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Nd_2BaCuO_5-Type Structure: Nickel in Square Planar Coordination and Copper Mixed Valency

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The new mixed-valence phases of copper and nickel $Nd_{2-x}A_xBaCu_{1-y}Ni_yO_5$ (A = Ba, Sr, Ca) with the Nd_2BaCuO_5-type structure were isolated. Structure calculations evidence a square planar coordination of nickel. The decrease of the cell volume as the substitution rate Ni/Cu increases is in agreement with the increase of the mean oxidation state of the transition elements in this square coordination. Influence of the Nd(III) ion in magnetic susceptibility is shown in this study. © 1993 Academic Press, Inc.

Introduction

Previous investigations of the system Ln_2O_3–BaO–MO, in which M is a transition element and Ln a rare earth cation, have shown the existence of a large family of oxides Ln_2BaMO_5 (*1–14*). The latter phases exhibit various structures which are closely related to the nature of the M ion and to the size of Ln. In this respect, the neodymium compounds, Nd_2BaCuO_5 (*2, 14*) and Nd_2BaNiO_5 (*11*), are of interest, since in the first one Cu(II) exhibits a square planar coordination (Fig. 1), whereas in the second Ni(II) is octahedrally coordinated (Fig. 2). For this reason it seems to us interesting to investigate mixed systems with similar formulation involving both nickel and copper in the same structure. Moreover, up to now, no mixed-valence oxide Ln_2BaMO_5, involving either Cu(II)–Cu(III) or Ni(II)–Ni(III) couples, has been synthesized. Such a possibility of mixed valency for those compounds is not obvious since the CuO_4 (or NiO_6) polyhedra are isolated from each other, i.e., there is no possibility of electronic delocalization, so that it should lead to the coexistence of localized M(II) and M(III) ions in the same structure. In order to test such an eventuality, Nd(III) has to be replaced by a divalent cation, such as alkaline earth cations. We report, in this study, on new oxides $Nd_{2-x}A_xBaCu_{1-y}Ni_yO_5$, with A = Ca, Sr, Ba with the Nd_2BaCuO_5 structure, i.e., characterized by a square coordination of both nickel and copper, and by a mixed valency of copper and (or) of nickel.

Experimental

Solid solutions of the $Nd_{2-x}A_xBaCu_{1-y}Ni_yO_5$ system for various values of x and y were prepared from the component oxides Nd_2O_3 (calcined at 900°C), $BaCO_3$, ACO_3 (A = Ba, Sr, Ca), CuO, and NiO. The mixtures were heated successively at 900, 1000,

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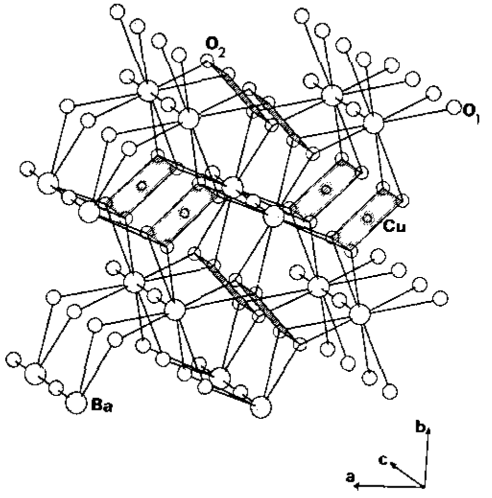

FIG. 1. Square planar coordination of copper in Nd_2BaCuO_5 structure.

and 1100°C for 1 day for each step with intermittent grinding.

The X-ray powder patterns at room temperature were recorded on a conventional Philips diffractometer using CuK_α radiation.

Oxygen stoichiometry of all the pure compounds was determined by hydrogen reduction using a Setaram TAG 24 thermogravimetric analyser.

The magnetic susceptibility was measured with a Faraday balance in the range of temperature 4–850 K with an applied magnetic field of 3000 G.

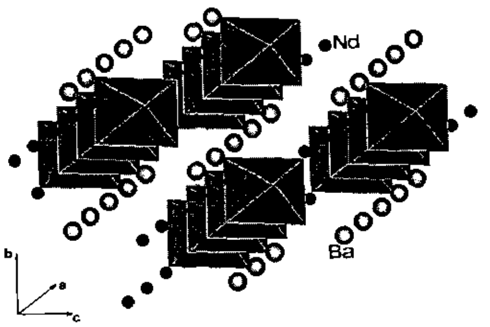

FIG. 2. NiO_6 octahedra chains along the [100] direction in Nd_2BaNiO_5 structure.

Results and Discussion

The Mixed-Valence Copper Oxides $Nd_{2-x}A_xBaCuO_5$

In order to investigate the possibility of stabilization of the mixed-valency Cu(II)–Cu(III) and Ni(II)–Ni(III) in these two structures, the replacement of neodymium by alkaline earth elements was first studied in the two oxides, Nd_2BaCuO_5 and Nd_2BaNiO_5. All the attempts to substitute an alkaline earth *A* element for neodymium in the Nd_2BaNiO_5 structure failed, whatever the nature of *A*, calcium, strontium, or barium, and whatever the experimental conditions. On the contrary, in the case of the copper oxide, three solid solutions were isolated; their formulation $Nd_{2-x}A_xBaCuO_5$, corresponding to the "O_5" stoichiometry, with the mixed valency Cu(II)–Cu(III) which was confirmed by the microthermogravimetric determination of the oxygen content by hydrogen reduction (Table I). The homogeneity range of these phases depends on the size of the *A* cation. One observes a larger domain for strontium, i.e., $0 \leq x \leq 0.40$, whose size is intermediate and is similar to that of neodymium, between those of barium and calcium, for which, $0 \leq x \leq 0.20$ and $0 \leq x \leq 0.30$, respectively.

The X-ray diffractograms of these phrases show that they are isotypic with Nd_2BaCuO_5 and consequently they could be indexed in a tetragonal cell whose parameters are given in Table I. These results show that in each series, barium and calcium cuprates, the cell volume increases and decreases respectively as the alkaline earth content increases in agreement with the size of these cations. In the strontium series, "*a*" increases, whereas "*c*" decreases as the strontium content increases, the cell volume increasing in agreement with the larger size of strontium compared to neodymium. It is worth pointing out that strontium cuprates exhibit a smaller *c* parameter than the calcium phases for the same *A* content, the cell volume be-

TABLE I

$Nd_{2-x}A_xBaCuO_5$: PARAMETERS OF THE TETRAGONAL CELL

	a (Å)	c (Å)	V (Å^3)	Oxygen content ±0.01	A
$x = 0$	6.6950(4)	5.8190(5)	260.82	5.00	Nd
$x = 0.1$	6.6947(5)	5.8128(5)	260.52	4.98	Ca
	6.6990(8)	5.8125(9)	260.85	5.00	Sr
	6.7032(6)	5.8116(6)	261.03	5.00	Ba
$x = 0.2$	6.6921(6)	5.8071(5)	260.07	4.99	Ca
	6.7065(5)	5.8034(7)	261.02	4.99	Sr
	6.7057(3)	5.8140(4)	261.43	5.00	Ba
$x = 0.3$	6.6884(6)	5.8033(6)	259.61	5.00	Ca
	6.7113(5)	5.7999(5)	261.47	5.00	Sr
$x = 0.4$	6.7226(5)	5.7932(5)	261.81	5.02	Sr

ing larger, in agreement with the relative size of these two cations.

Structural calculations of the most substituted phase $Nd_{1.6}Sr_{0.4}BaCuO_5$ was performed from powder X-ray data, using the Rietveld program, in the space group *P4/mbm*. The refinements of the variable parameters; atomic positions, isotropic thermal factors, and occupancy factor of every site, made in the first 80 *hkl* lead to reliability factor $R_I = 0.061$ (Table II). These calculations show that all of the sites are fully occupied, they confirm the "O_5" stoichiometry of this phase determined by hydrogen reduction. One observes that the replacement of Nd(III) by Sr(II) leads to a smaller Cu–O distance (Table VI), in agreement with the increase of oxidation state of copper.

Substitution of Nickel for Copper: The Oxides $Nd_{2-x}A_xBaCu_{1-y}Ni_yO_5$

The study of the system Nd_2BaCuO_5–Nd_2BaNiO_5 ($x = 0$) did not allow any pure phase, $Nd_2BaCu_{1-y}Ni_yO_5$, to be isolated. One always observes a mixture of the two limit phases, Nd_2BaCuO_5 and Nd_2BaNiO_5. The fact that Cu(II) does not enter the Nd_2BaNiO_5 structure can easily be explained by the flattened character of the NiO_6 octahedra, whereas Cu(II) in oxides tends to exhibit elongated CuO_6 octahedra. To the contrary, Ni(II), owing to its d^8 con-

TABLE II

STRUCTURAL DATA OF $Nd_{1.6}Sr_{0.4}BaCuO_5$ PHASE AFTER REFINEMENT, SG = *P4/mbm*, $Z = 2$

Atom	Site	x	y	z	B (Å^2)
Ba	2(*b*)	0.5	0.5	0.5	0.1(1)
Nd, Sr	4(*g*)	0.1737(1)	0.6737(1)	0.0	−0.3(1)
Cu	2(*c*)	0.5	0.0	0.5	0.2(1)
O(1)	2(*a*)	0.0	0.0	0.0	1.0(2)
O(2)	8(*k*)	0.3686(15)	0.8686(15)	0.2623(0.20)	0.3(2)

TABLE III

THE Ni-SUBSTITUTED OXIDES $Nd_{2-x}A_xBaCu_{1-y}Ni_yO_5$: HOMOGENEITY RANGE

A	$x = 0.1$	$x = 0.2$	$x = 0.3$	$x = 0.4$
Ba	$0 \leq y \leq 0.4$	$0 \leq y \leq 0.5$		
Sr	$0 \leq y \leq 0.4$	$0 \leq y \leq 0.4$	$0 \leq y \leq 0.4$	$0 \leq y \leq 0.4$
Ca	$0 \leq y \leq 0.4$	$0 \leq y \leq 0.4$	$0 \leq y \leq 0.4$	

figuration, seems to be compatible with a square planar coordination, so that the formation of a Nd_2BaCuO_5-type structure involving nickel should be possible.

When alkaline earth is introduced on the Nd-sites, with $x \geq 0.1$, nickel can be substituted for copper in a wide range as shown from Table III. Indeed, calcium and strontium phases can contain up to 40% ($y = 0.4$) of nickel on the copper sites, whatever the A content ranging from $x = 0$ to $x = 0.30$ and from $x = 0$ to $x = 0.40$, respectively. In the case of barium cuprates, up to 50% of copper can be replaced by nickel for the series $Nd_{1.80}Ba_{0.20}Cu_{1-y}Ni_yO_5$ ($x = 0.20$). The oxygen content of these phases are very close to the stoichiometric value "O_5." The evolution of the cell parameters (Table IV), shows that for a given content x of the A element, the c parameter of the tetragonal cell decreases significantly as the nickel content increases, whereas the a parameter remains approximately constant. Note also that the influence of the size of the A elements on the cell parameters is weaker than the influence of substitution rate Ni/Cu. This decrease of the cell volume with increase in y is in agreement with the increase of the mean oxidation state of the transition elements in square planar coordination, i.e., with the increase either of the ratio Cu(III)/Cu(II) or of the ratio Ni(III)/Ni(II). However, it is not possible to tell which of these two redox couples is predominant in the structure, considering the equilibrium Ni(II) + Cu(III) ↔ Ni(III) + Cu(II).

In order to verify that the structure of these nickel-substituted phases belong to the Nd_2BaCuO_5-type structure, the structure of the nickel-rich compound, $Nd_{1.80}Ca_{0.20}BaCu_{0.6}Ni_{0.4}O_5$, was determined from powder X-ray data in the space group $P4/$

TABLE IV

Ni-SUBSTITUTED OXIDES $Nd_{2-x}A_xBaCu_{1-y}Ni_yO_5$: TETRAGONAL CELL PARAMETERS

		$x = 0.20$			$x = 0.30$			$x = 0.40$		
A		a (Å)	c (Å)	V (Å³)	a (Å)	c (Å)	V (Å³)	a (Å)	c (Å)	V (Å³)
Ba	$y = 0.30$	6.7007(3)	5.7779(6)	259.42						
	$y = 0.50$	6.7062(2)	5.7623(3)	259.15						
Sr	$y = 0.20$	6.7067(10)	5.7871(10)	260.30	6.7154(7)	5.7758(7)	260.47	6.7217(6)	5.7720(6)	260.79
	$y = 0.40$	6.7055(5)	5.7614(5)	259.05	6.7136(6)	5.7638(6)	259.80	6.7194(6)	5.7551(6)	259.84
Ca	$y = 0.20$	6.6907(6)	5.7829(7)	258.87	6.6944(6)	5.7855(5)	259.28			
	$y = 0.40$	6.6909(4)	5.7601(4)	257.87	6.6831(5)	5.7501(10)	256.82			

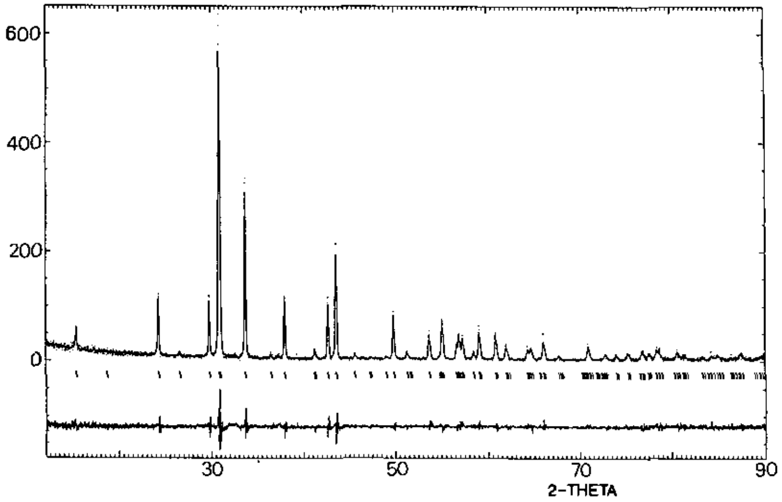

FIG. 3. Observed, calculated, and difference plot for $Nd_{1.8}Ca_{0.2}BaCu_{0.6}Ni_{0.4}O_5$ compound after refinement with Rietveld program.

mbm, from 72 reflections (Fig. 3). Ca^{2+} and Nd^{3+} were statistically distributed on the 4(*g*) sites, whereas copper and nickel were located on the 2(*c*) sites. After several cycles, the reliability factor calculated on the intensities was lowered to $R_I = 0.048$ for the atomic positions and thermal factors given in Table V. These atomic positions are close to those observed for Nd_2BaCuO_5 (*14*), confirming that copper and nickel sit in square planar coordination (Fig. 1). One observes that the Ba–O distances are slightly smaller in the nickel-substituted phases (Table VI), whereas the tricapped trigonal prism (Nd, Ca)O_8 exhibits a distortion different from that of the NdO_8 one in Nd_2BaCuO_5.

Magnetic Measurements

The magnetic susceptibility measurements performed in the range 4–850 K show a continuous evolution of the susceptibility versus temperature. Such a behavior is shown on Figs. 4 and 5 for the oxides $Nd_{2-x}Ca_xBaCu_{0.6}Ni_{0.4}O_5$ and $Nd_{2-x}Sr_xBaCuO_5$ respectively. The Curie–Weiss law is not observed. Consequently, the content of each species, Ni(II), Ni(III), Cu(II), Cu(III) cannot be determined in these phases. This particular behavior can be explained by the fact that the MO_4 groups are isolated one from the other, but they are connected by the paramagnetic ions Nd(III), which insure the magnetic coupling between copper and

TABLE V

ATOMIC PARAMETERS OF $Nd_{1.8}Ca_{0.2}BaCu_{0.6}Ni_{0.4}O_5$ COMPOUND AFTER REFINEMENT: SG = *P4/mbm*, *Z* = 2

Atom	Site	*x*	*y*	*z*	*B* (Å^2)
Ba	2(*b*)	0.5	0.5	0.5	1.0(1)
Nd, Ca	4(*g*)	0.1740(3)	0.6740(3)	0.0	0.4(1)
Cu, Ni	2(*c*)	0.5	0.0	0.5	1.1(3)
O(1)	2(*a*)	0.0	0.0	0.0	1.4(4)
O(2)	8(*k*)	0.3593(10)	0.8593(10)	0.2674(14)	1.4(4)

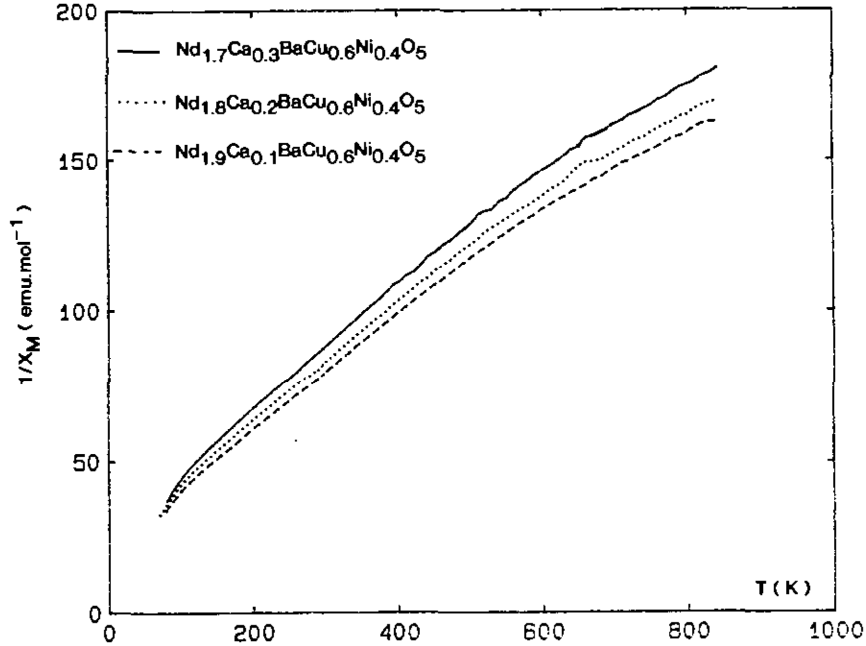

FIG. 4. Reciprocal molar magnetic susceptibility vs temperature of $Nd_{2-x}Ca_xBaCu_{0.6}Ni_{0.4}O_5$ oxides.

nickel through the O(2) oxygen atoms. Such a hypothesis implies that the Nd(III) content should influence the magnetic susceptibility of these phases. The decreasing susceptibility as x increases for a fixed molar ratio Ni/Cu (Fig. 4) supports this viewpoint. On the contrary, the influence of the Ni/Cu ratio on the magnetic susceptibility is weaker than the influence of the Nd(III) content. Consequently, for the given contents of A element (x) and of the substitution rate Ni/Cu (y), one observes the same curve of $1/X_M$ versus temperature, irrespective of the A element (Fig. 6).

Concluding Remarks

The study of the system $Nd_{2-x}A_xBaCu_{1-y}Ni_yO_5$ has shown evidence of large series of mixed valent compounds with the Nd_2BaCuO_5-type structure. As shown in the struc-

TABLE VI

CALCULATED DISTANCES (Å) IN $Nd_{1.8}Ca_{0.2}BaCu_{0.6}Ni_{0.4}O_5$, $Nd_{1.6}Sr_{0.4}BaCuO_5$, AND Nd_2BaCuO_5 (14) COMPOUNDS, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

M–O	$Nd_{1.8}Ca_{0.2}BaCu_{0.6}Ni_{0.4}O_5$	Nd_2BaCuO_5	$Nd_{1.6}Sr_{0.4}BaCuO_5$
Ba–$O_{(1)}$	2.880 (≤1) × 2	2.909(1) × 2	2.898(1) × 2
Ba–$O_{(2)}$	2.909(13) × 8	2.990(3) × 8	2.971(9) × 8
Nd, (Ca, Sr)–$O_{(1)}$	2.473(2) × 2	2.476(3) × 2	2.486(2) × 2
Nd, (Ca, Sr)–$O_{(2)}$	2.334(13) × 2	2.370(3) × 2	2.397(10) × 2
Nd, (Ca, Sr)–$O_{(2)}$	2.618(13) × 4	2.530(3) × 4	2.569(11) × 4
Cu, Ni–$O_{(2)}$	1.889(13) × 4	1.900(3) × 4	1.860(10) × 4

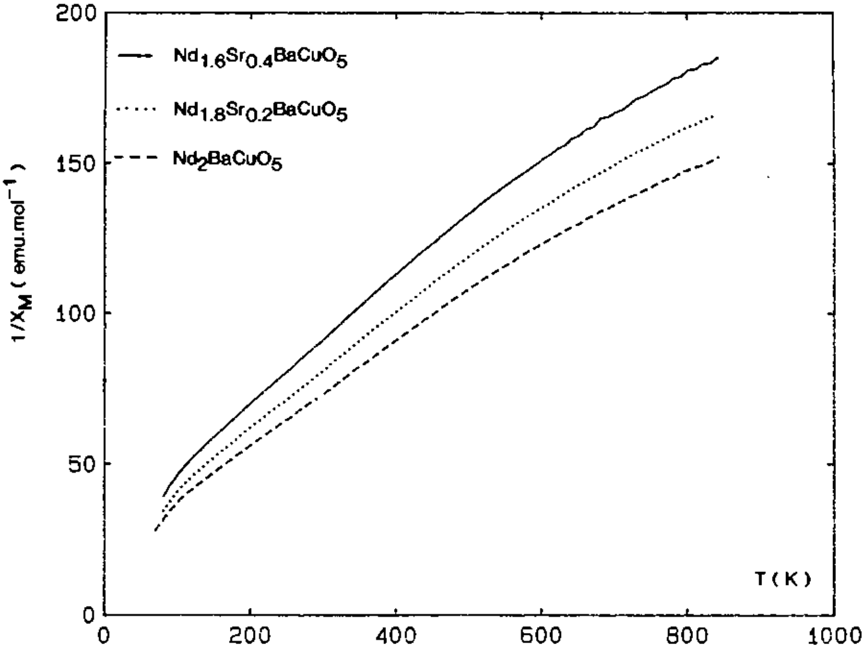

FIG. 5. Reciprocal molar magnetic susceptibility vs temperature of $Nd_{2-x}Sr_xBaCuO_5$ oxides.

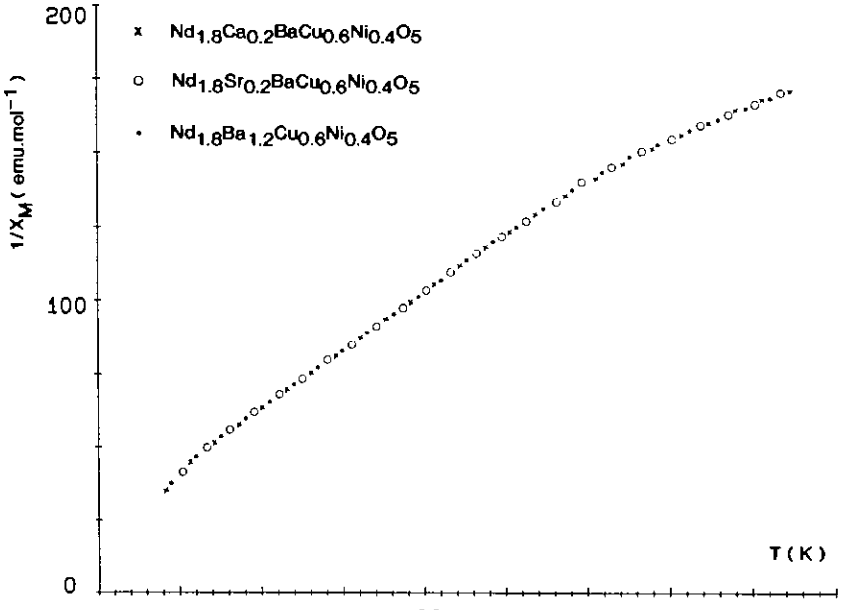

FIG. 6. Evolution of $1/X_M$ vs temperature of three compounds: $Nd_{1.8}A_{0.2}BaCu_{0.6}Ni_{0.4}O_5$ (A = Ba, Sr, Ca); we observe that they are superimposed.

tural calculations, nickel ion is stabilized in an square planar environment.

The susceptibility measurements of these phases confirm that the magnetic interactions in this structure are insured by Nd(III) ions.

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