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Solid state synthesis of $CuFe_2O_4$ from $Cu(OH)_2 \cdot CuCO_3$–$4FeC_2O_4 \cdot 2H_2O$ mixtures: mechanism of reaction and thermal characterization of $CuFe_2O_4$

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Abstract Copper Ferrite has been prepared by solid state synthesis of milled mixtures of copper basic carbonate [$Cu(OH)_2 \cdot CuCO_3$] and iron (II) oxalate dihydrate [$FeC_2O_4 \cdot 2H_2O$]. The reaction mechanism has been studied by simultaneous TG/DSC analysis: the different steps of the mass loss process have been individuated along with the relevant enthalpy terms starting from both physical and mechanically activated mixtures. $CuFe_2O_4$ has been synthesized by annealing the mechanically activated mixture at 750–800 °C while no pure $CuFe_2O_4$ is obtained by annealing the physical mixture at temperatures as high as 1100 °C. $CuFe_2O_4$ has been characterized as concerns the molar het capacity, the tetragonal–cubic transition enthalpy and the Curie point.

Keywords High energy milling · Thermally activated mechanosynthesis · TG-DSC · Copper ferrite ($CuFe_2O_4$) · Molar heat capacity

Introduction

Transition metal ferrites are a family of oxides that are key materials in a wide variety of fields. The reason for such a wide range of applications is related to the variety of transition metal cations that can be incorporated the parent lattice of magnetite ($Fe^{2+}{Fe_2}^{3+}O_4$). Ferrites are known to be used in electronics, magnetic storage, ferro-fluid technology, catalysis, microwave devices, gas sensors and many bio-inspired applications such as, for example, drug carriers for magnetic guided drug delivery and contrast agents in magnetic resonance imaging [1].

Usually ferrites are prepared by the conventional ceramic method that implies a number of stages, including homogenization of the precursors powder, compaction of the reactants, and, finally, prolonged heat treatment at considerably elevated temperatures.

On the other hand alternative routes to obtain ferrites have been worked out. In the case of copper ferrite $CuFe_2O_4$ has been prepared by the self-propagating high-temperature synthesis (SHS) [2], the precipitation in polymer matrix [3], the citrate route [4], the co-precipitation method [5], the hydrothermal method [6] and the combustion synthesis [7].

The present article is a third instalment in a series dedicated to the synthesis of metal ferrites the previous ones having been dealt with the synthesis of $NiFe_2O_4$ [8] and of $MgFe_2O_4$ [9]. First of all the mechanism of the thermal decomposition reactions of the precursors has been studied by simultaneous TG/DSC analysis. In this first stage of the work, the different steps of the mass loss process have been individuated along with the relevant enthalpy terms starting from both physical and mechanically activated mixtures. Afterwards we have dealt with the synthesis of $CuFe_2O_4$ by applying a combination of mechanical energy (high energy milling) and thermal energy (thermally activated mechanosynthesis) to mixtures of $Cu(OH)_2 \cdot CuCO_3$ and $FeC_2O_4 \cdot 2H_2O$. Furthermore, the transition enthalpy between tetragonal and cubic

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$CuFe_2O_4$, the Curie point of $CuFe_2O_4$ and its molar C_P have been determined by DSC and MDSC.

Experimental section

Starting chemicals and sample preparation

The starting chemicals were purchased from Aldrich Chimica (Italy): $Cu(OH)_2 \cdot CuCO_3$ (purity 99+%) and $FeC_2O_4 \cdot 2H_2O$ (purity 99.9%).

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

The mechanically activated mixtures were prepared by dry milling lots of 1 g of 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 9:1). The mill was operated at 450 rpm (rotation speed) for 12 h.

Experimental techniques

TG/DSC measurements were performed with a TG-DSC Q600 simultaneous TG/DSC analyser (TA Instruments Inc. USA). Samples of ≈50 mg of $Cu(OH)_2 \cdot CuCO_3$–4 $FeC_2O_4 \cdot 2H_2O$ mixtures were placed into alumina cups and heated (10 K/min, air flow 100 mL/min) from 25 °C up to a temperature where a constant mass value is reached (500 °C). Some of the thermal runs have been performed up to temperatures of 600, 700 and 800 °C.

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

The specific heat capacity of the copper ferrite samples were determined by MDSC (Q2000 DSC, T_{zero} technology, TA Instruments Inc. USA). The samples (≈10 mg) were placed in a closed aluminium pan and heated (5 K/min, $A = \pm 1$ °C, $P = 80$ s, nitrogen flow 50 mL/min) from 0 to 400 °C. The instrument, before the measurements, was calibrated under the same experimental conditions with a sapphire disk according to the manufacturer's instructions. The same experimental apparatus has been used (in conventional DSC mode) to determine the tetragonal–cubic transition enthalpy and the Curie temperature (under nitrogen flow of 50 mL/min, 10 K/min).

Results and discussion

TG-DSC measurements

Figure 1 compares the TG curves typical of a sample of physical mixture (dashed line) and of a sample of milled mixture (solid line).

The TG runs reported in Fig. 1 show that the mass loss process is subdivided into three stages for both kinds of sample:

(1) The TG curve of the sample of physical mixture (solid line) show that the mean mass value attained at the end of the first stage of mass loss is 83.51 ± 0.22% (mean of ten independent measurements). Such a value is sensibly higher than the mass expected (82.76%) if the dehydration of the mixture would be completed within the first stage according to the reaction:

$$Cu(OH)_2 \cdot CuCO_{3(s)} + 4\,FeC_2O_4 \cdot 2\,H_2O_{(s)} \rightarrow CuO_{(s)} + CuCO_{3\,(s)} + 4FeC_2O_{4\,(s)} + 9\,H_2O_{(g)} \uparrow \quad (1)$$

The first stage of mass loss of the milled mixture (dashed line) ends at 213.25 ± 0.79 °C and the mean mass value attained ($M_1 = 81.80 \pm 0.47\%$, mean of 13 independent measurements) is sensibly lower than the mass value expected (82.76%) for reaction (1).

(2) The second stage of mass loss of the physical mixture ends at ≈300 °C and the mean mass value attained (56.96 ± 0.52%, mean of 10 independent measurements) points to the fact that the conversion of FeC_2O_4 to Fe_2O_3 according to the reaction:

$$4FeC_2O_{4(s)} + O_{2(g)} \rightarrow 2\,Fe_2O_{3(s)} + 4CO_{(g)} + 4CO_{2(g)} \quad (2)$$

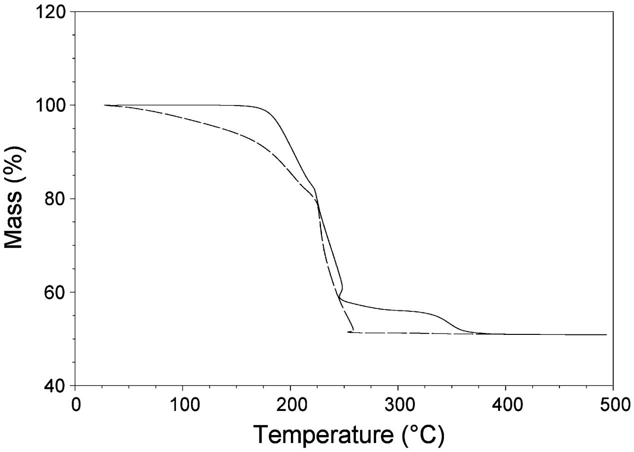

Fig. 1 TG curves (air flow, 10 K min^{-1}). *Solid line*: physical mixture; *Dashed line*: mechanically activated mixture

has not completed since the mass value expected at the end of such a process would be 55.54%.

The second stage of mass loss of the milled mixture ends at 296.63 ± 5.12 °C and the mean mass value attained ($M_2 = 51.41 \pm 0.27\%$, mean of 13 independent measurements) is well lower than that expected for the conversion of FeC_2O_4 to Fe_2O_3 (55.54%) according to the reaction (2). The lower mass value attained at the end of this stage suggests that a major share of the thermal decomposition of $CuCO_3$ to CuO has taken place under this stage.

(3) The last stage of mass loss of the physical mixture is constituted by the sum of the residual part of the conversion of FeC_2O_4 to Fe_2O_3 and by the decomposition of $CuCO_3$ to CuO since the mean mass value at 500 °C ($M_{500\ °C}$) is 50.84 ± 0.16% i.e. in very good agreement with that expected for the formation of a mixture $2CuO{:}2Fe_2O_3$ (50.86%).

The last stage of mass loss process of the milled mixture is constituted by the residual part of the decomposition of $CuCO_3$. The mean mass value at 500 °C is $M_{500\ °C} = 50.85 \pm 0.20\%$ that it is also in very good agreement with that expected for the formation of a mixture $2CuO{:}2Fe_2O_3$ (50.86%).

The DSC curves of the physical mixture show two peaks (see Fig. 2).

The first one is a very sharp exothermic peak with mean enthalpy $\Delta H_1 = -790.7 \pm 40.0$ kJ. The mean mass change under the peak ($-26.4 \pm 0.4\%$) fairly agrees with that expected for the conversion of FeC_2O_4 to Fe_2O_3 (-27.2%). If it is taken into account that the run is performed in flowing air it is likely that, besides reaction (2), also reaction (3) occurs under the peak:

$$4CO_{(g)} + 2O_{2(g)} \rightarrow 4CO_{2(g)} \quad (3)$$

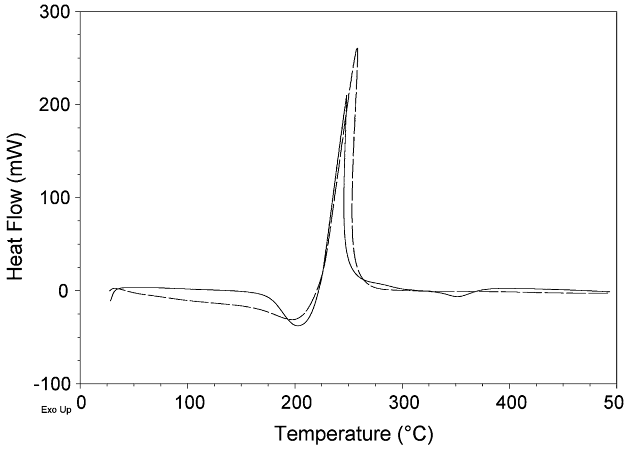

Fig. 2 DSC curves (air flow, 10 K min^{-1}). *Solid line*: physical mixture; *Dashed line*: mechanically activated mixture

The combined enthalpy change of the two reactions has been determined by performing DSC experiments in air on samples of pure iron (II) oxalate: the mean value obtained from five runs is $\Delta H = -208.1 \pm 4.6$ kJ. On the basis of this value the enthalpy change of the mixture should result $\Delta H = -832.4$ kJ. Therefore an enthalpy of +41.3 kJ is absorbed with respect to what expected but it is to note that the significance of such a value is doubtful as it is nearly equal to the standard deviation of ΔH_1 (±40 kJ).

The second peak is an endothermic one with mean enthalpy $\Delta H_2 = +67.5 \pm 1.8$ kJ. The mean mass change under the peak ($-4.56 \pm 0.43\%$) fairly agrees with the mass change expected for the decomposition of $CuCO_3$ to CuO (-4.68%).

The XRPD patterns of the residuals of the TG/DSC runs performed up to 500 °C shows the peaks of Fe_2O_3 and CuO produced by the thermal decomposition of the respective precursors; on the other hand no peaks characteristic of $CuFe_2O_4$ are evident.

The DSC traces of the milled mixture (see Fig. 2) show just one peak up to 500 °C. It is an exothermic peak with mean enthalpy $\Delta H_1 = -870.3 \pm 20.2$ kJ. This enthalpy value is higher than that of the corresponding peak of the physical mixture (-790.7 ± 40.0 kJ) and with half the standard deviation. The mean mass change under the peak ($-30.39 \pm 0.30\%$) is greater than that expected for the conversion of FeC_2O_4 to Fe_2O_3 (-27.2%).

On the other hand it has to be taken into account that part of the iron (II) oxalate conversion to Fe_2O_3 occurs within the first stage of mass loss, the reaction occurring under the exothermic peak is:

$$\begin{aligned} &n\,CuCO_{3\,(s)} + (4-m)\,FeC_2O_{4\,(s)} + \left[3 - \left(\frac{3}{4}m\right)\right] O_{2\,(g)} \rightarrow \\ &(8-2m+n)\,CO_{2\,(g)} + n\,CuO_{(s)} + \left[2 - \left(\frac{m}{2}\right)\right] Fe_2O_{3\,(s)} \end{aligned} \quad (4)$$

Reaction (4) is the algebraic sum of the following reactions:

$$FeC_2O_{4(s)} + (3/4)O_{2(g)} \rightarrow (1/2)Fe_2O_{3(s)} + 2CO_{2(g)} \quad (5)$$

$$CuCO_{3(s)} \rightarrow CuO_{(s)} + CO_{2(g)} \quad (6)$$

According to the relation: $(4) = (4 - m) \times (5) + n(6)$ and consequently the relevant enthalpy change can be calculated as $\Delta H_4 = (4 - m) \times \Delta H_5 + n \times \Delta H_6$.

The enthalpy values of reactions (5) and (6) have been determined by DSC runs performed respectively on samples of pure milled iron (II) oxalate and pure milled basic copper (II) carbonate. The following values have been determined: $\Delta H_5 = -212.3 \pm 4.7$ kJ, $\Delta H_6 = +63.4 \pm 0.9$ kJ. Hence $\Delta H_4 = (4 - m) \times (-212.3\ kJ) + n \times (+63.4\ kJ)$

The value of m and n can be deduced as follows:

$$(1-\mathrm{n}) = \frac{(\mathrm{M}_2 - \mathrm{M}_{500\,^\circ\mathrm{C}})}{100 \times \mathrm{M}_{\mathrm{CO}_2}} \times \mathrm{M}_{\mathrm{tot,mix}}$$

where $\mathrm{M}_{\mathrm{CO}_2}$ is the molar mass of CO_2 and $\mathrm{M}_{\mathrm{tot,mix}}$ (940.704 g is the mass of a mixture of composition $Cu(OH)_2 \cdot CuCO_3$–$4FeC_2O_4 \cdot 2H_2O$);

$$(4-\mathrm{m}) = \left[\frac{\mathrm{n} \times \mathrm{M}_{\mathrm{CO}_2}}{\mathrm{M}_{\mathrm{tot,mix}}} \times 100 + (\mathrm{M}_2 - \mathrm{M}_1)\right] \times \left(\frac{1}{27.2}\right) \times 4$$

By introducing into the above expressions the mean values of M_1, M_2 and $M_{500\,^\circ C}$ the values $(1 - n) = 0.1197$ and $(4 - m) = 3.8605$ can be obtained. Therefore $\Delta H_4 = 3.8605 \times (-212.3\ \mathrm{kJ}) + 0.8803 \times (+63.4\ \mathrm{kJ}) = -819.6\ \mathrm{kJ} + 55.8\ \mathrm{kJ} = -763.8\ \mathrm{kJ}$ vs. the experimental value of -870.3 ± 20.2 kJ. Hence in the case of the milled mixture an excess of heat is evolved −106.5 kJ) under the exothermic peak. However the thermal release cannot be due to the formation of $CuFe_2O_4$ from the constituent oxides since the XRPD patterns of the milled sample heated up to 500 °C show only broad peaks that cannot unambiguously assigned to the binary oxides or to copper ferrite (Fig. 3a).

By heating the milled sample beyond 500 °C, another exothermic peak appears that does not show up by heating the physical mixture at $T > 500$ °C. Such a peak has an enthalpy $\Delta H_3 = -43.5 \pm 6.3$ kJ but it has to be remarked that the XRPD patterns of the milled mixture heated up to 600 °C show the peaks of CuO and Fe_2O_3 with only very weak peaks characteristic of $CuFe_2O_4$ (Fig. 3b) and this allows to conclude that the enthalpy evolved under the exothermic peak at $T > 500$ °C is due to the crystallization of these oxides. The crystallization of both constituent oxides continues by heating the milled mixture up to 700 °C while the formation of $CuFe_2O_4$ only occurs to a very limited extent (Fig. 3c). The situation changes for samples of the milled mixture heated at $T > 700$ °C: the DSC trace of the milled samples shows an endothermic peak (onset temperature ≈700 °C $\Delta H_4 = +37.3 \pm 3.0$ kJ) that is not present in the DSC curve of the samples of the physical mixture. The XRPD patterns of the residuals recovered after the DSC runs show only the peaks of $CuFe_2O_4$ (Fig. 3d) so that it can be concluded that this endothermic peak corresponds to the reaction $2CuO + 2Fe_2O_3 \rightarrow 2\ CuFe_2O_4$.

From the formation enthalpies of the three oxides involved in the reaction [7], the endothermic value of +22.6 kJ can be calculated: so it can be seen that the enthalpy absorbed under the endothermic peak at ≈700 °C (+37.3 kJ) corresponds to ≈83% of the heat expected to be absorbed from the reaction $2CuO + 2Fe_2O_3 \rightarrow 2\ CuFe_2O_4$ (+45.2 kJ). Therefore it can be deduced that the reaction between the binary oxides to form $CuFe_2O_4$ occurs with appreciable rate only at $T > 700$ °C.

Solid state synthesis of $CuFe_2O_4$

Mixture samples have been annealed in air (17 h) at temperatures between 500 and 1000 °C (step of 100 °C, physical mixture) or between 500 and 800 °C (step of 100 °C, 12 h-mechanically activated mixture).

The XRPD patterns of all the annealed samples have been collected. Figure 4 shows the XRPD patterns of samples of the physical mixture.

The patterns of the samples annealed at temperatures between 500 and 700 °C (patterns a to c) show that the sample is constituted by a mixture of the two binary oxides

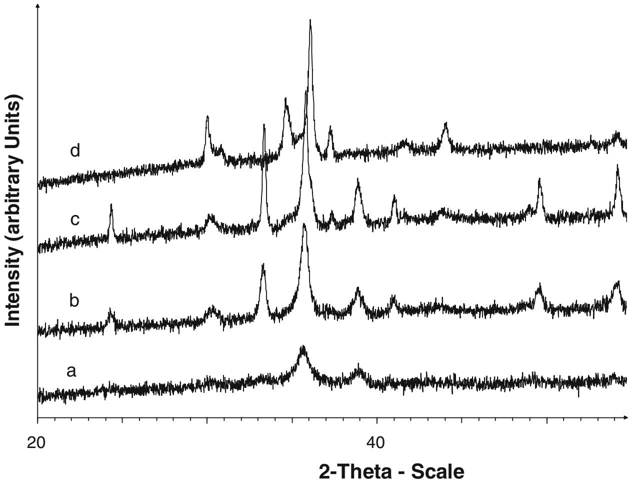

Fig. 3 XRPD Patterns of the residuals recovered from TG/DSC runs performed on the milled mixture (air) up to temperatures: *a* 500 °C; *b* 600 °C; *c* 700 °C; *d* 800 °C

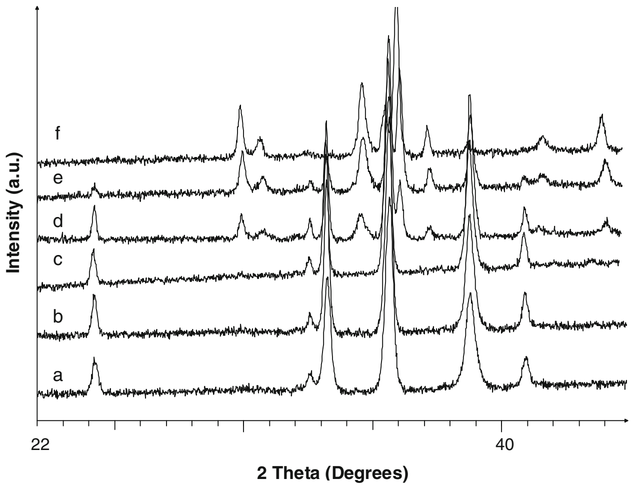

Fig. 4 XRPD patterns of samples of physical mixture annealed 17 h at: *a* 500 °C; *b* 600 °C; *c* 700 °C; *d* 800 °C; *e* 900 °C; *f* 1000 °C

formed by the decomposition of the two precursors. The peaks of tetragonal $CuFe_2O_4$ (peaks around 30° and at ≈37.5°) begin to appear in the patterns of the sample annealeds at 800 °C (d) and 900 °C (e) even if the peaks of CuO ($2\vartheta \approx 39°$) and of Fe_2O_3 ($2\vartheta \approx 24$ and 33.5°) are still well evident. Even a thermal treatment of 17 h at 1000 °C (f) does not lead to the complete formation of $CuFe_2O_4$: the peaks at $2\vartheta \approx 33.5°$ (Fe_2O_3) and at $2\vartheta \approx 39.5°$ (CuO) are still present though with reduced intensity.

Figure 5 shows the XRPD patterns of samples of the mechanically activated mixture.

The samples annealed at 500 and 600 °C show the peaks of CuO ($2\vartheta \approx 39.5°$) and Fe_2O_3 ($2\vartheta \approx 22.5$ and $2\vartheta \approx 33.5°$) even if at $2\vartheta \approx 30°$ and 34.5° some low-intensity reflections are observed that are characteristic of $CuFe_2O_4$. The peaks characteristic of $CuFe_2O_4$ are the main reflections of the pattern of the sample annealed at 700 °C but it has to be noted that the 100% peaks of CuO ($2\vartheta \approx 39.5°$) and Fe_2O_3 ($2\vartheta \approx 33.5°$) are present though with low intensity. A 17 h thermal treatment at 800 °C leads to the complete formation of tetragonal $CuFe_2O_4$.

The information that is obtained from the XRPD experiments in is agreement with that derived by the study of the mechanism of the reaction where it was demonstrated that $CuFe_2O_4$ forms only at $T > 700$ °C.

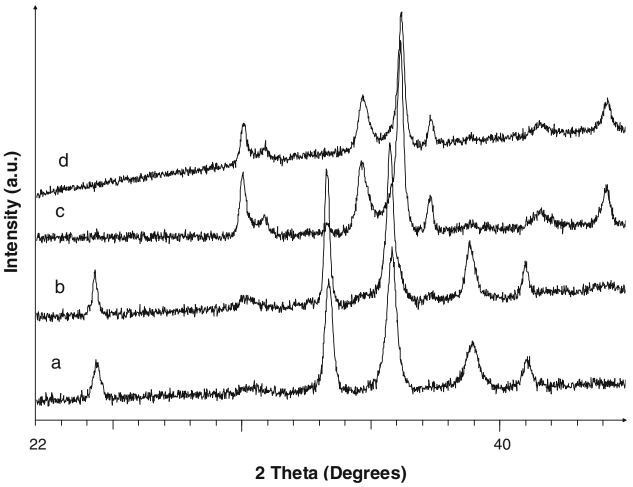

Fig. 5 XRPD patterns of samples of milled mixture annealed 17 h at: *a* 500 °C; *b* 600 °C; *c* 700 °C; *d* 800 °C

Thermal characterization of $CuFe_2O_4$

The thermal characterization of the samples obtained by annealing at 700, 750 and 800 °C for different times (between 1 and 17 h) the mechanically activated mixture has been performed by determining:

(1) the molar heat capacity (by MDSC) in the temperature range between 35 and 390 °C. The C_P determinations have been performed at 5 K/min (by using the reversing signal) and the data have been fitted by 2-order polynomials ($C_P = A + Bt + Ct^2$) whose mean coefficients are reported in Table 1.

It can be noted that the mean values of the coefficients A, B and C are close to each other for the samples annealed at 750 and 800 °C. The mean values of the coefficients of the samples annealed 17 h at 700 °C are instead sensibly different even if the relevant standard deviations are taken into account.

(2) The enthalpy change of the tetragonal → cubic transition has been determined by DSC. Such a transition is marked by an endothermic peak at a temperature 397.7 ± 1.1 °C. The enthalpy of the peak has been determined on samples produced by thermal treatment of milled mixture at 750 and 800 °C for different times. The values of the transition enthalpy are reported in Table 2: the mean enthalpy value is $\Delta_t H = +1041.4 \pm 49.1$ J/mol;

Table 2 Tetragonal–cubic phase transition enthalpy ($\Delta_t H$, J/g) and Curie point (°C) of $CuFe_2O_4$ obtained by annealing at 750 and 800 °C for different times

750 °C, t(h)	$\Delta_t H$	T_{Curie} (°C)	800 °C(h)	$\Delta_t H$	T_{Curie} (°C)
1	1006.5	463.8	1	1026.6	461.2
3	1193.8	467.5	2	1004.6	461.2
10	1097.9	461.8	5	1026.6	464.7
17	1104.3	462.8	8	1073.2	465.7
			10	1029.9	464.9
			13	1145.0	463.3
			17	984.7	461.5
			Mean	1065.8 ± 62.8	463.5 ± 2.1

Table 1 Coefficients of the 2-order polynomials ($C_P = A + Bt + Ct^2$) reported for annealing of 17 h (700 °C), between 1 and 17 h at 750 and 800 °C at heating rate of 5 K/min (reversing C_P)

T(°C)/t(h) of annealing, β (K/min)	A	B	C
700 °C, 17 h, 5 K/min	151.39 ± 2.10	0.2445 ± 0.0078	-2×10^{-4}
750 °C, 1 to 17 h, 5 K/min	155.13 ± 5.95	0.2134 ± 0.0133	$-1.38 \times 10^{-4} \pm 0.48 * 10^{-4}$
800 °C, 1 to17 h, 5 K/min	157.73 ± 3.38	0.2128 ± 0.0188	$-1.42 \times 10^{-4} \pm 0.63 * 10^{-4}$

(3) The Curie point of copper ferrite (see Table 2) has also been determined by DSC. Indeed, after the phase transition, a second endothermic peak is present at a mean temperature of 463.6 ± 1.9 °C that is in a satisfactory agreement with that reported in the literature as the Curie temperature of copper ferrite (455 °C) [10].

The phase transition enthalpy has been determined in a second heating run performed on the same samples of Table 2 after they were cooled down from 500 °C (i.e. just above the Curie point) to room temperature with different cooling rates:

(a) The sample has been rapidly cooled from 500 °C to room temperature by lifting off the furnace. The cooling has taken only a few minutes (3 ÷ 5 min). The second heating of this sample showed a transition peak with $\Delta H = 177$ J/g. By the ratio of such a transition enthalpy to the mean value of the transition enthalpy obtained in the first run (1065.8 J/g) it can be deduced that the cooled sample only contains ≈17% of tetragonal phase;

(b) The sample has been cooled from 500 °C to room temperature by blowing with a fan into the furnace. The cooling down to ≈200 °C took only about 10 min while further 30 min were needed to cool down the sample at room temperature. The second heating of this sample showed a transition peak with $\Delta H = 432$ J/g that leads to a content of ≈41% of tetragonal phase;

(c) The sample has been cooled down from 500 °C to room temperature by keeping it into the furnace that has been cooled naturally (without activating the cooling fan) to room temperature in about 1.2 h. The second heating of this sample showed a transition peak with $\Delta H = 523$ J/g that leads to a content of ≈50% of tetragonal phase;

(d) The sample has been cooled down from 500 °C to room temperature at 10 K/min. An additional isothermal stage (30 min) has been appended so to allow that the sample effectively reaches 25 °C. The second heating run of this sample showed a transition peak with $\Delta H = 885$ J/g that leads to a content of ≈85% of tetragonal phase;

(e) The sample has been cooled down from 500 °C to room temperature at 2 K/min. An additional isothermal stage (30 min) has been appended so to allow that the sample effectively reaches 25 °C. The second heating run of this sample showed a transition peak with $\Delta H = 1{,}090$ J/mole that coincides, within the standard deviation, with the mean value found for all the milled samples annealed at 750 and 800 °C (1065.8 ± 62.8). Therefore it can be observed that the tetragonal–cubic transition shows, on cooling, a pronounced extent of hysteresis.

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