the crystallite grain size, $\lambda$ is the wavelength of the X-ray source, $\theta_B$ is the Bragg angle of the considered XRDP peaks, and $B$ represents the FWHM line broadening obtained as follows:

$$B^2 = B^2_m - B^2_s$$

where $B^2_m$ is the FWHM line broadening of the material and $B^2_s$ represents the FWHM line broadening of the internal standard ($\alpha$-$Al_2O_3$). The resulting value of the crystallite size, obtained from the (111) strongest reflections, is 28 nm.

## 4. Conclusion

The possibility for mechano-chemical synthesis of $MnFe_2O_4$ ferrite has been investigated, starting in one case from the mixture of oxides $MnO_2$ and $Fe_2O_3$, and in the other from the mixture of the carbonate $MnCO_3$ and the oxide $Fe_2O_3$. It has been shown that the mechano-chemical treatment of the oxide mixture leads to the amorphization of the starting oxides and to their partial reaction, producing after 20 h of milling a mixture of $MnO_2$, $Fe_2O_3$ and $MnFe_2O_4$. In the other case, the mechanochemical treatment leads to the synthesis of $MnFe_2O_4$ after only 10 h. Prolonging the milling to 20 h yields the compound $MnFe_2O_4$ with nanocrystalline structure. Thermal treatment of the mechano-chemically treated powders at lower temperatures (up to 400 $^o$C) leads to formation of the mixture of $(Mn_{0.983}Fe_{0.017})_2O_3$ and $Fe_2O_3$, while in case of the mechano-chemically treated mixture of the carbonate and the ferric oxide structural arrangements and growth of $MnFe_2O_4$ grains occur up to 400 $^o$C, but at higher temperatures the two-phase system of $(Mn_{0.983}Fe_{0.017})_2O_3$ and $Fe_2O_3$ forms here too.

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