Superconductivity and microstructures of fluorinated and chlorinated YBa$_2$Cu$_3$O$_z$

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Superconductivity and microstructures of fluorinated and chlorinated YBa$_2$Cu$_3$O$_z$ were investigated with BaF$_2$ and BaCl$_2$ as the fluorination and chlorination agents. The incomplete decomposition of BaF$_2$ and BaCl$_2$ led to inhomogeneous phase and elemental distributions as shown by energy dispersive analysis of X-rays (EDAX) and X-ray diffraction (XRD) analysis. A high ($y \geqslant 2$) chlorine concentration stabilized a tetragonal perovskite structure in the YBa$_2$Cu$_3$Cl$_y$O$_z$ compositions while an orthorhombic structure was observed in samples with a lower chlorine concentration. The maximum superconductivity transition temperature, T_c, was $\leqslant 95$ K in these fluorinated and chlorinated samples. Thus, our data are contradictory to the claims of high transition temperatures (155 K) recently reported for some of these compositions. The microstructural and phase composition data reported here could provide useful information in the search for possibly high T_c phases in these fluorinated and chlorinated compositions.

1. Introduction

Recently there has been significant interest in the yttrium barium cuprate system since the discovery of its high temperature superconductivity by Wu *et al.* [1]. Several papers have reported solute substitutions in the cation sublattices of YBa$_2$Cu$_3$O$_7$ in an attempt to increase the superconductivity transition temperature, but without any significant success [2-6]. More recently, there has been a report on the use of fluorine anion substitution in YBa$_2$Cu$_3$O$_7$ to increase the superconductivity transition temperature to 155 K [7]. In this paper, we report the preparation and properties of YBa$_2$Cu$_3$O$_7$ samples with chlorine and fluorine substitution in the oxygen sublattice.

2. Experimental procedure

We prepared batches of powder with nominal compositions of YBa$_2$Cu$_3$F$_x$Cl$_y$O$_z$ by mixing appropriate quantities of Y$_2$O$_3$, BaF$_2$, BaCl$_2$ Ba(OH)$_2$ and CuO powders and reacting in oxygen at 900° C for 6 h. The reacted powder was granulated, pressed into discs at 13 500 p.s.i. (93.1 MN) and sintered at 950° C in oxygen for 5 h, followed by annealing at 500° C for 2 h prior to slow cooling at 200° C h^{-1}. X-ray diffraction studies of sintered samples were used to measure their phase composition. Furthermore, optical and scanning electron microscopes and X-ray energy dispersive analyses were used to study the distribution of different phases. The superconductivity of sintered samples was measured by the a.c. magnetic susceptibility and four-point resistivity methods.

3. Results and discussion

Table I shows the crystalline phase distribution in the sintered compositions investigated in this study. The concentration of the YBa$_2$Cu$_3$O$_7$ superconducting phase in the fluorinated and chlorinated samples decreased with the nominal fluorine and chlorine concentrations. When either BaF$_2$ or BaCl$_2$ was the exclusive barium source, i.e. $x = 4$ or $y = 4$, the

TABLE I Phase distribution in samples with nominal compositions of YBa$_2$Cu$_3$F$_x$Cl$_y$O$_z$ where $x + y + 2z \simeq 14$

x	y	YBa$_2$Cu$_3$O$_7$	Y$_2$BaCuO$_5$	BaF$_2$	BaFCl	CuO	Cu$_2$Y$_2$O$_5$	(BaCu)OCl$_2$ or (BaCu)OF$_2$	BaCl$_2$H$_2$O
0	0	1.00	0	0	0	0	0	0	0
1	0	0.33	0.30	0.25	0	0.03	0	0.09	0
2	0	0.15	0.20	0.48	0	0.05	0	0.12	0
4	0	0	0	0.73	0	0.09	0.18	0	0
0	1	0.35	0.13	0	0	0	0	0.51	0.01
0	2	0.24	0.07	0	0	0	0.14	0.51	0.04
0	4	0	0	0	0	0.29	0.50	0	0.21
4/3	4/3	0.09	0.26	0	0.45	0.16	0	0.04	0
1	1	0.26	0.15	0	0.48	0.07	0	0.04	0
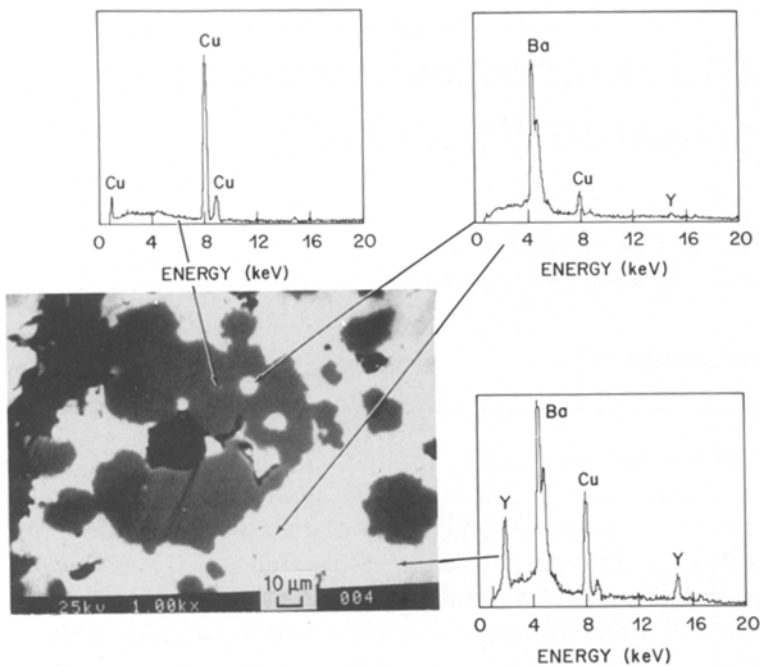
Figure 1 SEM and EDAX spectra of a fluorinated sample with a nominal composition of YBa_2Cu_3-F_2O_z where $z \simeq 6$.

$YBa_2Cu_3O_7$ superconducting phase was not detected. Because BaF_2 and $BaCl_2$ remained intact at the sintering temperature, not all barium was available to react with copper, yttrium and oxygen to form quaternary compounds of $YBa_2Cu_3O_7$ or Y_2BaCuO_5. However, a significant amount of the ternary compound of $Cu_2Y_2O_5$ was formed and this phase was readily detected by X-ray diffraction.

When part of the barium source originated from $Ba(OH)_2$, both the $YBa_2Cu_3O_7$ and Y_2BaCuO_5 phases were formed. $Ba(OH)_2$ decomposed to BaO at a relatively low temperature of 750 to 850° C and this oxide reacted with CuO and Y_2O_3 to form these quaternary compounds. In samples with a significant amount of $BaCl_2$, e.g. $y = 2$, the $YBa_2Cu_3O_7$ phase had a tetragonal crystalline structure with the lattice parameters $a \simeq b \simeq c/3$. This is probably because the chlorine atoms were too large to substitute in the vacant oxygen sites in the basal plane and the chloride compound prevented oxidation of these samples. However, an orthorhombic phase was found in $YBa_2Cu_3Cl_yO_z$ samples with a lower $BaCl_2$ content, e.g. $y = 1$, with the lattice parameters $a < b \simeq c/3$.

When both $BaCl_2$ and $Ba(OH)_2$ were used as the barium sources, part of these precursors reacted with CuO to form a rather stable compound of $(Ba, Cu)OCl_2$. Hydrated barium chloride, $BaCl_2 \cdot H_2O$, was also found in samples prepared by these barium precursors. However, a significant amount of mixed barium halide, BaFCl, was detected by X-ray diffraction (XRD) in samples prepared from a mixture of $Ba(OH)_2$, $BaCl_2$ and BaF_2 precursors.

Fig. 1 shows a scanning electron micrograph (SEM) and the spectra of X-ray energy dispersive analyses (EDAX) from different parts of a fluorinated sample with $x = 2$. The micrograph shows the multiphase nature of this specimen. The EDAX spectra show that the darker areas were copper-rich and they were probably the unreacted CuO phase revealed by X-ray diffraction. The light areas were barium-rich and they
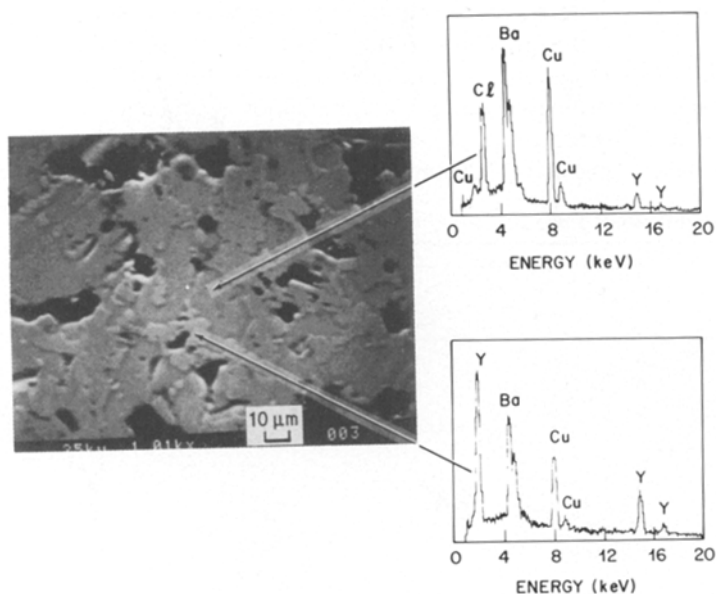

Figure 2 SEM and EDAX spectra of a chlorinated sample with a nominal composition of YBa_2Cu_3-Cl_2O_z where $z \simeq 6$.
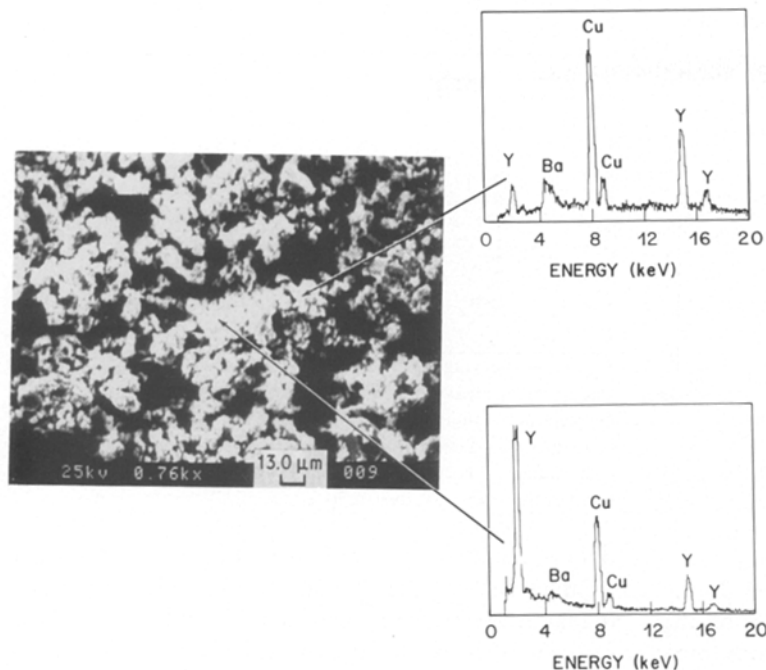
Figure 3 SEM and EDAX spectra of a chlorinated sample with a nominal composition of $YBa_2Cu_3Cl_4O_z$ where $z \simeq 5$.

were the unreacted BaF_2 phase which was also detected by the diffraction analyses. Fluorine was not detected by the present technique because of its low atomic number. Small quantities of copper and yttrium were also detected in these light areas probably because of their solubilities in BaF_2. Copper, barium and yttrium were detected in the grey areas of the micrograph and these areas were the $YBa_2Cu_3O_7$ superconducting phase.

Fig. 2 shows a scanning electron micrograph and the EDAX spectra from different parts of a chlorinated sample with $y = 2$. The scanning electron micrograph shows grains with differential etching rates when polished in isopropanol. The grans with a higher etching rate contained a significant amount of barium, copper and chlorine and only a small amount of yttrium was detected by EDAX. The unetched grains contained significant amounts of yttrium, barium and copper and the relative concentrations of these elements indicated that these grains were probably the Y_2BaCuO_5 phase.

In samples prepared from $BaCl_2$ as the exclusive barium source, $Y_2Cu_2O_5$ and CuO were the major phases detected by XRD. This was confirmed by the EDAX and SEM of a sample with $y = 4$ and they are shown in Fig. 3. Areas rich in $Y_2Cu_2O_5$ and CuO were identified by elemental analyses. The difference in the relative intensity of the $L\alpha$ emission at 1.48 keV and the $K\alpha$ emission at 14.9 keV of yttrium detected at two different areas of this specimen was probably due to the rough surfaces of the fractured sample. A further examination showed that the high intensity emission line near 1.5 keV detected in the lower part of Fig. 3 was not due to the zirconium $L\alpha$ or $L\beta$ emissions (near 1.4 keV) because other ($K\alpha$ and $K\beta$) zirconium emission lines were not detected in this sample. Thus, we conclude that the X-ray emission detected near 1.5 keV in this chlorinated sample was due to yttrium.

X-ray diffraction analyses showed that a significant amount of BaFCl was found in samples prepared from BaF_2, $BaCl_2$ and $Ba(OH)_2$ sources. This was confirmed by SEM and EDAX analyses of a sample

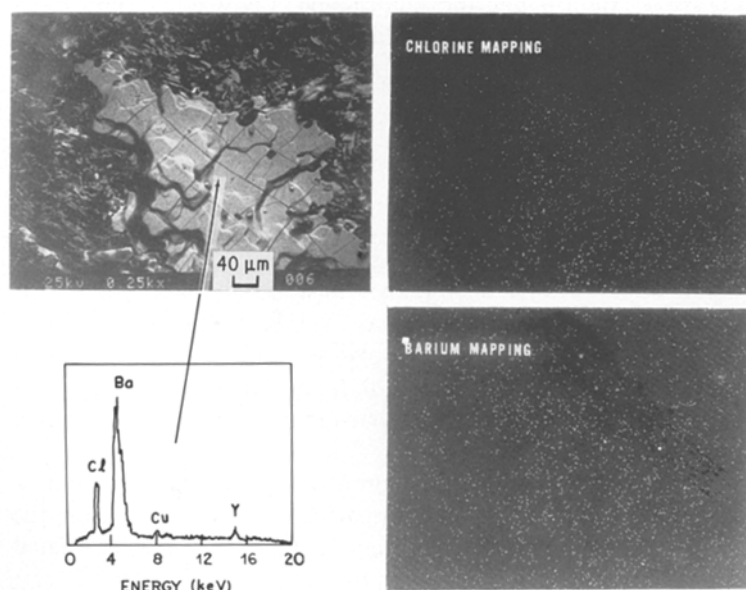*Figure 4* SEM, EDAX spectrum and X-ray mappings of barium and chlorine in a chlorinated and fluorinated sample with a nominal composition of $YBa_2Cu_3FClO_z$ where $z \simeq 6$.

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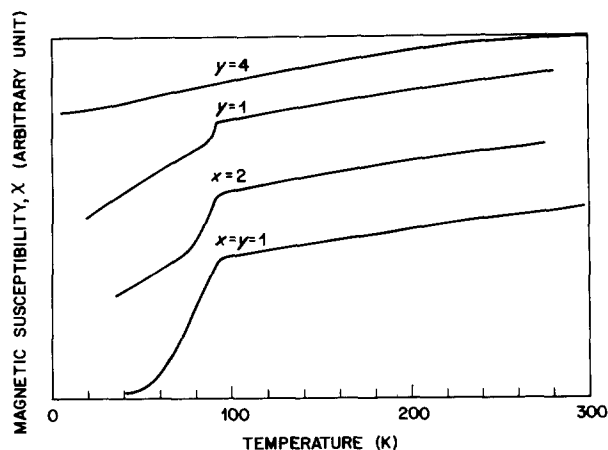*Figure 5* Magnetic susceptibility plotted against temperature for samples with different nominal compositions of $YBa_2Cu_3F_xCl_yO_z$ where $x + y + 2z = 14$.

with $x = y = 1$ and they are shown in Fig. 4. Large grains of $100\,\mu m \times 100\,\mu m$ in size were found on the as-sintered surface of specimens prepared from these barium precursors. EDAX analyses showed that these grains were rich in barium chlorine. Unfortunately, the EDAX analyses were not sensitive for fluorine detection because of its low atomic weight. X-ray mappings of barium and chlorine elements in Fig. 4 matched the location of the BaFCl grains detected on the as-sintered specimen surface.

Figs 5 and 6, respectively, show the magnetic susceptibility and resistivity measurements plotted against temperature for several compositions investigated. Table II summarizes the superconductivity
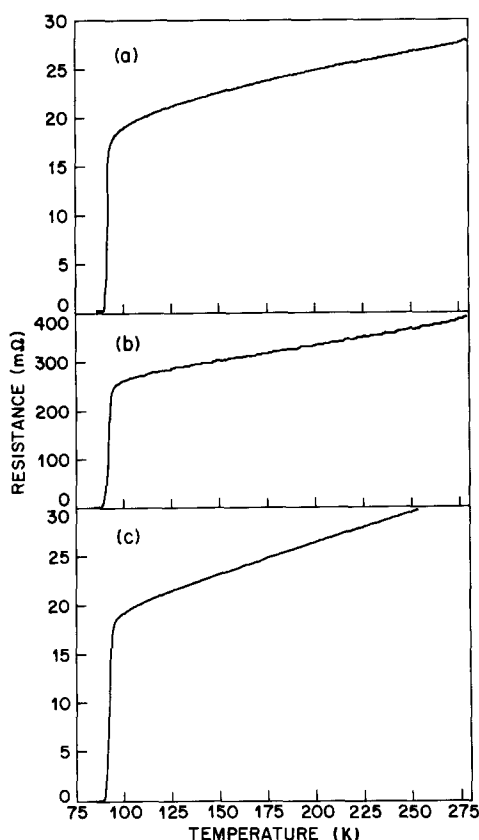

Figure 6 Resistance plotted against temperature for samples with different nominal compositions of $YBa_2Cu_3F_xCl_yO_z$: (a) $x = 2$; (b) $y = 1$ and (c) $x = y = 1$.

TABLE II The superconductivity data of nominal YBa_2Cu_3-$F_xCl_yO_z$ compositions where $x + y + 2z \simeq 14$

x	y	$T_c(\chi)$*	$T_0(\varrho)$*	$T(\varrho = 0)$*
0	0	94	94	92
1	0	94	93.8	91
2	0	93	93.3	89.6
4	0	<4	†	
0	1	92	94.3	88.4
0	2	<4	†	
0	4	<4	†	
4/3	4/3	89	93.0	<79
1	1	93	93.8	89.8

*$T_c(\chi)$ is the transition temperatures measured using magnetic susceptibility measurements. $T_0(\varrho)$ is the onset temperature for the decrease in resistivity and $T(\varrho = 0)$ is the temperature at which zero resistivity was detected by four-point measurements.
† Resistance exceeded $20\,M\Omega$ at $25°\,C$ and resistivity data at a lower temperature were not measured.

data of compositions investigated in this study. Most samples showed the diamagnetic susceptibility starting at a temperature between 89 and 94 K. These samples also exhibited zero resistivity below 88 to 91 K. In samples with high chlorine and fluorine concentrations, e.g. $x = 4$, $y = 2$ and $y = 4$, diamagnetic susceptibility was not detected above 4.2 K. Furthermore, as their electrical resistivities exceeded $2 \times 10^8\,\Omega cm$ at $25°\,C$, their resistivities have not been measured at a lower temperature. It is important to note that we have not observed any sign of superconductivity above 95 K in these fluorinated and chlorinated samples. Thus, our data are contradictory to those published by Ovshinsky *et al.* [7] who claimed a high transition temperature ($\geqslant 155$ K) in fluorinated samples. It is possible that among the many phases observed in these compositions, some of them could have a high T_c as suggested by their measurements [7], even though they were not confirmed by our data. Furthermore, the high T_c phase has not been identified by Ovshinsky *et al.* [7]. Our microstructural and phase composition data could provide useful information in the search for high T_c phases in these fluorinated and chlorinated compositions.

4. Conclusions

1. The superconductivity and microstructures of fluorinated and chlorinated $YBa_2Cu_3O_z$ were investigated using BaF_2 and $BaCl_2$ as the fluorination and chlorination agents, respectively.

2. The incomplete decomposition of the BaF_2 and $BaCl_2$ precursors led to inhomogeneous phases and elemental distributions as shown by EDAX and XRD analysis.

3. A high dopant level of chlorine seemed to stabilize the tetragonal perovskite structure.

4. The maximum transition temperature in the superconductivity was $\leqslant 95$ K in these fluorinated and chlorinated samples and our data are contradictory to the claims of high transition temperatures (155 K) recently reported in some of these fluorinated compositions [7].

5. The microstructural and phase composition data reported here could provide useful information in the search for possibly high T_c phases in these chlorinated and fluorinated compositions.

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