Influence of Cu-site substitution on the structure and superconducting properties of the $NdBa_2Cu_{3-x}M_xO_{7+\delta}$ (M = Fe,Co) and $NdBa_2Cu_{3-x}M_xO_{7-\delta}$ (M = Ni,Zn) systems

T. A. Mary, N. R. S. Kumar, and U. V. Varadaraju

Materials Science Research Centre, Indian Institute of Technology, Madras 600 036, India

The effect of substitution at the Cu site by the transition elements Fe, Co, Ni, and Zn on the structure and superconducting properties of $NdBa_2Cu_3O_7$ has been investigated. Compared to the $YBa_2Cu_{3-x}M_xO_{7+\delta}$ (M = Fe, Co, Ni, Zn) system, considerably high solid solubility and drastic T_c suppression is achieved in the Nd 1:2:3 system. The maximum solid solubilities achieved for the dopants are x = 1.0 for M = Fe and Co and x = 0.8 for M = Ni and Zn. An orthorhombic-to-tetragonal (O→T) transition is observed at x = 0.08 for M = Fe, Co similar to the case of the M-doped Y 1:2:3 system. However, a second T→O transition is observed in Nd 1:2:3 at x = 0.5 for M = Co and x = 0.8 for M = Fe. For the Ni- and Zn-doped phases, an O→T transition is observed at x = 0.4 for M = Ni and x = 0.5 for M = Zn. The doped phases are superconducting up to x = 0.2 (M = Fe, Co, Ni) and x = 0.08 (M = Zn). The initial rate of T_c suppression (up to 3.33 at. %) is ~14 K/at. % for M = Fe, Co, and Ni and ~28 K/at. % for M = Zn and is much higher than that reported for the Y 1:2:3 system. The Fe- and Zn-doped phases, heated in flowing N_2 gas at 800 °C followed by reoxygenation at 450 °C show higher T_c and sharper superconducting transition. Hole doping by Ca substitution (y) at the Nd site in the Zn-doped (x = 0.1) semimetallic-semiconducting Nd 1:2:3 phase induces metallicity and superconductivity for $y \geq 0.1$ and a T_c of 32 K is obtained for y = 0.2.

I. INTRODUCTION

The effect of substitution of transition and nontransition elements at the Cu site on the structural, electrical, and superconducting properties of the Y 1:2:3 material is of great importance for understanding the role of Cu in high-T_c superconductivity. The 1:2:3 structure consists of two crystallographically distinct Cu-O environments, CuO chains, and CuO_2 planes. The Cu in the chains [Cu(1) site] is fourfold oxygen coordinated [2×O(1) along the b axis and 2×O(4) along the c axis]. The Cu in the planes [Cu(2) site] is fivefold oxygen coordinated [2×O(2)] parallel to the a axis, 2×O(3) parallel to the b axis and O(4) along the c axis.[1-3] Though Cu site substitution studies in $YBa_2Cu_3O_7$ have been widely reported in the literature, there are only a few reports on corresponding substitutional studies in other $RBa_2Cu_3O_7$ (R = rare earth) systems. Recently we have studied the effect of Ga substitution at the Cu site in $NdBa_2Cu_3O_7$ and found that the solid solubility limit and T_c suppression rate are much higher in the Nd 1:2:3 system than in the Ga-doped Y 1:2:3 system.[4] We have also established single-phase formation in $RBa_2Cu_2GaO_7$ for R = La-Eu and in $RBa_2Cu_2CoO_{7+\delta}$ for all rare earths except when R = Ce,Tb, and Lu.[5] These observations show that the size of the lanthanide ion is also an important factor which determines the solid solubility, and the superconducting and other properties of the substituted R 1:2:3 systems. This prompted us to study the effect of other substituents also at the Cu site in the Nd 1:2:3 system. Presently, we report on the effect of substitution of Fe,Co,Ni, and Zn at the Cu site, on the structure and superconducting properties of $NdBa_2Cu_3O_7$.

II. EXPERIMENT

The phases with the following compositions have been synthesized and studied (i) $NdBa_2Cu_{3-x}Fe_xO_{7+\delta}$; x = 0.0 to 0.1 in steps of 0.02 and x = 0.2, 0.3, 0.6, 0.8, and 1.0; (ii) $NdBa_2Cu_{3-x}Co_xO_{7+\delta}$; x = 0.0 to 0.1 in steps of 0.02 and x = 0.1–1.0 in steps of 0.1 and x = 1.5; (iii) $NdBa_2Cu_{3-x}M_xO_{7-\delta}$ (M = Ni,Zn); x = 0.0 to 0.1 in steps of 0.02 and x = 0.2, 0.3, 0.4, 0.5, 0.8, and 1.0; (iv) $Nd_{1-y}Ca_yBa_2Cu_{2.9}Zn_{0.1}O_{7-\delta}$; ($y$ = 0.05, 0.1, 0.15, 0.2). The compounds were prepared by the high-temperature solid-state reaction from high-purity oxides; Nd_2O_3 (99.99%, IRE, India; preheated at 950 °C for 24 h and stored in a desiccator), $BaCO_3$, $CaCO_3$, CuO, Fe_2O_3, and NiO (all 99.999%, Cerac, USA), Co_3O_4 (99.999%, Fisher Scientific, USA), and ZnO [prepared by dissolving Zn metal (99.9%, Cerac, USA) in conc. HNO_3, evaporating the solution to dryness and decomposing at 600 °C and characterized by x-ray diffraction (XRD)]. Stoichiometric amounts of the oxides were mixed well and heated at 920 °C for 48 h with intermittent grindings. The reacted powder was pressed into pellets (8 mm diam, 1–2 mm thick tungsten carbide, lined stainless-steel die and plunger; hydraulic press at 2–3 tons pressure) and sintered at 940 °C for 24 h in air. The samples were oxygen treated in a tubular furnace at 900 °C for 24 h, cooled to 600 °C, held for 48 h and furnace cooled to room temperature in 1 atm oxygen flow. Select phases of the $NdBa_2Cu_{3-x}M_xO_{7+\delta}$ (M = Fe,Zn) system were heated in nitrogen atmosphere at 800 °C for 24 h and quenched in air. The quenched pellets were given a low-temperature (450 °C) oxygen treatment for 24 h and furnace cooled in flowing oxygen.

All the phases are black in color and are stable toward exposure to atmosphere. The compounds were characterized by powder XRD (Seifert, Germany, Cu $K\alpha$ radiation) and the lattice parameters were obtained by least-squares (LSQ) fitting of the high-angle reflections. Resistivity (ρ) measurements were done on well sintered, oxygen annealed pellets by the four-probe van der Pauw method as a function of temperature in the range 300–13 K using a closed-cycle He refrigerator (CTI-Cryogenics, USA, Model M22). The electrical contacts were given by ultrasonically (Fibra Sonics Inc., USA) impregnating indium metal and soldering fine-gauge copper wires to the samples to ensure Ohmic contact. A nanovoltmeter (Keithley, USA, Model 181) was used to measure the voltage drop across the sample for currents of the order of 5–20 mA, using a dc current source (Keithley, USA, Model 224). AC-magnetic-susceptibility studies were done on the compounds using a superconducting materials property measurement unit (Sumitomo, Japan, Model SCR 204T) in the temperature range 300–13 K using a field of the order of ~0.1 Oe and a frequency 300 Hz. Oxygen content of the phases in the $NdBa_2Cu_{3-x}M_xO_{7+\delta}$ (M = Fe,Co,Ni,Zn) systems was estimated by an iodometric titration method.[5] The δ values are accurate to ± 0.03.

III. RESULTS AND DISCUSSION

A. Structure and stoichiometry

1. $NdBa_2Cu_{3-x}M_xO_{7+\delta}$ (M = Fe,Co) system

For both M = Fe- and Co-doped systems, XRD patterns reveal good crystalline single-phase formation for $0.0 \le x \le 1.0$ (Figs. 1 and 2). The x = 1.5 composition is multiphasic. In $YBa_2Cu_{3-x}Fe_xO_{7+\delta}$, the maximum solid solubility reported was x = 0.6.[6] However, presence of additional peaks due to impurities were reported even for lower values of x ($x \ge 0.45$).[7,8] In Co-doped Y 1:2:3, the maximum solid solubility limit reported was x = 1.0.[5,6]

The lattice parameters vs x for the phases are plotted in Fig. 3 for M = Fe and in Fig. 4 for M = Co. The occurrence of the orthorhombic-to-tetragonal (O→T) transition at x = 0.08 for both M = Fe and Co is similar to that of Fe- and Co-doped Y 1:2:3 systems.[6,9–11] In the Fe-doped Nd 1:2:3 ($x \le 0.3$) system, Ren et al.[12] observe the O→T transition at x = 0.063. The second T→O transition at x = 0.8 for M = Fe and at x = 0.5 for M = Co presently observed is worth noting and the phases remain orthorhombic up to x = 1.0. The degree of orthorhombicity $[(b-a)/a]$ decreases in the ortho I region ($0.0 \le x \le 0.08$) and increases in the ortho II re-
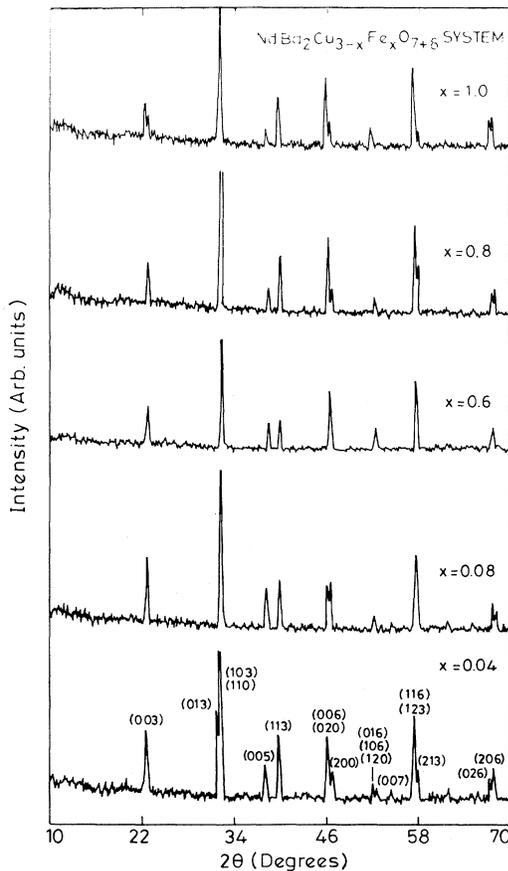
FIG. 1. XRD patterns for the $NdBa_2Cu_{3-x}Fe_xO_{7+\delta}$ system indicating the single-phase nature and the O→T→O transition.
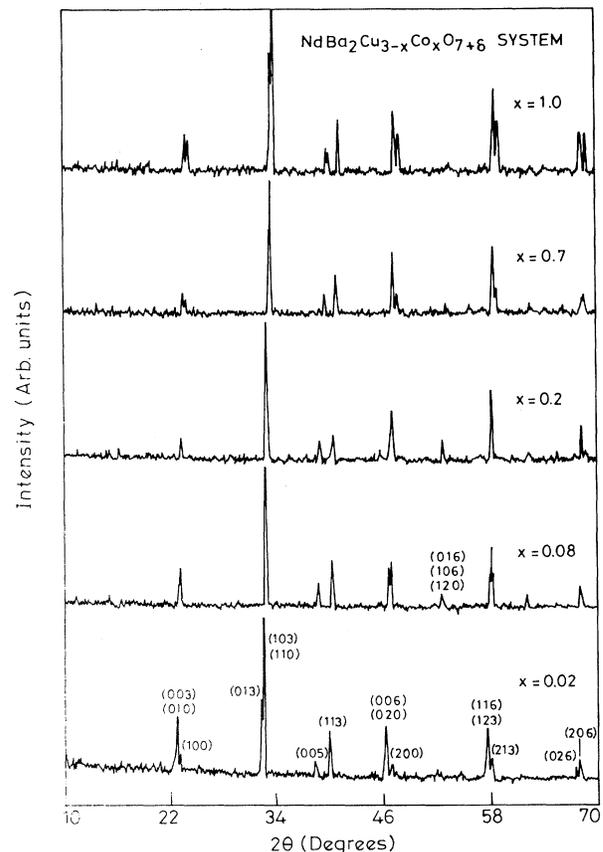
FIG. 2. XRD patterns for the $NdBa_2Cu_{3-x}Co_xO_{7+\delta}$ system indicating the single-phase nature and the O→T→O transition.
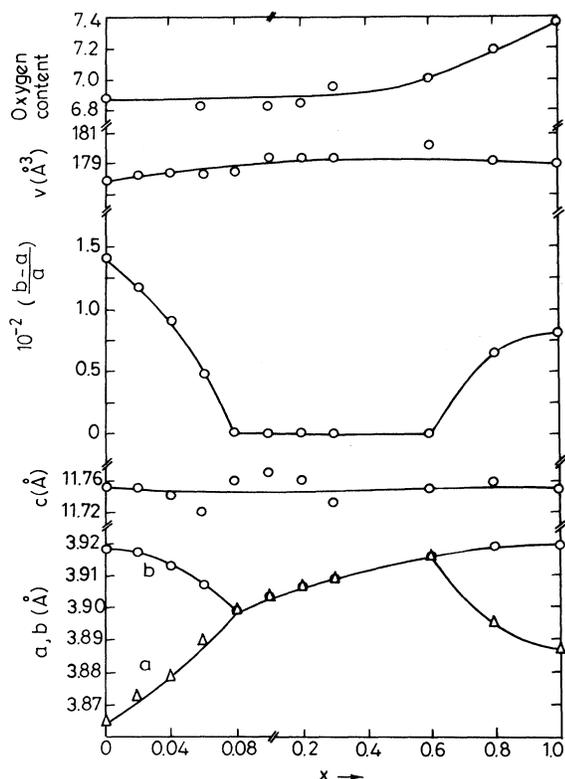
FIG. 3. Variation of lattice parameter, degree of orthorhombicity, unit-cell volume, and oxygen content as a function of x for the $NdBa_2Cu_{3-x}Fe_xO_{7+\delta}$ system.

FIG. 4. Variation of lattice parameter, degree of orthorhombicity, unit-cell volume, and oxygen content as a function of x for the $NdBa_2Cu_{3-x}Co_xO_{7+\delta}$ system.

gion ($0.8 \leq x \leq 1.0$ for Fe and $0.5 \leq x \leq 1.0$ for Co) as x increases. Thus, the two end members of the series $NdBa_2Cu_{3-x}M_xO_{7+\delta}$ (M = Fe, Co) show orthorhombic structure with an intermediate region of compositions having tetragonal structure. The oxygen content of the phases remains constant at 6.84 ± 0.03 for $x \leq 0.1$ and increases as x increases up to a maximum of 7.24 (M = Co) and 7.37 (M = Fe) for $x = 1.0$ (Table I; Figs. 3 and 4). The increase in unit-cell volume as the Fe and Co content increases can be attributed to the increase in oxygen content and this is similar to that observed for Fe- and Co-doped Y 1:2:3.[5,6]

It is generally agreed that Fe and Co occupy the Cu(1) site predominantly for low values of x with an increasing fraction on the Cu(2) site as the total dopant concentration increases.[6,7,9,10,13-18] Bridges et al.[15] proposed that Fe and Co, at the Cu(1) site in Y 1:2:3, aggregate into distorted zigzag chains along the $\langle 110 \rangle$ direction in the basal plane, with some of the Fe, Co, and oxygen displaced off center. Moderately long chains could promote microscopic twinning and, hence, lead to apparent (by XRD) tetragonality even at low concentrations of the substituent. However, electron microscopic studies[7,13,19] reveal that the tetragonal phase induced by the substituents actually consists of differently oriented orthorhombic microdomains, i.e., the phase is tetragonal only in a statistical sense. The reoccurrence of orthorhombicity for higher M content in the present case could be due to
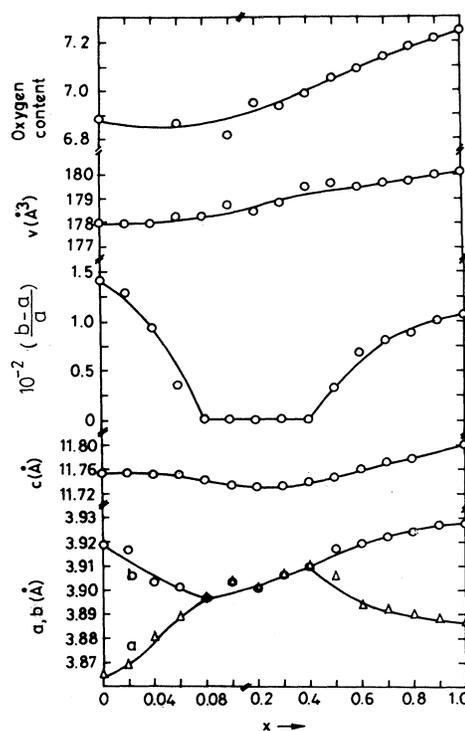
the increased clustering of M, leaving behind largely M-free orthorhombic domains. In other words, the size of the orthorhombic domains increases. An alternate mechanism is the occupancy of the excess oxygens (above 7.0) in the O(6) position (R plane) leaving the oxygen ordering in the basal plane intact.[20,21] Further studies using local probes such as x-ray-absorption spectroscopy (XAS), Mossbauer spectroscopy, etc. are needed.

2. $NdBa_2Cu_{3-x}M_xO_{7-\delta}$ (M = Ni, Zn) system

For both Ni- and Zn-doped systems, single-phase formation occurs for $0.0 \leq x \leq 0.8$. For M = Ni, the $x = 1.0$ composition is multiphasic and for M = Zn, the $x = 1.0$ phase crumbles and changes color (brown) after oxygen treatment and the XRD pattern revealed multiphase formation. Hence $x = 0.8$ can be taken as the upper limit of solid solubility of both Ni and Zn in the Nd 1:2:3 system and this is much higher (almost double) than the solubility limit reported for the Y 1:2:3 system. In Ni-doped Y 1:2:3, the maximum solubility reported is $x = 0.5$.[6,11] However, most of the reports show that the actual solid solubility limit is less than $x = 0.3$.[15,22,23] Though the maximum solid solubility limit reported for the $YBa_2Cu_{3-x}Zn_xO_7$ system is $x = 0.36$ (Ref. 24), several groups have reported that the upper limit of solubility of Zn is even less than $x = 0.3$.[7,25] However, such a high solubility limit of $x = 0.8$, as observed in the present case of Nd 1:2:3, was recently reported for the $LaBa_2Cu_{3-x}Zn_xO_{7-\delta}$ system[21] as well. But traces of

TABLE I. Oxygen content $(7\pm\delta)$ for the $NdBa_2Cu_{3-x}M_xO_{7\pm\delta}$ (M = Fe, Co, Ni,Zn) systems.

M	0.0	0.04	0.06	0.1	0.2	x in $NdBa_2Cu_{3-x}M_xO_{7\pm\delta}$ 0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
Fe	6.88		6.83	6.82	6.84	6.95			7.13		7.20		7.37
Co	6.88		6.86	6.81	6.94	6.93	6.97	7.05	7.08	7.13	7.18	7.21	7.24
Ni	6.88	6.87		6.86				6.99			7.05		
Zn	6.88			6.85	6.85		6.86	6.86			6.80		

ZnO impurity were observed in the neutron-diffraction pattern of $LaBa_2Cu_{2.2}Zn_{0.8}O_{7-\delta}$.

The lattice parameters of the phases with M = Ni and Zn in Nd 1:2:3 are shown in Figs. 5 and 6, respectively. The O→T transition observed at x = 0.4 in the case of M = Ni and at x = 0.5 in the case of M = Zn is in significant contrast to the Y 1:2:3 system. In the case of $YBa_2Cu_{3-x}M_xO_7$ (M = Ni,Zn) all the reports show that the phases retain orthorhombicity until the maximum solid solubility limit. In Zn-doped Eu 1:2:3 (Ref. 26) and La 1:2:3 (Ref. 21) O→T transition at x = 0.4 and x = 0.5, respectively, were also reported, as observed in the present case. For the M = Ni phases, the unit-cell volume remains almost constant throughout the solubility region and this could be attributed to the comparable size of Ni^{2+} and Cu^{2+} (0.63 Å and 0.65 Å, respectively, for fivefold coordination). For the Zn-doped system, since the ionic radius of Zn^{2+} is slightly larger than that of Cu^{2+}

(Cu^{2+} = 0.65 Å, Zn^{2+} = 0.68 Å for fivefold coordination) the unit-cell volume increases as expected as Zn content increases.

The oxygen content of the M = Ni phases increases only slightly, from 6.88 to 7.05 for x = 0.0→0.8 (Table I). For the Zn-doped system, the oxygen content values are in the range 6.88–6.80 ($\pm$0.03). The oxygen content remains unchanged for the orthorhombic phases, whereas a slight decrease (which may fall within the experimental error) in oxygen content is observed for the tetragonal phases. Similar behavior is reported for the Ni- and Zn-doped Y 1:2:3 systems also.

For a given value of Zn content (x = 0.1), we have synthesized and studied phases where Ca is substituted for Nd, viz., $Nd_{1-y}Ca_yBa_2Cu_{2.9}Zn_{0.1}O_{7-\delta}$ (y = 0.0–0.2 in steps of 0.05) and find that solid solubility exists up to y = 0.2 (Fig. 7). As the Ca content increases from x = 0.0 to 0.2, the lattice parameter a increases while b and c and
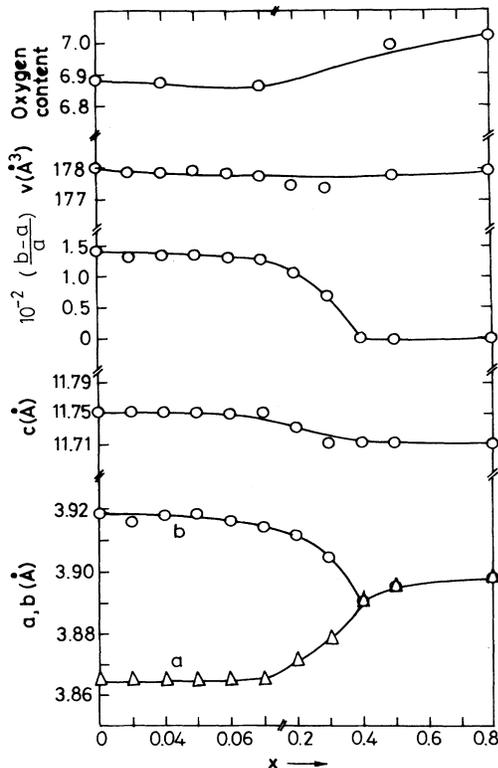
FIG. 5. Variation of lattice parameter, degree of orthorhombicity, unit-cell volume, and oxygen content as a function of x for the $NdBa_2Cu_{3-x}Ni_xO_{7-\delta}$ system.
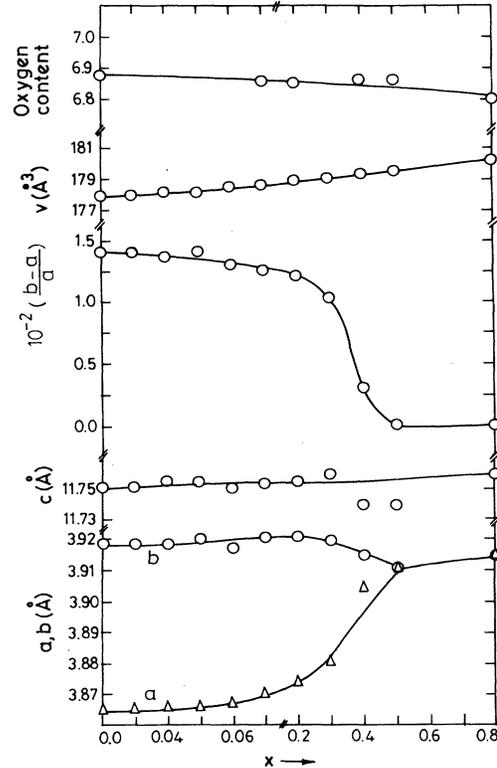
FIG. 6. Variation of lattice parameter, degree of orthorhombicity, unit-cell volume, and oxygen content as a function of x for the $NdBa_2Cu_{3-x}Zn_xO_{7-\delta}$, system.
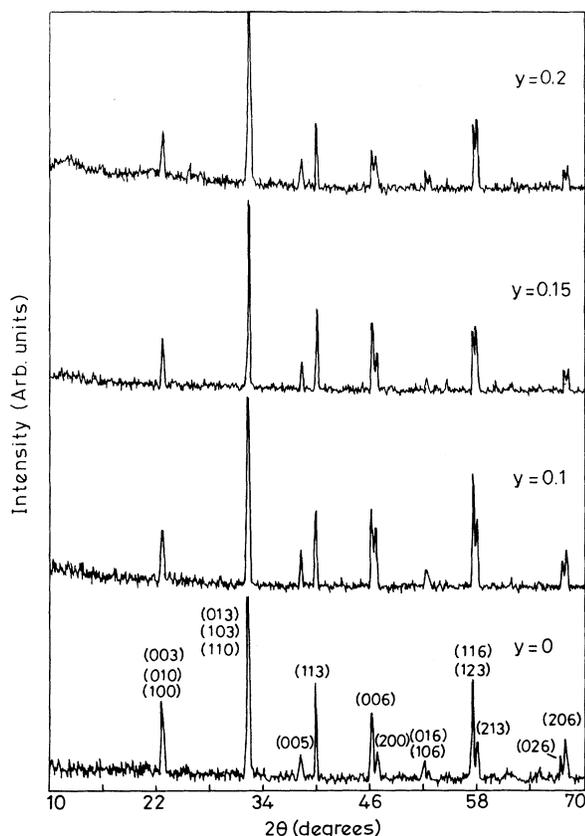
FIG. 7. XRD patterns for the $Nd_{1-y}Ca_yBa_2Cu_{2.9}Zn_{0.1}O_{7-\delta}$ system indicating the single-phase nature of the compounds.

the degree of orthorhombicity decrease slightly.

There is still no consensus about the exact location of the substituted Ni and Zn ions in the Y 1:2:3 lattice, whether they occupy the Cu(1) site or the Cu(2) site, or both. Occupancy of Ni[11,14,22] and Zn,[8,14,18,25] both at Cu(1) and Cu(2) sites and exclusively at the Cu(2) site[6,27−29] in Y 1:2:3, are also reported. However, the

present observation of an O→T transition in the case of M = Ni-, Zn-doped Nd 1:2:3 for higher values of x clearly indicates that, indeed, Ni and Zn occupy the Cu(1) site also and bring about a disorder in the oxygen occupancy in the basal plane resulting in tetragonal structure. The absence of an O→T transition in Ni- and Zn-doped Y 1:2:3 can be attributed to the lower solid solubility. In the $LaBa_2Cu_{3-x}Zn_xO_{7-\delta}$ system,[21] there is evidence from neutron-diffraction studies that 60% of the doped Zn occupies the Cu(2) site and 20% occupies the Cu(1) site for higher values of x.

B. Electrical, magnetic, and superconducting properties

In the $NdBa_2Cu_{3-x}M_xO_{7+\delta}$ (M = Fe,Co,Ni,Zn) system, for all the M ions, $\rho_{300 \text{ K}}$ increases as x increases and superconductivity is encountered only for lower concentrations of the M ion. An upturn in resistivity immediately before T_c(onset) is observed for $x \geq 0.08$ and it can be attributed to weak localization effects.[7,8] For the $x = 0.2$ phase (M = Fe,Co,Ni), resistivity measurements could not be done below 150 K due to fluctuations while passing current through the samples. The T_c values obtained from the ρ-T studies are in agreement with those obtained from ac-magnetic-susceptibility measurements (diamagnetic onset temperature) and are listed in Tables II and III. The $x = 0.2$ phase (M = Fe,Co,Ni) also exhibits superconducting transition.

From Tables II and III, it is clear that the T_c decreases monotonically as x increases. The effect of the M ion on T_c suppression is more drastic in the case of the Nd 1:2:3 system than in the corresponding Y 1:2:3 system. Of all the ions substituted, Zn shows the maximum effect on T_c suppression. The Zn-doped phases with $0.0 \leq x \leq 0.08$ only are superconducting; i.e., T_c disappears for less than 3 at. % of Zn doping with the rate of decrease of T_c as high as ~28 K/at. %. In Y 1:2:3, on the other hand, the rate of T_c suppression is 11–16 K/at. % of Zn only. For M = Fe,Co,Ni, the initial rate of decrease of T_c up to 3.3 at. % is ~14 K/at. % and is much higher than that reported for the corresponding Y 1:2:3 system (~4 at. %).

TABLE II. Electrical and superconductivity data for the $NdBa_2Cu_{3-x}M_xO_{7+\delta}$ (M = Fe, Co) system.

M	x	$\rho_{300 \text{ K}}$ mΩ/cm	Resistivity $(1/\rho_{300 \text{ K}})d\rho/dT_{(300-100 \text{ K})}$ $\times 10^{-3}$	T_c (onset)	$T_c(\rho-T)\pm 1$ K T_c (midpt)	T_c (zero)	ΔT_c	$T_c(\chi-T)\pm 1$ K
Fe	0.00	0.92	2.72	96	92	89	3	88
	0.02	1.09	2.84	90	83	79	8	84
	0.04	1.88	2.69	78	70	68	5	75
	0.06	2.46	2.64	75	68	63	9	65
	0.08	2.59	2.45	64	56	51	9	52
	0.10	6.53	2.38	63	47	41	12	47
	0.20	12.0						23
Co	0.02	1.90	2.47	80	73	68	9	71
	0.04	2.10	1.67	68	62	59	6	64
	0.06	2.42	2.46	66	58	53	11	57
	0.08	3.90	3.08	67	57	49	15	54
	0.10	7.50	2	59	50	43	14	50
	0.20	7.60						27

TABLE III. Electrical and superconducting data for the $NdBa_2Cu_{3-x}M_xO_{7-\delta}$ (M = Ni,Zn) system.

M	x	$\rho_{300\,K}$ mΩ/cm	Resistivity $(1/\rho_{300\,K})d\rho/dT_{(300-100\,K)}$ $\times 10^{-3}$	$T_c(\rho - T)\pm 1$ K				$T_c(\chi - T)\pm 1$ K-
				T_c (onset)	T_c (midpt)	T_c (zero)	ΔT_c	
Ni	0.00	0.92	2.72	96	92	89	3	88
	0.02	1.08	1.76	78	72	65	8	77
	0.04	1.11	2.03	69	65	61	4	72
	0.06	1.19	1.68	72	64	55	11	65
	0.08	1.26	1.59	71	59	51	15	61
	0.10	1.37	1.53	62	51	46	10	55
	0.20	1.55						33
Zn	0.02	1.16	1.64	70	64	60	6	73
	0.04	1.38	1.59	59	54	49	6	63
	0.06	1.49	1.91	58	46	31	19	40
	0.08	1.63	1.29	35				26

Ren et al.[12] also observed such a higher rate of T_c suppression for the Fe-doped Nd 1:2:3. Above $x = 0.1$, the T_c decreases at a lower rate of 7 K/at. % for M = Fe and Co and is similar to that observed in the Y 1:2:3 system.[10] Superconductivity vanishes for $x = 0.3$ in the case of M = Fe,Co,Ni. The minimum values of x at which T_c becomes zero for $YBa_2Cu_{3-x}M_xO_{7+\delta}$ are $x = 0.4$ (M = Fe,Co) and $x = 0.18$ (M = Zn).[9] The T_c behavior of Ni-doped Nd 1:2:3, however, is in contrast to the studies reported for the Ni-doped Y 1:2:3 system where the phases exhibit superconductivity ($T_c > 40$ K) throughout the solid-solution range. A similar detrimental effect on T_c for M = Fe,Zn was observed in the $LaBa_2Cu_{3-x}M_xO_{7-\delta}$ system also.[21]

Superconducting to semiconducting transition occurs at $x = 0.3$ for M = Fe,Co,Ni and $x = 0.1$ for M = Zn. For M = Zn, phases with $0.1 \le x \le 0.4$ exhibit a metallic or semimetallic behavior in the range 300–100 K and subsequently show semiconducting behavior down to 13 K. Phases with $x \ge 0.3$ for M = Fe,Co,Ni and $x = 0.5$ and 0.8

for M = Zn exhibit semiconducting behavior in the whole range of temperature measured (300–13 K). The activation energies for conduction have been calculated from an Arrhenius equation and are given in Table IV.

The different mechanisms suggested in the literature for the T_c suppression are (i) a pair-breaking effect as in the conventional Abrikosov-Gorkov (AG) theory, owing to the localized magnetic moment of Fe^{3+}, Co^{3+}, and Ni^{2+}.[8,11] Fe substitution in Y 1:2:3 and Gd 1:2:3 phases seems to increase the coherence length perpendicular to the ab plane and smears out the local distribution of charge carriers,[30] i.e., the density of superconducting charge carriers in the CuO_2 planes smears out along the c direction and the probability for direct interaction between the magnetic moment of Fe and the Cooper pairs increases. This interaction lifts the degeneracy of the two states that form the Cooper pair and hence, affects the pair breaking, resulting in the reduction of T_c in terms of AG theory; (ii) in an alternate model, Bridges et al.[15] suggest that the observed structural distortions induced

TABLE IV. Resistivity and activation energy data for the $NdBa_2Cu_{3-x}M_xO_{7\pm\delta}$ (M = Fe, Co, Ni,Zn) system. The temperature ranges for which the activation energies for conduction are calculated are given below.

	M	x in $NdBa_2Cu_{3-x}M_xO_{7\pm\delta}$ (M = Fe, Co, Ni, Zn)									
		0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
$\rho_{300\,K}$ mΩ/cm	Fe			18			53		128		161
	Co			19.8	108	112	149	981		3560	4185
	Ni			1.90	3.7	12.8			264		
	Zn	1.69	2.41	2.91	3.6	4.61			43		
$E_a \times 10^{-2}$ (eV)	Fe						2.0[d]		4.1[d]		4.4[d]
	Co			0.21[a]	4.2[e]	3.2[b]	5.3[a]	10[d]		13.6[d]	14[b]
	Ni			0.42[c]	0.39[h]	0.73[f]			5.5[b]		
	Zn	0.11[k]	0.18[j]	0.22[i]	0.23[g]	0.70[f]			3.7[d]		

[a]300–200.
[b]300–150.
[c]300–140.
[d]300–100.
[e]300–80.
[f]300–70.
[g]230–70.
[h]220–50.
[i]190–50.
[j]160–50.
[k]110–40.

by Fe and Co within the Cu(1) layer modifies the overlap of the Cu and O orbitals. This may reduce the electron-electron coupling within the layer, thereby making the Cu(1)-O layer in the basal plane a poor conductor. The distorted Cu(1) and O(1) sites will also change the coupling between the Cu(1) and Cu(2) layers through small changes in the positions of the O(4) oxygens and the Ba atoms in the structure, leading to the suppression of T_c. The T_c suppression has also been correlated to the change in the Cu(1)-O(4)/Cu(2)-O(4) bond length as a function of the dopant concentration.[31] The resulting electronic disorder between the CuO chains and the CuO$_2$ planes leads to reduction of carrier concentration. Indeed, the reduction of mobile carrier concentration in the Fe-doped[7] and Co-doped[32] Y 1:2:3 has been verified experimentally; (iii) in the case of Ni doping, the variation in the density of states near the Fermi level[33] has also been suggested as a possible reason. In addition, many suggestions have been made to account for the dramatic suppression of T_c by nonmagnetic Zn. They are (i) reduction of mobile charge-carrier concentration due to the filled $3d^{10}$ shell of Zn^{2+};[8,27,34,35] (ii) localization of Cu-$3d$ holes;[25,36] (iii) electronic disorder in the CuO$_2$ planes[37,38] and changes in the band structure.[39,40]

In the present study of Fe-, Co-, Ni-, and Zn-doped Nd 1:2:3, the reduction of carrier concentration alone cannot account for such drastic depression of T_c. In addition to the above, the site disorder and magnetic interaction of the M ion and Nd^{3+} may also partly play a role in the enhanced depression of T_c, similar to the Fe-doped La 1:2:3 and Gd 1:2:3 systems. In the $LaBa_2Cu_{3-x}Fe_xO_{7+\delta}$ system, the drastic T_c suppression is attributed to the disorder of the oxygen ions among the various sites in the lattice.[21] The increased rate of T_c suppression in the case of Fe-doped Gd 1:2:3 is attributed to the magnetic interaction of the Fe^{3+} and Gd^{3+} ion moments.[30]

C. Effect of N_2 treatment and low-temperature O_2 treatment

It has been reported that heat treatment in a reducing atmosphere can alter the ratio of distribution of the sub-

stituents between Cu(1) and Cu(2) sites in the $YBa_2Cu_{3-x}M_xO_{7+\delta}$ (M = Fe,Co) system and thereby modify the structure and superconducting properties.[41-46] In order to study the effect of thermal treatment on the structure and superconductivity of the $NdBa_2Cu_{3-x}M_xO_{7+\delta}$ (M = Fe,Zn) system, select phases have been treated at 800 °C in flowing N_2 gas and then reoxidized at 450 °C in oxygen (see Sec. II). These are designated as batch II, whereas the earlier 900 and 600 °C O_2-treated samples are denoted as batch I. The x-ray-diffraction patterns of $x = 0.08$ and 0.1 (M = Fe) and $x = 0.5$ (M = Zn) phases (which were otherwise tetragonal in batch I) showed weak orthorhombic splitting after the above treatment. However, we note that the upper limit of x to which the orthorhombic structure is extended in batch II is very much lower in Fe-doped Nd 1:2:3 compared to that of Fe-doped Y 1:2:3.[41-43] We are not aware of any similar heat treatment studies on the Zn-doped Y 1:2:3. We find that batch II samples possess the same oxygen content as batch I. This applies to the Y 1:2:3 system as well.

AC-magnetic-susceptibility studies on the batch II phases of Fe- and Zn-doped Nd 1:2:3 (Figs. 8 and 9, respectively) show that for $x < 0.04$, T_c is the same as that of batch I. For higher values of x, batch II samples show the diamagnetic transition at appreciably higher temperatures than that of batch I. Also, the T_c transition is sharp in batch II phases and shows well-defined saturation.

It is known that the heat treatment of $YBa_2Cu_{3-x}M_xO_{7+\delta}$ (M = Fe,Co) in a reducing atmosphere at high temperature (~ 800 °C) results in changes in the ratio of occupancy of the dopant ions at the Cu(1) and Cu(2) sites and clustering of Fe or Co in the CuO chains by sharing the oxygen (even though the total oxygen content is low), by which it can achieve the preferred coordination rather than remaining as isolated substituents. The different models proposed for the changes during the reduction treatment are (i) migration of Fe or Co from the Cu(1) site to the Cu(2) site,[41-44] (ii) migration of Co from the Cu(2) site to the Cu(1) site,[45,46] and (iii) Fe remains in the chain layer regardless of the heat
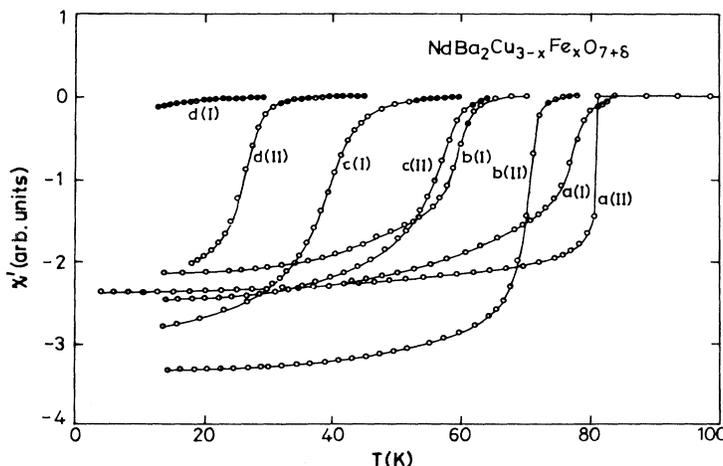
FIG. 8. Superconducting transition from ac-susceptibility measurements for select phases of the ordinary oxygen treated (batch I) and nitrogen gas treated and reoxygenated (batch II) phases of the $NdBa_2Cu_{3-x}Fe_xO_{7+\delta}$ system; (aI,aII) $x = 0.02$, (bI,bII) $x = 0.06$, (cI,cII) $x = 0.10$, and (dI,dII) $x = 0.20$, where (I) and (II) stand for batch I and batch II phases, respectively.
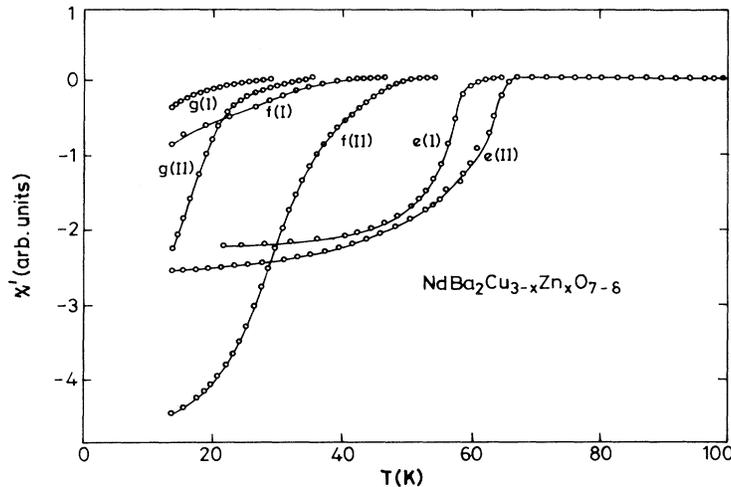
FIG. 9. Superconducting transition from ac-susceptibility measurements for select phases of the ordinary oxygen treated (batch I) and nitrogen gas treated and reoxygenated (batch II) phases of the $NdBa_2Cu_{3-x}Zn_xO_{7-\delta}$ system; (eI,eII) $x = 0.04$, (fI,fII) $x = 0.06$, and (gI,gII) $x = 0.08$, where (I) and (II) stand for batch I and batch II phases, respectively.

treatment.[47] The cluster formation occurs at lower temperatures in the case of Co than in the case of Fe (Refs. 45,46) and there exists a difference in the morphology of the clustering between the Co- and Fe-doped Y 1:2:3.[44] It is contended that the formation of ordered clusters varies with the exothermicity of the M-O bond.[48] The temperature at which the reoxygenation is done is too low to break the clusters. This results in the formation of phases with larger regions of relatively poor dopant concentration (i.e., the orthorhombic domain size will enlarge). Reoxygenation of the reduced phases at low temperature is found to increase the T_c in the case of both Fe- and Co-doped Y 1:2:3.[41-43,45,46] However, there are also reports of T_c remaining unchanged for the Fe-doped Y 1:2:3 (Ref. 47), as well as a decrease in the T_c in the case of Co-doped Y 1:2:3.[44] The differences in the behavior observed by various groups can be attributed to the different heat treatment conditions employed.

In the present study, since the orthorhombicity of the Fe- and Zn-doped Nd 1:2:3 phases (batch II) is not increased considerably, we can assume that the fraction of the dopants migrating to the Cu(2) site is negligible. The observation of higher and sharper diamagnetic onset temperature can be correlated to clustering of the dopants in the basal plane, resulting in the formation of larger orthorhombic domains with lesser dopant concentration as discussed above. However, without further studies, such a Mossbauer spectroscopy, it will be premature to speculate about the occupancy of the ions and the enhancement of T_c.

D. Recovery of superconductivity in Zn-doped Nd 1:2:3 by hole doping

It is well established that metallicity and superconductivity in the Y 1:2:3 system of compounds is due to the mixed valency of copper in the compound and more specifically, the hole doping of the CuO_2 planes, and the CuO chains acting as hole reservoirs. Therefore, any mechanism which either decreases the hole concentration [say, by decreasing the oxygen content in $YBa_2Cu_3O_7$ or by doping at the Cu(1) site of the chain] or the mobility of the mobile holes [either by doping at the Cu(1) or Cu(2)

sites], decreases the T_c and eventually destroys superconductivity above a critical concentration.[1-3] This is in accordance with the present studies as well as those reported in the literature. On the other hand, hole doping can be achieved by calcium doping at the Y site in oxygen deficient Y 1:2:3 (Refs. 49,50) or M-ion-substituted (at Cu site) Y 1:2:3.[51,52]

We have also tried and succeeded in inducing superconductivity in the Zn-doped Nd 1:2:3 by progressively substituting Ca at the Nd site to give phases of the type, $Nd_{1-y}Ca_yBa_2Cu_{2.9}Zn_{0.1}O_{7-\delta}$. The phase with $y = 0.0$ is semimetallic in the range 300–100 K and shows semiconducting behavior below 100 K. No superconductivity is encountered down to 13 K. The ac χ-T data show that superconductivity is induced for $y > 0.1$ and T_c increases from 13 K for $y = 0.1$ to 32 K when $y = 0.2$. (The solid solubility limit extends only up to $y = 0.2$ in this system.) The ρ-T studies for $y = 0.2$ clearly show a T_c (zero) of 27 K. Thus, the present study shows that hole doping of the CuO_2 phases can, indeed, be achieved by substitution at the Nd site by the bivalent Ca ion.

IV. CONCLUSIONS

The main observations of the present study are (i) increased solubility limit for the M = Fe, Co, Ni, and Zn in $NdBa_2Cu_3O_{7+\delta}$, compared to the Y 1:2:3 system, (ii) the O→T→O transition with Fe^{3+} and Co^{3+} substitution with increasing x, (iii) the O→T transition in the case of Ni and Zn substitution with increasing x, unlike in Y 1:2:3, and (iv) the drastic effect on T_c suppression of Nd 1:2:3 for all the substituents compared to Y 1:2:3. The following inferences can be drawn. (a) The radius-ratio and tolerance-factor criteria differ when the size of the lanthanide is changed from Y to Nd in R 1:2:3 and thus can lead to increased solid solubility at the Cu site. (b) The observed structural features from diffraction experiments are global in nature; (i) the microdomain structure can be different; (ii) the dopants form clusters; (iii) the O_6 position (Nd plane) can also be occupied. (c) The M^{2+} (Ni and Zn) ions also occupy the Cu(1) site at higher concentrations in Nd 1:2:3 leading to tetragonal structure.

(d) The higher rate of T_c suppression (~ 14 K/at. %) for $M =$ Fe, Co, Ni even at lower concentrations (unlike in the Y 1:2:3 system), and the catastrophic effect the Zn^{2+} ion has on the superconducting properties indicate that the mechanism of T_c suppression may not be common in all the 1:2:3 systems and could be dependent on the nature of the R ion.

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