

## Enhancement of $T_c$ in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ by fluorination

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A 4 K increase of  $T_c$  in Hg-1223 was achieved by the exchange with fluorine of the extra oxygen located in ( $\text{HgO}_\delta$ ) layer. Fluorination of the initially reduced Hg-1223 samples with  $T_c \approx 100$  K by  $\text{XeF}_2$  results in the increase of  $T_c$  up to 138 K while treatment in oxygen flow causes the enhancement of  $T_c$  not higher than up to 134 K. From x-ray and neutron diffraction data we conclude that shortening of the in-plane Cu-O distances without significant ( $\text{CuO}_2$ ) layers buckling in fluorinated Hg-1223 seems to be the main structural factor responsible for the enhancement of  $T_c$ .

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The third member of the superconducting  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$  homologous series exhibits the record  $T_c \approx 135$  K at ambient conditions.<sup>1</sup> Moreover an application of external pressure promotes its increase  $\geq 150$  K.<sup>2,3</sup> This result indicates the principal possibility of achieving in Hg-1223 of higher values of  $T_c$  at ambient pressure by proper modification of its composition and, subsequently, the crystal structure. Neutron powder diffraction experiments performed on Hg-1223 under high pressure<sup>4</sup> revealed shortening of both in-plane and apical Cu-O distances, and the most significant shrinkage was found for the apical bond length.

This pressure effect can be simulated by cation exchange. For this purpose many attempts of Hg substitution by other cations were undertaken.<sup>5</sup> However, in most cases such substitution resulted in the  $T_c$  decrease that probably can be explained by local structural distortions caused by simultaneous location of different cations in one crystallographic site.<sup>6</sup> The only exception was found for the Tl substitution. Tl incorporation into the Hg-1223 structure ( $\approx 10$ – $20$ %) causes the increase of  $T_c$  up to 138 K.<sup>7–9</sup> This replacement is accompanied by small compression of both lattice constants and by the increase of oxygen content in the (Hg, Tl) layer.

The variation of interatomic distances in Hg-based complex copper oxides can also be made by anion exchange. Fluorine has a lower formal valence than oxygen and therefore the larger amount of fluorine should be incorporated in the structure to achieve the same carrier concentration. Moreover, it has slightly smaller radius than oxygen. Both factors can promote variation of characteristic bond lengths. It was shown that fluorination of Hg-1201 resulted in the significant compression of the apical Cu-O distance, while the in-plane one did not vary in comparison with those in the oxygenated Hg-1201 samples exhibiting the same  $T_c$  values.<sup>10</sup> For this superconductor, fluorination does not enhance  $T_c$  and its optimal value for both series was 97 K. This fact allowed to conclude that compression of apical Cu-O bond could not be the main factor of  $T_c$  enhancement under high pressure. It was also shown that the same carrier concentration and  $T_c$ 's require double amount of fluorine in comparison with oxygen.

The large anion concentration can be also incorporated in the fluorinated Hg-1223 structure resulting in the Cu-O dis-

tances variation. The effect of oxygen-fluorine anion exchange may be different for the Hg-1201 and Hg-1223 phases due to different coordination polyhedra for Cu cations. Therefore we suggested that it would be interesting to study the influence of such anion substitution on structural and superconducting properties of the Hg-1223 phase.

Syntheses of the Hg-1223 samples were carried out in sealed silica tubes in two-temperature furnace. All operations with initial oxides and reduced Hg-1223 samples were made in the ‘‘MBraun’’ glove box filled with highly purified Ar to exclude presence of  $\text{H}_2\text{O}$ ,  $\text{O}_2$ , and  $\text{CO}_2$ . The mixture of oxides HgO, BaO, CaO, CuO with the nominal stoichiometry  $\text{Hg}_{1-x}\text{Cu}_x\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_8$  ( $0.0 \leq x \leq 0.2$ ) was placed in the zone at  $900^\circ\text{C}$ . The mixture of cobalt oxides ( $\text{CoO}/\text{Co}_3\text{O}_4$ ) to control oxygen pressure in the ampoule ( $p_{\text{O}_2} \approx 2.2$  bar) was placed in the other zone of the furnace at  $1000^\circ\text{C}$ . Mercury gaseous pressure was adjusted by the excess of HgO which was determined empirically. We found that an excess of copper in the starting mixture resulted in synthesis of Hg-1223 samples with the lower amount of impurity phases. This technique allowed to obtain samples with Hg-1223 content about 95%.

Thus obtained Hg-1223 samples were reduced by annealing in sealed silica tube with the use of Ti getter ( $P_{\text{O}_2} < 10^{-20}$  atm) at  $500^\circ\text{C}$ . After reduction samples had lattice parameters  $a = 3.856$  Å,  $c = 15.84$  Å, and exhibited  $T_c$  in the interval of 90–100 K. Reduced Hg-1223 samples were subjected to fluorination or treatment in oxygen flow during 20 h at  $300^\circ\text{C}$ . Fluorination was performed with the use of  $\text{XeF}_2$  (provided by the Laboratory of Inorganic Synthesis of the Institute of Applied Chemical Physics ‘‘Kurchatov Institute,’’ Moscow, Russia). Reduced Hg-1223 samples were mixed with  $\text{XeF}_2$  in different ratios and ground in an agate mortar, placed into Ni crucibles and then in copper tubes which were evacuated and sealed. Ampoules were annealed at  $200^\circ\text{C}$  for 10–15 h and then quenched.

Phase compositions and lattice parameters were determined by x-ray powder diffraction using a focusing Guinier-camera FR-552 ( $\text{Cu}_{K\alpha 1}$  radiation, Ge internal standard). ac susceptibility measurements were performed in the 12–160 K temperature range at external field amplitude of 1 Oe and frequency of 27 Hz.

TABLE I.  $T_c$  values and lattice parameters of the reduced (No. 1), fluorinated (Nos. 2–8), and oxygenated (No. 9) Hg-1223 samples.

$N$	$T_c^{\text{onset}}$	$a$ (Å)	$c$ (Å)
1	100	3.8566(8)	15.840(5)
2	120	3.8556(4)	15.840(3)
3	135	3.8536(4)	15.799(4)
4	137	3.8514(3)	15.771(2)
5	138	3.8501(2)	15.773(3)
6	138	3.8496(3)	15.724(3)
7	138	3.8495(7)	15.719(9)
8	137	3.8479(2)	15.721(2)
9	134	3.8524(4)	15.819(2)

Lattice parameters and  $T_c$ 's of different fluorinated, reduced and oxygenated Hg-1223 samples are listed in the Table I. Variation of  $\text{XeF}_2/\text{Hg-1223}$  molar ratio and treatment conditions allowed obtaining samples with different level of fluorination. It is remarkable that the incorporation of fluorine in the Hg-1223 structure is accompanied by the valuable decrease of lattice parameters, while  $T_c$  increases up to 138 K. The fluorinated samples are arranged in order of the  $a$  parameter decrease which is sensitive to carrier concentration and reflects different fluorine content. It should be noted that values of lattice parameters for the samples with the highest  $T_c$  (Nos. 5–8) are significantly lower than those for oxygenated one (No. 9). This fact gives us the indirect evidence of fluorine incorporation in Hg-1223 structure. Overdoped oxygenated Hg-1223 phase with close values of lattice parameters (prepared under 40 kbar pressure) revealed much lower  $T_c \approx 125$  K.<sup>11</sup>

The most important observation is that some samples after fluorination exhibit  $T_c = 138$  K which was not reached on samples annealed in oxygen flow. This fact was carefully investigated. The Hg-1223 sample preliminary reduced to  $T_c = 100$  K was divided on two parts. One of them was fluorinated (sample No. 5) while the other part was treated in oxygen flow. ac susceptibility measurements of these three samples are presented in the Fig. 1. Fluorinated sample ( $a = 3.8501(2)$  Å and  $c = 15.773(3)$  Å] showed onset of the transition at 138 K, while the oxygenated sample exhibited  $T_c = 134$  K and had significantly larger lattice parameters:  $a = 3.8524(4)$  Å and  $c = 15.819(4)$  Å. The observed difference of about 4 K between two transitions is clearly seen in Fig. 1. Moreover this result was reproduced several times and  $T_c = 138$  K was also found for some other fluorinated samples (Nos. 6, 7). So we can conclude that fluorine incorporation in Hg-1223 structure allows to increase  $T_c$  by 3–4 K in comparison with oxygen-treated samples.

To understand the reason of this phenomenon the sample No. 8 with the lowest impurity content was further investigated by NPD and XRD methods. The x-ray powder diffraction data were obtained on STADI P diffractometer ( $\text{Cu}_{K\alpha 1}$  radiation, linear PSD). It was found that the investigated sample contained 1% of CaO (which was introduced in the refinement) and a few not indexed reflections with the maxi-

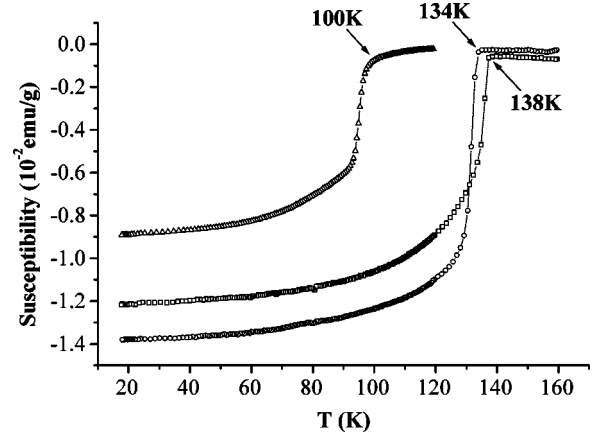


FIG. 1. Temperature dependence of ac susceptibility of Hg-1223: after reduction ( $\Delta$ ), heat treatment in oxygen flow (O), and fluorination ( $\square$ ).

mal intensity about 1%. The XRD experiment allowed us to refine the occupancy of the (Hg, Cu) position. It was found that this position is occupied together by mercury [82.4(6)%] and copper [17.6(6)%]. The obtained occupancy parameters are in a good agreement with the starting composition ( $\text{Hg}_{0.8}\text{Cu}_{0.2}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ ). Moreover, the NPD refinement showed a significant (10%) occupancy of the oxygen site in the middle of the edge which was attributed by a partial replacement of Hg by Cu.<sup>12</sup>

The neutron powder diffraction pattern was obtained at 7 K with the high-resolution Fourier diffractometer (HRFD) at the IBR-2 pulsed reactor. In our experiment the resolution of HRFD,  $\Delta d/d$  was near 0.0015, which allowed to obtain the precise structural information. In particular, the errors of the interatomic distances were about 0.002–0.003 Å. The Rietveld refinement was done in the  $d_{hkl}$  interval from 0.8 to 2.8 Å assuming 17.6% substitution of mercury by copper obtained from XRD data. Neutron diffraction pattern, theoretical peaks positions and difference curve are shown in Fig. 2. It is remarkable that the NPD pattern contained only one impurity phase of CaO with refined mass fraction less than 1%. This allowed us to obtain structural parameters with high precision, because incorrect handling of impurity phases in the refinement resulted in significant systematic errors especially for the occupancy parameters as it was shown by Wagner *et al.*<sup>13</sup> Structural parameters of this refinement are listed in the Table II. Calculated values for the main interatomic distances are presented in the Table III. In general, there is good agreement with the results obtained by Wagner *et al.* for oxygenated Hg-1223 samples. We have also found two types of positions of extra anion located in the (Hg) layer: A(1) in the middle of the mesh (0.5, 0.5, 0) and A(2) in the middle of the edge (0.5, 0, 0) with the occupancies 27(1) and 10(1) %, respectively. The latter value is close to Cu concentration in Hg site and may be attributed to additional bonding between Cu and anions. It is interesting to note that these values as well as positional parameters of atoms were practically insensitive to the variation of the Hg/Cu ratio in the Hg position within the 10–30 % range.

The same two types of extra anion positions were found

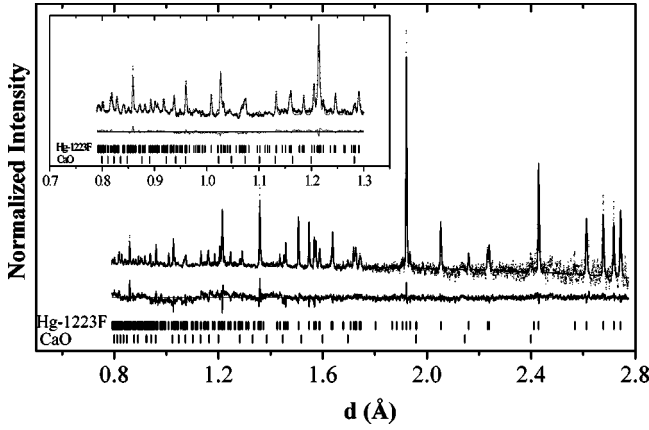


FIG. 2. Neutron-diffraction pattern of the fluorinated Hg-1223 sample (No. 8) measured at  $T=7$  K. Experimental points, calculated profile, and the difference curve are shown. The difference curve is normalized on the mean-square deviation. Tick marks at the bottom indicate the position of Bragg peaks for the main phase and CaO.

for oxygenated Hg-1223 sample ( $T_c=135$  K) and for reduced ones with  $T_c=95$  and 107 K by Wagner *et al.*<sup>13</sup> It was stated that in the reduced sample occupancies of both extra anion positions are equal to 8–10(2) % while oxygen treatment leads to the increase of oxygen occupancy in the A(1) position up to 18(2)%. This value is significantly lower in

TABLE II. Structural parameters for fluorinated Hg-1223 phase (No. 8 sample) refined from neutron powder diffraction data. The commonly used criteria for the quality of the refinement are given.

		$B$ ( $\text{\AA}^2$ )
$a$ ( $\text{\AA}$ )	3.84232(2)	
$c$ ( $\text{\AA}$ )	15.67451(15)	
$V$ ( $\text{\AA}^3$ )	231.4096	
Hg(0,0,0), $n$	0.824	1.28(3) <sup>a</sup>
Cu(0,0,0), $n$	0.176	1.28(3) <sup>a</sup>
Ba(0.5,0.5, $z$ ), $z$	0.1697(1)	0.42(2) <sup>b</sup>
Ca(0.5,0.5, $z$ ), $z$	0.3932(2)	0.42(2) <sup>b</sup>
Cu(1)(0, 0, 0.5)		0.42(2) <sup>b</sup>
Cu(2)(0,0, $z$ ), $z$	0.2973(1)	0.42(2) <sup>b</sup>
O(1)(0, 0.5, 0.5)		0.5 <sup>c</sup>
O(2)(0,0.5, $z$ ), $z$	0.3002(1)	0.5
O(3)(0,0, $z$ ), $z$	0.1261(1)	0.69(4)
A(1)(0.5,0.5,0), $n$	0.27(1)	0.5 <sup>c</sup>
A(2)(0,0.5,0), $n$	0.10(1)	0.5 <sup>c</sup>
$\gamma=n[A(1)]+n[A(2)]$	0.37(2)	
$\chi^2=3.45$		
$R_p, \%$ = 8.43		
$R_w, \%$ = 4.68		

<sup>a</sup>Parameters were varied with constraint to equality.

<sup>b</sup>Parameters were varied with constraint to equality.

<sup>c</sup>Fixed to 0.5  $\text{\AA}^2$ .

TABLE III. Selected interatomic distances and angles for fluorinated Hg-1223 phase.

Bond type	Length ( $\text{\AA}$ )
Hg-O(3)	1.976(2)
Cu(2)-O(3)	2.684(3)
Cu(1)-O(1)	1.92116(1)
Cu(2)-O(2)	1.92167(6)
Cu(1)-Cu(2)	3.177(1)
Ba-A(1)	2.660(2)
Ba-O(2)	2.805(2)
Ba-O(3)	2.8017(7)
$\angle \text{Cu(2)-O(2)-Cu(2)}$ ( $^\circ$ )	177.3(1)

comparison with that [27(1)%] obtained in the present study for fluorinated samples. Similar significant increase of extra anion concentration was found by NPD for fluorinated Hg-1201 in comparison with oxygenated samples exhibiting close  $T_c$ .<sup>10</sup> Unfortunately NPD could not distinguish fluorine and oxygen atoms due to their similar coherent scattering lengths. However, we can estimate the average copper valence ( $V_{\text{Cu}}$ ) on the base of different anion distribution between these two sites. The obtained values belong to the 2.12–2.18 range which is typical for Cu-based hole-doped superconductors exhibiting optimal  $T_c$ .

Incorporation of fluorine results in structure modifications indicated by changes in lattice parameters. The change of the  $a$ -parameter reflects the variation of the extra anion concentration in the structure. The dependencies of  $T_c$  vs  $a$  parameter for oxygenated and fluorinated Hg-1223 samples are shown in Fig. 3. The values of lattice parameters determined by XRD with internal standard were used to avoid possible systematic errors between the data obtained by different techniques. The right part (underdoped range) of the  $T_c(a)$  curve for fluorinated series is close to the oxygenated one down to  $a=3.852$   $\text{\AA}$  and  $T_c \approx 134$ –135 K. These values correspond to the optimally doped oxygenated Hg-1223 samples. However, further increase of extra anion concentration promotes the increase of  $T_c$  for the fluorinated series up to 138 K while oxygenated Hg-1223 exhibits the decrease of  $T_c$  due to overdoping. For the fluorinated series the optimal

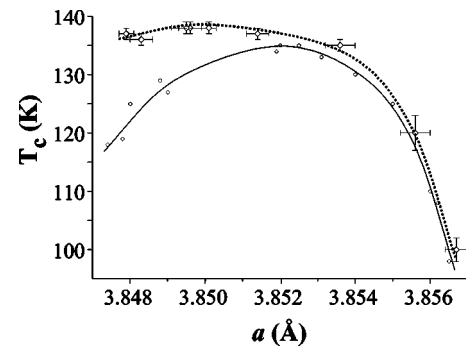


FIG. 3. The dependence of  $T_c$  vs  $a$  parameter for the fluorinated ( $\diamond$ ) and oxygenated (O) Hg-1223 samples. Data for oxygenated samples were taken from Ref. 11. Lines are guides to the eye.

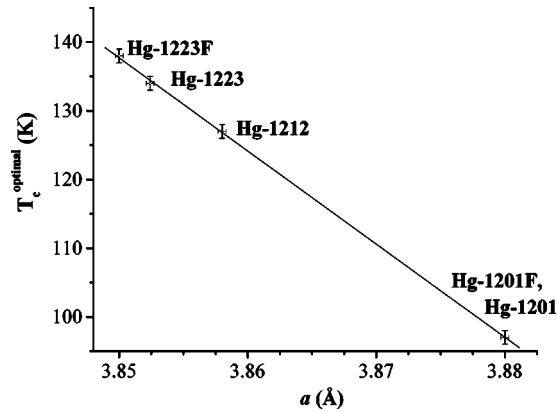


FIG. 4. The dependence of optimal  $T_c$  vs  $a$  parameter for Hg-based superconducting Cu mixed oxides.

value of the  $a$  parameter is smaller in comparison with the oxygenated series  $\sim 3.850$  and  $\sim 3.852$  Å, respectively. Therefore we can conclude that partial replacement of extra oxygen by fluorine in (Hg) layer results in compression of the structure in the ( $ab$ ) plane which is accompanied by the increase of optimal  $T_c$  value. This fact is different from the data recently found for Hg-1201, where the  $T_c(a)$  dependencies for oxygenated and fluorinated samples practically coincide and have the same values of optimal  $T_c = 97$  K and in-plane parameter ( $3.880$  Å).<sup>10</sup>

The dependence of optimal  $T_c$  vs  $a$  parameter for the first three members of the Hg-based series and fluorinated Hg-1201 and Hg-1223 is shown in Fig. 4. The perfect linear fit is clearly seen with a derivative of  $dT_c/da \approx -1.35 \times 10^3$  K/Å. Subsequent compression of the  $a$  parameter reflects shortening the in-plane Cu-O distance because buckling of the ( $\text{CuO}_2$ ) layers is absent for Hg-1201 and practically absent for Hg-1212 and Hg-1223 phases. This ‘‘chemical’’ in-layer compression is accompanied by significant  $T_c$  increase ongoing from Hg-1201 to Hg-1223 as it was previously reported in Refs. 14 and 15. For the latter phase anion substitution promotes small in-plane compression ( $\Delta a = 0.0023$  Å) which is accompanied by substantial (4 K) growth of  $T_c$ . Similar  $T_c$  growth was found for Tl-substituted Hg-1223 with similar change of the  $a$  parameter ( $\Delta a = 0.0024$  Å).<sup>8</sup> Our data show that the origin of this  $T_c$  enhancement cannot be explained by the increase of anion content as it was suggested by Dai *et al.*<sup>8</sup> It is supported by fluorination of optimally doped Hg-1223. These treated samples did not show  $T_c$  enhancement up to 138 K. It should be noted that the fluorination of highly reduced Hg-1223 is a crucial parameter for such  $T_c$  enhancement. Peacock *et al.* used less reduced Hg-1223 with  $T_c \approx 115$  K and could achieve only 135 K after fluorination.<sup>15</sup> Shortening of the apical Cu-O distance cannot be responsible for the  $T_c$  enhancement as it was revealed by the study of Hg-1201.<sup>10</sup>

Taking into consideration all data shown in Fig. 4 we can conclude that the origin of this phenomenon is a compressive strain of the ( $\text{CuO}_2$ ) layer produced by chemical modification of the crystal structure. It is interesting to notice that the compressive epitaxial strain for the deposited  $\text{La}_{1.9}\text{Sr}_{0.1}\text{CuO}_4$  single-crystal thin film resulted in doubling of  $T_c$  from 25 to 49 K with a derivative of  $dT_c/da \approx -1.0 \times 10^3$  K/Å which is close to our value.<sup>16</sup>

These derivatives are much larger than those produced by an application of external pressure. From crystallographic data of Armstrong *et al.*<sup>4</sup> and the value of  $dT_c/dP \approx 1.7$  K/GPa<sup>2</sup> we can estimate the  $dT_c/da$  derivative for Hg-1223 as equal to  $-1.6 \times 10^2$  K/Å which is the order of magnitude smaller as compared with chemical modification effect. What is the origin of this difference? If we consider structure modification caused by chemical pressure we notice, that there is no significant change in structural arrangement of ( $\text{CuO}_2$ ) layers in the row from Hg-1201 to fluorinated Hg-1223. These layers are flat (Hg-1201) or nearly flat in other phases. Fluorination or Tl substitution do not change significantly the Cu(2)-O(2)-Cu(2) angle which is close to  $180^\circ$ :  $178.4(4)^\circ$  for oxygenated Hg-1223,<sup>13</sup>  $177.3(1)^\circ$  for fluorinated Hg-1223, and  $178.3(4)^\circ$  for Tl-substituted Hg-1223.<sup>8</sup>

External pressure changes the arrangement of ( $\text{CuO}_2$ ) layers much stronger which is reflected in the larger compression of the apical Cu-O distance and buckling of these layers as a result. For instance, the Cu(2)-O(2)-Cu(2) angle becomes much smaller [ $175.0(5)^\circ$ ] in the Hg-1223 structure under 2 GPa pressure which promotes close  $T_c$  enhancement but with much larger compression of the in-plane bond distances.<sup>4</sup> This buckling angle is an important parameter influencing superconducting properties of layered cuprates, and the materials with the highest  $T_c$  have smaller buckling and longer apical distance for asymmetrical ( $\text{CuO}_5$ ) pyramids.<sup>13</sup> Finally we can conclude that chemical modification of the structure causing the in-plane compression without change of buckling angle is much more efficient factor enhancing  $T_c$  in layered cuprates in comparison with isotropic external pressure as it was shown for fluorinated Hg-1223.

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