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CHARACTERISTICS OF ND1+XBA2-xCU3O6.5+Y SPUERCONDUCTORS

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ABSTRACT

Five superconductors of the $Nd_1+x\ Ba_2-x\ Cu_3O_{6.5\pm y}$ type (x=0.00, 0.05, 0.10, 0.15, and 0.20) were prepared. The orthorhombic crystal lattice observed at x = o gradually transforms into a tetragonal structure with increasing values of x. Resistivity measurements (D.C.) showed a metalsemiconductor type transition at temperatures above Tc. The Tc ranges from 92K to 72K by increasing. Values of x from 0.00 to 0.20, respectively. The oxygen content (y) increases with increasing x. Comparison of calculated and experimental valued of y suggests that Nd is present in the form of Nd2O3. In contrast to early reports, it appears that the behaviors observed are due to Nd_2O_3 and $NdBa_2Cu_3O_{6.5\pm y}$ instead of $Nd_1+xBa_2-xCu_3O_{6.5\pm y}$ suggested earlier.

INTRODUCTION

Cuprate superconductors are multimetallic oxides composed of copper and 2 to 5 more electopositive metals. Most researches agree that copper and oxygen have a dominant effect on the electromagnetic behavior of these superconductors. The importance of other elements is less understood. A possible way to study effect of the constituting atoms on electromagnetic properties of cuprates is to compare behaviors with those in which these atoms are substituted by other atoms.

Substitution of rare earth elements for Y has usually little effect on the critical transition temperatures (Tc) of $YBa_2Cu_3O_{6.5+y}$ (1) when y<0.5. The oxygen content of $YBa_2Cu_3O_{6.5+y}$ never exceeds the value of 7(y=0.5) (1,2). In contrast, oxygen contents with y<0.5 were measured for some $REBa_2Cu_3O_{6.5\pm y}$ (RE =rare earth) superconductors. Examples are $LaBa_2Cu_3O_{7.27}$ (3) and $NdBa_2Cu_3O_{7.23}$ (4). In the $LaBa_2Cu_3O_{6.5+y}$ family of superconductors, the Tc of compounds with y<0.5 is significantly lower than the Tc of most other compounds containing oxygen at y<0.5 (1, 3, 5). For instance, 72K and 23K critical transition temperatures were for LaBa2Cu3O6.75 and LaBa2Cu3O7.27, respectively (3).

The $LaBa_2Cu_3O_{6.75}$ is an orthorhombic, while the $LaBa_2Cu_3O_{7.27}$ is a tetragonal version of the well - knon crystal structure of $YBa_2Cu_3O_{7-x}$ (3, 5-8). It is possible that an orthorhobic to tetragonal phase transformation is responsible for the drop of Tc Such changes are known for $YBa_2Cu_3O_{7-x}$ (6-8). However, in contrast to the La-superconductors, the formation of the non-superconducting retragonal phase is a result of oxygen loss in the $YBa_2Cu_3O_{7-x}$.

The ionic difference between the radii of La^{3+} (1.16A) and Ba^{2+} (1.61A) is smaller than between the radii of Y^{3+} (1.02A) [9]. Consequently, the possibility for some random La^{3+} -Ba^{2+} disorder is somewhat higher in superconductors of the type $LaBa_2Cu_3O_{6.5\pm y}$ than that of Y^{3+}-Ba^{2+}disorder in $YBa_2Cu_3O_{6.5+y}$. It is speculated [1, 3, 5] that a partial exchange between the $La^{3+}$and Ba^{2+}ions in the $LaBa_2Cu_3O_{6.5+y}$ crystal can result in a reorganized coordination of oxygen which manifests itself in an orthorhombic to tetragonal lattice symmetry transformation. Since the mutual replacement between the La^{3+} and Ba^{2+}ions does not introduce new positive charges into the molecule, it is not clear how and why would a La^{3+}-Ba^{2+} disorder $LaBa_2Cu_3O_{6.5+y}$ superconductors with oxygen contents of $y < 0.5$.

In contrast to the tetragonal $LaBa_2Cu_3O_{7.27}$, the $NdBa_2Cu_3O_{7.23}$ has an orthorhombic crystal structure [4]. Many other compounds of the type $NdBa_2Cu_3O_{6.5+y}$, containing various amounts of oxygen (y ranges from 0.00 to 0.75), have also been reported to be orthorhombic [1, 4, 10-12]. The critical transition temperature (roughly 8ok) of these superconductors remainel practically unchanged at different values of Y [1, 4, 10-12]. Since the ionic radius of Nd^{3+}, 1.29A, is closer that of Ba^{2+} (1.61A) than the radius of La^{3+} (1.16A) [9], one would expect a similar Nd^{3+}-Ba^{2+} disorder in $LaBa_2Cu_3O_{6.5+y}$. Provided that the reported [1] crystal symmetry and oxygen dependence of Tc are correct in $LaBa_2Cu_3O_{6.5+y}$, the decreasing of similar y-Tc relationship in superconductors of the type $NdBa_2Cu_3O_{6.5+y}$ is rather surprising. We try to show in this work that an orthorhombic to tetragonal transformation and subsequent decrease of Tc can also be observed in $NdBa_2Cu_3O_{6.5+y}$. However, in contrast to earlier suggestions for the $LaBa_2Cu_3O_{6.5\pm y}$ superconductors, the observed chages in $NdBa_2Cu_3O_{6.5+y}$ superconductors are probably due to the presence of excess neodymium and not to oxygen surplus over 7.

The idea that Nd^{3+} can substitute some Ba^{2+} in the perovskite-like structure of $NdBa_2Cu_3O_{6.5+y}$ is supported in many reports of the $Nd_{1+x}Ba_{2-x}Cu_3O_{6.5+y}$ solid solution [1, 4, 10-18]. Three essential observations were deduced from the results. They are: i) an orthorhombic to tetragonal phase transformation takes place when x is increased from 0 to 1, that is when Nd2O3 surplus and $BaCO_3$ deficit is used for synthesis of the superconductors; ii) y increases with increasing x; iii) Tc decreases with increasing x. It is cinjectured that the excess Nd^{3+} substitutes the missing Ba^{2+} ions. The surplus positive chargc of Nd^{3+} requores adsorption of additional oxygen ions. Consequently, the oxygen deficit, characteristic on the original orthorhombic structure, disappears and the compound becomes tetragonal. The orthorhombic to tetragonal phase transformation or the decreasing hole concentration (due to the increased oxygen content) is thought to cause a strong decrease in Tc [1, 4, 10 - 18].

Studying the physical behaviors of some superconductors of the type $Nd_{1+x}Ba_{2-x}Cu_3O_{6.5+y}$, most of our measurements confirmed results reported in the literature. However, we found that the oxygen content in these solid solutions is higher than one could expect from the excess amount of Nd^{3+}. The difference between the calculated and measured oxygen contents have not been taken into accunt in early reports. Based on the real oxygen contents of $Nd_{1+x}Ba_{2-x}Cu_3O_{6.5+y}$ solid solutions a new interpretation of experimental results is suggested in this paper.

EXPERIMENTAL

Solid solutions of $Nd_{1+x}Ba_{2-x}Cu_3O_{6.5+y}$ with x= 0.10, 0.15, and 0.20 were prepared from the stoichiometric mixtures of Nd_2O_3, $BaCO_3$ and CuO. The starting materials were wet ground in an electrical agate mortar for 120 minutes using isopropanal for moisturizing. The mixture was placed in an alumina crucible and heated at 850 °Cfor hours. After cooling at a rate of 50 °C/h, the mixture was wet ground and pressed into pellets at 12 tons/cm2 pressure. The pellets were reheated in air at 900 °C, 920 C, 940 °C, and 950 °C, for 10 hours , repeatedly. The rate of cooling between the heating cycles was 50°C/h. A last heat treatment was dine at 960 °C for 100 hours. Hereupon; the pellets were cooled to room temperature in flow of oxygen (2.0 L/h) ata rate of 10 °C/h.

D.C. electrical resistance measurements were performed using the conventional fourprobe technique [19]. platinum thermometer (pT-100) with ± 1°C accuracy was used to measure temperatures. Oxygen contents were measured by the iodometric titration method [20] in oxygen free nitrogen atmosphere. X-ray powder diffraction (XRD) patterns were measured using the Cuka (1.54178A) source in a philips diffractometer.

RESULTS AND DISCUSSION

X-ray Powder Diffraction

XRD of samples $Nd_{1+x}Ba_{2}$-$xCu_{3}O_{6.5+y}$ containing different amounts of Nd are shown in Fig. 1. Only one crystallized phase is to observe in all solid solution. The perovskite-like structure is reported to be similar to the structure of the well-known $YBa_{2}Cu_{3}O_{6.5+y}$ [1]. A typical orthorhombic to tetragonal change of lattice symmetry at different values of x is shown in Fig. 2. The lattice parameters a, b, and c were confirmed by Rietveld analysis [21]. The parameter a increases while c and b decrease with increasing x, respectively. The changes of symmetry are akin to those reported earlier [17] for these compounds. According to these reports [1,17], the orthorhombic to tetragonal phase transformation can be the reslt of replacement of some Nd^{3+} ions for Ba^{2+} ions in the $NdBa_2Cu_3O_{6.5+y}$ crystal lattice. The replacement is due to the presence of excess Nd.

OXYGEN CONTENT

Oxygen contents measured at various values of x are shown in Fig. 3. Since, except of the Nd content, there is no difference betwen the composition of solid solutins, $Nd_{1+x}Ba_{2-x}Cu_3O_{6.5+y}$,it seemed to be reasonable to assume that the increasing oxygen content is due to the gradual replacement of Ba^{2+} with Nd^{3+}. The dashed line in Fig. 3 represents the calculated oxygen contents for $Nd_{1+x}Ba_{2-x}Cu_3O_{6.5+y}$ at different values of x. For the calculaions it was assumed that : i) the basic Y = 0.73 value at x = 0 is correct; ii) each Nd atom replaces one Ba atom and each replacement causes 1+ increase in positive charges; iii) each new 2+ charge is neutralized by on O^{2-} ion. Fig.3 shows that the measured oxygen contents exceed significantly the values expected. The dotted line in Fig. 3 shows the calculated oxygen contents of the $Nd_{1+x}Ba_{2-x}Cu_3O_{6.5+y}$ samples assuming that the Nd atoms did not replace Ba but, instead, they are present as Nd_2O_3. These values nearly agree with the experimental results within the error of measurements (±0.5%).

It is believed therefore that, rather than $Nd_{1+x}Ba_{2-x}Cu_3O_{6.5+y}$, a mixture of Nd_2O_3 and $NdBa_2Cu_3O_{6.5\pm y}$ is prepared. The small, well distributed, probably amorphous amount of Nd2O3 is not visible in XRD.

At x=1.10 and 1.15, the measured oxygen contents are slightly than those calculated from the presence of Nd_2O_3. It is conjectured that this excess oxygen is actually built into the lattice of superconductors. The built in O-or O^{2-} ions acan be thought to represent the negative to equalize the excess positive charges of molecules in which some Nd^{3+} substitution for Ba^{2+} took part. However, we wish to stress that our results do not confirm the idea that the oxygen content of $Nd_{1+x}Ba_{2-x}Cu_3O_{6.5+y}$ superconductors, included the built in excess oxygen ions, can exceed the value of 7, as assumed earlier [1,4]. This conclusion is not in contradiction with the orthorhombic to tetragonal phase transformation observed (Fig. 2) which probably reflects some Nd^{3+}-Ba^{2+} disorder. It is known from the literature [1] that a phase transformation can take part when a very low portion of cations is exchanged. For example, incorporating as low as 0.04% Fe into the $YBa_2Cu_3O_{6.5+y}$ superconductor is enough to cause an orthorhombic to tetragonal change in crystal symmetry [2].

Resistivity Measurements

The temperature dependance of the D.C. electrical resistivity R(T) of different $Nd_{1+x}Ba_{2-x}Cu_3O_{6.5+y}$ samples are plotted in Fig. 4. At high temperatures (>95K), the linear decrease in R (T) of samples with x = 0.00 and 0.05 is typical on metallic conductors. These maerials became superconductors at critical temperatures (Tc) 91K and 91K, respectively. Samples with x>0.05 are semiconductors at gigh temperatures, but a sharp transition to superconductor occurs at critical temperatures from 72K to 89K.

The decreasing in Tc is probably due to the orthorhombic to tetragonal transition of $Nd_{1+x}Ba_{2-x}Cu_3O_{6.5+y}$ as also observed earlier [1, 4, 10-18]. The metal semiconductor type transition may be attributed to the presence of the non-reacted Nd_2O_3. Superconducting cuprates can lost superconductivity by heating them in the presence of a small portion of some types of metal oxide contaminants while they can tolerate remarkably big amounts from other oxides. For example, $BaCuO_2$ belongs to the first while $Ba_2Cu_3O_{5+y}$ to the second group of contaminants in the presence of $YBa_2Cu_3O_{6.5+y}$ [23, 24]. Although the nature of interactions between the second type of nonconducting and superconducting oxides is not understood, the resistivity curves in Fig. 4 are typical for the co-heated mixtures of such materials. Similar results were observed for $YBa_2Cu_3O_{6.5+y}$ in the presence of $Bs_2Cu_3O_{5+y}$ [23, 24]. It is believed that the mixture of $NdBa_2Cu_3O_{6.5+y}$ and Nd_2Cu_3 represents a new version of this type of mixed superconductors.

CONCLUSIONS

1) The orthorhombic to tetragonal phase transformation, the increasing oxygen content and the decreasing of the Tc of $Nd_{1+x}Cu_3O_{6.5+y}$ samples containing increasing amounts of Nd from x = 0 to x = 0.5 prove that properties of our superconductors are akin with those reported earlier.

2) Differences between the measured and calculated oxygen contents and the temperature dipendance of resistivities suggest that essentially a mixture of Nd_2O_3 and $NdBa_2Cu_3O_{6.5+y}$ is present.

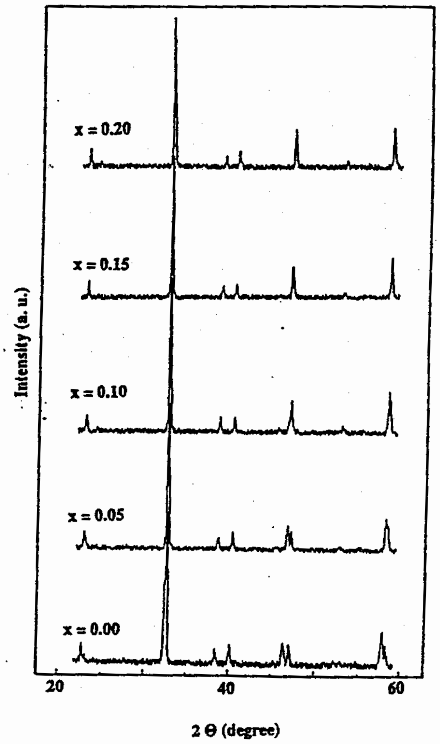

Fig (1) XRD of the Ne1+xBa2-xCu3O6.5+y samples

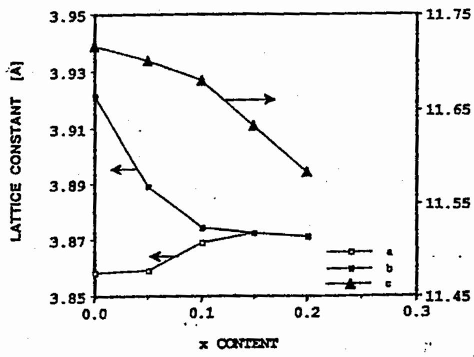

Fig.(2) Effect of change of Nd content (x) on the lattice constants, a, b, c, of Nd1+xBa2-xCu3O6.5+y

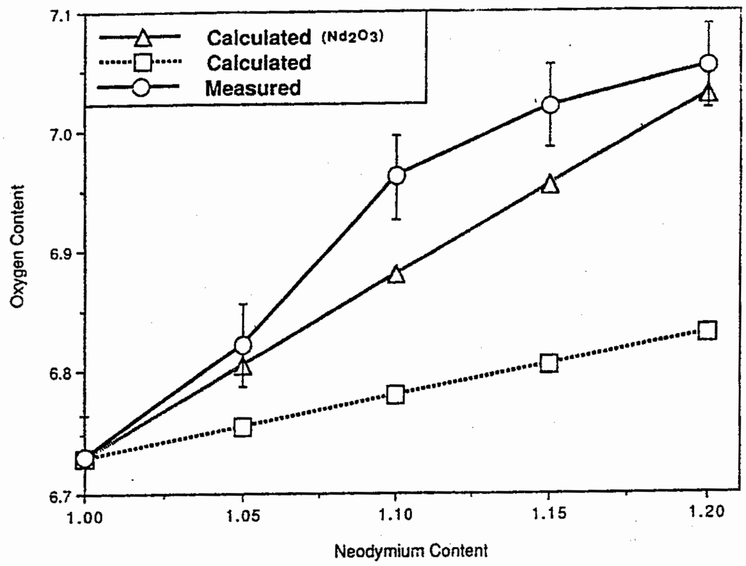

Fig.(3) Relationship between the oxygen content and the neodymeum content of different Nd1+xBa2-xCu3O6.5+y samples.

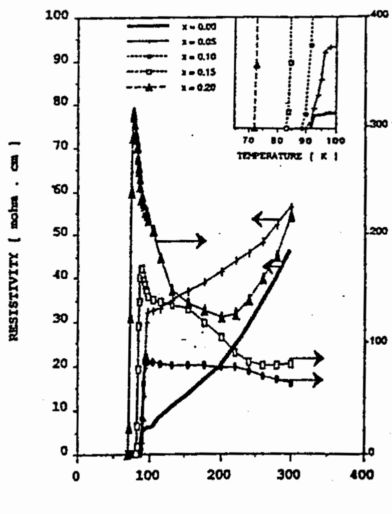

Fig. (4) Temperature dependence of D.C. electrical resistivity of different Nd1+xBa2-xCu3O6.5+y samples

Only a small portion of excess Nd can be built into the superconducting phase.

3) All results can simply explained based on the behaviors of a mixture of superconducting $NdBa_2Cu_3O_{6.5+y}$ and nonconducting Nd2O3. The explanation avoids assuming unusual exceptions for $Nd_{1+x}Ba_{2-x}Cu_3O_{6.5+y}$ solid solutions (e.g. higher than 7 oxygen content paired with a tetragonal crystal structure) from the general features of the 1-2-3 cuprate superconductors.

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