Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 27 (2007) 3911–3914
www.elsevier.com/locate/jeurceramsoc

Magnetic properties of $Cu_{1+x}Mn_{2-x}O_4$ and $Ni_{1+x}Mn_{2-x}O_4$ solid solutions

O. Peña [a,*], X. Cailleaux [a], B. Piriou [a], M. del Canto [b], S. Abarca [b], E. Ríos [b], J. Ortiz [b], J.L. Gautier [b], P.N. Lisboa-Filho [c], C. Moure [d]

[a] *Sciences Chimiques de Rennes, UMR-CNRS 6226, Université de Rennes 1, 35042 Rennes Cedex, France*
[b] *Materials Chemistry Department, Facultad de Química y Biología, Universidad de Santiago, Santiago, Chile*
[c] *Departamento de Física, Universidade Estadual Paulista (UNESP), Bauru, Brazil*
[d] *Instituto Cerámica y Vidrio, CSIC, Electroceramics Department, Campus de Cantoblanco, 28049 Madrid, Spain*

Available online 23 March 2007

Abstract

Magnetic properties of two spinel oxides solid solutions, $Cu_{1+x}Mn_{2-x}O_4$ and $Ni_{1+x}Mn_{2-x}O_4$, are reported. These series are characterized by two magnetic transitions: the upper one, of ferrimagnetic type, occurs at about 85 K (for copper-based) and at 105–110 K (for nickel-based spinels), independently of the *x*-content; the lower transition may be related to a Néel-type collinear ordering and takes place at 30 and 45 K, respectively. Application of moderate fields ($H > 250$ Oe) make both transitions to merge into one broad maximum in the magnetization, which takes place at lower temperature when applying larger fields. Magnetization cycles with temperature (ZFC/FC) or field (loops) allowed us to well characterize the ordered state. The effective moment follows the expected behavior when manganese ions are being substituted by ions of lower magnetic moment (Ni^{2+} and Cu^{2+}).

Keywords: Spinels; Magnetic properties; Soft magnets; Ferrimagnetism

1. Introduction

Oxide spinel materials based on 3d transition-metal have been well studied due to their outstanding semiconducting properties, well appropriated for temperature sensing devices, among many other applications.[1] For this reason, a thorough research has been developed, focused mainly on varying cation compositions, chemical phase relations, structural and electrical properties, etc. But, in contrast to other related compounds based mainly on Fe,[2] few reports have dealt with the low temperature magnetic properties.[3] Because of the relative complexity of the cationic distribution, any research in these materials must take into account the intrinsic duality among the tetrahedral and octahedral sites, and the possibility of the cations to adopt two, or even three, different oxidation states within the same specimen, leading to some particular properties in the ordered state(s).

During the recent years, we have developed a research centered on the crystallo-chemical and physical properties of manganite compounds of spinel structure. In a first stage, we have been looking into the magnetic properties of the parent compound $NiMn_2O_4$, already well described in the literature,[4] in order to characterize the influence of the partial oxygen pressure during annealing.[5] In a second step, the manganese cation has been partially substituted by other transition metal elements, in particular nonmagnetic ones in order to separate out the contribution of the main magnetic sublattice.[6] We report herein the magnetic behavior of pseudo-binary oxides of spinel structure in which manganese is now being substituted by magnetic ions, such as Cu or Ni, leading to a general formula $Me_{1+x}Mn_{2-x}O_4$, where Me = Cu and Ni.

2. Experimental procedure

Samples were prepared using different methods, based mainly on solid-state mixing of the corresponding oxides, or using hydrated nitrates as precursors. The synthetical route, described elsewhere,[6] basically consisted in calcinations steps at about 1173 K, with repeated milling and pre-sintering heating (usually, three times) and a final sintering step at about 1323–1373 K for 2 h, with a warming rate of 5 K/min and cooling in air at a rate of 2 K/min. Homogeneous, single-phase samples were found on different compositional ranges, depending on the

* Corresponding author. Tel.: +33 2 23 23 67 57; fax: +33 2 23 23 67 99.
E-mail address: pena@univ-rennes1.fr (O. Peña).

0955-2219/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2007.02.058

substituting element. In the case of Me = Ni, the series extended all over the range from $x = 0$ ($NiMn_2O_4$) till $x = 1$ (Ni_2MnO_4), while for Me = Cu, it was limited to $[0 \leq x \leq 0.4]$, that is, from $CuMn_2O_4$ until $Cu_{1.4}Mn_{1.6}O_4$. The metal-to-metal ratio was systematically verified by energy dispersive X-ray spectroscopy (EDX) and in all cases confirmed the nominal metallic composition, within an experimental error of 5–8%. X-ray diffraction (XRD) analyses performed using Cu Kα radiation confirmed the samples' purities (discarding the presence of any spurious phases within an accuracy of approximately 1 vol.%) and allowed the determination of the lattice parameters within the classical spinel group *Fd*3*m* of cubic symmetry.

Magnetic measurements were performed in a SHE VTS-906 and a Quantum Design MPMS XL5 SQUID susceptometers, between 2 and 300 K, on ceramic specimens glued to a thin rod in order to avoid disorientation due to torque forces exerted on the sample. When samples were only available in powder form, compact pellets were prepared to avoid any orientation of fine crystallites under the applied field.

3. Paramagnetic regime

The paramagnetic regime differs in these two systems. Fig. 1 shows the inverse susceptibility (defined hereafter as the ratio $(M/H)^{-1}$) and Table 1 gives the parameters obtained from a fit at $T > 200$ K (for the nickel series) and at $T > 150$ K (for the copper series). It can be immediately seen that the Weiss temperature constitutes the main difference in their magnetic behaviors: while it is largely negative in $Ni_{1+x}Mn_{2-x}O_4$, it stays positive and increasing with the x-content, in $Cu_{1+x}Mn_{2-x}O_4$.

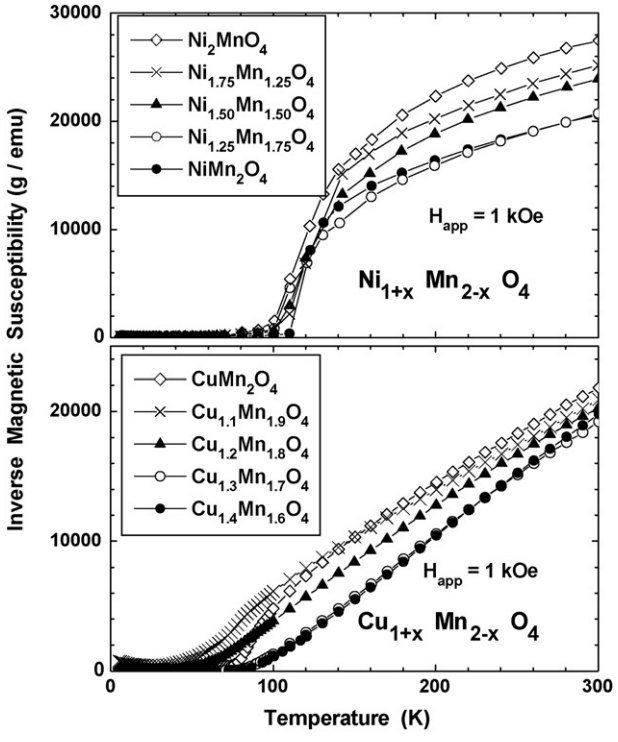

Fig. 1. Inverse susceptibility for the solid solutions $Ni_{1+x}Mn_{2-x}O_4$ and $Cu_{1+x}Mn_{2-x}O_4$.

Table 1
Magnetic data[a] for the series $Me_{1+x}Mn_{2-x}O_4$ (Me = Ni, Cu)

	Weiss temperature Θ (K) (±5 K)	Magnetic moment μ_{eff} (μ_B/f.u.)[b] (±0.05)
$NiMn_2O_4$	−86	6.62
$Ni_{1.25}Mn_{1.75}O_4$	−139	6.27
$Ni_{1.50}Mn_{1.50}O_4$	−183	6.15
$Ni_{1.75}Mn_{1.25}O_4$	−214	6.18
$Ni_{2.00}Mn_{1.00}O_4$	−245	6.10
$CuMn_2O_4$	+11	4.99
$Cu_{1.1}Mn_{1.9}O_4$	+14	5.22
$Cu_{1.2}Mn_{1.8}O_4$	+40	4.91
$Cu_{1.3}Mn_{1.7}O_4$	+84	4.61
$Cu_{1.4}Mn_{1.6}O_4$	+92	4.49

[a] Calculated in the ranges $T > 200$ K for $Ni_{1+x}Mn_{2-x}O_4$ and $T > 150$ K for $Cu_{1+x}Mn_{2-x}O_4$.
[b] Magnetic moment/formula unit.

However, in both cases, a strong negative curvature is observed at the approach of the magnetic transition, typical of a ferrimagnetic order.[7] It should be remarked that both $CuMn_2O_4$ and $Cu_{1.1}Mn_{1.9}O_4$ were analyzed by a modified Curie–Weiss law (not shown), of the type $\chi = C/(T - \Theta) + \chi_{TIP}$, with rather large values of a temperature-independent contribution ($\chi_{TIP} \sim 15 \times 10^{-3}$ and 30×10^{-3} emu K/mol, for $CuMn_2O_4$ and $Cu_{1.1}Mn_{1.9}O_4$, respectively). The origin of such paramagnetic contribution stays unknown but, as can be seen in Fig. 1, the corrected expression fits very well with the general trend of the series.

The effective moments of both solid solutions follow the expected behavior if one considers that manganese ions are being substituted by ions of lower magnetic moment (Ni^{2+} and Cu^{2+}, of 2.83 and 1.73 μ_B, respectively). The slow decrease of μ_{eff} with x(Ni) and a somewhat larger decrease in the case of x(Cu) correlates well with expected variations (Table 1).

4. Ordered regime

In order to fix the experimental conditions, we first of all performed the magnetic characterization of the non-substituted spinel $NiMn_2O_4$, under various conditions of preparation and applied field. Fig. 2 shows the magnetic response of a $NiMn_2O_4$ sample annealed at 1100 °C and quenched in air, and measured on a ZFC/FC mode under an applied dc field of 5 Oe. Two well-defined anomalies can be observed: during the ZFC mode, a first broad maximum occurs at about 45 K followed by an antiferromagnetic-type transition at $T_N = 101$ K. The paramagnetic state is reached at $T_c = 105$ K. During the field cooling (FC) procedure, the magnetization increases abruptly at the magnetic transition temperature T_c, while the low temperature anomaly is seen as a leveling of the magnetization variation. Such double-transition feature (confirmed by ac susceptibility measurements; not shown) have been already observed[3,8] and it is a signature of a complex magnetic structure which reflects the competition between ferromagnetic (F) and antiferromagnetic (AF) magnetic sublattices leading to a ferrimagnetic-like state. A possible scenario for the lowest magnetic transition is the occurrence of

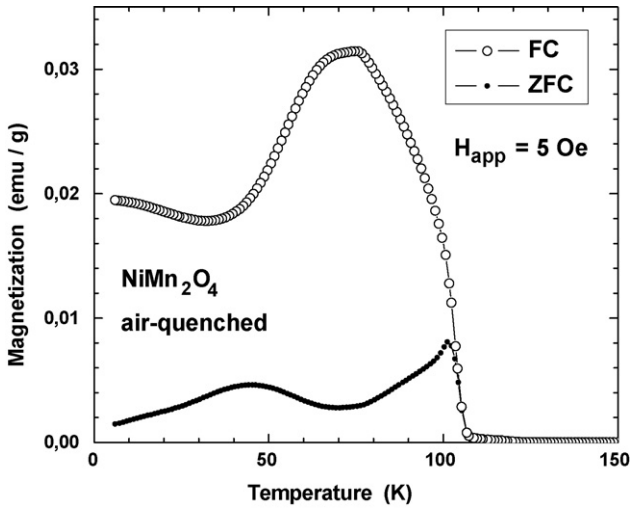

Fig. 2. ZFC/FC cycle of a $NiMn_2O_4$ sample annealed at 1100 °C and quenched in air.

a Néel-type collinear structure or a canted arrangement of the Yafet–Kittel type.[9] These transitions merge into a single broad transition, which gets broader and takes place at lower temperatures when applying larger fields. This maximum, which occurs at T_{max}, defines the antiferromagnetic-like ordering, typical of non-compensated ferromagnetic systems (either ferrimagnetic sublattices or canted antiferromagnetism).

Similar observations were recorded for the whole series $Ni_{1+x}Mn_{2-x}O_4$, for which the upper transition at T_c stayed absolutely constant at 105 K as a function of the nickel content (Fig. 1). Substitutions of manganese by non-magnetic (Ga, Zn) or strongly magnetic (Cr) elements gave exactly the same value for T_c, while substitutions by Co showed a large increase of T_c, from 105 up to 210 K for $NiMn_{1.3}Co_{0.7}O_4$.[6,10]

The case of the $Cu_{1+x}Mn_{2-x}O_4$ solid solution seems to be more complex since the nature of the ordered state changes with composition. Fig. 3 shows ZFC/FC cycles performed under an applied field of 50 Oe. For the parent compound $CuMn_2O_4$, two well-identified transitions occurred, the upper one at 80 K, and

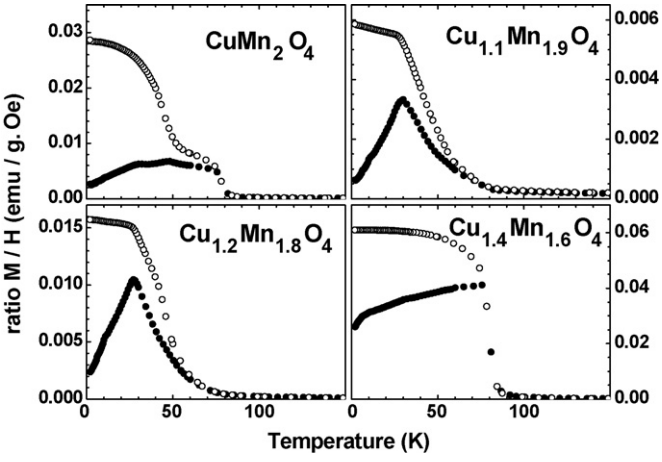

Fig. 3. ZFC (filled symbols) and FC magnetizations (open symbols) measured under 50 Oe on given samples of $Cu_{1+x}Mn_{2-x}O_4$.

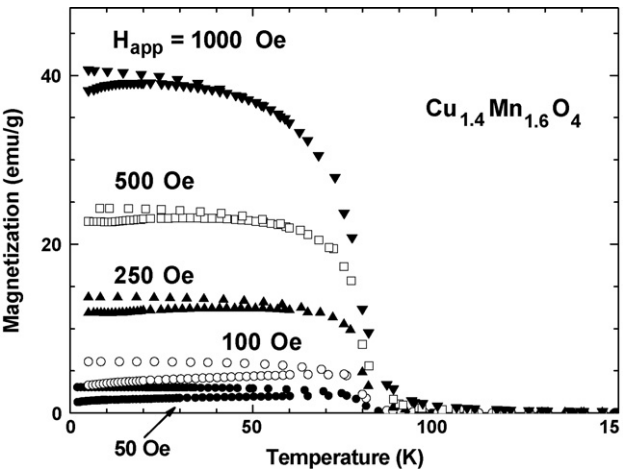

Fig. 4. ZFC/FC cycles performed under given applied fields for $Cu_{1.4}Mn_{1.6}O_4$.

the lowest one at about 30 K. An intermediate peak is observed at 45 K, which is just the added contribution of the other two transitions. This trend is found again in the $Cu_{1.1}Mn_{1.9}O_4$ and $Cu_{1.2}Mn_{1.8}O_4$ samples, where the lowest anomaly corresponds to a pronounced peak characteristic of an antiferromagnetic transition (in the ZFC mode) and a tendency to a plateau characteristic of a ferromagnetic order (in the FC mode). The ferromagnetic behavior is well seen in the $Cu_{1.4}Mn_{1.6}O_4$ sample, where the ZFC branch still shows a weak antiferromagnetic contribution, while the FC magnetization is characteristic of long-range ferromagnetic interactions. Under increasing magnetic fields such ferrimagnetic character slowly evolves toward a 100% ferromagnetic state, as shown in Fig. 4.

Fig. 5 summarizes the general behavior of this series, shown as magnetization loops measured at 2 K, between −50 kOe and +50 kOe: at low contents of copper, the loops are characterized by small coercive fields due to the ferromagnetic interactions and by a magnetization which keeps increasing with the applied field; at larger contents of copper, that is for $Cu_{1.4}Mn_{1.6}O_4$, the saturation magnetization is reached at rather low fields (∼10 kOe)

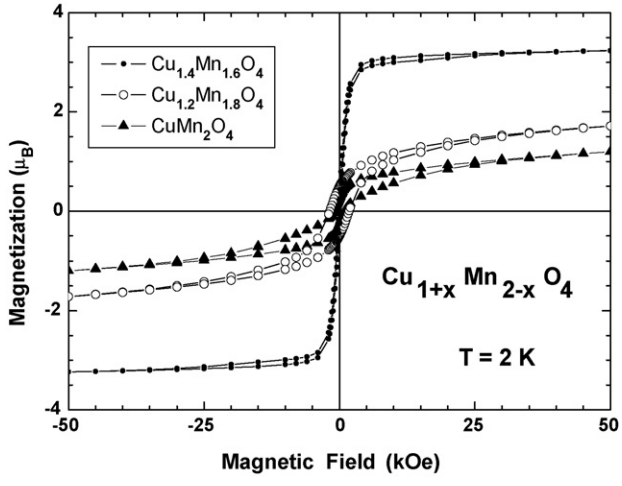

Fig. 5. Magnetization loops performed at 2 K on given samples of $Cu_{1+x}Mn_{2-x}O_4$.

although the coercive field decreases rapidly, as in soft ferromagnets.

5. Conclusion

The magnetic properties of two families of manganese spinel oxides have been described, one based on $NiMn_2O_4$ and the other on $CuMn_2O_4$. Quite different behaviors were observed in the paramagnetic parameters, mainly in the Weiss temperature Θ, one being strongly negative (nickel samples), the other being highly ferromagnetic (copper samples). This trend was also observed in the ZFC/FC cycles, since antiferromagnetic interactions are well developed in the $Ni_{1+x}Mn_{2-x}O_4$ solid solution, while there is a clear evolution from antiferromagnetism toward ferromagnetism in the $Cu_{1+x}Mn_{2-x}O_4$ solid solution. As a whole, both systems behave as ferrimagnetic systems, as expected from their spinel nature.

Acknowledgements

Authors from Chile and O.P. thank project Fondecyt-Chile 1050178. Authors also acknowledge the bilateral exchange programs France-Brazil CAPES-COFECUB, project no. 416/03, and France-Spain CNRS-CSIC, project no. 18873.

References

[1]. Grimes, N. W., The spinels: versatile materials. *Phys. Technol.*, 1975, **6**, 22–27.

[2]. Ferreira, T. A. S., Waerenborgh, J. C., Mendonça, M. H. R. M., Nunes, M. R. and Costa, F. M., Structural and morphological characterization of $FeCo_2O_4$ and $CoFe_2O_4$ spinels prepared by a co precipitation method. *Solid State Sci.*, 2003, **5**, 383–392 (and references therein).

[3]. Boudaya, C., Laroussi, L., Dhahri, E., Joubert, J. C. and Cheikh-Rouhou, A., Preparation and characterization of the spinel series $Co_{6+x}Ni_{4-x}Mn_8O_{24}$ ($0 \leq x \leq 4$). *Phase Transit.*, 1999, **68**, 631–642.

[4]. Tang, X.-X., Manthiram, A. and Goodenough, J. B., $NiMn_2O_4$ revisited. *J. Less-Common Met.*, 1989, **156**, 357–368.

[5]. Lisboa-Filho, P. N., Bahout, M., Barahona, P., Moure, C. and Peña, O., Oxygen stoichiometry effects in spinel-type $NiMn_2O_{4-\delta}$ samples. *J. Phys. Chem. Solids*, 2005, **66**, 1206–1212.

[6]. Peña, O., Moure, C., Bodenez, V., Cailleaux, X., Piriou, B., Ortiz, J., Zúñiga, G., Gautier, J. L. and Lisboa-Filho, P. N., Magnetic properties of spinel-type oxides $NiMn_{2-x}Me_xO_4$. *J. Chil. Chem. Soc.*, 2005, **50**, 617–623.

[7]. Srinivasan, G. and Seehra, M. S., Magnetic properties of Mn_3O_4 and a solution of the canted-spin problem. *Phys. Rev. B*, 1983, **28**, 1–7.

[8]. Shen, Y., Nakayama, T., Arai, M., Yanagisawa, O. and Izumi, M., Magnetic phase transition and physical properties of spinel-type nickel manganese oxide. *J. Phys. Chem. Solids*, 2002, **63**, 947–950.

[9]. Herpin, A., *Théorie du Magnetism*. Presses Universitaires de France, Paris, 1968, pp. 630–635.

[10]. Ma, Y., Bahout, M., Peña, O., Duran, P. and Moure, C., Magnetic properties of $(Co,Ni,Mn)_3O_4$ spinels. *Bol. Soc. Esp. Ceram. Vidrio*, 2004, **43**, 663–667.