Processing-dependent CMR properties of $Ca(Cu,Mn)_7O_{12}$ manganites

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A strong dependence of physical properties on preparation conditions was found for the perovskite-like $CaMn_{3-x}Cu_xMn_4O_{12}$ solid solution demonstrating a record negative magnetoresistance of –65% at 35 K in a field of 5 T, for $x = 1.0$.

The family of manganites $CaMn_{3-x}Cu_xMn_4O_{12}$ with a perovskite-like structure[1–8] is known to exhibit a unique mechanism of colossal magnetoresistance (CMR), advanced CMR properties at comparably low fields and better thermal stability of the effect that attracts renewed fundamental[4–8] – and also practical[1–3] – interest to these compounds due to potential applications as magnetic sensors and read heads. At the same time, the reported MR properties of $CaMn_{3-x}Cu_xMn_4O_{12}$ vary drastically in different experiments,[5] and the origin of this contradiction is not yet established. Therefore, in this work, a new simple preparation technique was developed to study the physical properties of $CaMn_{3-x}Cu_xMn_4O_{12}$ solid solution prepared under different conditions.

$CaCO_3$, CuO and Mn_2O_3 reagents mixed in stoichiometric ratios were stirred at 40–80 °C in an excess of 65% nitric acid with about 10–20% of H_2O_2 added to reduce the Mn_2O_3 powder to soluble Mn^{II} nitrate. After complete dissolution of the reagents, the nitrate solution was kept at ~100 °C for 1 h to evaporate the water and then slowly heated up to ~500 °C. The dark flaky product thus obtained was ground to form the oxide precursor powder used in all the subsequent syntheses. The $CaMn_{3-x}Cu_xMn_4O_{12}$ samples were prepared by a solid-state reaction using the oxide powder milled with a planetary micromill in heptane for 15–120 min in agate bowls. The fine powder obtained was then pressed in air into pellets under 0.8–5.4 kbar uniaxial pressure at 250 °C for 3–4 h using a standard press with hot plates [mechanically-activated-and-densified precursor (MAD) method]. The pellets were placed in alumina boats, isothermally annealed at 600–1050 °C in a simple tubular furnace under a dry oxygen flow for 50–150 h with intermediate grindings, and air-quenched from respective temperatures.

Powder X-ray diffraction patterns for phase identification were collected in the 2θ range of 20–70° (STOE diffractometer, $CuK_{\alpha 1}$). The unit cell parameters were determined by the least-

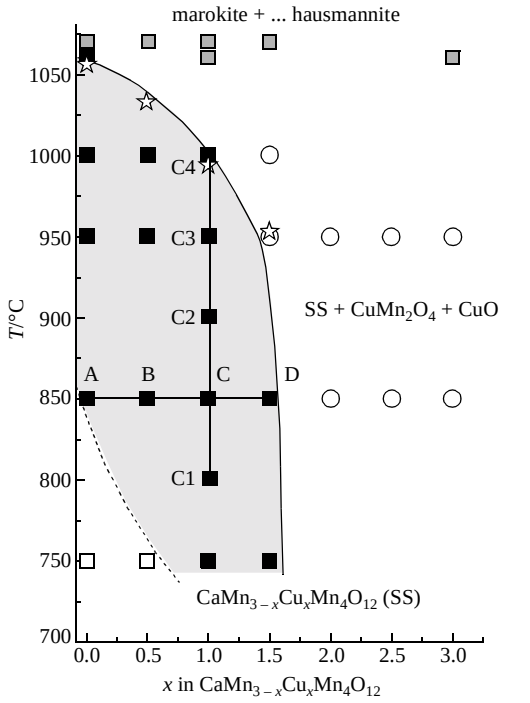

Figure 1 The homogeneity field of the $CaMn_{3-x}Cu_xMn_4O_{12}$ solid solution (SS) at $p_{O_2} = 1$ bar along the $CaMn_7O_{12}$–$CaCu_3Mn_4O_{12}$ polythermal section according to XRD, EDX and TGA/DTA data.[5] A, B, C and D denote compositions prepared at 850 °C and used to measure the MR properties of the solution, while the C, C1, C2, C3 and C4 points are samples of the same composition ($x = 1.0$) obtained at different temperatures in the range of 800–1000 °C.

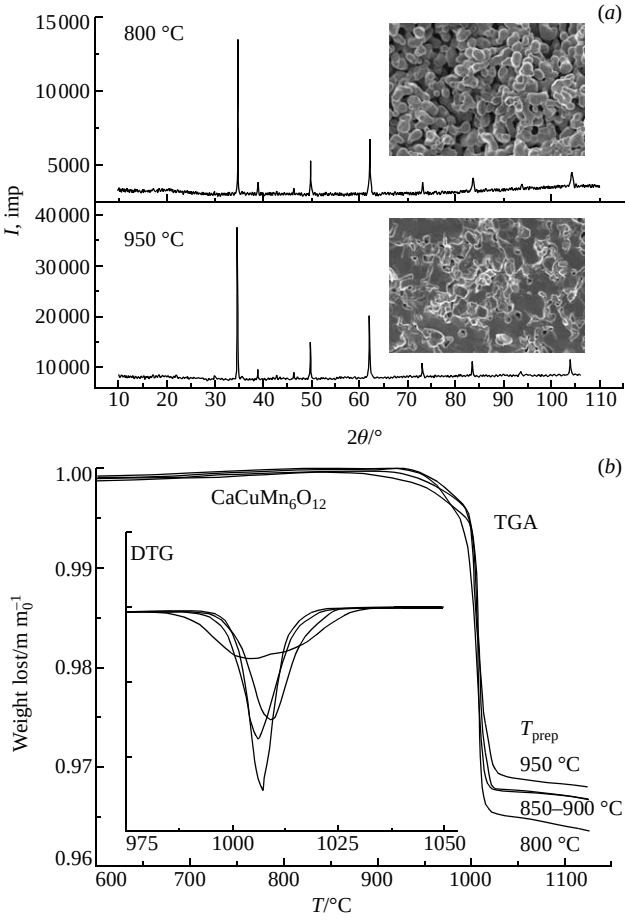

Figure 2 Chemical and phase composition analysis data of CMR samples. (*a*) Powder XRD patterns of single phase $CaCuMn_6O_{12}$ samples obtained from the same precursor at different temperatures [≤ 1–2% of impurity phases as confirmed by XRD and SEM, Ca:Cu:Mn = = 0.99(5):1.01(5):5.99(3), as determined by EDX]; insets show the difference in microstructures; (*b*) TGA data of the samples; inset shows DTG curves demonstrating the beginning points of weight loss; according to iodometric titration, the average oxidation state of Mn is 3.33–3.34 for the samples obtained at 800–900 °C, as expected for this compound.

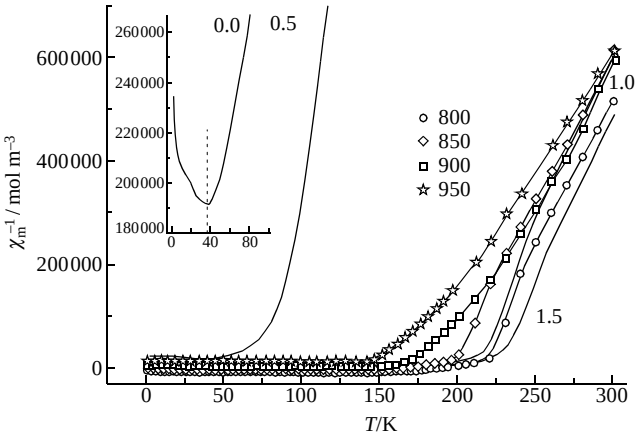

Figure 3 Magnetic properties of $CaMn_{3-x}Cu_xMn_4O_{12}$ samples. Solid curves correspond to the samples of different compositions obtained at 830 °C, x values are denoted near the curves. In some cases, only a part of curves is shown like in the inset (x = 0.0 sample). Symbols connected by curves show the behaviour of samples of the same (x = 1.0) composition obtained at different temperatures.

squares fit of the peak positions obtained with a focusing FR-552 Guinier camera ($CuK_{\alpha1}$, germanium as an internal standard). Microstructure investigations and electron probe microanalysis were performed with a Leo Supra 50VP digital scanning electron microscope (SEM) equipped with an Inca (Oxford) energy-dispersive X-ray detector (EDX) with the spot size < 3 μm. To confirm chemical compositions, EDX spectra were collected for each test sample from about 10 randomly selected grains or areas; the oxygen content was additionally determined using iodometric titration and thermal analysis (Perkin Elmer Pyris Diamond, temperature range of 20–1100 °C, 5 K min^{-1} heating rate, Al_2O_3 standard, 10–15 mg of samples). Magnetic properties were measured on an MPMS XL SQUID magnetometer (Quantum Design) in a ZFC regime. Magnetoresistance measurements were carried out with a standard four-probe technique with silver paste contacts using a PPMS 6000 SQUID magnetometer in the temperature range of 5–300 K at magnetic fields (H) from 0 to 7 T. CMR effect magnitudes were calculated as MR = = $[R(H) - R(0)]/R(0)\times100\%$.

The optimization of preparation conditions gives a possibility to find tentatively the boundaries of the $CaMn_{3-x}Cu_xMn_4O_{12}$ solid solution homogeneity field (Figure 1) being potentially the most important guidance in the controllable preparation of this compound with desired CMR properties. In particular, this solid solution can be obtained under ambient conditions with different compositions of $0 \le x \le 1.5$ and in a wide temperature range of 750 °C ≤ T ≤ 1060 °C. The homogeneity field has a maximum compositional width (x = 0–1.5) at ~850 °C (points A–D, Figure 1), while it is possible to prepare the $CaCuMn_6O_{12}$ (x = 1) phase in the broadest range of temperatures from 750 to 1000 °C (points C, C1, ..., C4, Figure 1). Thus, there are at least three degrees of freedom in the variation of properties of the solution: composition, microstructure and temperature.

Intergrain spin-polarised tunneling (TMR) makes a large contribution to the total magnetoresistance in this particular system[1–4] thus demanding an optimised microstructure for improved CMR properties. Indeed, we found recently[5] that there is a drastic influence of microstructure on MR properties as is easily controlled by a pre-treatment stage including, mostly, milling time and pressing effort during warm compacting of mechanically activated precursors. Furthermore, the magnitude of MR was believed to increase monotonically with increasing x, and the highest values were reported for the $CaCu_3Mn_4O_{12}$ (x = 3) or $Na_{0.5}Ca_{0.5}Cu_3Mn_4O_{12}$ solid solutions with a maximum copper content.[1–4] In contrast, our samples exhibit a maximum of MR for x = 1 achieved as soon as other preparation conditions (precursor pre-treatment, annealing temperature, atmosphere and microstructure) were optimised.[5] Fixing both composition and optimal precursor pre-treatment conditions may allow us to achieve the best CMR performance of the

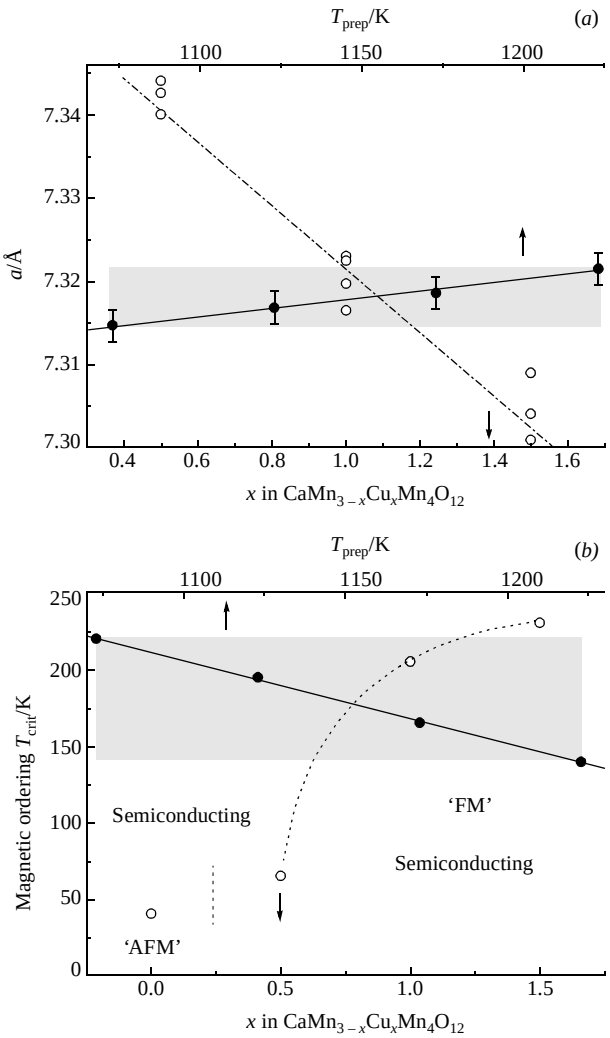

Figure 4 Fundamental constants as functions of preparation temperature (T_{prep}) of the $CaCuMn_6O_{12}$ CMR phase (C1, C2, C3 and C4 points in Figure 1) as compared to changes caused by a composition variation (A, B, C and D points in Figure 1). (*a*) Lattice constants [a = 7.268(4) + + 4.4(4)×10$^{-5}T_{prep}$, R = 0.9943], open circles correspond to a combined set of our and published data; dark circles are given for the x = 1.0 samples obtained at different temperatures; (*b*) experimental magnetic ordering temperatures, T_c = 800(16) – 0.54(1)T_{prep} (R = 0.9993) for the x = 1.0 series. In (*a*) and (*b*), gray shading shows the range of parameter changes *vs* changes in the same parameters for the samples with different compositions.

samples. Our ceramic samples prepared by the MAD technique reproducibly demonstrate record CMR values for this system, exceeding –65% at 35 K and 5 T, which is twice as high as previously published values. Hence, the only $CaCuMn_6O_{12}$ compound, having the same cation and anion composition and same pre-treatment (120 min of precursor milling and 4.6 kbar of pressing at 250 °C for 3 h), was used then to clarify the role of thermal preparation history.

Temperature is the most common parameter varied to prepare a desired material. Indeed, annealing at different temperatures (at least in the range of 800–1000 °C, Figure 2) preserves same chemical composition and phase assemblage; however, it causes evident microstructural changes [Figure 2(*a*), insets]. The microstructure is composed of micron- and submicron-sized rounded grains connected with each other in a highly interlinked percolation network.[5] Sintering at higher temperatures allows us to achieve larger well-developed and strongly linked grains of this CMR solution. In both cases, sintering temperatures and annealing durations are moderate and do not exceed 1000 °C and 50 h, respectively. Therefore, it is easy to vary the microstructure from porous to dense ceramics having very different grain sizes and the numbers of intergrain contacts.

The test solid solution, as found, has an unexpectedly large dependence of its properties on preparation temperature influ-

encing both microstructural features of the material (Figure 2) and also fundamental characteristics of the crystal lattice (Figures 3, 4); therefore, this is the most complex preparation parameter in the case of the Ca–Cu–Mn–O system. It was found that $CaCuMn_6O_{12}$ single-phase samples quenched from different temperatures (800–950 °C) demonstrate a linear increase of cubic cell parameters, 0.004 Å per 100 °C [Figure 4(*a*)]; the temperature of magnetic ordering exhibits [Figures 3 and 4(*b*)] the same tendency decreasing by 60–70 °C per 100 °C (Figure 4). The samples were found (Figure 2) to be a single phase (XRD) of the same composition ($CaCuMn_6O_{12}$, EDX) with the same crystal lattice (space group $Im\bar{3}$, Rietveld refinement) and identical oxygen content (TGA and iodometric titration). Therefore, the observed anomaly may indicate different ordering of Mn^{3+} and Cu^{2+} ions in the A and B positions of the $A_3B_4C_7O_{12}$ structural type. This situation seems to be typical of complex oxides with perspective magnetic and electrical properties.[9–11] Thus, the CMR properties of manganites as multicomponent solid solutions are determined not only by the solid solution composition and sample microstructure but also depend on possible cation disordering in its lattice controlled by a preparation temperature and, therefore, demanding for more careful control of preparation conditions of the $CaMn_{3-x}Cu_xMn_4O_{12}$ magnetoresistive solid solution.

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