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Abstract

Bulk superconductivity with $T_c$ up to 94 K has been induced by fluorination of non-superconducting YBa$_2$Cu$_3$O$_{6.1}$ using XeF$_2$ as a fluorination agent. Strong changes on X-ray patterns were found after fluorination of reduced YBCO. High resolution electron microscopy of superconducting samples showed the presence of a new phase with $c = 13$ Å which exists as noticeable areas included within a matrix of the 123 structure or which occurs as isolated defects with a limited extension. All fluorinated compounds exhibited a strong disorder along the $c$-direction resulting in a 'loss' of $c$-parameter on X-ray patterns. The present results demonstrate that fluorine indeed enters the YBCO structure with a significant structural rearrangement for the high level of fluorination. The structure of the fully fluorinated YBa$_2$Cu$_3$O$_x$F$_2$ phase, possibly responsible for superconductivity, has been deduced from high resolution electron microscopy. © 1997 Elsevier Science B.V.

Keywords: YBCO; Fluorination; Electron microscopy

1. Introduction

After the discovery in 1987 of the YBa$_2$Cu$_3$O$_{6+\delta}$ superconductor, several groups reported the enhancement of $T_c$ (up to 159 K) for the 123 phase with partial replacement of oxygen by fluorine [1–3]. These results however were not reproduced despite a great activity in this field. The main results achieved in this field up to now may be summarized as follows.

(1) For the partially reduced or fully oxygenated YBa$_2$Cu$_3$O$_{6+\delta}$ compound ($\delta \geq 0.65$), the F incorporation occurs in the Cu1 layer and fluorine preferentially occupies vacant sites along the $a$-direction reducing the orthorhombic strain in the unit cell; this was proved by neutron powder diffraction [4]. This process does not change the symmetry; it causes the decrease of the $c$- and $b$-parameters while the $a$-parameter increases. For the fluorinated 123 phase with starting stoichiometry YBa$_2$Cu$_3$O$_{6.7}$, an enhancement of $T_c$ from 65 K to 90 K was reported whereas at the higher level of fluorination superconductivity was suppressed [5–8]. In the latter case the 123 phase becomes tetragonal with $c = 11.634$ Å.

(2) Fluorination of highly reduced non-superconducting YBa$_2$Cu$_3$O$_{6+\delta}$ ($0 < \delta < 0.35$) preserves the tetragonal symmetry with an increase of the $a$-
parameter, while the c-parameter decreases again [4–6, 9, 10]. This fluorine uptake induces superconductivity with $T_c = 55 - 60$ K which is close to the value for the YBa$_2$Cu$_3$O$_{6.5}$ phase. Magnetic susceptibility measurements exhibited a broad transition and a low volume of superconducting fraction. Note that for all 123 phases the structure shrinks along the c-axis, independent of the initial oxygen content. This indicates that fluorine incorporation creates a similar structural arrangement for the CuI-cations as the oxigens do.

In 1987 Kistenmacher [11] suggested, based on simple considerations of the F$^-$ and O$^{2-}$ similarities, that a fluorine substituted YBa$_2$Cu$_3$O$_{6.5}$F$_2$ phase should have tetragonal symmetry, because of the replacement of one-dimensional Cu-O chain by two-dimensional Cu-F layers. It may enhance superconductivity properties of the fluorinated compound in comparison with YBa$_2$Cu$_3$O$_7$.

However, for a high level of fluorine incorporation into the reduced 123 phase a structural rearrangement should occur due to the instability of the CuI-cation in octahedral coordination with practically equivalent Cu-O$_{apical}$ and Cu-F$_{equatorial}$ bonds. It is well-known that Cu-cations, in an oxidation state close to +2 and surrounded by six oxygen or fluorine atoms, form a strongly distorted octahedron due to a Jahn-Teller effect. Obviously, such effect should take place for the CuI-cation when it is surrounded by six anions in the fully fluorinated YBa$_2$Cu$_3$O$_{6.5}$F$_2$ phase. A significant structural transformation leading to an elongation of the Cu(1)-O(F)$_{apical}$ separation occurs during fluorination of Sr$_2$CuO$_3$ with the formation of the superconducting oxyfluoride Sr$_2$CuO$_2$F$_{2+}$ [12]. One may expect a similar distortion of the Cu(1) octahedral environment for the fully fluorinated YBa$_2$Cu$_3$O$_{6.5}$F$_2$ phase. In this case the structural rearrangement should take place with a significant elongation of the apical Cu-O bonds and an increase of the c-parameter. The effect of a significant elongation of the c-parameter of the unit cell in the fluorinated phases was never reported and all authors found only a continuous decrease of the c-parameter with an increase of fluorine concentration in the lattice. Therefore, one may conclude, that in all previous studies the variation of the reported lattice constants only suggests a partial incorporation of F-anions, whereas a highly fluorinated 123 phase with a composition close to YBa$_2$Cu$_3$O$_{6.5}$F$_2$ and a significantly enlarged c-parameter has never been obtained.

Fluorination of YBCO at equilibrium conditions should lead to the formation of simple oxyfluorides and fluorides (BaF$_2$, YOF, etc.) [13]. Therefore, a soft-chemistry technique (low temperature and a soft fluorinating agent) is more favourable to obtain fluorinated 123 compounds. Earlier we showed that XeF$_2$ may be successfully used as a fluorinating agent at temperatures around 300°C [14]. In the case of YBCO, an anion deficient starting material looks more promising than an oxidized one, since anion exchange in the latter phase should require higher temperatures leading to the formation of thermodynamically stable admixtures.

Our present investigation shows that an intercalation of fluorine into the YBCO structure induces bulk superconductivity and is accompanied by a significant structural rearrangement leading to the formation of a new phase with an enlarged c-parameter of the unit cell ($\approx 13$ Å).

### 2. Experimental

BaCO$_3$, Y$_2$O$_3$, CuO and XeF$_2$ were taken as starting materials. First YBa$_2$Cu$_3$O$_{6.5}$ was obtained by annealing a stoichiometric mixture of the initial compounds at 850°C in air for 48 h and at 930°C for 100 h with intermediate regrinding and then furnace cooled in air. Resulting samples had a composition YBa$_2$Cu$_3$O$_{6.95}$. The reduced material YBa$_2$Cu$_3$O$_{6.1}$ was prepared by annealing YBa$_2$Cu$_3$O$_{6.95}$ pellets in an Ar-flow under a controlled partial oxygen pressure ($P_{O_2} = 10^{-3}$ atm) at 780°C for 10 h. After annealing, the samples were quenched into a massive metal vessel (in an Ar-flow). All initial YBa$_2$Cu$_3$O$_{6.5}$ compounds used for fluorination were obtained as single phase samples.

All subsequent operations were carried out in a glove box in dried N$_2$ atmosphere excluding the presence of O$_2$. 0.4 g of YBCO was mixed with 0.07–0.2 g of XeF$_2$ and intimately ground in an agate mortar. Syntheses were carried out in Ni-crucibles placed in a hermetically closed steel or Ni-container ($V = 30$ cm$^3$ or 15 cm$^3$). In some cases Ni-crucibles were placed into N$_2$-filled and sealed cop-
per-tubes. Time and temperature of annealings were varied from 3–70 h and from 100–350°C. Phase compositions and lattice parameters of the compounds were determined by X-ray powder diffraction using a focusing Guinier-camera FR-552 (Cu $K_{\alpha1}$-radiation, germanium internal standard) and a STADI/P diffractometer (Cu $K_{\alpha1}$-radiation, scintillation counter). The formal copper valence ($V_{Cu}$) in the initial and fluorinated samples was determined by iodometric titration.

AC susceptibility measurements were performed in the temperature range 12–100 K at an external field amplitude of 1 Oe and a frequency of 27 Hz.

Calculations of thermodynamic equilibria and partial gas pressures were made using data from [15].

Electron diffraction (ED) and high resolution electron microscopy (HREM) were performed using a Jeol 4000 EX instrument operating at 400 kV. EDX analysis and electron diffraction were performed using Philips CM 20 microscope with a LINK-2000 attachment. Image simulations were made using the MacTempas software.

3. Results

3.1. X-ray study and magnetic measurements

Two compounds, tetragonal YBa$_2$Cu$_3$O$_{6.11}$ ($V_{Cu} = +1.74$) and orthorhombic YBa$_2$Cu$_3$O$_{6.95}$ ($V_{Cu} = +2.30$), were selected for fluorination treatment. The conditions of the treatment, lattice constants and the superconducting properties for some of the prepared samples are presented in the Table 1.

![Graph](https://via.placeholder.com/150)

**Fig. 1.** X-ray patterns of YBa$_2$Cu$_3$O$_{6.95}$ before (sample 1) and after (sample 2) fluorination.

The fluorination of YBa$_2$Cu$_3$O$_{6.95}$ did not lead to significant changes on the X-ray diffraction pattern (Fig. 1) except a small increase of an orthorhombic distortion and the value of the $c$-parameter. The fluorination also did not change the $T_c$ value (Fig. 2) but the superconducting volume decreased. Iodometric titration revealed a decrease of $V_{Cu}$ to +2.22.

The fluorination starting from YBa$_2$Cu$_3$O$_{6.11}$ (sample 3) (YBCO: XeF$_2 = 1.5:1$) revealed a strong dependence of the X-ray patterns of the resulting materials on the synthesis conditions. Sample 4 did

| Sample No. | Fluoridation conditions | Cell parameters (Å) | Formal Cu valence | $T_c$ (K) 
<table>
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<tbody>
<tr>
<td>1</td>
<td>non-fluorinated</td>
<td>$a = 3.8221(7)$, $b = 3.8676(8)$, $c = 11.664(1)$</td>
<td>+2.30</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>350°C, 70 h</td>
<td>$a = 3.8208(2)$, $b = 3.8876(2)$, $c = 11.6852(8)$</td>
<td>+2.22</td>
<td>93</td>
</tr>
<tr>
<td>3</td>
<td>non-fluorinated</td>
<td>$a = 3.8591(5)$, $c = 11.815(3)$</td>
<td>+1.74</td>
<td>NS</td>
</tr>
<tr>
<td>4</td>
<td>200°C, 30 h</td>
<td>$a = 3.8619(4)$, $c = 11.817(2)$</td>
<td>NS</td>
<td>-75</td>
</tr>
<tr>
<td>5</td>
<td>250°C, 24 h</td>
<td>$a = 3.8685(7)$</td>
<td>+2.14</td>
<td>94</td>
</tr>
<tr>
<td>6</td>
<td>300°C, 70 h</td>
<td>$a = 3.8688(9)$</td>
<td>+2.03</td>
<td>94</td>
</tr>
<tr>
<td>7</td>
<td>350°C, 50 h</td>
<td>$a = 3.8688(6)$</td>
<td>+2.03</td>
<td>94</td>
</tr>
<tr>
<td>8</td>
<td>350°C, 70 h</td>
<td>$a = 3.8724(6)$</td>
<td>-76</td>
<td>NS</td>
</tr>
<tr>
<td>9</td>
<td>325°C, 50 h; Cu-tube</td>
<td>$a = 3.8688(2)$</td>
<td>+2.03</td>
<td>94</td>
</tr>
<tr>
<td>10</td>
<td>350°C, 50 h; Cu-tube</td>
<td>$a = 3.8696(8)$</td>
<td>+2.03</td>
<td>94</td>
</tr>
</tbody>
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not reveal any noticeable interaction with XeF$_2$. Significant changes were detected on the X-ray pow-der patterns of the samples prepared above 200°C. Sample 5 contained two phases and one of them was an unreacted tetragonal YBCO as an admixture (about 10%). The increase of temperature and time of fluo-ration led to a dramatic decrease of the intensity of reflections with $l \neq 0$ (Fig. 3). Mainly $h00$ reflections are present in the X-ray pattern of samples 5–7 and therefore only $a$-parameters can be determined correctly. The fluorination is accompanied by an increase of the $a$-parameter from 3.859 Å to 3.869 Å. Apart from sharp $hk0$ reflections a few very broad $hkl$ ($i \neq 0$) reflections are also present in the X-ray patterns. Their peak height positions cor-respond to a tetragonal phase with $c = 11.658(1)$ Å. These peaks have a strong asymmetry at the low angle side, which may be attributed to the existence of several phases with a variable c-parameter. Such X-ray patterns suggest a well established in-plane order and a strong disorder along the c-direction or the presence of numerous defects in the microstruc-ture of the phase. A further increase of annealing time from 50 to 70 h (sample 8) led to an increase of

the $a$-parameter to 3.872 Å but the overall aspect of the X-ray pattern remained the same. It should be noted that a small amount of badly crystallized admixture of cubic (Ba,Y)-oxyfluoride ($a = 5.975(4)$ Å) was also present on some X-ray patterns (samples 6–8).

The presence of ill crystallized oxyfluorides on the X-ray patterns of samples 6–8 indicates that some other processes occur. Under the synthesis conditions (closed volume) decomposition of YBCO as well as anion exchange may take place. This may lead to a release of oxygen which may interact with YBCO, producing an oxygenated orthorhombic phase. However, the orthorhombic 123 phase has never been observed in our experiments.

To decrease the partial oxygen pressure during fluorination several syntheses were performed in N$_2$-filled and sealed copper tubes. Only the fluori-nated tetragonal phase with $a = 3.868$ Å was ob-tained and no amorphous phase was revealed on X-ray patterns (Fig. 3, sample 9). The internal sur-

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**Fig. 2.** Temperature dependence of the magnetic susceptibility for YBa$_2$Cu$_3$O$_{6.95}$ before (sample 1) and after (sample 2) fluorination.

**Fig. 3.** X-ray patterns of YBa$_2$Cu$_3$O$_{6.11}$ before (sample 3) and after (samples 7,9) fluorination. The arrow indicates an admixture peak.
face of the Cu-ampoule after reaction was covered by a small amount of Cu$_2$O.

In contrast to YBa$_2$Cu$_3$O$_{6.95}$, the synthesis conditions here critically influence the superconducting properties of materials obtained from reduced YBCO (Fig. 4). The initial tetragonal phase is known to be non-superconducting, but annealing with XeF$_2$ at 250°C during 1 day already revealed a very broad superconducting transition (sample 5). A further increase of the annealing temperature led to a sequential increase of the superconducting volume and $T_{c,\text{onset}}$ (samples 6,7). The highest value of $T_{c,\text{onset}} = 94$ K was found for samples 7,9 and they exhibited also the largest superconducting volume fraction ($\sim 25\%$). However, a further increase of the annealing time led to a decrease of the superconducting fraction as well as of $T_c$ (sample 8).

3.2. Electron microscopy analysis

Since X-ray diffraction only allows to deduce clear information about the cell dimensions in the $ab$-plane, an electron microscopy study was performed to determine the cell dimension along the $c$-axis as well as the microstructure of the fluorinated samples. The $a$-parameter determined from X-ray data was further used for calibration of the ED patterns as well as the HREM images. The samples 5,7,8 were investigated by ED and HREM.

ED patterns for the best superconducting sample 7 are shown in Fig. 5. The [001]$^*$ diffraction pattern (DP) shows an intensity and spot distribution typical for tetragonal symmetry with $a = 3.86$ Å (Fig. 5a). The [hk0]$^*$ diffraction patterns however are strongly dependent on the area selected; they can be divided into two categories. The first one is typical for a 123-structure with $c$-parameter 11.66 Å (Fig. 5c,e) whereas the second one exhibits streaks along the $c^*$-direction (Fig. 5b,d). Careful analysis of these patterns allowed us to separate two diffraction grids with equal $ab$-parameters but with different dimensions along the $c$-axis: $\sim 11.66$ Å and $\sim 13$ Å [16].

DP along the [110]$^*$-zone axis (Fig. 5d) often show, besides streaks along the $c^*$-axis, additional streaks or rows of diffusion spots parallel to the $c^*$-direction.

Fig. 5. Electron diffraction patterns for sample 7. (a) [001]$^*$-zone; (c) and (e) [100] and [110] patterns corresponding to the ordered F1 phase with $c = 11.66$ Å; (b) and (d) [100] and [110] patterns corresponding to an intergrowth of the F1 and F2 phases.
Under the used defocus conditions, the bright dots correspond to heavy atoms. It is visually clear that in the phase marked as F2 the contrast, corresponding to Cu1 atoms, has drastically changed in comparison with that in areas of the F1 phase and becomes similar to contrast for Cu2 atoms. This may be explained by the similar equatorial arrangement for Cu1 and Cu2 atoms in the F2 structure. At the same time the distance between the Cu1 layers as well as between neighbouring BaO layers increased, pointing towards a fluorine uptake within the Cu1 plane. Areas of the F2 phase were observed also on HREM images of sample 5. Non-superconducting compounds never showed the presence of the F2 phase.

The limited extension of the F1 and, especially, the F2 areas as well as the modulation along the c-axis of the atom displacements around the Cu1 layers produced by an inhomogeneous F-intercalation into the 123 structure explains the broadening and the ‘loss’ of the hkl (l ≠ 0) reflections on the X-ray patterns (see before).

Details on the electron microscopy investigation will be published separately [16].

at the position $h + 1/2, k + 1/2, l$. These streaks are always very weak and sensitive to the electron beam. Their origin has not been deduced until now.

EDX analysis inside the electron microscope, revealed the presence of fluorine in all crystallites but the fluorine distribution is not homogeneous, even inside one crystallite (Fig. 6). A quantitative analysis of the fluorine content however is not straightforward, because of its low Z-number. Nevertheless, the F-content in the crystallites of the F1 phase is definitely smaller than in crystallites exhibiting streaks along the $c^*$-direction (F2 phase).

HREM images of the F1 phase along different zone axes, reveal a contrast similar to that for undoped YBCO [16]. The HREM image of a region, showing a diffraction pattern as in Fig. 5b revealed that the F2 phase (with an enlarged c-parameter of about 13 Å) exists as noticeable bands included within a matrix of the F1 structure or occurs as isolated defects with a limited extension (Fig. 7).
4. Discussion

The present investigation showed that the results of fluorination of the 123 phase strongly depends on its initial oxygen content. No significant changes of $T_c$ and lattice parameters were found when YBa$_2$Cu$_3$O$_{6.95}$ was used in contrast to the reduced YBa$_2$Cu$_3$O$_{6.11}$. The insertion of the F-oxidizer into the 123 structure should increase the average copper valence which differs significantly for both compounds, +2.30 and +1.74, respectively. For YBa$_2$Cu$_3$O$_{6.95}$, the insertion of an additional oxidizer should result in a very high oxidation state of Cu-cations, this problem no longer existing for the reduced compound.

The insertion of F atoms into the YBCO structure may occur at two different positions. Mostly probable is the occupation of the positions in the $xy0$ plane (Cu1-layer). A small amount of fluorine, up to a composition YBa$_2$Cu$_3$O$_6$F (F1 phase), may either occupy one of two positions and form a square Cu1 coordination polyhedron or may be statistically distributed in the 1/2,0,0 and 0,1/2,0 sites. In the first case such intercalation should be accompanied by an orthorhombic distortion of the initial tetragonal unit cell similar to that in the YBa$_2$Cu$_3$O$_7$ structure. A statistical arrangement on the other hand will maintain the tetragonal symmetry. If the fluorine content is more then one atom per unit cell (F2 phase), the extra atoms can occupy the remaining sites in the Cu1 plane. The full occupation of 1/2,0,0 and 0,1/2,0 positions in this plane results in the formation of an octahedral coordination for the Cu1 atoms. Such an arrangement should lead to a distortion of the formed octahedra due to a Jahn-Teller effect and to a significant increase of the Cu1–O$_{apical}$ separation. One may expect an increase of the Cu1–O$_{apical}$ distance by 0.5–0.7 Å which leads to a new c-parameter for the F2 phase in the order of 12.8–13.2 Å; this is exactly what one observes. Such fluorination will result in an increase of the formal valence for Cu and keep the conducting CuO$_2$ layers unaltered. The structural transformations during this fluorination are shown and summarized in Fig. 8.

The second possibility for the intercalation of fluorine atoms in the YBCO structure is to insert them into the Y-layer. Such intercalation would create an octahedral arrangement of copper atoms with an apical Cu–O(F) separation of more than 2 Å, whereas the YBCO structure has a relatively short Cu2–Cu2 distance (3.3 Å). If this intercalation would take place, it would result in a similar increase of the c-parameter (1.0–1.4 Å). However, HREM observations would clearly make the distinction. Image simulations for both models showed that intercalation of fluorine into the Y-layers did not occur.

Fluorination of YBCO with XeF$_2$ leads to the formation of ill ordered structures where a new phase with an enlarged c-parameter (F2) is incorporated in a matrix of F1. Taking into account the

![Fig. 8. Crystal structure of the reduced YBCO, together with the F1 structure and the fully fluorinated F2 structure.](image-url)
formal Cu valence for sample 7 (+2.14) the bulk composition of the sample may be deduced as YBa$_2$Cu$_3$O$_{6.11}$F$_{1.2}$. The intercalation of fluorine into the YBCO structure occurs inhomogeneously (this is evident from the HREM observations), therefore one may assume that the ideal F2 phase has a composition close to YBa$_2$Cu$_3$O$_6$F$_2$. The elongation of the cell parameter is due to an increase of the fluorine content followed by a structural rearrangement of the Cu(O,F)$_6$ polyhedra.

It is reasonable to assume that the intercalation of fluorine occurs in different steps. The first one:

$$\text{YBa}_2\text{Cu}_3\text{O}_6 + \text{XeF}_2 \rightarrow \text{YBa}_2\text{Cu}_3\text{O}_6\text{F}_8 + \text{Xe}$$

\[X(0 < \delta \leq 1), \tag{i}\]

yields an F1 phase with reduced c-parameter (c = 11.66 Å in our experiment). A decrease of the c-parameter for fluorinated YBCO is typical and was observed before. It supports the idea that fluorine atoms intercalate into the YBCO structure similar to oxygen atoms. Reported $T_c$ values for fluorinated phases obtained from reduced YBCO did not exceed 60 K.

During the second stage:

$$(i) + \text{XeF}_2 \rightarrow \text{YBa}_2\text{Cu}_3\text{O}_6\text{F}_8 + \text{Xe} \quad (1 \leq \delta \leq 2), \tag{ii}$$

a new F2 phase is formed as areas within the F1 phase. Areas of F2 were observed in different samples which exhibited superconductivity. The broad superconducting transition is, probably, due to inhomogeneity of the F intercalation, which was confirmed by HREM. One could object that a $T_c$ of about 90 K corresponds to the orthorhombic 123 phase with an oxygen content $\geq 6.8$. However, no orthorhombic phase was observed either on X-ray patterns or on ED and HREM images. We therefore have to attribute the observed superconductivity with $T_c > 60$ K to the appearance of the fluorinated F2 phase.

It is reasonably to suggest the presence of two different competing reactions taking place during the fluorination process in closed vessels. The first one is an intercalation of the fluorine-oxidizer into the YBCO structure and the formation of partially (F1) or fully (F2) fluorinated compounds: reactions (i) and (ii). This should lead to an increase of the formal copper valence and the appearance of superconductivity. The second type of reaction is an anion exchange with a replacement of oxygen atoms by F ones in the YBCO structure:

$$\text{YBa}_2\text{Cu}_3\text{O}_6 + \text{XeF}_2 \rightarrow \text{YBa}_2\text{Cu}_3\text{O}_{6-\delta}\text{F}_8 + [\text{O}] + \text{Xe}. \tag{iii}$$

The differences between a-parameters and $T_c$ values for samples 7 and 8 may be attributed to their distinct anion compositions (e.g. oxygen/fluorine ratio) due to an anion exchange. Moreover, an anion exchange can also take place during a fluorination of the YBa$_2$Cu$_3$O$_{6.95}$ compound. This leads to a decrease of the superconducting fraction and a reduction of $V_{Cu}$ from +2.30 to +2.22. A decrease of $T_c$ after fluorination of oxidized YBCO was observed by several groups [4–8].

The reactions of fluorination with XeF$_2$ occur via the gaseous state. According to thermodynamic calculations of the gaseous phase equilibrium composition, mainly XeF$_2$, XeF$_4$ and Xe are present in the reaction volume at the synthesis conditions. Therefore the partial pressures of XeF$_2$ and XeF$_4$ as well as the microstructure of the initial YBCO strongly influence the chemical reactions between gaseous and solid phases, leading to different fluorination reactions.

The final equilibrium products of fluorination should be fluorides and oxyfluorides of Ba, Y and Cu. The presence of diffuse maxima on some X-ray patterns, corresponding to mixed (Ba,Y)-oxyfluoride supports this idea. Their formation is accompanied by a release of oxygen into the closed vessel. Oxygen may be adsorbed either by YBCO with the formation of the orthorhombic phase (which was not observed) or by other material, for instance the Cu-container. In the sealed copper tube extra oxygen is adsorbed by a getter of Cu/Cu$_2$O forming on the internal tube surface. Assuming that the partial oxygen pressure is determined by the equilibrium O$_2$ pressure under the mixture of Cu/Cu$_2$O, one can estimate that $\ln P_{O_2} = -22.2$ at 600 K. This value is comparable with the partial $P_{O_2}$ under reduced YBCO ($\delta = 0.1$) at the same temperature ($\ln P_{O_2} = -21.1$).

The present results demonstrate unambiguously the possibility of inducing a fluorine-oxidizer (using
XeF$_2$ as a fluorination agent) into strongly reduced YBCO, with the formation of a new compound YBa$_2$Cu$_3$O$_6$F$_2$. It is known, that the average $V_{Cu}$ in the highest $T_c$ orthorhombic YBa$_2$Cu$_3$O$_7$ is +2.33. The same $V_{Cu}$ should exist for the tetragonal YBa$_2$Cu$_3$O$_6$F$_2$ phase. However, the occurrence of two types of competing fluorination processes (insertion and anion exchange) results in an opposite change of $V_{Cu}$ and, probably, $T_c$ of the fluorinated materials. This feature together with the decomposition of fluorinated YBCO creates difficulties to isolate the pure fully fluorinated superconducting phase with ideal composition YBa$_2$Cu$_3$O$_6$F$_2$. Nevertheless, this way appears to have considerable promise for synthesis of new high-$T_c$ superconductors and optimizing of their properties. The increase of $T_c > 150$ K under high pressures for the Hg-1223 superconductor clearly demonstrates the ability of the CuO$_2$ layers to have a specific structural arrangement to produce such high-$T_c$ at ambient pressure. Probably, a change of anion composition may provide the structural change necessary for the enhancement of $T_c$.

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