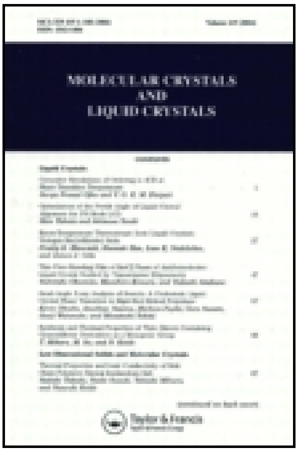

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Nickel/Lanthanum Ordering in $YBa_2Cu_3O_{7-\delta}$

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NICKEL/LANTHANUM ORDERING IN $YBa_2Cu_3O_{7-\delta}$

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Abstract Replacement of the formally d^8 Cu^{+3}-ion in $YBa_2Cu_3O_{7-\delta}$ with the isoelectronic d^8 Ni^{+2}-ion and Ba^{+2} with La^{+3} for charge compensation has been studied. In the composition series $YBa_{2-x}La_xCu_{3-x}Ni_xO_{7-\delta}$ x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7, and 1.0, a systematic change from orthorhombic to tetragonal symmetry was observed along with a decrease in the resistive transition temperature. Composition x = 0.3 has been the most thoroughly studied and is near the limit of the nickel solubility which results in a mixture of $YBa_{2-x}La_x(Ni_{.05}Cu_{.95})_3O_{7\pm\delta}$, $Ni_{1-x}Cu_xO$ and $Y_2Ba(Cu,Ni)O_5$. The small amount of nickel incorporated eliminates superconductivity and magnetic ordering is observed in the susceptibility around 50 K in addition to a paramagnetic background.

INTRODUCTION

In order to understand the properties and chemistry of $YBa_2Cu_3O_{7-\delta}$ and other high temperature superconductors, a large number of studies have been done based on the similarities of known high Tc materials; features that include approximately planar copper-oxide layers and formal mixed valency. This has led to new structures including $LaSrAlCuO_5$[1] and $LaSrGaCuO_5$ where roughly planar copper-oxide layers are interleaved with aluminum oxide and gallium oxide layers, respectively. At the less extreme end are a host of substitutions attempting to substitute iron[2], zinc[3], silver[4], nickel[3], the lanthanide series[5] and many other elements into the $YBa_2Cu_3O_{7-\delta}$ structure. The substitutions lead to more changes than is desired; ideally these substitution reactions would not also entail the relaxation of structure, changing its bond lengths, atomic positions and electronic structure. In this paper we report on our efforts to replace the d^8 Cu^{+3}-ion in $YBa_2Cu_3O_{7-\delta}$ with the isoelectronic d^8 Ni^{+2}-ion. Lanthanum was reacted in equimolar amounts with nickel to provide the necessary charge compensation.

Structural complexities associated with both superstructure/solid solution can be formidable. In general the superstructure formed depends upon the electronic configuration (d^n) and preferred coordination of the smaller B-site cation and the ionic radius of the larger, electropositive A-cation[6]. Complex pseudocubic and oxygen-deficient structures based on perovskite are known for manganese[7], iron[8] and copper[9]. In addition to pseudocubic structures, ABO_3 compounds form an extraordinary number of structures based on mixed cubic (c) and hexagonal (h) close-packed AO_3 layers[10]. Some of this polytypism has been shown to be associated with the oxygen composition[11,12]. The combination of mixed sequences (c,h), cation composition, and oxygen stoichiometry can give rise to a large number of complex structures and a range in properties[13]. The B cations in $Ba_2Bi_{2-x}La_xO_6$ can be ordered or disordered depending on oxygen history of the sample[14]. High resolution electron microscopy of quenched $YBa_2Cu_3O_{7-\delta}$ samples indicates the presence of trigonal phases[15] as well as the common observations of small regions of $BaCuO_x$ on the surface of $YBa_2Cu_3O_{7-\delta}$ particles.

The other possibility that must be addressed is segregation and inhomogeneity in these complex oxide systems and the sensitivity of the available methods of detection. At what scale must the mixing occur to be considered one phase rather than an intergrowth of many structurally similar phases. As a first probe of this we have done extensive SEM/EDAX of our samples to determine if they are homogeneous on the SEM length scale (.1 μm).

EXPERIMENTAL

Samples of composition $YBa_{2-x}La_xCu_{3-x}Ni_xO_{7-\delta}$ with x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.7 and 1.0 were prepared by solid state reaction described elsewhere[16] along with the method of X-ray, susceptibility and resistivity characterization. After initial measurements during the first two weeks, the samples were then returned to a 900°-920° furnace in air for 6-8 months.

A Hitachi S-570 SEM equipped with a Tracor Northern energy dispersive X-ray spectrometer was used to determine the stoichiometry of individual grains. The Tracor Northern computer program SQ was used the fit the spectra and apply an initial matrix correction based on the atomic number, absorption and fluorescence (ZAF) and generate approximate metal atom ratios. To correct the calculated percentages of constituent metal atoms for variations in their absorbance/fluorescence due to variations in the geometry of individual grains, a first order correction was arrived at by monitoring the intensity of the Y_L-line verses the Y_K-line. The Y_K-line is only weakly affected by absorption/fluorescence (~.2%) where as the Y_L is strongly affected (~200%). Observed amounts of yttrium, barium and copper based on the Y_K, Ba_L and Cu_K-lines were collected on the same grain as the stage was tilted between collections so varying absorption could be calibrated by the Y_L to Y_K ratio which was the most strongly affected line. The zero point for the elements was corrected by averaging approximately 50 points of $YBa_2Cu_3O_7$. The correction for Ni was determined from Ni_4CuO_5 and that of La from $La_3Ba_3Cu_6O_{14.1}$. Data points were usually collected for 300 to 500 seconds yielding ~$3 \cdot 10^5$ counts of the Cu_K-line.

RESULTS AND DISCUSSION

TABLE I Initial lattice constants

x	a	b	c
0.0	3.823	3.888	11.670
0.1	3.821	3.886	11.666
0.2	3.819	3.891	11.678
0.3	3.824	3.885	11.653
0.4	3.840	3.879	11.638
0.5	3.837	3.879	11.642
0.7	3.863	-	11.592
1.0	3.858	-	11.574

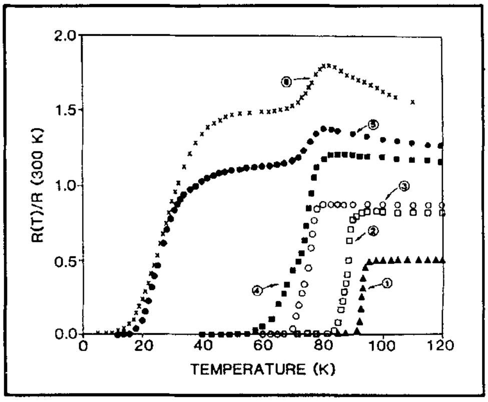

FIGURE I The normalized resistance verses temperature for the composition $YBa_{2-x}La_xNi_xCu_{3-x}O_{7\pm\delta}$. (1)x=0.0; (2)x=0.1; (3)x=0.2; (4)x=0.3; (5)x=0.4; (6)x=0.5.

Initial results[16] appeared surprisingly tolerant of the nickel and lanthanum. Unlike the magnetic lanthanide ion substitution which did not affect superconductivity, incorporated nickel would be occupying a site associated with the fermi surface and should affect the electrical properties strongly. The resistivity (Figure I) showed a drop in T_c while the lattice constants (Table I) shift from orthorhombic to tetragonal. Combined these results suggested that these compositions were complex mixtures. These data demonstrate the limitations of X-ray powder diffraction in determining lattice constants when similar compounds are present so that the result is the average of lattice constants.

To address this problem we used EDAX following the prolonged heat treatment (see figure II). The measurements are plotted on a pseudo ternary phase diagram. Our original intention was a substitution of nickel for copper and lanthanum for barium so that the combined fraction of nickel and copper (and lanthanum with barium) is one axis. The phase diagram for the Y_2O_3-BaO-CuO is superimposed on the diagram as a reference and if the solid solution were successful the only points would be centered on the $YBa_2Cu_3O_{7-\delta}$ point. Lanthanum incorporation on the yttrium site would cause the points to drift to the right.

The majority of the x = 0.3 sample is $YBa_2Cu_3O_7$-like, though a large fraction of the nickel is contained in a relatively few grains of $Ni_{1-x}Cu_xO$ ($0 \leq x \leq .35$, typically $x \approx .25$). For larger nickel and lanthanum fractions (not shown) the products are $Ni_{1-x}Cu_xO$, $(La,Y)_4Ba(Cu,Ni)_5O_{15-\delta}$, $YBa_{2-x}La_xNi_{.15}Cu_{2.85}O_{7\pm\delta}$ and $Y_2Ba(Cu,Ni)O_5$. The compounds are not easily detected by X-ray powder diffraction. $La_4BaCu_5O_{15-\delta}$ and any other perovskite-like phases are going to diffract in the same regions as $YBa_2Cu_3O_7$. $Ni_{1-x}Cu_xO$ is not visible in the diffraction pattern. The incorporation of the nickel is also evident from the elimination of superconductivity and magnetic ordering in the susceptibility (see Figure III) at approximately 50 K along with a paramagnetic background.

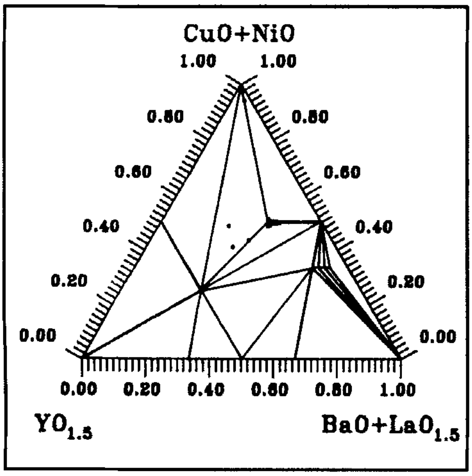

Figure II EDAX results of plotted on a pseudo ternary phase diagram for $YBa_{1.7}La_{.3}Ni_{.3}Cu_{2.7}O_{7\pm\delta}$.

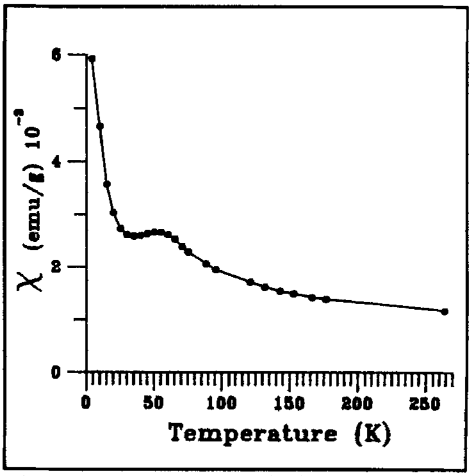

Figure III Susceptibility of the composition $YBa_{1.7}La_{.3}Ni_{.3}Cu_{2.7}O_{7.1}$ after long term annealing.

TABLE II Representative EDAX for the composition $YBa_{1.7}La_{.3}Ni_{.3}Cu_{2.7}O_{7\pm\delta}$

Y	Ba	La	Ni	Cu	phase type
1.09±0.39	1.42±0.13	0.31±0.12	71.21±0.38	25.98±0.26	$Ni_{1-x}Cu_xO$
16.49±0.59	27.38±0.29	6.33±0.23	2.03±0.16	47.77±0.42	$YBa_2Cu_3O_{7\pm\delta}$
16.59±0.76	27.52±0.36	5.53±0.27	2.12±0.22	48.23±0.54	"
16.42±0.71	27.71±0.34	5.43±0.26	2.29±0.21	48.18±0.50	"
15.38±0.48	27.62±0.24	6.58±0.20	2.24±0.12	48.19±0.34	"
44.07±0.59	24.66±0.32	1.11±0.24	2.26±0.17	27.90±0.36	Y_2BaCuO_5

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