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BRIEF COMMUNICATION

Phase Relations of the Nd_2O_3–Pr_6O_{11}–CuO Ternary System

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The subsolidus phase relations of the Nd_2O_3–Pr_6O_{11}–CuO ternary system sintered in air at 950°C have been investigated by X-ray powder diffraction. The system can be divided into one ternary phase region and three binary phase regions. The solid solution $Nd_{2-x}Pr_xCuO_{4-\delta}$ has been observed to exist over the composition region $0 < x < 2$. The solid solution has a tetragonal structure, and its lattice parameters increase linearly with the increasing of the praseodymium content. © 1995 Academic Press, Inc.

I. INTRODUCTION

Due to the important theoretical and practical interest of the discovery of *n*-type superconductors (1, 2), studies on the structure and properties of compounds Nd_2CuO_4 and Pr_2CuO_4, which are parent compounds of the *n*-type superconductors $[Ln_{1-x}Ce_x]_2CuO_4$(*Ln* = Nd, Pr, Sm) (1), have been stimulated extensively (3, 4). In the Ln_2CuO_4 family (*Ln* = rare earth), three types of crystal structures have been found. These are referred to as the T-, T′-, and T*-phases. The crystal structure of La_2CuO_4 is known as the T-phase. In this structure a Cu atom is octahedrally surrounded by six oxygen atoms. When La is replaced by Nd (or Pr, Sm, Gd, Eu), the structure changes to the so-called T′-phase; the apex oxygen atoms of the T-phase move to the faces of the tetragonal cell but the two-dimensional CuO_2 planes remains intact. $LaNdCuO_4$ forms the T*-phase, in which the Cu atoms have pyramidal coordination by oxygens.

It is well known that knowledge of phase relations is a precondition for improving materials and processing. Experiments show that superconductivity in rare earth cuprates depends on sample preparation. Thus knowledge of phase relations is helpful for improving superconducting materials. To date, the phase relations in the systems R_2O_3–BaO–CuO (*R* = Y, La, Pr, Nd, Sm, Eu, Gd, Er, Ho, Tm, Yb) (5–9), La_2O_3–SrO–CuO (10), Nd_2O_3–CeO_2–CuO (11), and Nd_2O_3–SrO–CuO (12) have been studied.

Pieczulewski *et al.* (11) investigated the phase relations in the Nd_2O_3–CeO_2–CuO ternary system. The 1000°C subsolidus phase diagram for the $NdO_{1.5}$–CeO_2–CuO system in air was determined. The solid solution $Nd_{2-x}Ce_xCuO_4$ was found to be the only ternary phase, and the terminal solid solubility was confirmed to be $x = 0.2$. A binary $(1-y)\,CeO_2$–$yNdO_{1.5}$ solid solution was detected to exist with $y = 0.4$. Oka and Unoki (13) determined the phase diagram of the Nd_2O_3–CuO system. Nd_2CuO_4 is the only binary phase, and melts incongruently at about 1240°C. The eutectic point of this system is located at 1040°C with 7 mol% Nd_2O_3.

The present work investigates subsolidus phase relations in the Nd_2O_3–Pr_6O_{11}–CuO ternary system.

II. EXPERIMENTAL PROCEDURE

2.1. Preparation of the Samples

A series of Nd_2O_3–Pr_6O_{11}–CuO samples with different compositions were prepared by firing stoichiometric mixtures of Nd_2O_3 (99.9%), Pr_6O_{11} (99.5%) and CuO (99.95%). The raw oxides powders were heated 3 hr at 800°C, before being weighed. The weighed powders were thoroughly mixed, ground, and fired for 12 hr at 950°C in air, then pressed into pellets with diameter 10 mm and thickness about 2 mm. These pellets were sintered at 950°C for 72 hr in air. If it was necessary, the samples were sintered again several times after being intermittently ground and repelletized. The sintering procedures were stopped when the phase compositions of the samples had no more changes. Thirty-seven samples with different compositions were prepared and sintered (see Table 1).

2.2. X-Ray Powder Diffraction

Phase identifications were carried out using a Guinier–de Wolff monochromatic focusing transmission camera or a Rigaku automatic diffractometer using Cu$K\alpha$

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TABLE 1
Composition and Their X-Ray Diffraction Analyses

No.	Comp. (mol%) Nd	Pr	Cu	XRD analysis	No.	Comp. (mol%) Nd	Pr	Cu	XRD analysis
1	66.7	33.3	0	S–A S–B	20	30	50	20	S–B S–214(ss) W–A
2	50	50	0	S–A S–B	21	32	48	20	S–B S–214(ss) W–A
3	33.3	66.7	0	S–A S–B	22	34	46	20	S–214(ss) S–B W–A
4	30	60	10	S–B S–214(ss) W–A	23	36	44	20	S–214(ss) S–B W–A
5	14	60	26	S–B S–214(ss)	24	50	30	20	S–214(ss) S–A M–B
6	40	40	20	S–214(ss) S–B M–A	25	64	16	20	S–214(ss) S–A W–B
7	60	30	10	S–A M–214(ss) M–B	26	66	14	20	S–214(ss) S–A W–B
8	60	14	26	S–214(ss) M–B	27	68	12	20	S–214(ss) S–A W–B
9	10	10	80	S–C S–214(ss)	28	70	10	20	S–214(ss) S–A
10	10	40	50	S–214(ss) M–C	29	72	8	20	S–214(ss) S–A
11	40	10	50	S–214(ss) M–C	30	56.7	10.0	33.3	S–214(ss)
12	0	66.7	33.3	S–214	31	50.0	16.7	33.3	S–214(ss)
13	66.7	0	33.3	S–214	32	43.3	23.3	33.3	S–214(ss)
14	5	95	0	S–B W–A	33	33.3	33.3	33.3	S–214(ss)
15	10	90	0	S–B W–A	34	23.3	43.3	33.3	S–214(ss)
16	20	60	20	S–B S–214(ss)	35	16.7	50.0	33.3	S–214(ss)
17	24	56	20	S–B S–214(ss)	36	10.0	56.7	33.3	S–214(ss)
18	26	54	20	S–B S–214(ss)	37	3.3	63.3	33.3	S–214(ss)
19	28	52	20	S–B S–214(ss)					

Note. *A* is Nd_2O_3, *B* is Pr_6O_{11}, *C* is *CuO*, *214(ss)* is $Nd_{2-x}Pr_xCuO_{4-\delta}$, and *214* is Pr_2CuO_y or Nd_2CuO_4. *S* is strong, *M* is middle, and W is weak.

radiation. High purity Si was added to the samples as an internal standard. Lattice parameters were determined by the least-squares method from film X-ray patterns.

2.3. Oxygen Content Determination

The oxygen content of the $Nd_{2-x}Pr_xCuO_{4-\delta}$ (x = 0.3, 0.5, . . . , 1.9) was determined by iodometric titration (14). Spectral purity CuO was used as a standard to calibrate the concentration of $Na_2S_2O_3$ solution. The measurement error was less than 0.5%.

TABLE 2
The Cell Parameters of the Solid Solution $Nd_{2-x}Pr_xCuO_{4-\delta}$

No.	x	a	c	V
1	0	3.940	12.160	188.76
2	0.3	3.944	12.177	189.47
3	0.5	3.940	12.158	188.70
4	0.7	3.947	12.190	189.94
5	1.0	3.951	12.193	190.37
6	1.3	3.950	12.203	190.36
7	1.5	3.950	12.193	190.20
8	1.7	3.957	12.215	191.23
9	1.9	3.960	12.229	191.76
10	2.0	3.958	12.288	192.50

III. RESULTS AND DISCUSSION

3.1. Binary Subsolidus Relations and Compounds

One compound, Nd_2CuO_4, is identified in the Nd_2O_3–CuO binary system. It crystallizes in a tetragonal unit cell, *I4/mmm*, with Cu–O squares, the so-called T′ phase. Its lattice parameters are $a = b = 3.940$ Å, $c = 12.160$ Å. Under the present experimental conditions, $NdCuO_2$, which is stable only under reducing conditions (15), was not synthesized.

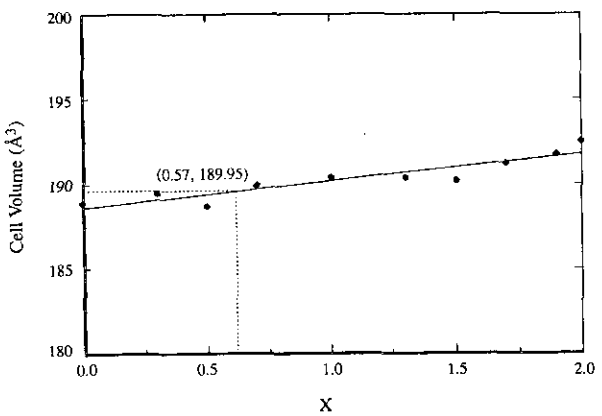

FIG. 1. Dependences of cell volumes on x in solid solution $Nd_{2-x}Pr_xCuO_{4-\delta}$.

One compound, Pr_2CuO_y, was synthesized at 950°C in air, with starting composition is 66.7 mol% $PrO_{11/6}$ and 33.3 mol% CuO. It should be pointed out that when praseodymium oxide is heated, the oxygen content and the valence of the Pr ion change with variation of temperature (16). Pr_2CuO_y crystallizes in a tetragonal unit cell with space group *I4/mmm* as well, and is isomorphous to Nd_2CuO_4. Its lattice parameters are $a = b = 3.958$ Å, $c = 12.288$ Å.

In all the Nd_2O_3–R_2O_3 (R = Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu) binary systems, considerable solid solubility has been reported (17). In the Nd_2O_3–Pr_6O_{11} system, negligible solid solubility has been observed, and no compounds have been synthesized, possibly due to the effect of the Pr^{4+} ions.

3.2. Solid Solution $Nd_{2-x}Pr_xCuO_{4-\delta}$(214(ss))

In the Nd_2O_3–Pr_6O_{11}–CuO ternary system, the solid solution $Nd_{2-x}Pr_xCuO_{4-\delta}$ has been observed to exist over the composition region $0 < x < 2$. X-ray powder diffraction patterns show that the solid solution exhibits a Nd_2CuO_4-like structure, and all lines from the X-ray powder diffraction patterns can be indexed with a tetragonal unit cell with space group *I4/mmm*. The lattice parameters of the solid solution are shown in Table 2 and Fig. 1. The lattice parameters increase slowly with increased x. The increase of unit cell volume with Pr content suggests that the valence of Pr in the solid solution is +3, because the effective ionic radius of Nd^{3+} (1.109 Å) is smaller than that of Pr^{3+} (1.126 Å) but larger than that of Pr^{4+} (0.960 Å) (18). Figure 2 shows the variation of oxygen content (4–δ) vs Pr content (x) of the solid solution. The oxygen content is below 4 when the samples are sintered in air.

3.3. Ternary Subsolidus Relations

Based on the results of phase identification and structure determination of the 37 samples (see Table I), the phase relations of the Nd_2O_3–Pr_6O_{11}–CuO ternary system sintered at 950°C in air are shown in Fig. 3. The solid solution $Nd_{2-x}Pr_xCuO_{4-\delta}$ is found to be the only ternary phase in this system. The system can be divided into one ternary compatibility, (I) Pr_6O_{11} + 214(ss) + Nd_2O_3, and three binary compatibilities, (II) 214(ss) + Nd_2O_3, (III) 214(ss) + CuO, and (IV) 214(ss) + Pr_6O_{11}.

The 214(ss) apex of the Pr_6O_{11} + 214(ss) + Nd_2O_3 triangle was determined by careful placement of the tie line connecting the 214(ss) phase with the Pr_6O_{11} (or Nd_2O_3) according to the phase relationships (see Table I). As drawn, the praseodymium content in the 214(ss) apex is $x = 0.57$, expressed as $Nd_{2-x}Pr_xCuO_{4-\delta}$. The X-ray powder diffraction lines of $Nd_{1.43}Pr_{0.57}CuO_{4-\delta}$ were collected and indexed. The lattice parameters are $a = b = 3.946$ Å, $c = 12.199$ Å. The volume of the unit cell is 189.95 Å^3, which agrees very well with Fig. 1.

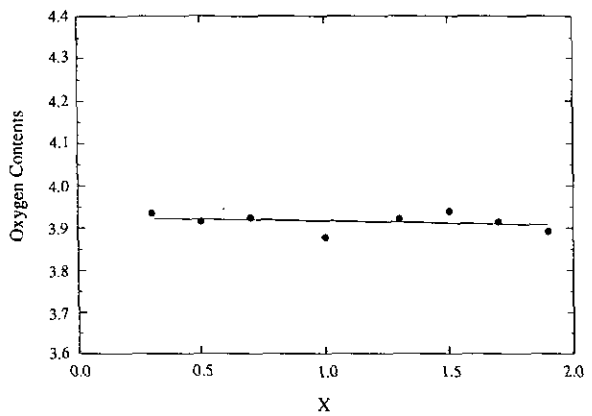

FIG. 2. Variations of oxygen contents (4−δ) vs Pr content (x) of $Nd_{2-x}Pr_xCuO_{4-\delta}$.

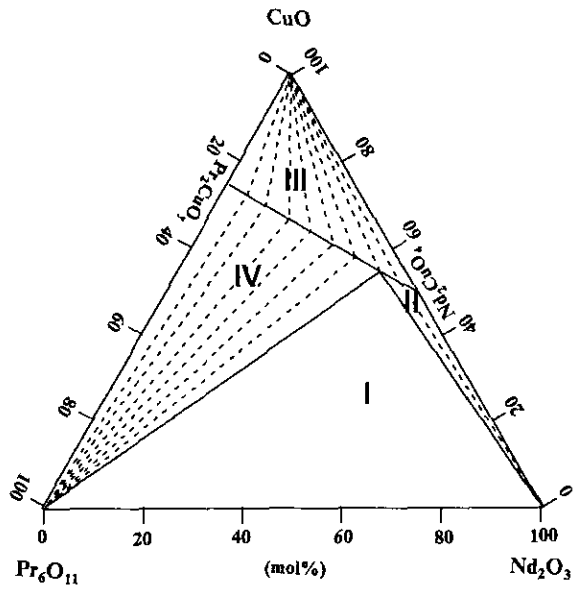

FIG. 3. Subsolidus phase relations in the Nd_2O_3–Pr_6O_{11}–CuO system sintered at 950°C in air.

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