The Effect of Mechanical Activation on the Synthesis of $MgFe_2O_4$ from Mixtures of $MgCO_3 \cdot Mg(OH)_2 \cdot xH_2O$ and $FeC_2O_4 \cdot 2H_2O$

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The synthesis of $MgFe_2O_4$ has been attempted starting from mixtures of $4MgCO_3 \cdot Mg(OH)_2 \cdot xH_2O$ and $FeC_2O_4 \cdot 2H_2O$ by combining mechanical activtion of the mixtures (by high-energy milling) with annealing at temperatures between 673 and 1073 K. TG measurements of mixtures of the precursors have been performed to assess the reaction mechanism, and to determine the minimum temperature where the two binary oxides (MgO and Fe_2O_3) are formed. X-Ray powder patterns of the milled / annealed mixtures have shown that $MgFe_2O_4$ is formed in an amorphous state already upon thermal treatment at 673 K, while annealing of the mixtures (not mechanically activated) at temperatures as high as 1473 K of the mixtures does not lead to the complete formation of $MgFe_2O_4$. The molar specific heat and the Curie temperature of the milled / annealed mixtures have been determined by DSC: $MgFe_2O_4$ is obtained provided that the annealing of the milled mixture is performed at temperatures as low as 873 K. The effect of the annealing temperature on the surface area of $MgFe_2O_4$ has been determined by BET measurements.

Key words: Magnesium Ferrite, Mechanical Activation, Solid State Synthesis, Molar Heat Capacity, Surface Area

Introduction

Spinel ferrites of the type MFe_2O_4 (M is a divalent metal cation) are key materials for advanced electronic devices, magnetic storage, ferrofluid technology, and many bioinspired applications such as, for example, drug carriers for magnetically-guided drug delivery and contrast agents in magnetic resonance imaging [1].

Conventional processing (*i. e.* by the ceramic method) of ferrites requires a number of stages, including homogenization of the precursor powders, compaction of the reactants, and finally prolonged heat treatment at considerably elevated temperatures. A goal of present ferrite research is the identification of processing schemes not relying on high-temperature treatments to induce solid-state reactions [2]. Following this guideline I. Bergmann *et al*. [3] reported a single-step synthesis of $MgFe_2O_4$ *via* a room temperature mechanochemical route that starts from the constituent oxides. In other studies the spinel ferrites MFe_2O_4 (M = Ba, Mg, Co, Ni, Cu, Zn) were prepared by self-propagating high-temperature synthesis (SHS) [4] or also by a coprecipitation method [5]. Other researchers performed the synthesis of $MgFe_2O_4$ by a microwave hydrothermal [6] or sol-gel method [7]. Furthermore, $MgFe_2O_4$ has been prepared by the polymeric-precursor method [8] that is based on the formation of a polymeric resin, followed by heat treatment at 1073 K.

In the present paper, we report a solid-state synthetic process to obtain $MgFe_2O_4$ that applies both mechanical (by high-energy milling) and thermal energy to mixtures of $4MgCO_3 \cdot Mg(OH)_2 \cdot xH_2O$ and $FeC_2O_4 \cdot 2H_2O$. The stages of the thermal decomposition processes occurring in the mixtures were studied by TG measurements. The XRPD patterns of mechanically activated mixtures subjected to thermal treatment (6 h at temperatures between 673 and 1073 K, in steps of 100 K) suggest that $MgFe_2O_4$ can be obtained at temperatures as low as 673 K. However, heat capacity measurements showed that $MgFe_2O_4$ can be effectively prepared by annealing for 6 h at $T \geq 873$ K of mechanically activated mixtures. No clear evidence of $MgFe_2O_4$ formation could be obtained after prolonged annealing at 1473 K of samples of the physical mixtures. The specific surface area of the mixtures me-

chanically activated and annealed at temperatures between 673 and 1073 K has been determined by BET.

Experimental Section

Starting chemicals and sample preparation

The starting chemicals were purchased from Aldrich Chimica (Italy) with purities of 99 + or 99.9 %.

TG measurements were performed on samples of the precursors $FeC_2O_4 \cdot 2H_2O$ and $4MgCO_3 \cdot Mg(OH)_2 \cdot xH_2O$. In the case of the Fe(III) precursor, the mean residual mass attained at 673 K was 44.6 ± 0.1 % in good agreement with the value expected (44.4 %) for the formation of Fe_2O_3. In the case of the Mg precursor, the mean residual mass attained at 1073 K was 41.9 ± 0.6 % that fairly agrees, by taking into account the standard deviations, with the value expected (41.5 %) for the formation of MgO if $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ is the starting compound.

Physical mixtures of the molar ratio Fe/Mg = 2.0 were prepared by weighing the appropriate amounts of the precursors and by stirring the powders in an acetone suspension for 3 h; finally the solvent was allowed to evaporate in an oven at 60 °C over night.

The mechanically activated mixtures were prepared by dry milling lots of 2 g of the physical mixtures. The powders were put into zirconia jars (12.5 mL) of a planetary mill (Pulverisette 7 by Fritsch, Germany) with 5 zirconia balls (12 mm diameter; the mass ratio between the milling balls and the sample powder was 7 : 1). The mill was operated at a 450 rpm rotation speed for 90 h.

Experimental techniques

TG measurements were performed (in triplicate) with a TG Q5000 thermogravimetric analyzer (TA Instruments Inc. USA). Samples of ≈ 50 mg of the $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O / 10FeC_2O_4 \cdot 2H_2O$ mixtures were placed in a platinum pan and heated (10 K min^{-1}, air flow 100 mL min^{-1}) from 298 K up to a temperature where a constant mass value was reached (1073 K).

X-Ray powder diffraction patterns were recorded in a step scan mode (step 0.015° in 2θ, 1s/step, 40 kV, 30 mA, 2θ range = 10 – 55°, CuK_α radiation) with an X-ray powder diffractometer (Bruker D5005) equipped with a position-sensitive detector (PSD, Braun).

The specific heat capacities of the magnesium ferrite samples were determined using a Q2000 DSC instrument (T_{zero} technology, TA Instruments Inc. USA). The samples (≈ 10 mg) were placed in a closed aluminum pan and heated (20 K min^{-1}, air flow 50 mL min^{-1}) from 273 to 673 K. The instrument was calibrated under the same experimental conditions with a sapphire disk according to the manufacturer's instructions. The same experimental apparatus was used to determine the Curie temperature (under air flow of 50 mL min^{-1}, 10 K min^{-1}).

The specific surface area of the reacted mixtures (see the Results and Discussion section for details) was determined by N_2 adsorption (BET method). The nitrogen adsorption curve was recorded by a Sorptomatic 1990 instrument (Thermo Electron Corporation, operated following the static volumetric principle). The correction for the volume of the sample was introduced by measuring the He sorption.

Results and Discussion

TG Measurements on mixture samples $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O / 10FeC_2O_4 \cdot 2H_2O$

TG measurements were performed in triplicate on samples of the milled mixtures. Fig. 1 shows a typical thermogram. Three stages of mass loss can be observed in the whole process: (1) the first stage ends at ≈ 500 K with a mean mass value of 80.8 ± 0.5 % that corresponds, within the standard deviations, to the mass expected for complete dehydration of the mixture (80.5 %); (2) the second stage ends at ≈ 630 K with a mean mass value of 51.9 ± 0.8 % that is in fair agreement, considering the rather high standard deviations, with the mass value expected for the dehydration of the mixture and for the complete conversion of Fe(II) oxalate to Fe(III) oxide (52.4 %); (3) the mean mass value at the end of the TG runs is 44.1 ± 0.4 % that coincides, within the standard deviations, with the mass value expected (43.9 %) if the decomposition of both Mg hydroxide and carbonate takes place so forming a mixture $5MgO + 5Fe_2O_3$.

It is worth to note that the identification of such processes of mass loss was not possible in cases where the TG studies were performed on physical mixtures (without milling).

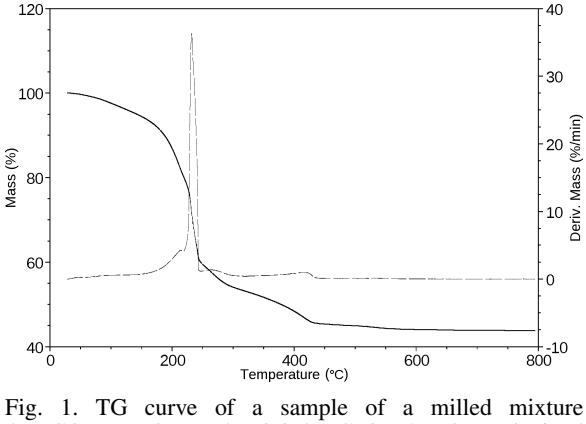

Fig. 1. TG curve of a sample of a milled mixture $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O / 10FeC_2O_4 \cdot 2H_2O$ obtained under an air flow with 10 K min^{-1}.

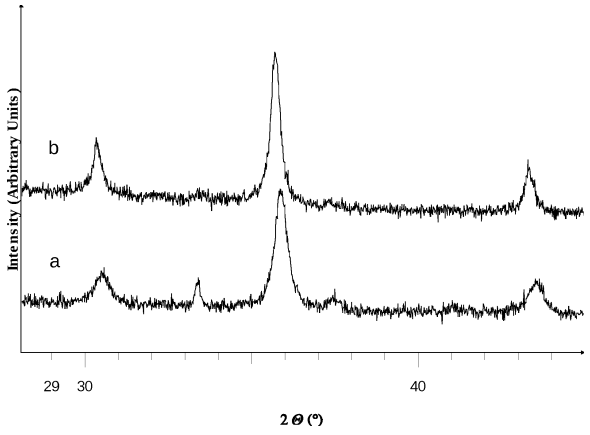

Fig. 2. Comparison between the XRPD patterns of the residuals recovered after the TG/DSC measurements performed on samples of physical mixtures (a) and of milled mixtures (b).

Fig. 2 shows the XRPD patterns of the samples recovered after the TG runs performed up to 1073 K on samples of both milled and physical mixtures. The peaks of $MgFe_2O_4$ are the only ones present in the samples of the milled mixture while also the reflections of unreacted hematite (see the peak at $2\theta \approx 33.5^\circ$) are showing up in the patterns of the samples of the physical mixtures.

Thermal treatment of samples of physical and milled mixtures

Samples of the physical mixtures were annealed for 12 h at temperatures between 973 and 1373 K (in steps of 100 K). The relevant XRPD patterns are shown in Fig. 3. It can be noted that the thermal treatment performed up to 1173 K led to samples whose XRPD patterns show only the reflections of the constituent oxides (MgO and Fe_2O_3) formed by decomposition of the precursors. The reflections of $MgFe_2O_4$ (*e. g.* the peak at $2\theta \approx 30^\circ$) can be observed in the XRPD patterns of the samples annealed at 1273 and at 1373 K but the peaks of Fe_2O_3 are still discernible. This indicates that the complete formation of $MgFe_2O_4$ requires a much longer thermal treatment at 1373 K or at even higher temperatures. Therefore a thermal treatment at 1473 K was performed for increasing times (up to 100 h). The XRPD patterns of these samples show that the peaks located at $2\theta \approx 43.0^\circ$ and 62.5° have shoulders towards low angles. This suggests the presence of unreacted MgO. On the other hand the peaks of Fe_2O_3 have disappeared after such thermal treatment. This fact can be explained by allowing for the formation of Fe_3O_4 besides $MgFe_2O_4$. It is known that $MgFe_2O_4$ and Fe_3O_4 cannot be distinguished with XRPD.

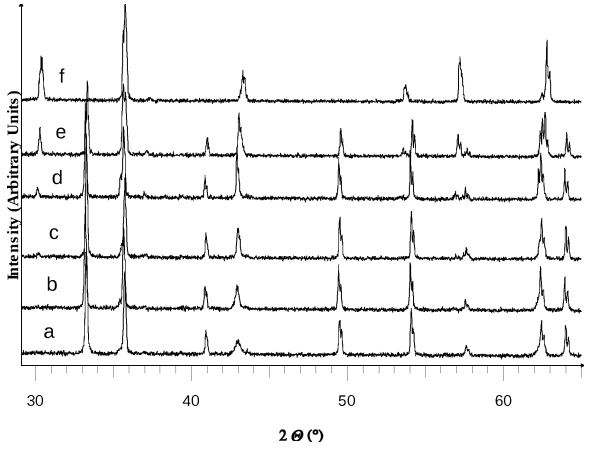

Fig. 3 XRPD patterns of physical mixture samples annealed for 12 h in air at 973 K (a), 1073 K (b), 1173 K (c), 1273 K (d), 1373 K (e). The pattern (f) refers to a sample annealed for 103 h at 1473 K.

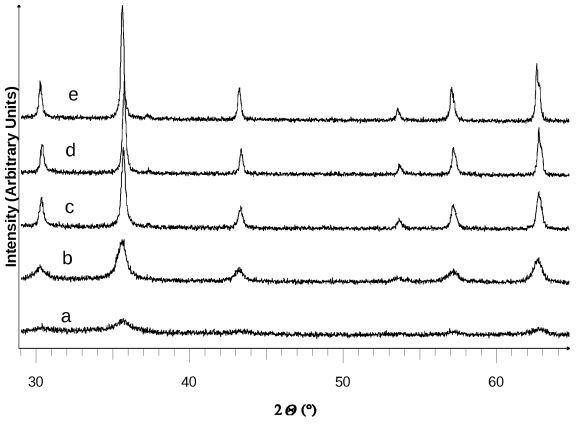

Fig. 4. XRPD patterns of milled mixtures annealed for 6 h in air at 673 K (a), 773 K (b), 873 K (c), 973 K (d), and 1073 K (e).

Fig. 4 shows the XRPD patterns of samples of the milled mixture annealed for 6 h at temperatures from 673 to 1073 K (in steps of 100 K). The patterns of the samples annealed at all these temperatures show the peaks characteristic of $MgFe_2O_4$ whose intensity increases with the annealing temperature. Thus the XRPD evidence shows that $MgFe_2O_4$ can be prepared from the mechanically activated mixture by annealing for 6 h at a temperature as low as 673 K although the crystallinity of the sample obtained at the lower temperatures (673 and 773 K) appears to be quite low.

Table 1. C_p data of milled mixtures annealed 6 h at temperatures from 673 to 1073 K. The columns *A*, *B* and *C* report the values of the coefficients of the square polynomials that fit the experimental data. T_c represents the Curie temperature.

T anneal. (K)	A	B	C	T_c (K)
673	67.1	0.30	$+4\times10^{-4}$	–
773	59.9	0.45	$+1\times10^{-4}$	–
873	94.2	0.43	-20×10^{-5}	618
973	92.4	0.45	-90×10^{-5}	590
1073	96.7	0.43	-2×10^{-4}	600

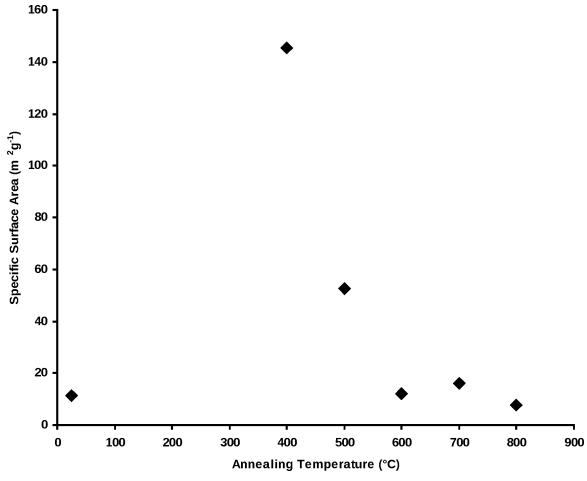

Fig. 5. Surface area values of milled samples as a function of the annealing temperature (between 673 and 1073 K).

The C_p data of the samples obtained by annealing at temperatures between 673 and 1073 K were determined between room temperature and 673 K. These data could be fitted by the square polynomial $C_p = A + B\ t + C\ t^2$. The values of the parameters (*A*, *B* and *C*) are reported in Table 1. The coefficients *A* and *B* of the polynomials are very similar for the samples annealed at 873, 973 and 1073 K, while the value of *C* tends to decrease with increasing the annealing temperature, which means that the data show a curvature and go through a maximum with increasing temperature. Table 1 also reports the maximum temperature that likely corresponds to the Curie temperature of $MgFe_2O_4$ (597 K according to literature data). The maximum temperatures that are close to 597 K are those of the samples annealed at 973 and 1073 K.

Values of the specific surface area of the samples of the milled mixture annealed for 6 h at temperatures between 673 and 1073 K (in steps of 100 K) are shown in Fig. 5. The specific surface area of the milled mixture is 11.3 $m^2\ g^{-1}$. The very significant increase of the surface area after the annealing at 673 K (145.4 $m^2\ g^{-1}$) is the consequence of the dehydration / decomposition processes that occurred. By performing the annealing at 773 K, the surface area of the sample becomes considerably smaller (57.4 $m^2\ g^{-1}$). Only for annealing temperatures $T \geq 873$ K the values of the specific surface area are constant.

Conclusion

The results of the thermoanalysis measurements performed on samples of milled mixtures allow to conclude that the reaction in air proceeds through the following stages: 1) dehydration of the two precursors; 2) thermal conversion of Fe(II) oxalate into Fe_2O_3; 3) simultaneous decomposition of $Mg(OH)_2$ and $MgCO_3$ to MgO. The XRPD patterns of the residuals of the thermal runs show that the products obtained at the end of the experiments consist of $MgFe_2O_4$ only when starting from the milled mixtures, while considerable amounts of the two unreacted oxides are present when starting from the physical mixtures.

X-Ray diffraction data suggest that $MgFe_2O_4$ could be prepared, though in an amorphous form, by annealing for 6 h of a mechanically activated mixture at a temperature as low as 673 K. On the other hand, no complete $MgFe_2O_4$ formation could be effected by thermal treatment of the physical mixtures at temperatures as high as 1473 K.

The C_p measurements have shown, on the contrary, that $MgFe_2O_4$ samples can be obtained from the mechanically activated mixture by a thermal treatment of 6 h at 873 K. The results of measurements of the specific surface area indicate that quite constant values of this parameter are obtained when the annealing of the mechanically activated mixture is performed at temperatures $T \geq 873$ K.

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