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12 PERSONAL AUTHOR(S): S.M. Fine, S.M. Zahurak, D.W. Murphy, M. Greenblatt, S. Nakahara, W.W. Warren, Jr., D.M. Krol, A.M. Thayer, D.C. Douglass, G.F. Brennert

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Solid State Ionics

EFFECTS OF FLOURINATION ON THE 90 K SUPERCONDUCTOR $Ba_2RCu_3O_{7-\delta}$ (R = Y, Eu; $0 \leq \delta \leq 1$)

S.M.Zahurak, S.M.Fine, D.W.Murphy, M.Greenblatt*, S.Nakahara, W.W.Warren,Jr., D.M.Krol, A.M.Thayer, D.C.Douglass, G.F.Brennert*
AT&T Bell Laboratories Murray Hill, New Jersey 07974
* Rutgers, the State University of New Jersey
Piscataway, N.J. 08854

ABSTRACT

Sintered pellets of $Ba_2RCu_3O_{7-\delta}$ (R= Y, Eu; $O \leq \delta \leq 1$) were allowed to react with fluorine gas at temperatures between 200 and 300°C. Fluorination of $Ba_2YCu_3O_{6.92}$ affords a nominal composition of $Ba_2YCu_3O_{6.4}F_{1.3}$ and T_c(onset) = 92K. Fluorination of $Ba_2YCu_3O_{6.15}$ gives a nominal composition of $Ba_2YCu_3O_{4.7}F_{3.0}$, which is not superconducting to 4.2K. Fluorinated pellets appear to be single-phase as determined by X-ray powder diffraction. However, Raman, NQR, ESR, X-ray diffraction, and TEM data suggest that fluorine is not incorporated into the superconducting phase, but rather is incorporated into a secondary amorphous phase.

MATERIALS INDEX: superconductors, fluorine, copper, yttrium, barium

Introduction

The 90K superconductor, $Ba_2YCu_3O_7$, has a particularly rich substitutional chemistry. (1,2,3) The possibility of substitution of fluorine for oxygen is intriguing since oxygen and fluorine have about the same ionic radius (4) and a variety of metal oxyfluorides are known to exist (5). A recent report claims to have observed superconductivity at 155K in a mixed phase sample in the Ba-Y-Cu-O-F system (6). A number of workers, including ourselves, have been unable to reproduce this result.

However, the possible existence of compounds of the type $Ba_2YCu_3O_xF_y$ and their properties remain as interesting questions. Recent reports (7,8,9) suggest that while solid state reaction methods do not yield oxyfluorides of the type $Ba_2YCu_3O_xF_y$, the reaction of $Ba_2YCu_3O_{7-\delta}$ with fluorine gas does yield $Ba_2YCu_3O_xF_y$ which is either superconducting with a reduced T_c (7) or not superconducting at all (8). We have also studied the reaction of $Ba_2RCu_3O_{7-\delta}$ (R = Y, Eu) with fluorine gas. Much of our data is similar, but additional data leads us to quite different conclusions.

Results and Discussion

Pellets of $Ba_2RCu_3O_{7-\delta}$ were prepared by standard solid-state reaction techniques which have been previously reported (10). Ceramic pellets of $Ba_2RCu_3O_{7-\delta}$ were allowed to react in a monel fluorine/vacuum line with a static pressure ~ 525 mm of fluorine gas at temperatures between 200°C and 300°C. In general, the reaction conditions for samples of $Ba_2YCu_3O_{7-\delta}$ ($\delta \sim 1$) were optimized to a pressure of 525 mm F_2 for 16 hr at 200 °C. Pellets of $Ba_2RCu_3O_{(7-\delta)}$ ($\delta \sim 0$) do not react with fluorine gas at an appreciable rate at 200 °C, therefore a slightly higher reaction temperature (~250°C) was necessary for these samples. Using these conditions, the fluorinated pellets are bluish-black in color throughout, and appear to have interference patterns on the surface much like those on the surface of silicon due to thin layers of SiO_2. X-ray diffraction patterns of these pellets are sharp and correspond to single phase $Ba_2YCu_3O_{7-\delta}$.

Both fluorine and oxygen analyses were performed on all samples. The fluorine content was determined using a calibrated fluoride ion selective electrode. The average oxidation state of Cu was determined by iodometric titration (11). Combined with fluorine analysis, the oxygen stoichiometry was calculated assuming no change in R:Ba:Cu. The T_c (onset) and relative magnitude of the diamagnetic susceptibility were determined by AC susceptibility measurements. In all cases, lattice parameters were determined from x-ray powder diffraction patterns for samples both before and after fluorination.

The composition, lattice parameters, and T_c (onset) of specimens both before and after reaction with fluorine are listed in Table 1. As can be seen, in all cases (except for the Eu containing samples) the lattice parameters and T_c (onset) change remarkably little upon fluorination. The a and b axes of the Eu containing samples do not change to any significant degree, however the c-axis shortens by 0.028(3) Å . The generally small changes in the lattice parameters and T_c (onset) of our samples upon fluorination is perhaps surprising, since in all cases the fluorinated species have compositions very different from those of the corresponding unfluorinated starting materials. For example, in sample 1 there are 6.15 anions per formula, while in sample 1F there are nominally 7.7 anions per formula unit. In contrast, the maximum average Cu

oxidation state does not change substantially upon fluorination and does not exceed ~ +2.33. Also, while compositions of the type $Ba_{2-x}YLa_xCu_3O_{7-\delta}$(12), $La_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ (13), and $Nd_{1+x}Ba_{2-x}Cu_3O_{7-\delta}$ (14) have tetragonal symmetry when $\delta > 0.4$, sample 3F, which nominally has 7.7 anions per formula, has orthorhombic symmetry and lattice parameters which are almost the same as those of sample 3. Davies et. al. (7) suggest that there is a change in the crystal symmetry upon fluorination of partially ($\delta \sim 0.5$) reduced samples. We have found that in partially reduced samples oxygen re-ordering can take place even at the relatively low reaction temperature of 300°C and this may account for their observations.

TABLE I

Composition, Lattice Parameters, and T_c (onset) of samples both before and after fluorination.

Sample No.	Composition	a(Å)	b(Å)	c(Å)	T_c(onset)(K)
1	$YBa_2Cu_3O_{6.15}$	3.863(1)	-	11.833(3)	-
1F[a]	$YBa_2Cu_3O_{4.7}F_{3.0}$	3.863(1)	-	11.829(3)	-
2	$YBa_2Cu_3O_{6.92}$	3.822(1)	3.889(1)	11.690(3)	91
2F[b]	$YBa_2Cu_3O_{6.2}F_{1.3}$	3.825(1)	3.890(1)	11.688(3)	93
3	$EuBa_2Cu_3O_{6.91}$	3.851(1)	3.909(1)	11.734(3)	95
3F[c]	$EuBa_2Cu_3O_{6.4}F_{1.3}$	3.849(1)	3.899(1)	11.702(3)	95
4	$YBa_2Cu_3O_{6.99}$	3.821(1)	3.891(1)	11.686(3)	93
4F[d]	$YBa_2Cu_3O_{5.8}F_{2.1}$	3.825(1)	3.887(1)	11.674(3)	93
5	$YBa_2Cu_3O_{6.99}$	3.822(1)	3.890(1)	11.688(3)	93
5F[e]	$YBa_2Cu_3O_{6.6}F_{0.8}$	3.826(1)	3.889(1)	11.683(3)	92

Reaction conditions: [a]525 mm F_2, 16 h, 200°C; [b]525 mm F_2, 24 h, 250°C; [c]525 mm, 16 h, 245°C; [d]525 mm F_2 120 h, 250°C; [e]500 mm F_2, 285° C, 16h. (Fluorinated samples have the same sample number as the corresponding starting materials).

The one significant change which is evident upon fluorination is broadening of the diamagnetic transition and a decrease in the magnitude of the diamagnetic suseptibility (see Fig.1). This is consistent with data presented by Davies et. al. (7) that fluorinated samples are superconducting but with lower full zero resistance temperatures. Resistivity measurements on heavily fluorinated pellets (3F, 4F) showed semiconducting transport behavior, even though AC susceptibility measurements on these samples showed a substantial superconducting fraction. Wang et. al. (8) reported no superconductivity in fluorinated $Ba_2YCu_3O_7$, but only measured samples resistively.

FIG. 1

A.C. susceptibility vs. temperature measurements before (sample 2) and after (sample 2F) fluorination.

The ^{19}F (I = 1/2) NMR spectra were obtained at room temperature for several fluorinated pellets. The spectra resulting from a solid-echo pulse are symmetric, and approximately Lorentzian in shape with full-width at half height of 270ppm. The decay rate of a $\pi/2_x - \tau - \pi_y$ spin echo pulse sequence indicates that the line is in part inhomogeneously broadened. The width of the absorption makes identification of the chemical species impossible. Spin lattice relaxation is composite, indicative of a broad distribution of magnetic environments for the fluorine; for that part of the ^{19}F signal recoverable from a $\pi_x - \tau - \pi/2_y$ sequence, the apparent T_1 is distributed between 2ms and 25ms. The short ^{19}F spin-lattice relaxation times are consistent with relaxation times reported by Davies et. al.[7] The integrated intensity of the NMR absorption corresponds to less fluorine than expected from chemical analysis, which is consistent with the extremely short relaxation times measured.

The ESR spectrum of a fluorinated pellet (sample 4F) exhibits a large ESR absorption near g=2. No ESR signal is observed for the unfluorinated $Ba_2YCu_3O_7$ ceramic, (15) therefore the signal at g=2 suggests the presence of some other Cu containing species. Comparison of estimated integrated intensities for similar volumes of fluorinated superconductor and CuF_2, suggests that a substantial portion of the copper in the sample is converted to a different compound.

The Raman spectra of $Ba_2YCu_3O_7$ both before and after fluorination have been measured (see Figure 2). Raman is a good probe for this system because of the sensitivity to oxygen stoichiometry and the detection of impurity phases (16,17,18). Upon fluorination the position of the Cu-O vibrational bands between 200 and 800 cm^{-1} do not shift. This is illustrated in Figure 2 where the band observed at 500 cm^{-1}, assigned to symmetric stretching of the apical oxygen, and the band at 435 cm^{-1}, assigned to in-phase bond bending (19) of the planar oxygens, show no shift upon fluorination. These bands would be expected to shift in frequency if a substantial fraction of these sites were occupied by fluorine. Because of the weak intensity of the Raman scattering from the superconductor, very low concentrations (<1%) of crystalline impurity phases would easily be detected. None of the bands due to other cuprates in the Ba-Y-Cu-O phase diagram or crystalline fluorides such as BaF_2 are present. In some cases, a slight broadening and increase in the intensity of the feature at ~ 600 cm^{-1} is observed. This band is ascribed to a stretching vibration of the oxygen in the chains. In a structure where all the chain sites are occupied, this vibration is Raman-forbidden, but it becomes allowed by disorder on the chain sites either created by O vacancies or by substitution such as with fluorine. Thus, the Raman spectra indicate that no new crystalline phases are formed with fluorine treatment and if fluorine is incorporated in the $Ba_2YCu_3O_{7-\delta}$ stucture at all it would be predominantly on the chain sites.

FIG. 2
Raman spectra before (2) and after (2F) fluorination.

The ^{63}Cu nuclear quadropole resonance (NQR) spectrum of $Ba_2YCu_3O_{6.2}F_{1.3}$ (sample 2F) was obtained at 100K (see Figure 3) using spin-echo NQR techniques. (20) The frequency was scanned in the region of the two lines found previously (20) in $Ba_2YCu_3O_7$, roughly 22 and 31.5 MHz. The resonance lines observed in the present samples were essentially identical in position and width with those of a standard sample of $Ba_2YCu_3O_7$. Although the intensities were not calibrated, the signal strengths were comparable to those observed in the standard material. There is therefore no evidence of appreciable modification of the local environments of either the Cu(1) or Cu(2) sites.

FIG. 3
NQR spectra before (2) and after (2F) fluorination.

The lack of substantial change in either the lattice parameters, T_c (onset), Raman spectrum, or ^{63}Cu NQR spectrum of our samples upon fluorination raises the question of whether fluorine is actually being incorporated into the $Ba_2YCu_3O_7$ lattice, or alternatively, is being incorporated into a second amorphous phase which cannot be detected by the above mentioned techniques. To determine if fluorination does cause the formation of substantial amounts of an amorphous phase, a transmission electron microscopic (TEM) study was performed on $Ba_2YCu_3O_7$ and $Ba_2YCu_3O_6$ both before

and after fluorination (see Figure 4). Figure 4a shows the prominent twinned domain structure characteristic of single-phase, orthorhombic, $Ba_2YCu_3O_7$ which has been previously reported (21). The TEM micrograph of $Ba_2YCu_3O_7$ after fluorination (Fig. 4b) shows large regions of randomly distributed amorphous material with the metals ratio approximately equal to that of the crystalline regions. Electron diffraction patterns of these samples clearly show the formation of amorphous material amidst the crystalline orthorhombic $Ba_2YCu_3O_7$. The TEM micrographs of $Ba_2YCu_3O_6$ before and after fluorination are similar to those of $Ba_2YCu_3O_7$, but contain relatively more amorphous material. Therefore, the TEM clearly indicates that the reaction of $Ba_2YCu_3O_{7-\delta}$ with fluorine gas, using the conditions described above, results in the formation of significant amounts of a secondary-amorphous phase.

FIG. 4

TEM micrograph and corresponding electron diffraction pattern before (a) and after (b) fluorination.

The data presented here, as well as that published by other workers (7,8) can all be explained by a simple model consisting of microcrystalline $Ba_2YCu_3O_7$ particles coated with an amorphous layer containing the majority of the fluorine. The three strongest pieces of evidence for this model are the direct observation of amorphous regions by TEM, the overall semiconducting transport behavior of samples with relatively large amounts of superconductivity as measured magnetically, and the large ESR absorption at g=2 which indicates the presence of Cu in a phase other than $Ba_2YCu_3O_7$. Evidence for regions of the sample remaining unchanged by the reaction with fluorine arises from the lack of significant changes in the NQR, Raman, and x-ray diffraction data upon fluorination. This indicates that the amount of fluorine incorporated into the crystalline $Ba_2YCu_3O_{7-\delta}$ lattice is minimal and is consistent with fluorine being present only in the amorphous 'layer' phase.

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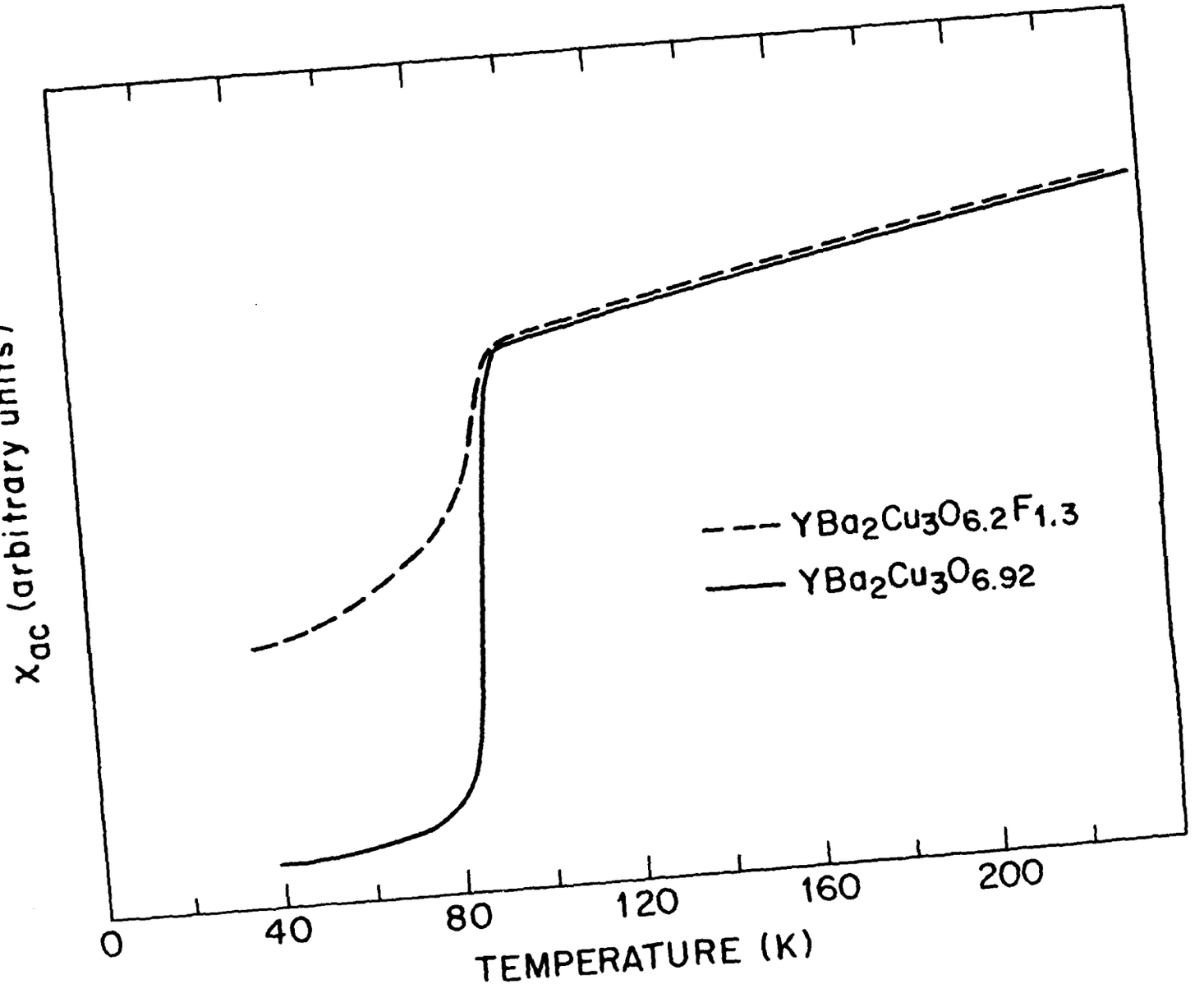
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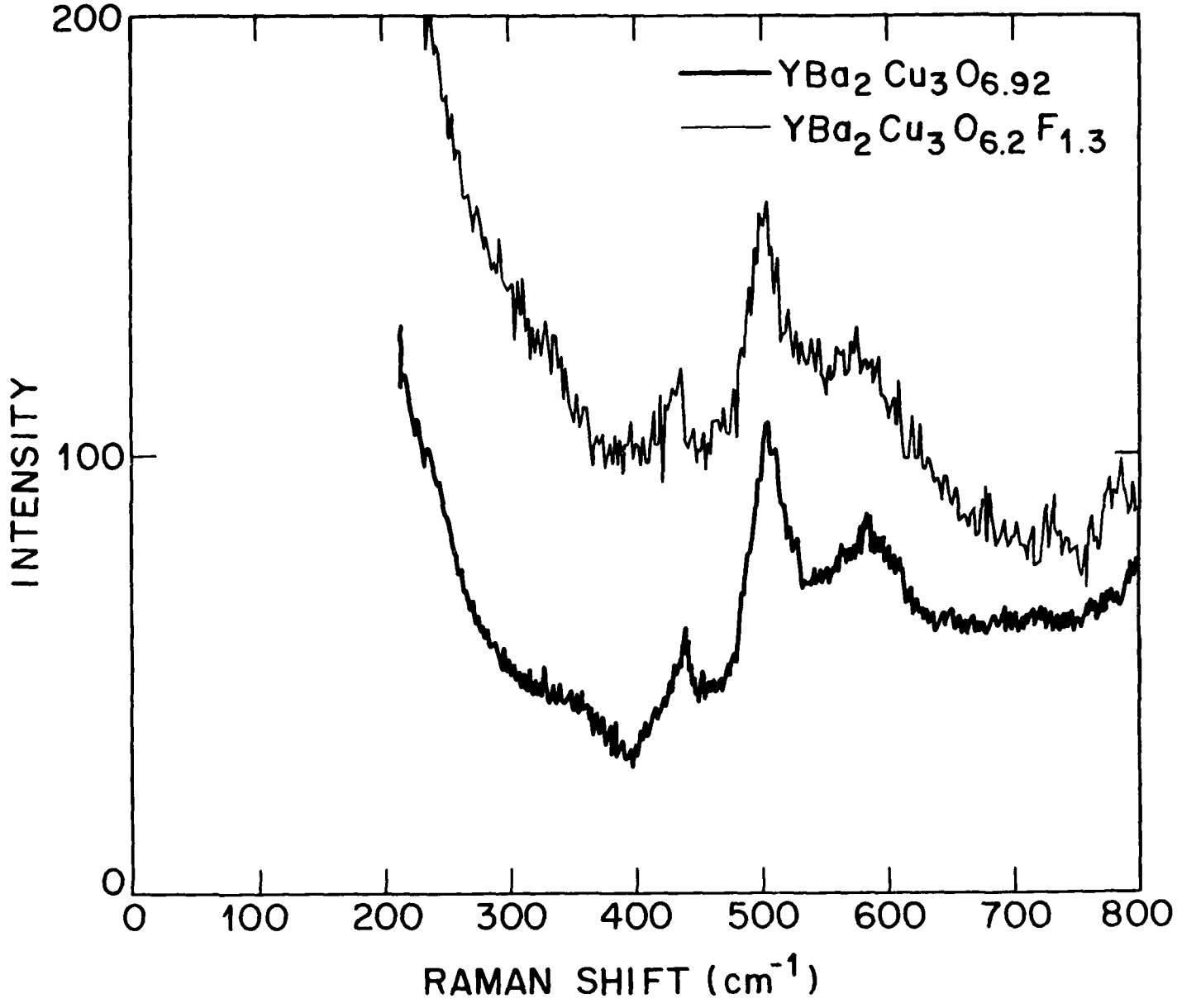
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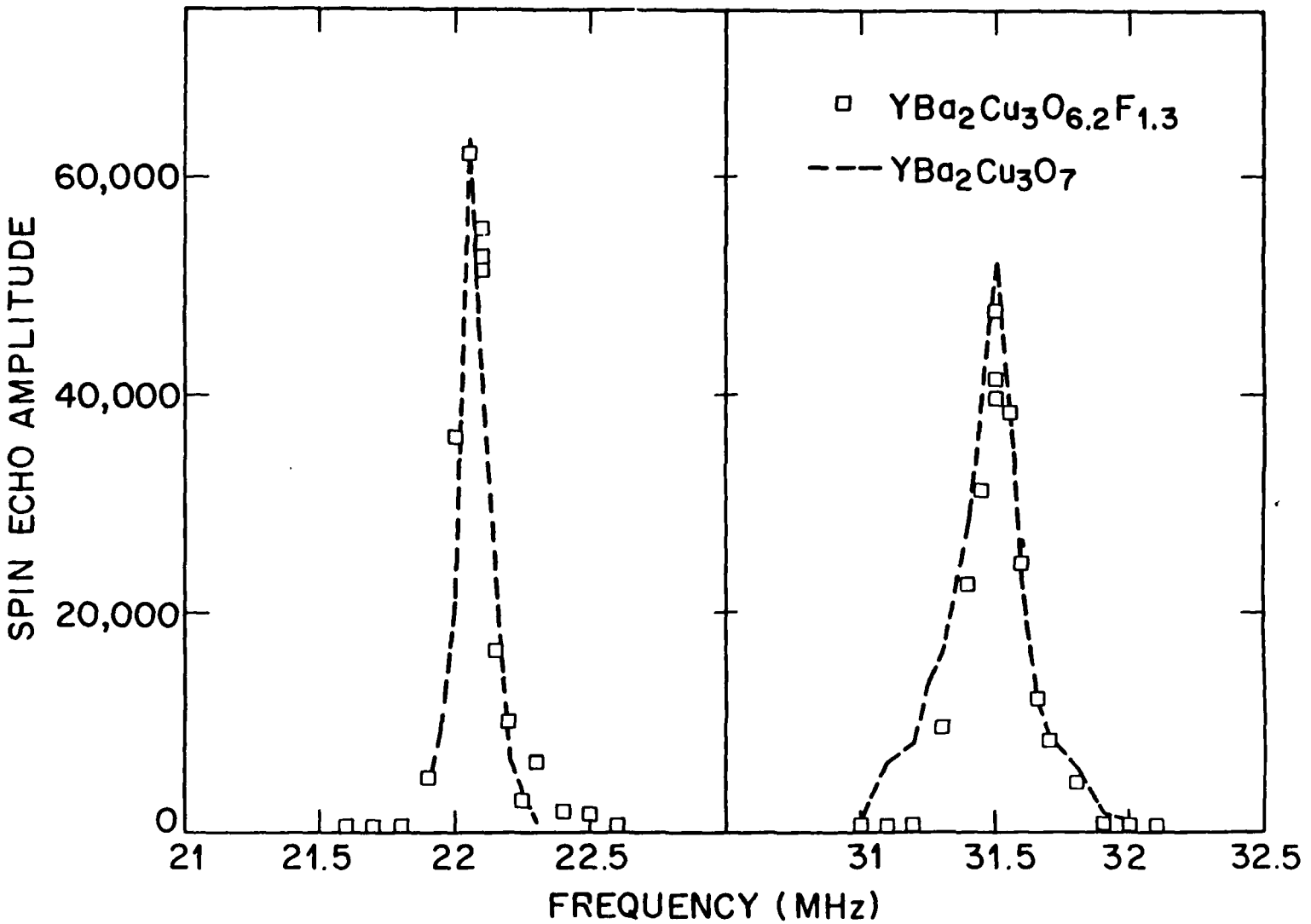
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