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Synthesis, Composition, and Magnetic Properties of the Ferrimagnetic $NdCu_{3-x}Mn_{4+x}O_{12}$ Perovskite-like Phases

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A magnetic oxide with composition close of $NdCu_3Mn_4O_{12}$ with a perovskite-related cubic structure ($a \simeq 7.30$ Å, space group $Im3$, $Z = 2$) has been synthesized by using either the high-pressure or the hydrothermal technique. The composition is strongly dependent on the synthesis conditions. A partial reduction of Mn^{4+} in the octahedral sites, resulting in a partial substitution of Cu^{2+} by Mn^{3+} in the Jahn–Teller sites, leads to the actual formula $Nd(Cu^{2+}_{3-x}Mn^{3+}_{x})(Mn^{4+}_{3-x}Mn^{3+}_{1+x})O_{12}$. For the compound synthesized at 650°C/2 kbar, the value of the substitution parameter x, as determined by neutron diffraction, is 0.32. For samples synthesized at higher temperatures, larger values of x are obtained. The compound is ferrimagnetic with Néel temperature of 390 K and a spontaneous magnetization of 93 emu/g at 4 K (52 emu/g at room temperature). For larger x values, magnetizations up to 118 emu/g at 4 K are obtained.

1. Introduction

The $[AC_3]B_4O_{12}$ compounds have a perovskite-like arrangement with a cubic cell parameter $a \simeq 7,30$ Å (space group $Im3$, $Z = 2$), which is twice the parameter of the simple ABO_3 perovskite structure. The doubling of the cell is due to an ordered arrangement of A and C cations, resulting in a tilting of the BO_6 octahedra tridimensional network. This tilting (~20°) gives rise to an important distorsion of $\frac{3}{4}$ of the 12-coordinated sites of the ideal perovskite structure: the C cations in the $[AC_3]B_4O_{12}$ compounds are surrounded by four oxygen nearest neighbors forming a square. This type of coordination is perfectly adapted to Jahn–Teller cations such as Cu^{2+} or Mn^{3+} (high spin). Consequently, two series of compounds ($C = Cu^{2+}$ or Mn^{3+}) have been prepared so far (*1–10*). The slightly distorted icosahedra of the A sites can be occupied by various cations of large ionic radius (or even be empty (*11*)) such as Sr^{2+}, Ca^{2+}, Y^{3+}, R^{3+} (lanthanides) the B cations ensuring the electrostatic equilibrium.

The existence of solid solutions between the two series has already been reported in the system $CaCu_3Mn_4O_{12}$–$CaMn_7O_{12}$ (*12, 14*). In the present article we examine the possibility of synthesizing solid solutions with the general formula $R(Cu^{2+}_{3-x}Mn^{3+}_{x})(Mn^{4+}_{3-x}Mn^{3+}_{1+x})O_{12}$. A systematic research of the synthesis conditions has been under-

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taken in order to study the influence of the rare earth and of the Cu and Mn concentration on the magnetic properties of the series. Some preliminary results of the magnetic study are presented here.

2. Synthesis Experiments

If the octahedral *B* sites are to be occupied by cations with a relatively stable valence state, the synthesis can be performed by firing the stoechiometric mixtures of the components at temperatures close to 1000°C. This is for instance the case for titanium (*11*) or ruthenium compounds (*12*, *13*). For the manganese compounds the use of high-pressure conditions has been proved necessary in order to prevent a complete reduction of Mn^{4+} to Mn^{3+} (*14*).

All the members of the series $RCu_3Mn_4O_{12}$ (R = La to Lu or Y) has been synthesized by high-pressure techniques (*15*). A systematic investigation of the synthesis conditions has been undertaken with the neodymium compound. A series of high-pressure synthesis experiments has been performed in a Belt X type apparatus by firing the corresponding oxides (MnO_2 for Mn) in the temperature–pressure range 700 to 1200°C and 20 to 80 kbar. In hydrothermal synthesis, starting with the corresponding oxides in stoechiometric proportions, various solvents such as H_2O, HCl, HNO_3, and $HClO_3$ have been tried. The synthesis, performed at 600°C and pressures between 1 and 2 kbar in a sealed gold tube, gives the compound a rather poor yield. The best yields (15–20%) have been obtained with $HClO_3$ and with HNO_3 solutions of $pH < 4$. The most important impurities were the spinel $CuMn_2O_4$ and the starting oxides CuO and MnO_2.

The above observations are indicative of (a) an insufficient protection of the valence state Mn^{4+} against reduction, (b) a poor solubility of the oxides, and (c) the importance of an acid environment. Starting materials such as $NdCl_3$, $CuSO_4 \cdot 5H_2O$ or $CuCl_2$, and $KMnO_4$ have then been utilized in various proportions. In this highly oxidizing environment due to the reduction of Mn^{7+} to Mn^{4+} and Mn^{3+}, yields as high as 70% have been obtained. The solvent was distilled water, the dissolved SO_4^{2-} anions ensuring the necessary acidity. It has been found that the composition of the starting mixture can vary between large limits without any influence on the yield; nevertheless an excess of $CuSO_4 \cdot 5H_2O$ has proved to be necessary.

The temperature and pressure conditions have a drastic influence on the yield and on the crystallization as well. The best results have been obtained for temperatures T = 600 to 750°C, the latter giving a product formed of small crystals (~1/100 mm). The pressure, related to temperature, must be higher than 1,2 kbar for the top of the temperature range, whereas at 500°C a pressure of 800 bar is sufficient.

3. X-Ray Characterization

The reaction products have been magnetically separated, purified by repeated washings in oxalic acid and ammonium chloride, and examined by X rays. The diffractograms performed on a Guinier focusing camera with the Fe$K\alpha$ radiation have been indexed in a *bcc* cell. An internal standard of Si powder was incorporated in order to eliminate possible errors due to origin imprecision. The refined cell parameters of the samples prepared under various temperature–pressure conditions, by using either the high pressure or the hydrothermal technique, are presented in Table I.

As can be seen, the cell parameters are largely dependent on synthesis conditions, indicating a variation of the chemical formula of the products. As a matter of fact, solid solutions with formula $R(Cu^{2+}_{3-x}Mn^{3+}_{x})(Mn^{4+}_{3-x}Mn^{3+}_{1+x})O_{12}$ could be formed by an excessive reduction of Mn^{4+}, owing to the

TABLE I

SYNTHESIS CONDITIONS AND CUBIC CELL PARAMETERS OF $NdCu_{3-x}Mn_{4+x}O_{12}$ PHASES PREPARED BY THE HIGH-PRESSURE (HP) AND HYDROTHERMAL (HS) TECHNIQUE

Technique	*T* (°C)	*P* (kbar)	Cell parameter in Å (±0.001)
HS	500	1	7.293
HS	500	1	7.292[a] 7.327
HS	600	1,5	7.310
HS	600	1	7.296
HS	650	1,5	7.292
HS	650	1,2	7.309
HS	650	2	7.296[b]
HS	650	1,5	7.306
HS	700	1,3	7.304
HS	700	1,2	7.302
HS	700	1,5	7.300
HS	750	2	7.298
HP	700	60	7.306
HP	800	40	7.351
HP	800	80	7.339
HP	900	20	7.373
HP	1000	80	7.340
HP	1200	50	7.341

[a] Quadratic cell; the second parameter is *c*.

[b] Sample studied by neutron diffraction.

ability of Mn^{3+} to occupy the Jahn–Teller *C* sites. The cell parameter of such solid solutions must strongly depend on the substitution parameter x, due to the large difference in ionic radii of Mn^{4+} and Mn^{3+} (*16*).

4. Neutron Diffraction Study

The powder sample intended to neutron diffraction has been prepared by hydrothermal synthesis at 650°C and 2 kbar in a 60-cm^3 autoclave protected by a gold sleeve. The pressure was applied at room temperature and maintained at his value during the temperature rise. The cubic cell parameter measured by X rays was $a = 7{,}296(1)$ Å. The neutron diffraction diagram has been recorded at 523 K (in the paramagnetic region) at the ILL high flux reactor in Grenoble by means of a two-circle spectrometer working at a wavelength $\lambda = 1.618$ Å, in 2θ-scanning, by steps of 5/100°.

As it has been already stated above, an amount of Mn^{3+} is probably contained in the *C*-sites besides Cu^{2+}. The occupancy of these sites cannot be determined by X-ray diffraction because the difference of form factors of Cu^{2+} and Mn^{3+} is less than 4 electrons. On the contrary, neutron diffraction can provide a check of this occupancy because the coherent neutron scattering amplitudes for Cu and Mn are very different: $b(\mathrm{Cu}) = +0{,}76 \times 10^{-12}$ cm, $b(\mathrm{Mn}) = -0{,}387 \times 10^{-12}$ cm (*17*).

The measured intensities have been corrected by Lorentz polarization. As a first approximation it was assumed that the composition of the sample corresponded to $NdCu_3Mn_4O_{12}$. Therefore, six Cu atoms were placed in the 6*b* $(0, \frac{1}{2}, \frac{1}{2})$ position (*C* sites) of the *Im*3 space group and eight Mn in the 8*c* $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ position. For the oxygens in 24*g* (*xy*0) the parameters found in $CaCu_3Mn_4O_{12}$ (3) were used as initial values. The refinement of (a) the positional parameters for the oxygens, (b) the Fermi lengths of atoms in 6*b*, and (c) the isotropic thermal factors was carried out by means of the AFISTR program (*18*). The *R* and *wR* factors were 0,027 and 0,023, respectively. The final values of the parameters are reported in Table II. A comparison between observed and calculated intensities is shown in Table III.

TABLE II

POSITIONAL, FORM FACTOR, AND THERMAL PARAMETERS OF $Nd(Cu_{2.68}Mn_{0.32})Mn_4O_{12}$

	Nd	Cu,Mn	Mn	O
Position (*Im*3)	2*a*	6*b*	8*c*	24*g*
x	0	0	0.25	0.2998(9)
y	0	0.5	0.25	0.1805(8)
z	0	0.5	0.25	0
Fermi length (10^{-12} cm)	0.72	0.636(10)	−0.387	0.577
B ($Å^2$)	0.9(3)	2.0(3)	2.0(3)	2.2(3)

TABLE III

COMPARISON BETWEEN OBSERVED AND CALCULATED NUCLEAR NEUTRON DIFFRACTION INTENSITIES IN $Nd(Cu_{2,68}Mn_{0,32})Mn_4O_{12}$

hkl	I_{obs}	I_{calc}
110	0.2	0.04
200	57.0	61.4
211	5.5	6.8
220	9.7	10.9
310	198.2	197.1
222	441.2	440.4
321	240.2	239.6
400	75.4	74.1
411 330	325.9	402.9
420	153.2	156.0
332	122.0	182.9
422	975.3	918.7
510 431	35.8	39.8

The determined Fermi length for the atoms in 6*b* positions gives the substitution parameter x of Cu atoms replaced by Mn in these sites $x = 0{,}32 \pm 0{,}04$ (a proportion of 11%) and confirms the formation of the solid solutions stated above, in accordance with the observed cell dependence on synthesis conditions. As a matter of fact, a rise in the synthesis temperature favors the reduction of Mn^{4+} to Mn^{3+} and yields a product richer in Mn^{3+} having a larger cell.

The alternative assumption compatible with the observed cell's rise, namely a partial substitution of Cu by Nd atoms, cannot be retained: a Fermi length smaller than that of Nd could not be observed in this case. On the other hand, the higher values of spontaneous magnetization observed for samples with larger cells (Section 5) clearly indicates that the Cu^{2+} ions have been replaced by ions of higher atomic moment, such as Mn^{3+}.

A speculated inverse influence of the pressure on the cell's size, namely its reduction with increasing synthesis pressure, probably masked by that of the temperature, has not been possible to have it unambiguously proved.

5. Magnetic Properties of the $Nd(Cu_{2,68}Mn_{0,32})Mn_4O_{12}$ Phase

The magnetic susceptibility of the sample whose chemical formula was determined by neutron diffraction has been measured by means of a vertical translation Faraday balance in the temperature range 300–800 K. The reciprocal susceptibility vs temperature curve (Fig. 1) shows a hyperbolic behavior, typical of a ferrimagnetic compound above the transition temperature ($T_N = 390$ K). Due to the absence of linear part in the $1/\chi(T)$ curve, no Curie constant has been determined.

The magnetization measurements have been performed by means of a vibrating-sample magnetometer in magnetic fields up to 50 kOe down to liquid-helium temperature. Some isotherm $\sigma(H)$ curves are given in Fig. 2; they can be represented by a law $\sigma = \sigma_0 + \chi H$. The spontaneous magnetization is 93 emu/g (12,4 μ_B/f.u.) at 4 K and 52

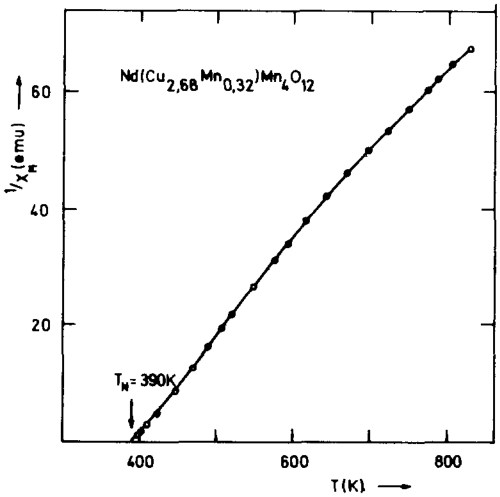

FIG. 1. Reciprocal susceptibility vs temperature.

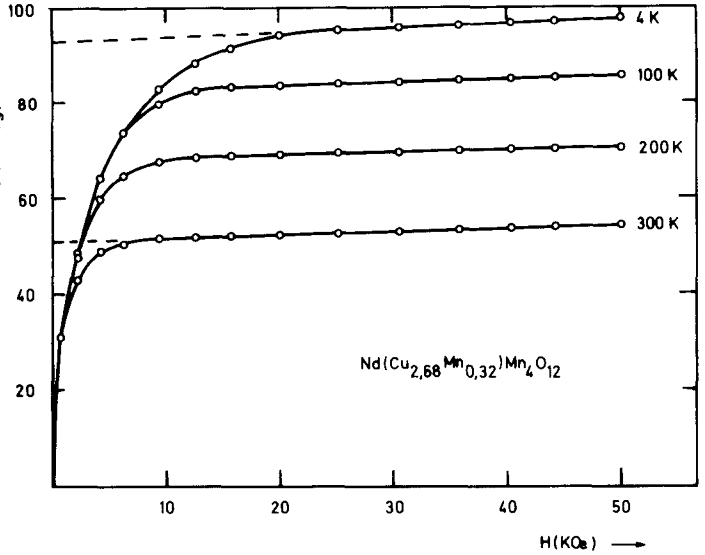

FIG. 2. Isothermal $\sigma(H)$ curves at different temperatures.

emu/g at room temperature. For samples with larger cell parameters and so presumably richer in Mn^{3+}, larger values of spontaneous magnetization up to 118 emu/g at 4 K have been found (for comparison, in YIG, $\sigma_0 = 28{,}5$ emu/g at 4 K). The important superimposed susceptibility ($\chi = 7 \times 10^{-5}$ emu/g at 4 K) indicates a paramagnetic behavior of the neodymium sublattice. A hypothetic umbrella-like noncollinear ferrimagnetic structure of the Cu and Mn sublattices, as it has been observed, for example, in $CaCu_3Mn_4O_{12}$ (*14*) cannot give alone a satisfactory explanation for such a large value of the susceptibility (for comparison, $\chi = 15 \times 10^{-6}$ emu/g at 4 K in $CaCu_3Mn_4O_{12}$).

The thermal variation of the spontaneous magnetization is represented in Fig. 3. The increase of magnetization at 60 K must be attributed to the positive polarisation of the Nd sublattice by the molecular field of the ordered Cu and Mn sublattices. A similar behavior, but with a negative polarization, has been observed at 80 K for the compound $HoCu_3Mn_4O_{12}$ (*15*). This is not an unexpected result since the exchange interaction between the transition element sublattice and the rare earth one is proportional to the quantity $(g - 1)/g$, which has opposite signs for Nd^{3+} and Ho^{3+}.

The number of magnetic sublattices and the complex chemical formula of the sam-

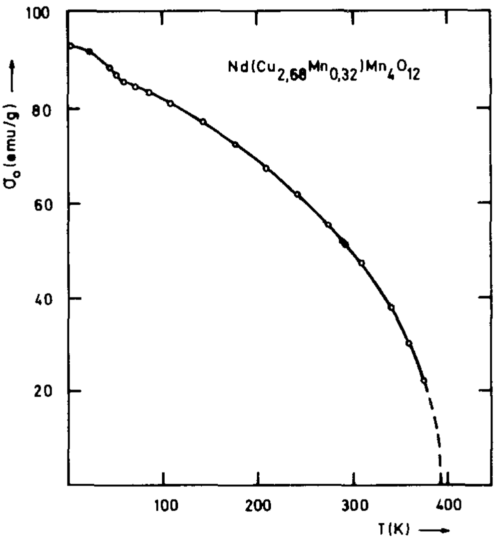

FIG. 3. Thermal variation of the spontaneous magnetization.

ple do not allow an identification of the magnetic structures' model by simple magnetic measurements. The magnetic structure is actually being studied by neutron diffraction.

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