Solid State Synthesis of $CaMnO_3$ from $CaCO_3$-$MnCO_3$ Mixtures by Mechanical Energy

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Z. Naturforsch. **61b,** 281 – 286 (2006); received December 14, 2005

A solid state synthesis of calcium manganite ($CaMnO_3$) is described where equimolecular mixtures $CaCO_3$:$MnCO_3$ have been subjected to mechanical stress (high energy milling) so yielding $CaCO_3$-$MnCO_3$ solid solutions of nanometric particle size. TG measurements have shown that a link exists between milling time, the extent of non-stoichiometry and the milling-induced decomposition of $MnCO_3$ to Mn_3O_4. A short (2 h) annealing at 850 °C performed on a sample mixture milled for 25 h leads to non-stoichiometric $CaMnO_{3-x}$. No sure conclusion could be drawn for the stoichiometry of $CaMnO_3$ obtained, under the same annealing conditions, from a mixture milled for longer time (150 h). No synthesis of $CaMnO_3$ could be effected by long (48 h) annealing at 1200 °C of mixtures that had not been subjected to mechanical stress.

Key words: TG Analysis, $CaMnO_3$, Mechanical Activation, Solid State Synthesis

Introduction

$CaMnO_3$ is the end member of the perovskite related mixed oxides $Ca_{1-x}M^{III}{}_xMnO_3$ where M^{III} is a trivalent cation that substitutes for Ca in the perovskite structure so that Mn is stabilized into the mixed valence status (Mn^{III}/Mn^{IV}). Such a status is also exhibited by the non-stoichiometric calcium manganite ($CaMnO_{3-x}$) with oxygen vacancies that significantly affect the magnetic and electronic properties of the compound. Indeed the stoichiometric oxide $CaMnO_3$ has an orthorhombic perovskite structure and it is a G-type antiferromagnetic insulator with a Néel temperature of 120 K. With decreasing oxygen content the $CaMnO_{3-x}$ phases show stronger ferromagnetic interactions with a slight increase in Néel temperature and an increase in conductivity becoming *n*-type semiconductors. The synthesis of $CaMnO_{3-x}$ oxide has usually been performed by solid state reaction involving high temperature and long reaction time (1400 °C, 15 h) so leading to samples with large particle size [1].

To try and solve this problem, different synthetic routes have been devised such as for example the thermal decomposition of metallo-organic precursors (Ca, Mn malonates) [2 – 4]. Other authors have simply modified the solid state route by using as precursor the solid solution $CaCO_3$-$MnCO_3$ prepared by wet methods [5 – 6] or by using the Pechini process [7].

The present work describes a solid state synthesis of $CaMnO_3$ where equimolecular mixtures $CaCO_3$:$MnCO_3$ have been subjected to mechanical stress by milling to yield $CaCO_3$-$MnCO_3$ solid solutions of nanometric particle size. By TG measurements it has been shown that a link exists between milling time and the extent of non-stoichiometry. A short (2 h) annealing at 850 °C of a sample milled for 25 h leads to non-stoichiometric $CaMnO_{3-x}$ whereas no sure conclusion could be drawn on the stoichiometry of $CaMnO_3$ synthesized under the same annealing conditions from a sample milled for longer time (150 h). The mechanochemical process seems cleaner than that where the precursor is prepared by a wet method. Moreover high energy milling is deemed to be a very effective route to introduce variable amounts of M^{III} to obtain $Ca_{1-x}M^{III}{}_xMnO_3$ perovskites.

Experimental Section

Starting chemicals and sample preparation

The starting chemicals were purchased from Aldrich Chimica (Italy): $MnCO_3$ (purity 99.9%) and $CaCO_3$ (purity 99.9%).

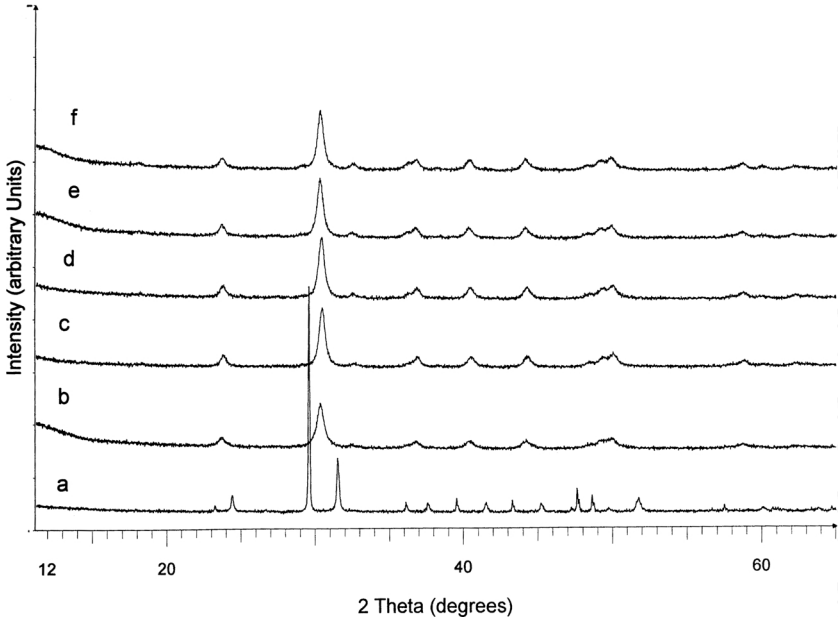


Fig. 1. XRPD patterns of samples of a physical mixture (a) and of a mixture milled for different times (b) 25 h, (c) 65 h, (d) 95 h, (e) 150 h, (f) 203 h.

Equimolecular physical mixtures were prepared by weighing the appropriate amounts of the two components and by stirring them in acetone suspension for 3 h. Then the solvent was allowed to evaporate in an oven at 60 °C overnight.

The mechanically activated mixtures were prepared by dry milling lots of 15 g of physical mixtures: the powders were put into stainless steel jars (200 ml) of a vibro-planetary mill (Pulverisette 4 by Fritsch, Germany) with 5 stainless steel balls (20 mm diameter; the mass ratio between the milling balls and the sample powder was 10 : 1). The mill was operated at 400 rpm rotation speed (up to 270 h).

Experimental techniques

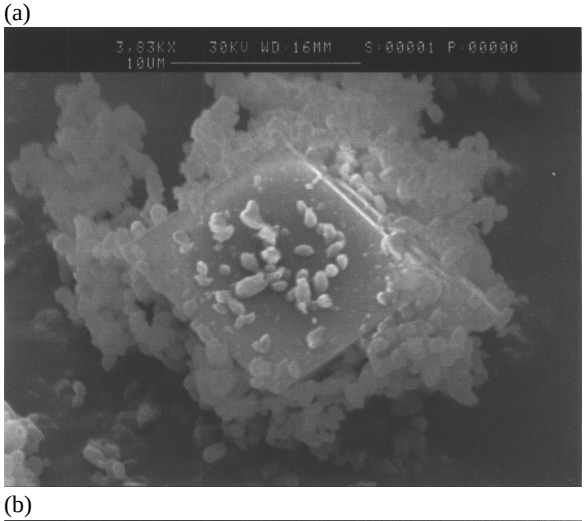
- TGA measurements were performed with a Q5000 thermogravimetric analyser (TA Instruments Inc. USA) connected to a computer fitted with an appropriate software. Samples of $\approx$ 50 mg were placed in a platinum pan and heated at 10 K/min (under air flow of 100 ml/min) from 25 °C up to 950 °C. Simultaneous TG/DSC measurements were performed under the very same experimental conditions in a Q600 Simultaneous TG/DSC analyser (TA Instruments Inc. USA) connected to a computer fitted with proprietary software;
- X-ray powder diffraction patterns were recorded in step scan mode (step 0.015°, 1s/step, 40 kV, 30 mA, $2\vartheta° = 10-65$) with an X-ray powder diffractometer (Bruker D5005) equipped with a Position Sensitive Detector (PSD, Braun). The crystal size of the milled mixtures was calculated from the XRD line broadening by the Scherrer equation. The instrumental line broadening was determined from the patterns of a physical mixture;
- Samples of both physical and milled mixtures (for 25 h and for 150 h) were examined by scanning electron microscopy (SEM, Model Stereoscan 200 by Cambridge, UK). Before analysis the samples were sputtered under vacuum with gold metal;
- Specific surface area of the starting reactants (milled and unmilled) and of the mixtures (physical and milled for 150 h) was determined by N_2 adsorption (BET method). The nitrogen adsorption curve was recorded by a Sorptomatic 1990 (Thermo Electron Corporation, operating with the static volumetric principle). The correction for the volume of the sample was introduced by measuring the He adsorption (in the case of the mixtures) and the N_2 adsorption with an empty sample burette (in the case of pure components the density of which is known).
- About 500 mg of both milled (25 h and 150 h) and physical mixtures were put into alumina boats and treated in a tube furnace (Carbolite, UK) at 10 K/min (static air) up to 850 °C. At the end of the ramp isothermal stages of 2, 12 and 48 h were appended. After cooling down at 5 K/min to r.t., the residual mass after each thermal treatment was determined before recording the XRPD patterns.

Results and Discussion

Preliminary measurements

Fig. 1 shows the XRPD patterns of the mixture milled for different times. For sake of comparison the

(a)



(b)

(c)

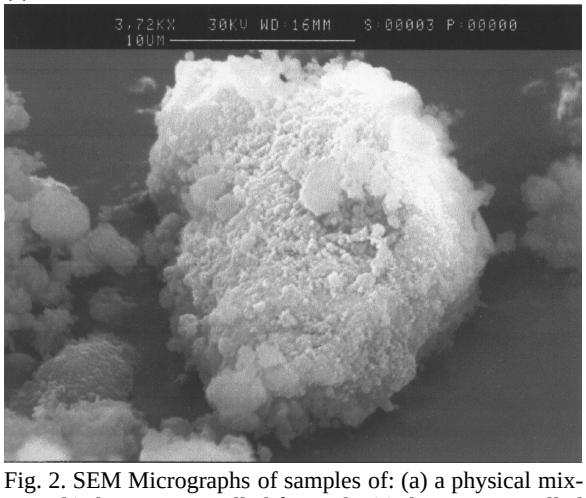


Fig. 2. SEM Micrographs of samples of: (a) a physical mixture, (b) the mixture milled for 25 h, (c) the mixture milled for 150 h.

Table 1. Specific surface area obtained by nitrogen adsorption (BET).

Sample	A (m^2/g)	Sample	A (m^2/g)
$MnCO_3$	4.06	$MnCO_3$ milled 100 h	76.18
$CaCO_3$	0.69	$CaCO_3$ milled 100 h	32.39
Physical mixture	2.68	Milled mixture	39.64

patterns of samples of physical mixtures are also reported. It can be seen that the peaks of the reactants, well separated in the patterns of physical mixtures, merge to give very broad single peaks. As $CaCO_3$ and $MnCO_3$ both crystallize in a calcite-type structure, it can be deduced that a solid solution forms in the milling process. The crystal size of the solid solution is obtained by applying the Scherrer equation to the peaks: a mean crystal size of 11.0 ± 1.5 nm results. By further milling (times > 25 h) the intensity of the peaks tends to increase: this fact is likely to be due to the crystallization of the solid solution. For samples milled for 150 h and more, the peaks of Mn_3O_4 (produced by $MnCO_3$ decomposition during milling) begin to appear (see the 100% peak at $2\vartheta \approx 18.5°$).

Fig. 2 shows the comparison between the SEM micrographs of samples of a physical mixture (2a) and of mixtures milled respectively for 25 h (2b) and 150 h (2c). No morphological differences are present between the samples milled for different times whereas two well distinct morphological features are present in the sample of physical mixture.

Another effect of milling is the increase of the specific surface area. Table 1 reports the data relevant to the starting reagents (both as purchased and milled) and of the mixtures (both physical and milled).

It can be noted that the specific surface area of the physical mixture is almost the double of that of the weighted mean of the specific surface areas of the pure components (1.17 m^2/g). On the contrary, the specific surface area of the milled mixture is $\approx 20\%$ lower than the weighted mean of the surface areas of the two milled components (49.79 m^2/g). This fact speaks for an enhanced surface interaction having occurred during milling that could then favour the solid state reaction by annealing the milled mixture.

Thermoanalytical measurements

In order to study how the solid state reaction proceeds going to higher temperatures and with the final aim to devise a thermal schedule to prepare $CaMnO_3$, TG measurements have been performed under air flow

Table 2. TG Measurements performed (10 K/min) under air flow.

t_{BM} (h)	M_1	T_1	$\Delta M_{HT,1}$	M_2	M_{fin}
5	83.95	565	−18.53	65.32	64.85
10	85.11	549	−19.35	65.76	65.30
15	83.35	562	−17.94	65.41	64.91
20	83.90	554	−18.32	65.58	65.11
25	83.65	555	−18.12	65.53	65.08
35	74.22	657	−8.18	66.04	65.55
65	74.32	658	−8.38	65.94	65.49
95	74.67	659	−8.36	66.31	65.83
110	75.35	658	−8.86	66.49	66.04
150	75.13	655	−9.00	66.87	66.39
203	75.80	656	−8.20	67.40	66.91
270	76.96	658	−8.53	68.43	67.90

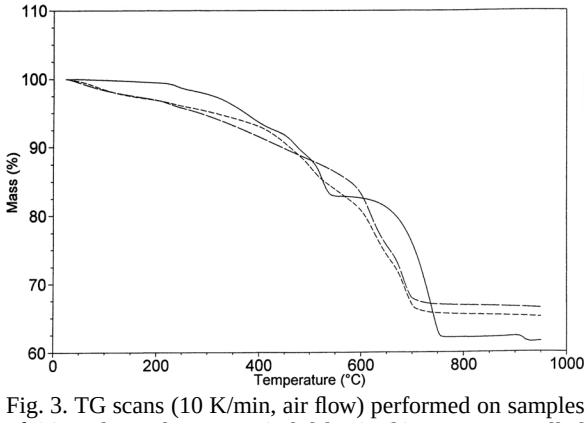


Fig. 3. TG scans (10 K/min, air flow) performed on samples of (a) a physical mixture (solid line); (b) a mixture milled 25 h (short-dashed line); (c) a mixture milled 150 h (long-dashed line).

up to 950 °C on samples milled for different times (up to 270 h).

Table 2 reports the results and Fig. 3 shows the TG curves of samples of a physical mixture (3a), and mixtures milled for 25 h (3b) and for 150 h (3c). Three stages of mass loss are present in all the samples.

- In the case of the physical mixture stage 1 ends at ≈ 577 °C with $M_1 = 82.67 \pm 0.31\%$ (mean of three independent runs). Such a value is only slightly lower than expected for the formation of a mixture $CaCO_3$-$0.5Mn_2O_3$ (83.25%). During the first stage an exothermic DSC peak is present the area of which corresponds to −3.3 kJ/g of mass loss;
- In the case of the mixtures milled up to 25 h stage 1 ends at ≈ 577 °C with $M_1 = 83.95 \pm 0.55\%$, slightly higher than expected for the formation of a mixture $CaCO_3$-$0.5Mn_2O_3$ (83.25%). The decomposition of $MnCO_3$ gives, at the end of stage 1, Mn_2O_3 as it is the case with pure milled $MnCO_3$ which at ≈ 600 °C produces a residue of 68.50% (expected for Mn_2O_3 68.67%). During the first stage the exothermic peak present has an enthalpy of −4.4 kJ/g of mass loss *i.e.* higher than it is the case with the physical mixture;
- For milling times > 25 h, stage 1 ends at a significantly higher temperature (658 °C) and with a higher mass value ($75.21 \pm 0.89\%$) than it is the case with samples milled for up to 25 h. Such a mean mass value corresponds to that calculated for the formation of a mixture constituted of MnO_2 and ≈ 0.6 moles of CaO (0.4 moles of $CaCO_3$ still remaining undecomposed);

At $T > T_1$ a mass loss process begins that ends at ≈ 800 °C (stage 2). Table 2 reports the mass loss values ($\Delta M_{HT,1}$). The mean value of the three independent measurements performed on the physical mixture is $-20.67 \pm 0.15\%$ which nearly coincides with the value expected for complete $CaCO_3$ decomposition (−20.47%). The endothermic DSC peak that corresponds to this part of the TG run has an enthalpy of 2.1 kJ/g of mass loss.

The values of $\Delta M_{HT,1}$ are lower for the milled mixtures: for milling times of up to 25 h the mean value is $-18.45 \pm 0.49\%$, and such a lower than expected mass loss allows to conclude that a share of $CaCO_3$ decomposes during stage 1. For milling times > 25 h the mean value is $-8.50 \pm 0.29\%$ which nearly corresponds to the value expected for the decomposition of 0.4 moles of $CaCO_3$ (−8.19%) that did not decompose during stage 1. The endothermic DSC peak which corresponds to this part of the TG run has an enthalpy of 0.50 kJ/g of mass loss which is lower than the value obtained with the physical mixture. This decreased enthalpic absorption suggests that some reaction between Mn oxides and CaO formed in the process is taking place. The mean mass value at the end of stage 2 (M_2 in Table 2) is, for the physical mixture, $62.00 \pm 0.44\%$, lower than the value expected (62.79%) for the formation of a mixture CaO-Mn_2O_3.

For the samples milled for up to 25 h the mean M_2 value is $65.52 \pm 0.15\%$, lower than the mass expected for the formation of a mixture CaO-MnO_2 (66.51%). It has to be noted that the XRPD patterns of the residuals recovered after TG runs performed up to 800 °C show reflexions of a mixture of poorly crystalline Mn(IV) compounds (mainly $Ca_2Mn_3O_8$ and $Ca_4Mn_3O_{10}$). The M_2 values for the samples milled for $t > 25$ h show an

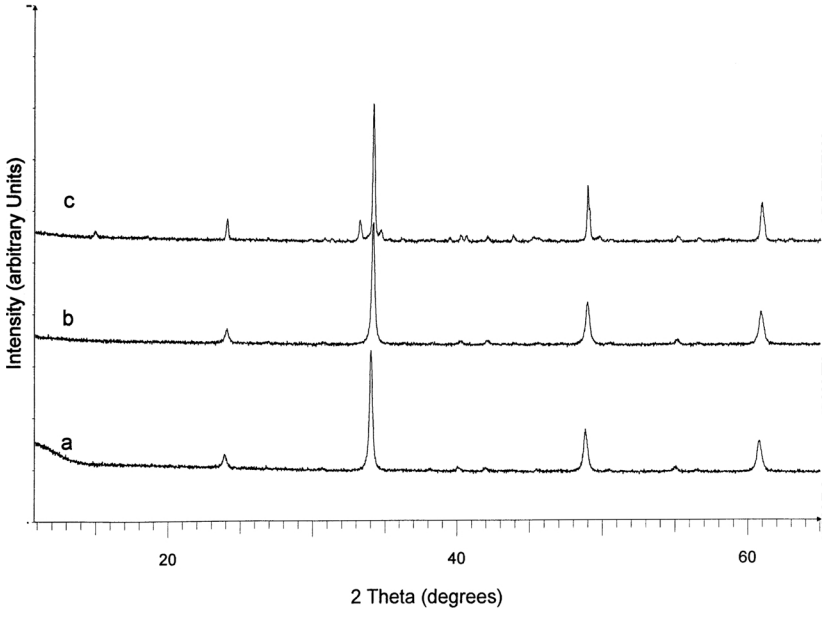


Fig. 4. XRPD patterns of.milled mixtures annealed for 2 h at 850 °C: (a) sample milled for 25 h; (b) sample milled for 150 h. Trace (c) is the XRPD spectrum of a physical mixture annealed for 48 h at 1000 °C.

increasing trend and, for milling times ≥ 150 h, they become higher than the value expected (66.51%) for the formation of a mixture CaO-MnO_2.

By further heating a slow mass loss process is taking place between 850 °C and 950 °C that leads to the M_{fin} values reported in Table 2. Such a mass loss according to the literature [6] could be due to the $CaMnO_3$ decomposition to give CaO, $CaMn_2O_4$ and O_2. If this were the case from the mean mass loss ≈ 0.13 moles of $CaMnO_3$ would decompose so that the final residue would contain $\approx 10\%$ by mass of $CaMn_2O_4$ while the relevant XRPD patterns only show the reflexions of $CaMnO_3$. Therefore what is happening is the formation at 950 °C of non-stoichiometric, oxygen-deficient $CaMnO_{3-x}$: for milling times up to 65 h the mean value of $(3-x) = 2.83 \pm 0.03$ is obtained. For milling time > 65 h, the M_{fin} values increase by increasing milling time and they even overcome the stoichiometric value for milling times > 150 h: the M_{fin} values higher than 66.51% can be explained by allowing for the fact that $MnCO_3$ decomposition begins to take place to some extent during milling (see Fig. 1). Finally it has to be noted that the XRPD patterns of the residuals of all the TG measurements performed up to 950 °C show the reflexions of $CaMnO_3$. On the contrary, the XRPD patterns of a residue obtained from a sample of a physical mixture (subjected to TG runs up to 950 °C) show completely different reflexions that cannot be ascribed to $CaMnO_3$.

Table 3. Annealing experiments performed in tubular furnace.

Mixture type	Thermal Schedule		M_{fin} (%)	$3-x$
Physical	2 h	850 °C	64.62	–
Physical	12 h	850 °C	64.10	–
Physical	48 h	850 °C	64.19	–
Milled 25 h	2 h	850 °C	65.83	2.91
Milled 25 h	12 h	850 °C	65.92	2.92
Milled 25 h	48 h	850 °C	65.94	2.92
Milled 150 h	2 h	850 °C	67.75	
Milled 150 h	12 h	850 °C	67.15	
Milled 150 h	48 h	850 °C	66.87	

Solid state synthesis

Table 3 reports the data of mass residuals obtained from samples of a physical mixture and from samples of mixtures milled for 25 h and for 150 h (annealed at 850 °C for 2, 12 and 48 h). The mean residual mass is $64.29 \pm 0.23\%$ for the sample of the physical mixture whereas, in the case of the milled mixture, the mean value becomes $65.90 \pm 0.05\%$ for the samples milled for 25 h that corresponds to the formation of $CaMnO_{2.92}$.

The mean value becomes higher by 150 h of milling ($67.26 \pm 0.37\%$) and this fact can be explained by allowing that some decomposition of $MnCO_3$ to Mn_3O_4 has occurred during milling. Hence no conclusion on the stoichiometry of the obtained calcium manganite can be drawn.

Fig. 4 shows that the XRPD patterns of the milled samples (both for 25 h and for 150 h) annealed at 850 °C for 2 h are indistinguishable and that they only show the reflexions of $CaMnO_3$. On the contrary, the patterns of samples of a physical mixture heated up to 1000 °C (with 48 h of annealing) show that the reflexions of $CaMn_2O_4$, $CaMn_3O_7$ and $Ca_4Mn_3O_{10}$ are present instead of those characteristic of $CaMnO_3$.

Conclusions

By milling mixtures $CaCO_3$-$MnCO_3$ the synthesis of $CaMnO_3$ is made easier with respect to the conventional solid state route. The essential features of the synthesis process are the following:

1. A nanocrystalline ($\approx$ 11 nm) solid solution is obtained which is a well suited precursor [5–6] to yield $CaMnO_3$ at $\approx$ 900 °C.
2. SEM micrographs show that no distinct morphological features can be detected in the milled mixtures.
3. Milling results in an increased surface area of the pure components. Such an increase is less in the case of mixtures where milling results in an enhanced homogeneity rather than in an increased particle comminution.
4. By milling for up to 25 h a mixture $CaCO_3$-0.5 Mn_2O_3 is the intermediate phase which forms at $\approx$ 560 °C. By longer milling times the reaction course is different in that $MnCO_3$ decomposition to MnO_2 takes place and also $\approx$ 60% of $CaCO_3$ decomposes to CaO up to 660 °C.
5. Up to 950 °C non-stoichiometric $CaMnO_{3-x}$ is formed ($3 - x = 2.83 \pm 0.04$). Upon increasing milling time an increasing share of $MnCO_3$ decomposes to give Mn_3O_4 during milling. This makes it impossible to assess the exact stoichiometry of calcium manganite.
6. By annealing for 2 h at 850 °C samples of mixtures milled for 25 h, $CaMnO_{2.92}$ is obtained.
7. No complete formation of $CaMnO_3$ occurs by annealing samples of physical mixtures for times up to 48 h at 1000 °C.

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