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Superconductivity in sulfur-containing *R*-Ba-Cu-O compounds

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We have prepared samples of $R\text{Ba}_2\text{Cu}_3\text{O}_7\text{S}_y$ (R = Y, Er, Nd) and studied them by x-ray powder diffraction, dc resistivity, and thermoelectric power measurements. All the compounds present a large proportion of secondary phases which are dominated by BaSO_4, as confirmed by the x-ray-diffraction patterns. Samples with R = Y or Er are still high-temperature superconductors confirming the fact that the sulfur atoms are not inserted, or with a very low proportion, in the 1:2:3 phase. In contrast, for the R = Nd samples, a semiconducting behavior is observed. A gradual transition from an orthorhombic to a tetragonal structure is obtained as the sulfur content is increased in $\text{NdBa}_2\text{Cu}_3\text{O}_7\text{S}_y$ ($0 \leq y \leq 1$). This is not due to a sulfur insertion in the 1:2:3 phase. In fact, this phase is Ba deficient because of the formation of BaSO_4 and some of the Nd substitutes for Ba in the 1:2:3 phase. That is, the resulting perovskitelike composition is $\text{Nd}(\text{Ba}_{2-x}\text{Nd}_x)\text{Cu}_3\text{O}_{7+\delta}$. This interpretation is consistent with a previous study of the solid solubility in the $R(\text{Ba}_{2-x}R_x)\text{Cu}_3\text{O}_{7+\delta}$ systems.

INTRODUCTION

Recently, much interest has been given to the effect of substituting the metallic elements in the Y-Ba-Cu-O compounds by transition metals and rare-earth metals.[1-7] The replacements concerning the Cu atoms generally lead to a superconducting transition that is broadened with a lower T_c, while the substitution of Y by most rare-earth elements does not really affect T_c. In the same way, several workers report studies of sulfur substitution for O in the Y-Ba-Cu-O compound.[8-14] However, here the results are contradictory. While certain authors[8-13] claim that the resistive and magnetic properties of $\text{YBa}_2\text{Cu}_3\text{O}_6\text{S}$ are very similar to the ones of $\text{YBa}_2\text{Cu}_3\text{O}_7$, Matsubara *et al.*[14] claim that the sulfur atoms are not incorporated into the crystal lattice of the 1:2:3 phase and make it multiphasic. Felner and Barbara,[10] in particular, studied $R\text{Ba}_2\text{Cu}_3\text{O}_6\text{S}$ compounds with R = Nd, Eu, Gd, and Er, and all their samples were reported to be superconductors demonstrating the Meissner effect. In this paper, we show that sulfur is not significantly inserted in the 1:2:3 phase for R = Nd, Y, or Er. X-ray-diffraction spectra and dc resistivity measurements clearly indicate this fact. However, an important difference exists between the Nd and the Y (or Er) sulfur-containing ceramics. When R = Y or Er, the materials are still superconducting at about 90 K with an orthorhombic structure, while the Nd compound is found to be a semiconductor and to adopt a tetragonal structure. This is well explained by the presence of BaSO_4 in the ceramics, together with the ability of Nd to substitute for Ba in $R(\text{Ba}_{2-x}R_x)\text{Cu}_3\text{O}_7$.[15,16]

EXPERIMENTAL RESULTS AND DISCUSSION

Samples of nominal composition $R\text{Ba}_2\text{Cu}_3\text{O}_7$ and $R\text{Ba}_2\text{Cu}_3\text{O}_7\text{S}_y$ were prepared by thoroughly mixing appropriate amounts of $R_2\text{O}_3$ (R = Y, Er, Nd), BaCO_3, CuO, and CuS powders. The mixed powders were fired at 920 °C in air for 12 h, and furnace cooled to room temperature. The powders were then ground and pressed into pellets at 1800 kg/cm^2, before being annealed under flowing oxygen for 2 days at 950 °C. The temperature was decreased slowly to 600 °C and then to 200 °C in 100 °C steps each lasting 12 h. Pellets were then removed from the furnace. The resistivity measurements were carried out using a four-probe technique on samples with typical dimensions $10 \times 2 \times 2$ mm^3. A current density around 10^{-1} A/cm^2 was used and low-resistance electrical contacts were made with silver paint.

Figure 1 presents the x-ray powder-diffraction spectra of $R\text{Ba}_2\text{Cu}_3\text{O}_7$. All the samples possess a 1:2:3 structure and are characterized by a single phase. Important traces of BaCuO_2 are present on the other hand in the diffraction spectrum of $\text{NdBa}_2\text{Cu}_3\text{O}_7$, as visible in the region of 30°. The splitting between the associated (020) and (200) peaks is present for the three samples (around 47°). This reflects an orthorhombic crystal structure. The lattice parameters that we obtained for each compound are as follows: a = 3.82 Å, b = 3.88 Å, c = 11.65 Å for R = Y; a = 3.81 Å, b = 3.89 Å, c = 11.66 Å for R = Er; and a = 3.87 Å, b = 3.90 Å, c = 11.74 Å for R = Nd. These results are consistent with Ref. 1. On the other hand, in Ref. 2, a very slight orthorhombic shouldering rather than a splitting is obtained with R = Nd. This discrepancy is probably due to an inadequate heat treatment in oxygen flow since we have observed that maximal oxygen entry in Nd-Ba-Cu-O is obtained around 300 °C instead of 450 °C as in Y(Er)-Ba-Cu-O. We noticed this phenomenon by a simple magnetic levitation experiment. Furthermore, the presence of BaCuO_2 in our spectra is indicative of the difficulty of growing pure $\text{NdBa}_2\text{Cu}_3\text{O}_7$. In fact, the ability of Nd to substitute for Ba is this com-

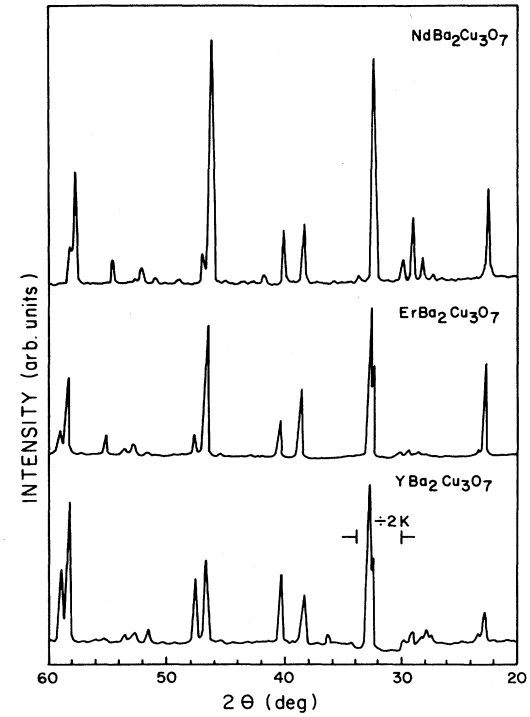

FIG. 1. X-ray-diffraction patterns of $RBa_2Cu_3O_7$ ceramics (R = Nd, Er, Y). The spectra are obtained with the Cu *Kα* radiation.

pound is responsible for the appearance of this secondary phase, just as La substitutes for Ba in $LaBa_2Cu_3O_7$.[17,18] After a comparison of the lattice parameters and the resistivity curve (in Fig. 4, discussed later in the text) with the ones presented in Refs. 15 and 16, we must conclude that our $NdBa_2Cu_3O_7$ sample is in fact a mixture of $Nd(Ba_{1.85}Nd_{0.15})Cu_3O_7$, $BaCuO_2$, and other undetected phases. A too long annealing time at 950 °C could promote the formation of these phases.[17]

In Fig. 2, we can see a large difference between the x-ray diffraction patterns of Nd and Y (or Er) sulfur-containing compounds. In fact, there is a great proportion of secondary phases which are clearly visible with R = Y and Er. The 1:2:3 pattern is still present for these compounds, but no significant peak shift is observed. We also observe an increase of the (005) peak as reported previously.[10,12] In contrast, the x-ray spectrum of Nd-Ba-Cu-O-S is largely dominated by the perovskitelike structure (in proportion). For this compound, the lattice parameters are $a = b = 3.87$ Å and $c = 11.62$ Å.

An attempt was made to identify the origin of the secondary phases. As shown in Fig. 2, many peaks are due to the presence of $BaSO_4$, a compound which has been observed also in Ref. 13 in small amounts. This reference makes a distinction between old and fresh $YBa_2Cu_3O_6S$ samples. Our x-ray patterns would be those of fresh samples, since the measurements were made within two days after the pellets were removed from the furnace. There was no detectable change in the spectra several months after the sample preparation (maintained under vacuum). Therefore, there is no distinction to be made between old and fresh samples. The two most intense lines of the 2:1:1 phase[19] are visible near 30° for Y and Er, but they are absent for the Nd sample.

All these x-ray results can be well accounted for if we suppose that all the sulfur used in the starting material (in the form of CuS powder) reacts with barium and oxygen to form $BaSO_4$. This implies that the remaining material becomes Ba deficient in a ratio 1:1 with the sulfur content, if one tries to grow a 1:2:3 phase. It is therefore possible to reconstitute the composition of the ceramic, knowing the origin of the secondary phases. We give here as an example a nominal composition $RBa_2Cu_3O_yS$ ($\frac{1}{3}$ CuS for $\frac{2}{3}$ CuO in the starting materials). Two different cases are considered: (i) substitution of Ba by R is efficient, which is the case for R = La, Nd, Sm; (ii) substitution of Ba by R does not occur, as for R = Y, Er, Dy. This choice follows the solubility studies of Zhang *et al.*[16]

In the first case, looking at the Nd compound under study, Ba-deficient samples lead to a solid solution of the form $Nd(Ba_{2-x}Nd_x)Cu_3O_{7+\delta}$ with $x = 0.5$. The excess of Cu simply appears in the form of CuO:

$$NdBa_2Cu_3O_yS \rightarrow BaSO_4 + \tfrac{2}{3}\,Nd_{1.5}Ba_{1.5}Cu_3O_{7+\delta} + CuO\,. \tag{1}$$

The two most intense CuO peaks are identified in Fig. 2 at 35.6° and 38.8°. These peaks have about the same relative intensity and the reason why the second appears higher than the first is that it is superimposed on the (005)

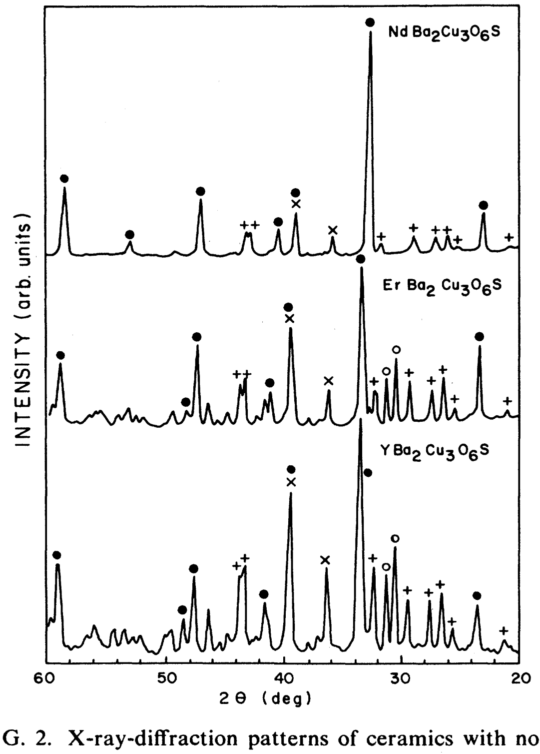

FIG. 2. X-ray-diffraction patterns of ceramics with nominal compositions $RBa_2Cu_3O_6S$ (R = Nd, Er, Y). The symbols represent the following: +, $BaSO_4$; ×, CuO; ○, R_2BaCuO_5; and ●, $Y(Er)Ba_2Cu_3O_7$ or $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$.

peak of the perovskitelike phase. The $Nd_{1.5}Ba_{1.5}Cu_3O_{7+\delta}$ compound that we obtained accidentally had been studied earlier.[16] The consistency is good, since the compound is tetragonal as in our case and the lattice parameters practically coincide. Moreover, as shown in Fig. 3, there is a gradual disappearance of the orthorhombic splitting as the sulfur content is increased, an evolution equivalent to an increase of x in $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$. The first tetragonal compound is observed for a sulfur composition of around $y=0.6$ corresponding to a solid-solution formation with $x \cong 0.25$, in agreement with Zhang *et al.*[16] The contribution due to the sulfur addition on the x value is given by $x=y/(3-y)$, according to a generalization of Eq. (1).

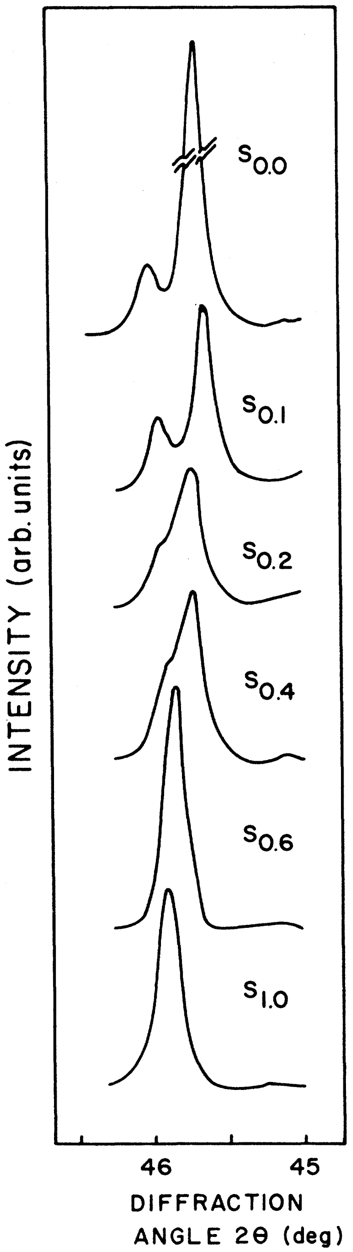

FIG. 3. X-ray-diffraction pattern illustrating the splitting between the (200) and (020) peaks for six samples (the same as in Fig. 4) of $NdBa_2Cu_3O_yS_y$.

The resistivity curves for the samples considered in Fig. 3 are shown in Fig. 4 and may be compared to the ones of Hinks *et al.*[15] We also observe a gradual decrease of T_c with increasing substitution. The evaluation of the x value at $x=0.15$ for our sulfur-free sample is made by an interpolation between their $x=0.1$ and 0.2 curves.

One remarkable effect is that T_c drops off more rapidly with x in our samples, an effect that could be attributed to the presence of an important fraction of secondary phases. In addition, compositional inhomogeneities could affect T_c in such an important way. Figure 5 presents the thermoelectric power measurements of some of our compounds. A metalliclike behavior is observed for the superconducting compounds ($S \propto T$), and the superconducting transition is clearly visible. The transition temperature is higher when observed by thermoelectric power rather than resistivity. This might be due to a current-density effect because $Nd_{1+x}Ba_{2-x}Cu_3O_{7+\delta}$ included in grains in the samples is not perfectly homogeneous. In fact, thermoelectric power measurements imply a very small current flow in the sample and the measured Seebeck voltage is related to most conducting path (superconducting) through the sample as the temperature is lowered. The $y=1$ sample does not present a superconducting transition and its Seebeck-coefficient behavior looks like the one obtained for $YBa_2Cu_3O_6$.[20] Variable-range hopping may explain the $S \propto T^{1/2}$ behavior.

In the second case, i.e., when the substitution of Ba by R is not possible ($R=$Y, Er in the present work), the

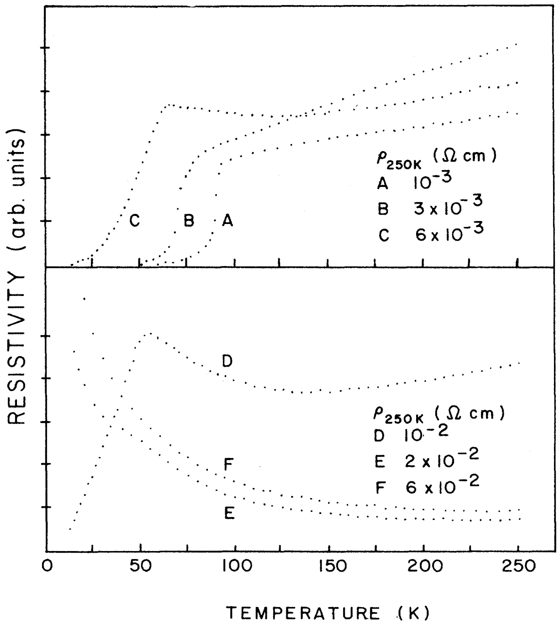

FIG. 4. dc-resistivity curves of six different samples of $NdBa_2Cu_3O_yS_y$: A, $y=0$; B, $y=0.1$: C, $y=0.2$; D, $y=0.4$; E, $y=0.6$; F, $y=1.0$. Also shown are the resistivity values taken at 250 K. Each curve refers to a different arbitrary scale.

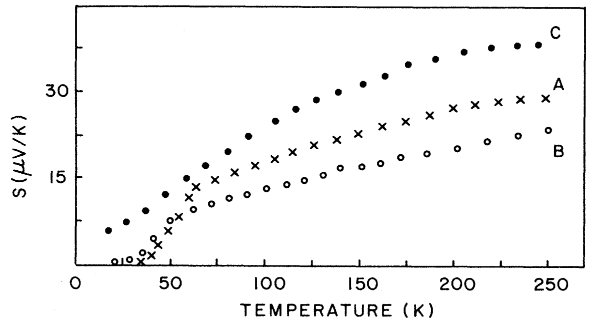

FIG. 5. Thermoelectric power curves of three samples of $NdBa_2Cu_3O_yS_y$ with compositions A, $y=0.2$; B, $y=0.4$; C, $y=1.0$.

chemical reaction becomes

$$RBa_2Cu_3O_yS \rightarrow BaSO_4 + \tfrac{1}{3} RBa_2Cu_3O_7 + \tfrac{1}{3} R_2BaCuO_5 + \tfrac{5}{3} CuO\,. \quad (2)$$

The 2:1:1 phase stemming from the reaction is due to the excess of *R* atoms that could not replace Ba atoms in the 1:2:3 phase, after the $BaSO_4$ formation. The 1:2:3 pattern occupies here a lower fraction of the sample than in the Nd case. That is why the secondary phase peaks are more prominent in the Y(Er) sulfur-containing samples, as visible in Fig. 2. Moreover, the CuO peak at 38.8° is superimposed over the (005) peak of $Y(Er)Ba_2Cu_3O_7$. The increase in the reflection peak with increasing sulfur content previously reported,[10,12] is actually due to CuO instead of sulfur insertion in the 1:2:3 phase.

Our resistivity results for $Y(Er)Ba_2Cu_3O_6S$ samples are very similar to the ones previously published in Ref. 11. These materials are still superconductors with T_c around 90 K and display a large transition width. It appears that sulfur is not incorporated into the 1:2:3 phase in these cases. Rather, we have $Y(Er)Ba_2Cu_3O_7$ grains sufficiently interconnected to favor percolation throughout the ceramic. The widening of the transition would be just due to the presence of the other phases between the superconducting grains, as usually observed.

The results of Felner and co-workers[8,9] on $YBa_2Cu_3O_6S$, showing a larger Meissner effect than in the pure oxide, are inconsistent with the present results as are the magnetic-susceptibility measurements inspired by Felner and Barbara[10] which indicate that $NdBa_2Cu_3O_6S$ is single phase and superconducts. This reference also presents magnetic susceptibility data for $R=$Gd and Eu, with about the same T_c for the pure oxides as for O_6S compounds. These compounds have a limited solid solubility region for the formation of $R(Ba_{2-x}R_x)Cu_3O_{7+\delta}$ and are thus intermediate cases between $R=$Y or Er and $R=$Nd.[16]

Matsubara *et al.*[15] concluded that the substitution of oxygen by sulfur is not achieved in the 1:2:3 phase of Y-Ba-Cu-O by replacing CuO by CuS in the ceramic preparation. Our work leads to the same conclusion.

CONCLUSION

We have presented measurements on the transport properties and structural aspects of ceramics with nominal composition $RBa_2Cu_3O_{7-x}S_x$ ($R=$Nd, Y, and Er). In the three cases, sulfur is not substitutional in the 1:2:3 phase but goes in $BaSO_4$. This reaction causes a Ba deficiency that makes the materials multiphasic. X-ray diffraction and transport properties of the ceramics are related to the solid solubility of $R(Ba_{2-x}R_x)Cu_3O_{7+\delta}$ as a function of the rare-earth element. All the secondary phases have been identified and are consistent with our interpretation for the chemical reactions. Some works previously published on *R*-Ba-Cu-O-S should be reinterpreted in view of the present results.

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