Effect of High-energy Milling on the Solid State Formation of Zinc Manganites ($Zn_xMn_{3-x}O_4$, $0.5 \leq x \leq 1.5$) from the System $ZnC_2O_4 \cdot 2H_2O$-n $MnCO_3$ (n = 1, 1.5 and 2)

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By combination of TG/DSC and XRPD measurements it has been shown that zinc manganites form ($Zn_xMn_{3-x}O_4$ with $0.5 \leq x \leq 1.5$) starting from mixtures of zinc oxalate dihydrate and manganese carbonate subjected to mechanical activation by high energy milling. Solid solutions ZnO-Mn_3O_4-$ZnMn_2O_4$ are the products obtained by the same experimental conditions, when starting from a physical mixture. Furthermore milling, besides changing the enthalpy of dehydration of zinc oxalate, induces a partial formation of amorphous Mn_3O_4 at r. t. In particular $ZnMn_2O_4$ can be prepared by annealing the milled mixture for 18 h at 650 °C while a temperature > 1000 °C is needed to prepare $ZnMn_2O_4$ from a physical mixture. Finally, the calorimetric data suggest that the mechanism of the reaction is different in the two kinds of mixtures.

Key words: Zink Manganites, $ZnMn_2O_4$, Mechanical Milling, Simultaneous TG/DSC

Introduction

Zinc manganites ($Zn_xMn_{3-x}O_4$) are potential candidates for high-temperature applications and catalysis. The vast majority of pertinent studies is concerned with the normal spinel $ZnMn_2O_4$ [1] with a tetragonal structure similar to that of Mn_3O_4. However, solid solutions $Zn_xMn_{3-x}O_4$ in a wide composition range ($0.5 \leq x \leq 1.5$) have also been the subject of study regarding their structure and thermal stability [2].

We report in this paper the solid state reactions in the system $ZnC_2O_4 \cdot 2H_2O - n$ $MnCO_3$ [composition ratio Mn/Zn (n) = 1, 1.5 and 2.0] and compare the results obtained starting from physically prepared mixtures and from high-energy milled ones with the aim to prepare zinc manganites. This is the most recent instalment on a research project of our group concerning the study on the influence exerted by mechanical energy on the course of solid state reactions [3 – 7].

Experimental Section

Starting chemicals and sample preparation

The starting chemicals were purchased from Aldrich Chimica (Italy): $MnCO_3$ (purity 99.9 %) and $ZnC_2O_4 \cdot 2H_2O$ (purity 99.9 %). Physical mixtures were prepared by weighing appropriate amounts of the two components and by stirring the powders in acetone 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 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 6 zirconia balls (12 mm diameter; the mass ratio between the milling balls and the sample powder was 7 : 1). The mill was operated at 400 rpm rotation speed (up to 100 h).

Experimental techniques

TG/DSC measurements were performed on samples of both physical and milled mixtures with a Q600 thermogravimetric analyser (TA Instruments Inc., USA) connected to a computer fitted with an appropriate software. Samples of $\approx$ 50 mg were placed in an alumina pan and heated at 10 K min^{-1} (under a flow of air of 100 mL min^{-1}) from 298 K up to 923 K where a constant mass value is reached.

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

Table 1. Dehydration enthalpy (kJ mol^{-1} H_2O, physical and milled mixtures).

	$\Delta_{dis}H$, $n = 1.0$	$\Delta_{dis}H$, $n = 1.5$	Δ_{dis}, $n = 2.0$
Phys. mixture	46.1 ± 0.1	45 ± 3	45 ± 1
Milled mixture	41 ± 2	40 ± 6	40 ± 7

About 500 mg of physical and milled mixtures was put into alumina boats, heated at 10 K min^{-1} (static air) in a furnace (tube furnace Carbolite, UK) up to different temperatures (from 923 K to 1000 K in steps of 50 K) and annealed for 18 h. The samples after the annealing were examined first by XRPD and afterwards by TG/DSC in flowing air (at 20 K min^{-1}) up to 1573 K.

Results

Pure components

Milling exerts an effect on the dehydration enthalpy of zinc oxalate. Indeed the mean value for the commercial sample is 49 ± 2 kJ mol^{-1} H_2O while the corresponding mean value for milled zinc oxalate is 33 ± 2 kJ mol^{-1} H_2O. Table 1 reports the mean dehydration enthalpy values (kJ mol^{-1} H_2O) obtained for the physical mixtures of different composition. The values do not greatly differ from those obtained for pure $ZnC_2O_4 \cdot 2H_2O$. The same Table reports the mean values of the dehydration enthalpy obtained with the milled mixtures: a noticeable decrease of the dehydration enthalpy of $ZnC_2O_4 \cdot 2H_2O$ has been confirmed to take place in the milled mixtures although, in this last case, the results are affected by a rather high standard deviation.

On the contrary, milling does not exert any effect on the mass loss observed when heating $ZnC_2O_4 \cdot 2H_2O$ up to 773 K: the mean value of the residual mass is 43.0 ± 0.5 % for the commercial zinc oxalate and the mean value for the milled zinc oxalate is 43.07 ± 0.04 % (expected value: 42.96 %). As concerns the milling of pure commercial $MnCO_3$, the mean residual mass at 923 K is 68.6 ± 0.2 % (expected value for the formation of Mn_2O_3 is 68.66 %). The value is slightly lower in the milled $MnCO_3$ samples (67.85 %) probably due to moisture absorption during milling.

Mixtures

Fig. 1 shows the XRPD patterns of the milled mixtures. It is observed that no peaks of zinc oxalate are present (the 100 % peak of this compound is at $2\theta \approx 18.5°$). Moreover all other peaks (characteristic of $MnCO_3$) appear much broader and less intense than in the XRPD patterns of the physical mixtures. Finally no peaks of other possible phases that could be formed during milling are present.

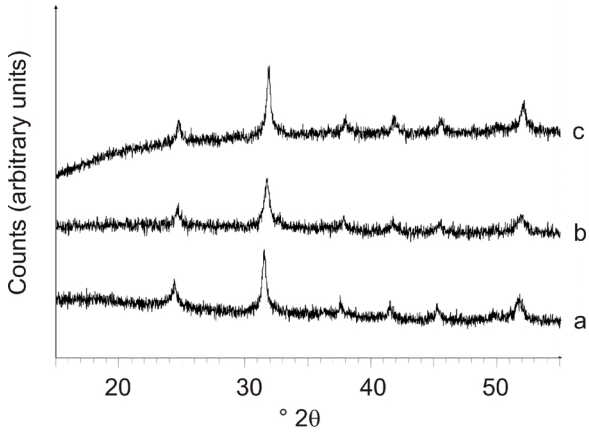

Fig. 1. XRPD patterns of the milled mixtures: a: $n = 1$; b: $n = 1.5$; c: $n = 2.0$. CuK_α radiation.

In the following the results of the TG/DSC measurements along with those of the XRPD are reported for each of the three compositions studied.

ZnC_2O_4-$MnCO_3$

TG curves show that a constant mass value is reached at 650 °C. The mean value of final mass of the physical mixtures at 923 K is 52.7 ± 0.3 %. Such a value nearly coincides with that expected (52.4 %) for the formation of a mixture ZnO+ (1/2) Mn_2O_3.

Indeed the XRPD patterns (Fig. 2, lower pattern) of a sample of a physical mixture annealed for 18 h at 923 K show only the peaks of ZnO (for example see the peaks at $2\theta \approx 32°$ and 34.7° which are characteristic of ZnO) and Mn_2O_3 (for example see the peak at $2\theta \approx 23.3°$ which is characteristic of Mn_2O_3). By increasing the annealing temperature the peaks of $ZnMn_2O_4$ appear while those of Mn_2O_3 gradually vanish until they disappear after annealing at 1123 K. The samples annealed at $T > 1123$ K show the peaks of $ZnMn_2O_4$ and excess ZnO. However, since the peaks of $ZnMn_2O_4$ are close to those of the other spinel phase Mn_3O_4 the disappearance of the Mn_2O_3 peaks could partly be due to the reaction $Mn_2O_3 \rightarrow$ (2/3) Mn_3O_4 +(1/6)O_2 which occurs instead of the formation of $ZnMn_2O_4$. On the other hand DSC runs performed on all the samples annealed for 18 h at temperatures from 923 K to 1273 K show at $\approx$ 1463 K

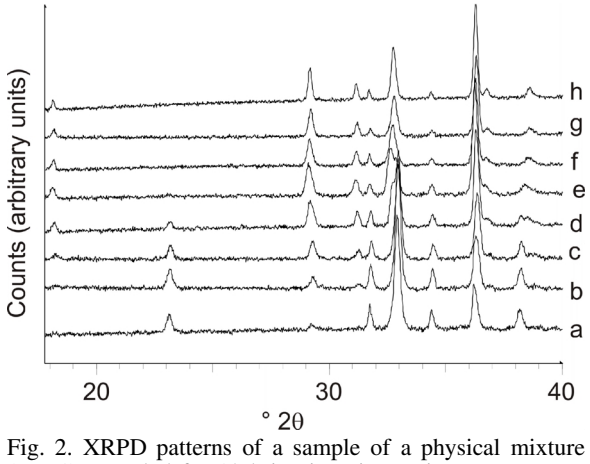

Fig. 2. XRPD patterns of a sample of a physical mixture (n = 1) annealed for 18 h in air at increasing temperature. a: 923 K; b: 973 K; c: 1023 K; d: 1073 K; e: 1123 K; f: 1173 K; g: 1223K; h: 1273 K. CuK_α radiation.

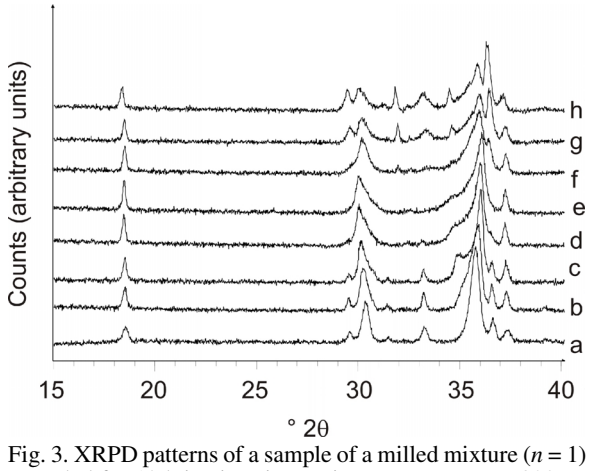

Fig. 3. XRPD patterns of a sample of a milled mixture (n = 1) annealed for 18 h in air at increasing temperature. a: 923 K; b: 973 K; c: 1023 K; d: 1073 K; e: 1123 K; f: 1173 K; g: 1223K; h: 1273 K. CuK_α radiation.

an endothermic peak (mean enthalpy of 38 ± 7 J g^{-1}) which is known to be due to the tetragonal-cubic phase transition of Mn_3O_4. Evidently Mn_3O_4 produced by the reduction of Mn_2O_3 forms a solid solution with $ZnMn_2O_4$ rather than reacting with ZnO to yield $ZnMn_2O_4$. Therefore the combined XRPD and DSC evidence shows that the product obtained is a solid solution $ZnMn_2O_4$-Mn_3O_4 plus unreacted ZnO.

In the case of the milled mixture the mass values attained in TGA at 923 K first increase during a milling time of up to 53 h while the final mass value reaches a nearly constant mean value (56.1 ± 0.2 %) which is much higher than that obtained for the samples of physical mixtures. Such a mass value higher than the expected one could be accounted for by allowing a process of mass loss that occurs during milling. On the basis of our previous studies [7], the candidate process is the formation of Mn_3O_4 from oxidative decomposition of $MnCO_3$ according to the reaction:

$$MnCO_{3(s)} + (1/6)O_{2(g)} \rightarrow (1/3)Mn_3O_{4(s)} + CO_{2(g)}$$

As the XRPD patterns of the milled mixture do not show peaks characteristic of this compound (see the comment on Fig. 1), Mn_3O_4 can be present only in an amorphous form.

The XRPD pattern (Fig. 3) of a sample of a milled mixture heated to 923 K does not show peaks due to ZnO and Mn_2O_3 but those of $ZnMn_2O_4$, though of low intensity. Broad peaks at angular positions ($2\theta \approx 30^\circ$ and 36°) between those of $ZnMn_2O_4$ and Mn_3O_4 are also present. With increasing temperatures (up to 1173 K) the peaks become broader, until at temperatures of 1223 K and 1273 K, they begin to separate showing the most intense peaks of ZnO ($2\theta \approx 32^\circ$ and 34.7°) and of $ZnMn_2O_4$ ($2\theta \approx 29.5^\circ$). What is likely to happen at $T > 1173$ K is the decomposition of $Zn_xMn_{3-x}O_4$. Indeed a TG run performed on the sample obtained at 923 K from the milled mixture demonstrates that $x = 1.5$ since a mass loss of -1.55 % occurs between ≈ 1170 K and 1520 K which fairly agrees with the expected value (-1.63 %) if the following reaction would take place:

$$Zn_{1.5}Mn_{1.5}O_{4(s)} \rightarrow (3/4)ZnMn_2O_{4(s)} + (3/4)ZnO_{(s)} + (1/8)O_{2(g)}$$

Therefore the reaction that occurs by heating the sample up to 923 K is:

$$(n/3)Mn_3O_{4(s)} + (1-n)MnCO_{3(s)} + ZnC_2O_4 \cdot 2H_2O_{(s)} + [(2-n)/6]O_{2(g)} \rightarrow (2/3)Zn_{1.5}Mn_{1.5}O_{4(s)} + 2H_2O_{(g)} + CO_{(g)} + (2-n)CO_{2(g)}$$

From the mass loss value it can be calculated that the initial milled mixture contains ≈ 10 % Mn_3O_4 by mass.

The DSC part of the thermoanalytical curve shows an exothermic peak between 470 K and 650 K whose enthalpy attains an appreciably constant value starting from the sample milled for 53 h. This value

is -211.7 ± 0.8 kJ. In this temperature region the thermal decomposition of zinc oxalate occurs (enthalpy: $+136.7$ kJ mol^{-1}) which releases CO_2 and CO which, in turn is oxidized to CO_2 (enthalpy: -283.1 kJ mol^{-1}). The difference between the enthalpy of the exothermic peak and the sum of the above mentioned ones (-146.4 kJ) is -65.3 kJ if referred to one mol $MnCO_3$. This value, calculated in the same way, is -38.5 kJ per mole of $MnCO_3$ for DSC runs performed on samples of physical mixtures. The DSC peak referring to the third stage of mass loss (residual decomposition of $MnCO_3$) is a combination of an endothermic and an exothermic effect and no quantitative calorimetric information on this stage of the process can be obtained. Furthermore, no endothermic peak is present at ≈ 1460 K so that it can be concluded that no tetragonal $\rightarrow$ cubic phase transition of Mn_3O_4 occurs meaning that no "free" Mn_3O_4 is present.

ZnC_2O_4-(3/2) $MnCO_3$

The physical mixture attains at 923 K a constant mean mass value of $53.3 \pm 0.20\,\%$ which fairly agrees with the value expected for the formation of a mixture ZnO+(1/2)Mn_3O_4 (54.1 %). Actually the XRPD pattern (Fig. 4) of a sample of a physical mixture annealed for 18 h at 923 K shows the peaks of ZnO, Mn_2O_3 and $ZnMn_2O_4$. After annealing at 1023 K the peaks of Mn_2O_3 disappear (see the peak at $2\theta \approx 23.3^\circ$ which is characteristic of Mn_2O_3). No peaks of Mn_3O_4 are present and this absence is confirmed as no DSC endothermic peak at ≈ 1460 K (indicating the presence of Mn_3O_4) appears for samples annealed at temperatures higher than 1073 K. Therefore pure $ZnMn_2O_4$ and excess ZnO are the phases formed that remain stable up to 1273 K.

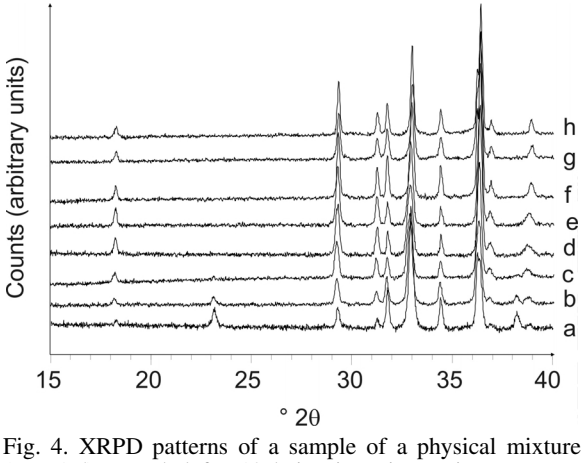

Fig. 4. XRPD patterns of a sample of a physical mixture (n = 1.5) annealed for 18 h in air at increasing temperature. a: 923 K; b: 973 K; c: 1023 K; d: 1073 K; e: 1123 K; f: 1173 K; g: 1223K; h: 1273 K. CuK_α radiation.

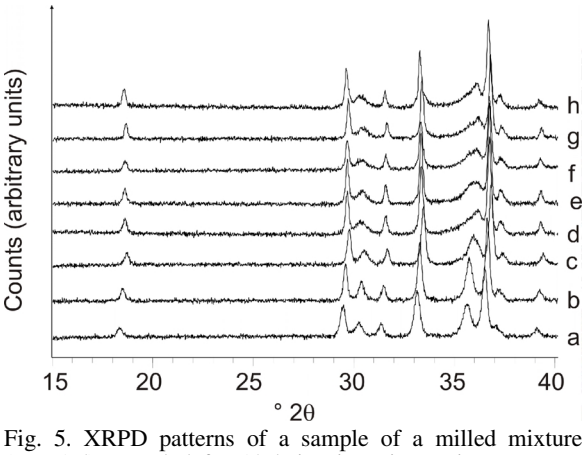

Fig. 5. XRPD patterns of a sample of a milled mixture (n = 1.5) annealed for 18 h in air at increasing temperature. a: 923 K; b: 973 K; c: 1023 K; d: 1073 K; e: 1123 K; f: 1173 K; g: 1223K; h: 1273 K. CuK_α radiation.

As concerns the milled mixture the residual mass at 923 K, for milling times ≥ 65 h, attains a mean value of $57.3 \pm 0.2\,\%$ which is much higher than that recorded for the physical mixtures. The XRPD pattern (Fig. 5) of a sample of a milled mixture heated up to 923 K shows the peaks of $ZnMn_2O_4$ and of Mn_3O_4 while no peaks of ZnO and Mn_2O_3 are present. By annealing at increasing temperatures the peaks of both spinel oxides tend to coalesce suggesting the formation of $Zn_xMn_{3-x}O_4$ phases. Indeed no endothermic peak is present at ≈ 1460 K so that it can be concluded that no tetragonal $\rightarrow$ cubic transition occurs, and this in turn means that no "free" Mn_3O_4 is present. The value of x = 1.2 has been deduced by performing a TG run on the sample obtained at 923 K from the milled mixture. It can be deduced that above 1370 K the following reaction takes place:

$$Zn_{1.2}Mn_{1.8}O_{4(s)} \rightarrow$$
$$0.9ZnMn_2O_{4(s)} + 0.3ZnO_{(s)} + 0.05O_{2(g)}$$

since a mass loss of $-0.77\,\%$ (expected $-0.71\,\%$) is observed between ≈ 1370 K and 1570 K. The reflexions of ZnO do not appear in the XRPD patterns of the samples treated up to 1273 K demonstrating that $Zn_{1.2}Mn_{1.8}O_4$ is thermally stable up to $T > 1273$ K. Therefore the reaction that occurs on heating the sam-

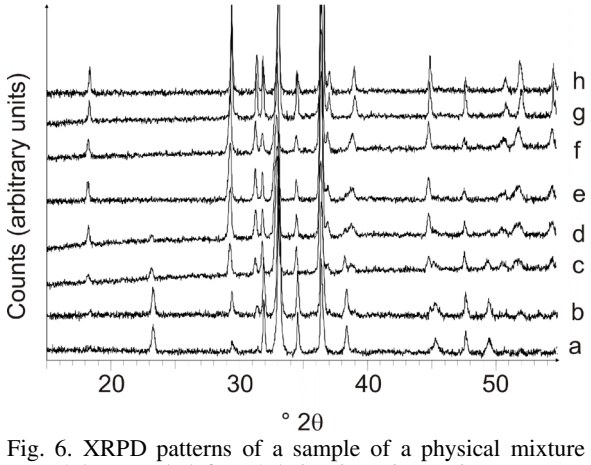

Fig. 6. XRPD patterns of a sample of a physical mixture (n = 2.0) annealed for 18 h in air at increasing temperature. a: 923 K; b: 973 K; c: 1023 K; d: 1073 K; e: 1123 K; f: 1173 K; g: 1223K; h: 1273 K. CuK_α radiation.

ple to 923 K is:

$$(n/3)\mathrm{Mn_3O_{4(s)}} + (1.5-n)\mathrm{MnCO_{3(s)}} + \mathrm{ZnC_2O_4\cdot 2H_2O_{(s)}} + [(2.5-n)/6]\mathrm{O_{2(g)}} \rightarrow 0.83333\mathrm{Zn_{1.2}Mn_{1.8}O_{4(s)}} + 2\mathrm{H_2O_{(v)}} + \mathrm{CO_{(g)}} + (2.5-n)\mathrm{CO_{2(g)}}$$

From the mass loss value it is deduced that the initial milled mixture contained $\approx 6\,\%$ mass of amorphous Mn_3O_4.

The enthalpy of the exothermic peak between 470 K and 650 K is -244 ± 10 kJ. The difference between this value and the expected enthalpy (-146.4 kJ) is -98.0 kJ which is higher than the difference, calculated in the same way, for the samples of the physical mixtures (-65.3 kJ). The DSC peak referring to the third stage of mass loss (residual decomposition of $MnCO_3$) is an exothermic peak with an enthalpy of -5.7 ± 0.8 kJ. The total excess enthalpy for the milled mixture is -103.3 kJ, *i. e.* -69.1 kJ if referred to one mole of $MnCO_3$.

ZnC_2O_4-2$MnCO_3$

The mean mass value reached by samples of physical mixtures at 923 K ($57 \pm 1\,\%$) is in fair agreement with the value expected for the formation of a mixture ZnO+Mn_2O_3 (57.04 %), though showing rather a high standard deviation. The XRPD pattern of a sample of a physical mixture annealed at 923 K (Fig. 6) shows mainly the peaks of ZnO and Mn_2O_3 (for example see the peak at $2\theta \approx 23.3^\circ$ which is characteristic of Mn_2O_3) along with low intensity peaks of $ZnMn_2O_4$. The intensity of the peaks of $ZnMn_2O_4$ increases with increasing temperature. After annealing at 1123 K the peaks of Mn_2O_3 vanish and only those of $ZnMn_2O_4$ and ZnO (for example see the peaks at $2\theta \approx 32^\circ$ and 34.7° which are characteristic of ZnO) remain. This situation does not change even after thermal treatment for 18 h at 1273 K: this means that the product formed up to 1273 K is not the tetragonally deformed spinel as expected on the basis of the phase diagram.

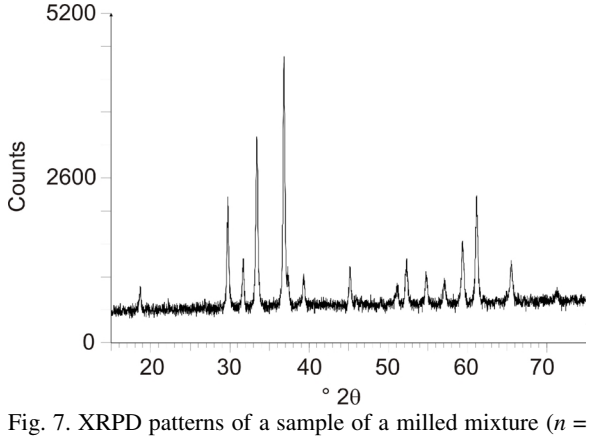

Fig. 7. XRPD patterns of a sample of a milled mixture (n = 2.0) annealed for 18 h in air at 923 K. CuK_α radiation.

The mean final mass value of samples of milled mixtures heated at 923 K is (for milling times $\geq$ 52 h) $58.2 \pm 0.2\,\%$, *i. e.* slightly higher than the value expected for the formation of a mixture ZnO-Mn_2O_3 (57.0 %). The XRPD pattern of a sample of a milled mixture heated up to 923 K shows only the reflexions of tetragonal $ZnMn_2O_4$ (Fig. 7). These peaks become sharper upon increasing the sample temperature to 1273 K. The reaction taking place in the milled mixture is:

$$(n/3)\mathrm{Mn_3O_{4(s)}} + (2-n)\mathrm{MnCO_{3(s)}} + \mathrm{ZnC_2O_4\cdot 2H_2O_{(s)}} + [(3-n)/6]\mathrm{O_{2(g)}} \rightarrow \mathrm{ZnMn_2O_{4(s)}} + 2\mathrm{H_2O_{(g)}} + \mathrm{CO_{(g)}} + (3-n)\mathrm{CO_{2(g)}}$$

Therefore $\approx 3\,\%$ by mass of amorphous Mn_3O_4 is calculated to be present in the milled mixture. A TG run performed up to 1623 K shows that $ZnMn_2O_4$ is thermally stable.

The enthalpy of the exothermic peak between 470 K and 650 K is -265 ± 6 kJ, and the difference between this value and the expected enthalpy (-146.4 kJ)

is −118.6 kJ, which is higher than the difference calculated in the same way for the samples of physical mixtures (−62.6 kJ). The DSC peak referring to the third stage of mass loss (residual decomposition of $MnCO_3$) is an exothermic peak with an enthalpy of -10.4 ± 0.4 kJ. The total enthalpy for the milled mixture is −129.0 kJ, *i. e.* −64.5 kJ if referred to one mole of $MnCO_3$.

Discussion

The TG measurements (supported by XRPD evidence) have shown that solid solutions of the type $Zn_xMn_{3-x}O_4$ form at 923 K starting from milled mixtures of composition n = 1 (x = 1.5) and n = 1.5 (x = 1.2). Partial formation of Mn_3O_4 ($\approx$ 10 and 7 % mass, respectively, for n = 1 and n = 1.5) occurs during milling at r. t. which could not be demonstrated on the basis of the XRPD powder patterns of the milled mixtures. The products are thermally stable up to $T \approx$ 1170 K (n = 1) and $\approx$ 1370 K (n = 1.5). None of them shows an endothermic DSC peak at $\approx$ 1460 K which would mark the tetragonal-cubic transition typical of the spinel phase Mn_3O_4. When starting from physical mixtures (n = 1, n = 1.5), a solid solution of Mn_3O_4 and $ZnMn_2O_4$ plus ZnO are the products obtained at 1273 K.

The combined TG and XRPD measurements show that the milled mixture of composition n = 2 contains some Mn_3O_4 ($\approx$ 3 mass%), and that $ZnMn_2O_4$ is formed at 923 K while the formation of $ZnMn_2O_4$ from the physical mixture is only accomplished by a 50 h annealing at 1573 K.

The different reactions are also reflected in the reaction enthalpy: the mean ΔH for the reactions (expressed per mole of $MnCO_3$) is -66 ± 2 kJ for the milled mixture *vs.* -38 ± 5 kJ for the pysical mixture.

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