

**METALS
AND SUPERCONDUCTORS**

Thallium-Based High-Temperature 2212 Superconductor with Partial Substitution of Oxygen by Fluorine and of Calcium by Cerium

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Abstract—Fluorine- and cerium-substituted thallium-based high-temperature 2212 superconductors are synthesized, the limits of solubility of the substitutes are investigated, the critical temperatures of the superconducting transitions are measured, and the local structure is refined using the Mössbauer technique.

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1. INTRODUCTION

It is generally accepted that the density of charge carriers (holes) in the Cu–O planes determines the superconducting properties of cuprate superconductors. Successful attempts to reduce the hole density and thereby increase the superconducting transition temperature have been related to either producing oxygen nonstoichiometry or substituting elements with a higher valence for the cations. Partial substitution of fluorine for oxygen in a complex cuprate reduces the hole concentration in the cuprate planes; so most of the

oxyfluorides synthesized in the past years have higher superconducting transition temperatures T_c than do their oxide counterparts (Table 1) [1–12]. High-temperature superconducting oxyfluorides of various compositions (based on Y, Sr, Hg, Bi, or Tl) and structural types (2223, 2212, 2201, 1223, 1234, 123) have been synthesized and studied.

It is known [1, 5] that fluorination of thallium-based superconductors increases the critical currents and is sometimes accompanied by a phase transformation, for example, Tl-2223 into Tl-1223, as shown in [5]. It is

Table 1. Published data on oxyfluorides of cuprate superconductors

Material	Crystal structure	T_c , K	Reference
$(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_{1.6}\text{Ba}_{0.4}\text{Ca}_2\text{Cu}_3\text{O}_y\text{F}_x$	1223	128	[1]
$(\text{Tl}_{0.5}\text{Pb}_{0.5})\text{Sr}_{1.6}\text{Ba}_{0.4}\text{Ca}_3\text{Cu}_4\text{O}_y\text{F}_2$	1234	128	[2]
$(\text{Tl}_{0.6}\text{Pb}_{0.5})\text{Sr}_{1.8}\text{Ba}_{0.2}\text{Ca}_{1.9}\text{Cu}_3\text{O}_y\text{F}_{0.6}$	1223	116	[3]
$\text{Tl}_{1.9}\text{Sn}_{0.1}\text{Ba}_2\text{CuO}_y\text{F}_{1.2}$	2201	97	[4]
$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_y\text{F}_2$	2223	119	[5]
$\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_y\text{F}_2$	1212	115	[5]
$\text{Bi}_{2.2}\text{Sr}_2\text{CaCu}_2\text{O}_y + 2 \text{ wt } \% \text{ NH}_4\text{HF}_2$	2212	105	[3]
$\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_8\text{F}_4$	2223	105	[6]
$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_6\text{F}_4$	2212	75	[6]
$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_x\text{F}_{0.4}$	1223	131.1	[7]
$\text{Hg}_{0.8}\text{Rc}_{0.2}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_y\text{F}_{0.08}$	1223	132	[8]
$\text{YBa}_2\text{Cu}_3\text{O}_y\text{F}_{1.2}$	123	90	[9]
$\text{SrBaYCu}_3\text{F}_2\text{O}_6$	123	105	[10]
$\text{YBa}_2\text{Cu}_3\text{O}_y\text{F}_2$	123	155	[11]
$\text{SrCa}_2\text{Cu}_3\text{O}_6\text{F}_2$	–	111	[12]

Table 2. Phase composition and superconducting transition temperatures of $Tl_2Ba_2Ca_{1-y}Ce_y(Cu_{1.98}Fe_{0.02})O_{8-x/2}F_x$ samples

Sample number	Composition (projected)	Phase composition	T_c , K	
			resistive measurements	magnetic measurements
1	$x = 0.1 Tl_2Ba_2Ca(Cu_{1.98}Fe_{0.02})F_{0.1}O_{7.95}$	Tl-2212	110	111
2	$x = 0.2 Tl_2Ba_2Ca(Cu_{1.98}Fe_{0.02})F_{0.2}O_{7.9}$	Tl-2212, BaCuO ₂ , BaCO ₃ at the background level	109	111
3	$x = 0.3 Tl_2Ba_2Ca(Cu_{1.98}Fe_{0.02})F_{0.3}O_{7.85}$	Tl-2212, CuO, BaCuO ₂ , BaCO ₃ , BaF ₂	101	106
4	$y = 0.1 Tl_2Ba_2(Ca_{0.9}Ce_{0.1})(Cu_{1.98}Fe_{0.02})O_8$	Tl-2212	99	103
5	$x = 0.2 y = 0.1 Tl_2Ba_2(Ca_{0.9}Ce_{0.1})(Cu_{1.98}Fe_{0.02})F_{0.2}O_{7.9}$	Tl-2212	103	106
6	$y = 0.1 Tl_2Ba_2(Ca_{0.9}Ce_{0.1})Cu_2O_8$	Tl-2212, BaCO ₃	100	102
7	$y = 0.2 Tl_2Ba_2(Ca_{0.8}Ce_{0.2})Cu_2O_8$	Tl-2212, BaCO ₃	103	103
8	$y = 0.3 Tl_2Ba_2(Ca_{0.7}Ce_{0.3})Cu_2O_8$	Tl-2212, BaCO ₃ , BaCuO ₂	Has no HTSC properties	
9	$y = 0.4 Tl_2Ba_2(Ca_{0.6}Ce_{0.4})Cu_2O_8$	Tl-2212, BaCO ₃ , BaCuO ₂	The same	

demonstrated in [1] that fluorination of $(Tl_{0.5}Pb_{0.5})Sr_{1.6}Ba_{0.4}Ca_2Cu_3O_y$ by partially substituting CuF_2 for CuO shifts the onset of the superconducting transition up to 128 K and causes the critical current to increase threefold as compared to that in the original high-temperature superconductors (HTSCs).

The $Tl_2Ba_2CaCu_2O_8$ HTSC with the 2212 structure was first created by Kikuchi et al. [13]. However, there have been no reports on the fluorination of double-layer thallium-based Tl-2212 HTSCs or studies of the effect of substitutions on the electrical properties and local structure of these HTSCs.

Taking into account the positive effect of fluorination on the properties of thallium-based HTSCs, we had the following objectives for this study: (i) to perform substitutions in the thallium-based double-layer superconductor $Tl_2Ba_2CaCu_2O_8$ (Tl-2212), namely, to substitute cerium and fluorine for calcium and oxygen, respectively; (ii) to find the solubility limits for the substitutes; and (iii) to investigate the effect of the substitutes on the electrophysical properties and local structure of $Tl_2Ba_2CaCu_2O_8$.

2. COMPOSITIONAL RANGES OF SINGLE-PHASE SUBSTITUTED TL-2212

The calcium and oxygen in the thallium-based superconductor $Tl_2Ba_2CaCu_2O_8$ with the 2212 structure were partially substituted for by cerium and fluorine, respectively. The contents of the substitutes in $Tl_2Ba_2Ca_{1-y}Ce_yCu_{1.98}Fe_{0.02}O_{8-x/2}F_x$ were $y = 0.1, 0.2, 0.3$, or 0.4 and $x = 0.1, 0.2$, or 0.3 . Thallium-based HTSCs were obtained by the solid-state synthesis technique; specifically, a mixture of powdered ingredients was pressed at a pressure of 100 MPa and then sintered for 4 h at $T = 840^\circ C$. The details of the procedure can

be found in [14]. The composition and the phase structure of the synthesized products are given in Table 2.

According to x-ray phase analysis, the samples crystallize into a tetragonal structure, which is preserved over the entire concentration range covered.

Based on the results of the x-ray phase analysis (Fig. 1), we determined the limits of solubility of the substitutes in the 2212 phase ($Tl_2Ba_2CaCu_2O_8$, $I4/mmm$). The results are as follows.

(1) When oxygen is substituted for by fluorine, the fluorine content is $x \leq 0.1$. The x-ray diffraction patterns of the fluorinated samples with $x = 0.20$ contain weak peaks related to extraneous phases (CuO , $BaCO_3$, and others [14]).

(2) When calcium is substituted for by cerium, the cerium content is $y \leq 0.1$. As the cerium content is increased further, extraneous phases appear in the synthesized compound.

(3) In the presence of cerium, the fluorine content in the 2212 phase of the superconductor can be increased further. Namely, if the substitutions of cerium for calcium and of fluorine for oxygen are made simultaneously, the solubility limits are $0 \leq x \leq 0.2$ and $0 \leq y \leq 0.1$.

In order to perform Mössbauer studies, a small part of the copper (2 at. %) was substituted for by the ^{57}Fe isotope. This small amount of iron has no effect on the formation of phases in the system. It was shown in [15–18] that this addition can only lead to an insignificant decrease in the superconducting transition temperature T_c (by 1–2 K). In our case, two samples were prepared in order to check this conclusion: one sample with a cerium content $y = 0.10$ and 2 at. % iron and another with $y = 0.10$ but without iron. No difference between the phase compositions or transition temperatures was found.

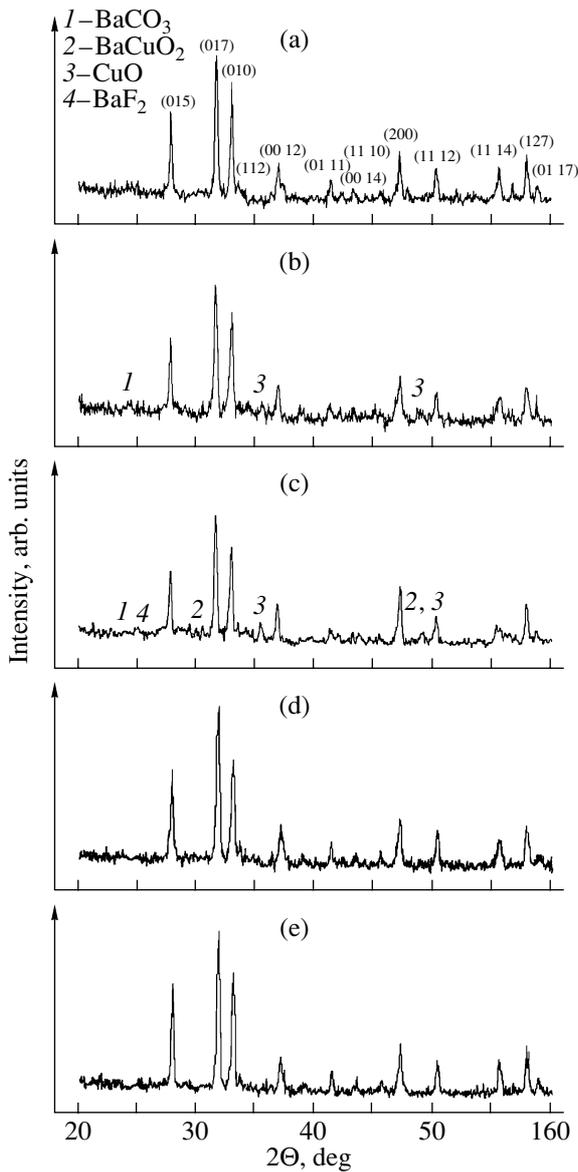


Fig. 1. X-ray diffraction patterns of samples (a) 1, (b) 2, (c) 3, (d) 4, and (e) 5.

3. EXPERIMENTAL RESULTS AND DISCUSSION

We studied the microscopic structure of the original and substituted Tl-2212 samples using a LEO electron microscope. The studies showed that the samples are conglomerates of randomly oriented lamellar microcrystals of the 2212 phase with average dimensions ranging from $(2-3) \times 4 \times 8 \mu\text{m}$ for $x = 0.10$ to $3 \times 4 \times 10 \mu\text{m}$ for $x = 0.30$.

The sizes of the superconducting grains in some areas of a cleavage plane reached $6 \times 10 \mu\text{m}$ (Fig. 2).

The parameters of the superconducting transition were determined for all synthesized samples by measuring the resistivity using the dc four-probe method.

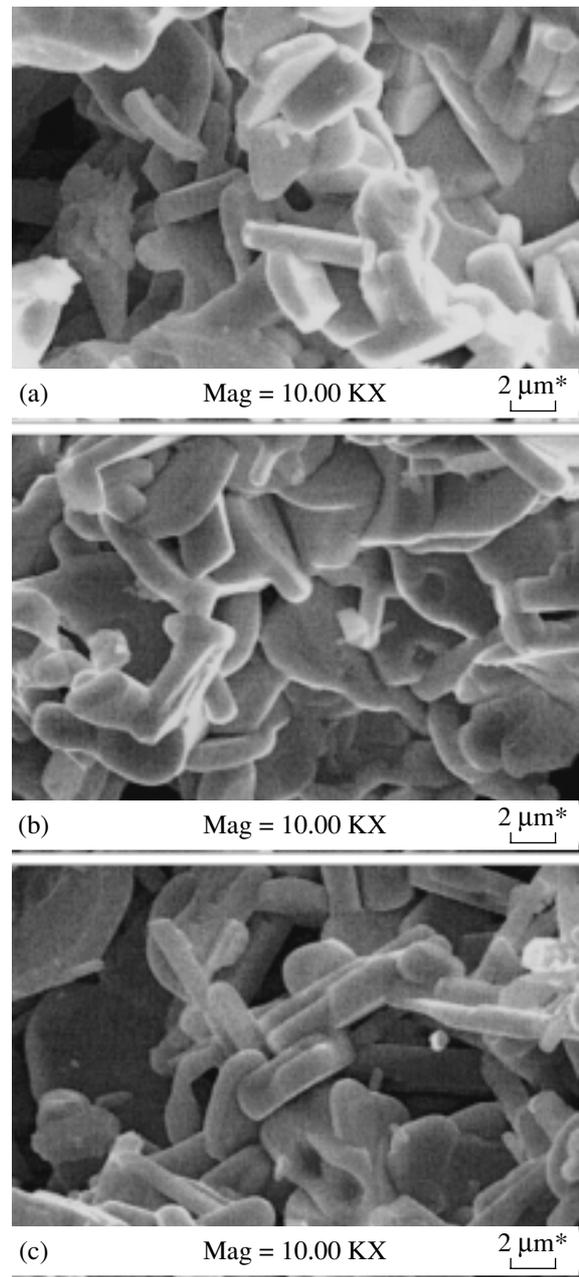


Fig. 2. Microstructure of the original and substituted Tl-2212: x is equal to (a) 0, (b) 0.1, and (c) 0.2.

The sensitivity of the null detector used was 5×10^{-9} V. The temperature T_c was determined as the midpoint [aw1] of the interval between the temperatures corresponding to 10 and 90% of the signal. The temperature dependences of the resistance and magnetic susceptibility were studied over the range 77–300 K. Inductive measurements were performed by observing the inductance of a coil with a superconducting material inside it. Using this method, the temperature dependence of the ac susceptibility was measured at a frequency $f = 6.7$ Hz. The accuracy of the measurements of the supercon-

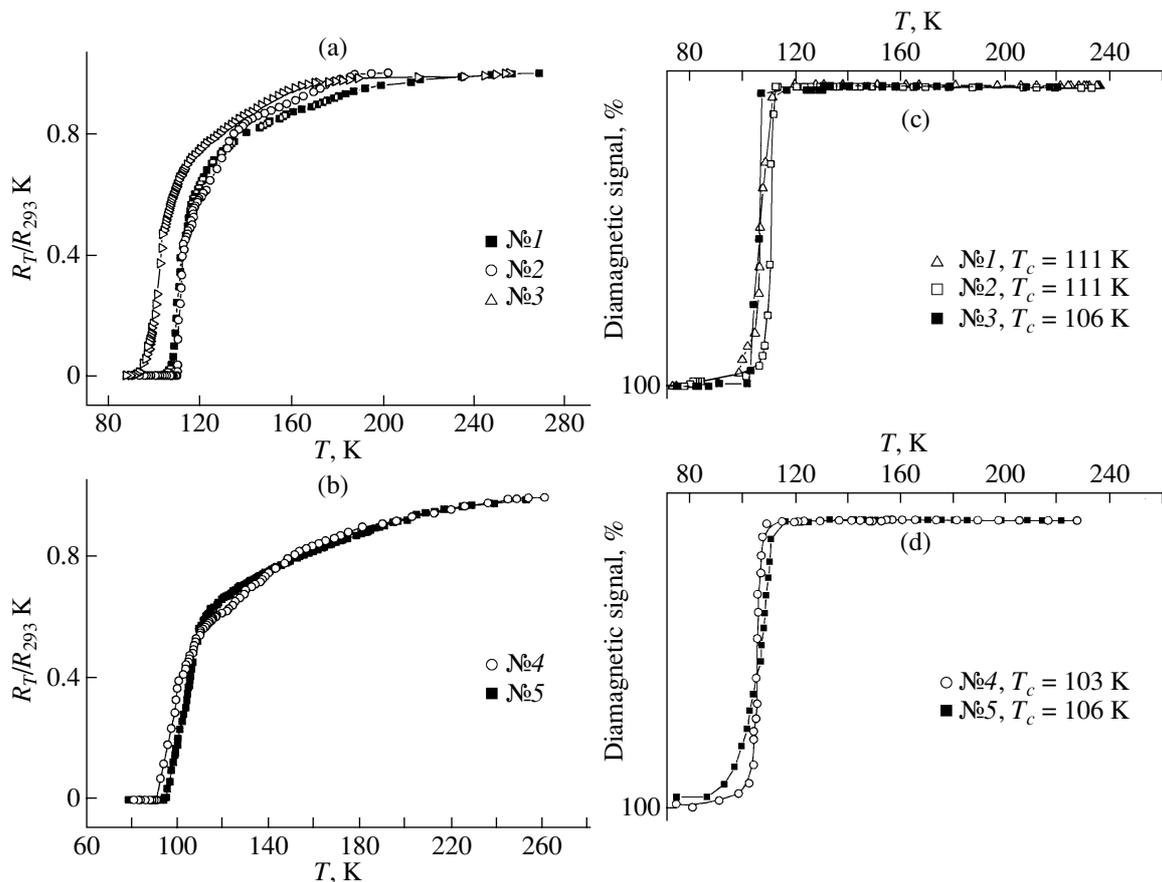


Fig. 3. Temperature dependences of the resistance of samples (a) 1–3 and (b) 4 and 5 and temperature dependences of the diamagnetic signal for samples (c) 1–3 and (d) 4 and 5.

ducting transition temperature by the resistive and inductive methods was ± 1 K.

The results of the measurements are shown in Table 2 and Fig. 3. It follows from Table 2 that the samples with a high cerium content $y \geq 0.3$ have no HTSC properties at all and that two samples with fluorine substituting for oxygen (namely, $\text{Tl}_2\text{Ba}_2\text{Ca}(\text{Cu}_{1.98}\text{Fe}_{0.02})\text{F}_{0.1}\text{O}_{7.95}$ and $(\text{Tl}_2\text{Ba}_2\text{Ca}(\text{Cu}_{1.98}\text{Fe}_{0.02})\text{F}_{0.2}\text{O}_{7.9})$) have transition temperatures higher than the T_c of the unsubstituted Tl-2212. The fluorinated samples have a smaller room-temperature resistivity than the unsubstituted HTSC (the resistivity of the samples with $x = 0.0, 0.10, 0.20,$ and 0.30 is 63.43, 7.95, 9.96, and 44.8 m Ω cm, respectively).

In order to refine the lattice parameters obtained experimentally, the main interatomic distances of the unsubstituted and fluorine-substituted ($x = 0.10$) thallium-based superconductors are calculated using the Rietveld method [19, 20]. The calculations are performed using the Quanto software package. The Tl-2212 crystal is tetragonal (space group $I4/mmm$). The Pearson VII function is chosen as a profile function, and the background of the x-ray scans is fitted by sixth-degree polynomials. A similar model was employed in [21, 22]. We assumed, as in [23], that fluorine atoms

substitute for oxygen atoms in the copper-containing planes. The results of the calculations are shown in Table 3.

In order to refine the local environment of the iron atoms located at the copper sites in the substituted Tl-2212 samples, Mössbauer effect measurements on the ^{57}Fe isotope were performed for the $\text{Tl}_2\text{Ba}_2\text{Ca}_{1-y}\text{Ce}_y\text{Cu}_{1.98}\text{Fe}_{0.02}\text{O}_{8-x/2}\text{F}_x$ samples with $0 \leq x \leq 0.2$ and $0 \leq y \leq 0.1$. The experiment was carried out in the usual transmission geometry at $T = 293$ and 4 K.

The Mössbauer data for the original $\text{Tl}_2\text{Ba}_2\text{CaCu}_{1.98}\text{Fe}_{0.02}\text{O}_8$ with the 2212 structure are similar to those obtained in [23] for Bi-2212. The spectrum measured at room temperature is a quadrupole-split line and it is fitted using a two-doublet model. The magnitudes of the isomer shifts of the subspectra are the same, $\text{IS}_1 = \text{IS}_2 = 0.275$ mm/s, but the magnitudes of the quadrupole splitting (QS) are different, $\text{QS}_1 = 1.245$ mm/s and $\text{QS}_2 = 0.882$ mm/s. The observed spectrum agrees well with the crystallographic features of the double-layer structure and the experimental data on the microstructure of the superconductor. The first subspectrum (with larger QS_1) corresponds to iron atoms located at the regular copper sites inside grains of the

superconducting 2212 phase. In a grain, the iron atoms have only one type of environment. Each iron atom at a copper site is situated in the center of a strongly distorted oxygen pyramid with a quadrilateral base formed by oxygen atoms. The distance between an iron[aw2] atom (located at a copper site) and an oxygen atom within the copper-containing layers (the Cu–O(1) distance) is 1.92 Å, and the Cu–O(2) distance between a copper (Fe) atom and the oxygen at the pyramid apex is 2.70 Å. Such a distortion of the pyramid produces an electric field gradient. The nonuniform electric field interacts with the quadrupole nucleus moment and causes a quadrupole splitting of the QS₁ line, which is observed experimentally in the Mössbauer spectrum of ⁵⁷Fe.

Some of the iron atoms at grain boundaries belong to imperceptible superconducting nonmagnetic phases. These iron atoms give rise to a second doublet in the Mössbauer spectrum with a smaller quadrupole splitting (QS₂). The slight broadening of the line in the subspectra can be caused by defects in the local environment of the iron atoms at copper sites inside superconducting phase grains and at the grain boundaries.

The Mössbauer spectra of the substituted samples are similar to those of the unsubstituted Tl-2212. The spectra observed in the superconducting state (at 4 K) are shown in Fig. 4, and the refined parameters are given in Table 4.

The spectra are fitted by a single doublet corresponding to iron atoms at the regular copper sites. The second subspectrum in the spectrum of the superconductor vanishes, because, as the temperature decreases to 4 K, the paramagnetic phases turn into magnetic phases, which are difficult to detect. Below the transition point, the probability of the Mössbauer effect is strongly reduced. Apparently, this is due to a softening of the HTSC lattice on the transition into the superconducting state, which causes anomalous changes in the probability of the Mössbauer effect and in the magnitudes of the isomer shifts and quadrupole splitting [24].

The anomalous change in the isomer shift at 4K (IS = 0.367–0.382 mm/s) as compared to the IS of the room-temperature spectrum (IS = 0.275 mm/s) is probably due to the formation of Cooper pairs (Bose condensation) upon transition of the HTSC into the superconducting state. Indeed, the formation of a Bose condensate leads to a redistribution of the electron density in the HTSC and, as is well known [25], it is the electron density at Cu(Fe) sites that determines the magnitude of the IS of the Mössbauer spectrum of iron.

The Mössbauer data obtained for the HTSCs with $x = 0.1$ and 0.2 and with $x = 0.1$ and $y = 0.1$ reveal no manifest dependence of the QS on the type and number of substituting elements over the compositional range studied. However, to make definite conclusions, we are performing more detailed comparative Mössbauer studies.

Table 3. Rietveld-refined parameters of the tetragonal structure (space group $I4/mmm$) of Tl₂Ba₂CaCu₂O₈ and Tl₂Ba₂CaCu₂O_{7.95}F_{0.1} samples

Sample	Tl ₂ Ba ₂ CaCu ₂ O ₈	Tl ₂ Ba ₂ CaCu ₂ O _{7.95} F _{0.1}
Lattice parameters		
a , Å	3.864	3.864
c , Å	29.28	29.27
Main interatomic distances, Å		
Tl–O(2)	2.398	2.468
Tl–O(3)	2.739	2.752
Ca–O(1)	2.495	2.478
Ba–O(1)	2.764	2.787
Ba–O(2)	2.750	2.743
Ba–O(3)	2.893	2.910
Cu–O(1)	1.934	1.935
Cu–O(2)	2.205	2.146
O(1)–O(1)	2.732	2.732
O(2)–O(1)	2.991	2.963
R , %*	8.6	8.65
R_{wp} , %*	11.52	11.43

* R and R_{wp} are the criteria for closeness of the measured and theoretically calculated x-ray scans.

Table 4. Parameters of the Mössbauer spectra of ⁵⁷Fe for Tl₂Ba₂Ca_{1–y}Ce_yCu_{1.98}Fe_{0.02}O_{8–x/2}F_x at 4 K

Sample number	x	IS*, ±0.01 mm/s	QS, ±0.01 mm/s	Γ, ±0.01 mm/s
1	$x = 0.10$	0.38	0.82	0.23
2	$x = 0.20$	0.39	0.73	0.28
3	$x = 0.20$ $y = 0.10$	0.37	0.89	0.29

* The values of IS are measured relative to α-Fe.

It is known that the quadrupole splitting in Mössbauer spectra is very sensitive to interatomic distances and the covalence degree of the bonds. Therefore, the appearance of a fluorine atom in place of an O(1) atom in the local environment of Fe can be expected to have a strong effect on the QS magnitude, because oxygen atoms in this position are the closest to resonant ⁵⁷Fe atoms. However, the data on the interatomic distances in the original and fluorine-substituted samples (Table 3) show that it is in the Cu–O planes that the interatomic distances remain almost unchanged. The reason for this can be that the ionic radii of fluorine and oxygen are close to each other (for a coordination number of 2, they are $r_F^- = 1.29$ Å and $r_O^{2-} = 1.35$ Å). Also, it is possible that fluorine atoms substitute for oxygen atoms not in the copper-containing planes (as was sug-

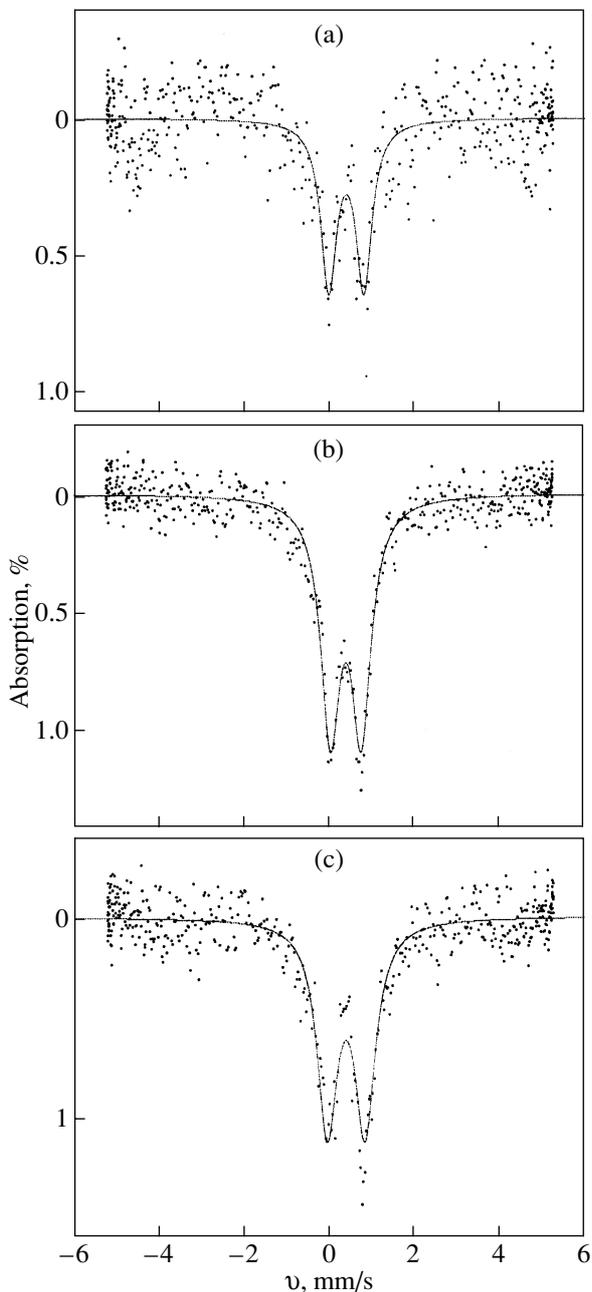


Fig. 4. Mössbauer spectra ($T = 4$ K) of substituted Tl-2212 samples with various fluorine (x) and cerium (y) contents: (a) $x = 0.1$, (b) $x = 0.2$, and (c) $x = 0.2$ and $y = 0.1$.

gested, e.g., in [22]) but rather at O(2) sites. This suggestion is supported by the decreased Cu(Fe)–O(2) distance (see the dependence of the lattice parameters a and c on x in Fig. 5). Since the Cu(Fe)–O(2) distance is much larger than the Cu(Fe)–O(1) distance, the oxygen pyramid around ^{57}Fe is distorted only slightly in this case and the quadrupole splitting observed in the Mössbauer spectrum of ^{57}Fe does not change significantly.

The situation where fluorine atoms occupy vacant crystallographic positions in the Tl-2212 structure

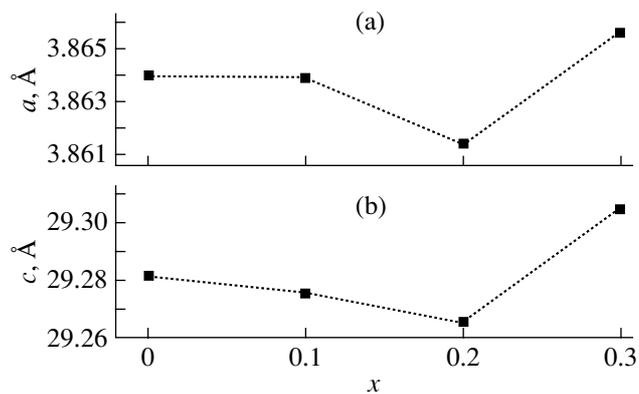


Fig. 5. Dependence of the lattice parameters a and c of the $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_{8-x/2}\text{F}_x$ superconductor on the fluorine content x .

seems less likely. Indeed, the lattice parameters should increase in this case, which has not been observed in experiment; on the contrary, the lattice parameters decrease slightly at $x = 0.10$ (Fig. 5).

Due to the difference between the electronegativities of oxygen and fluorine, the substitution leads to the appearance of free electrons, which partly compensate the holes, thereby causing an increase in the superconducting transition temperature T_c . We stress once again that this reasoning is valid for substitute contents at which the 2212 phase is retained, i.e., if x in $\text{Tl}_2\text{Ba}_2\text{CaCu}_{1.98}\text{Fe}_{0.02}\text{O}_{8-x/2}\text{F}_x$ does not exceed 0.10.

4. CONCLUSIONS

Substitution of cerium for calcium in the Tl-2212 superconductor has been shown to cause a slight decrease in the superconducting transition temperature. The addition of cerium to Tl-2212 increases the solubility of fluorine. Substitution of fluorine for oxygen leads to an increase in the superconducting transition temperature; the maximum increase relative to the unsubstituted $\text{Tl}_2\text{Ba}_2\text{CaCu}_{1.98}\text{Fe}_{0.02}\text{O}_{8-x/2}\text{F}_x$ compound is observed for a fluorine content $x \sim 0.10$ – 0.20 and amounts to 10 K. The Mössbauer data indicate that the most probable scenario is that fluorine substitutes for oxygen at the apexes of the oxygen pyramids.

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