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Preparation of $Tl_2Ba_2Ca_{1-y}Ce_yCu_2O_{8-x/2}F_x$ Ce- and F-Substituted Superconductors

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Abstract—High-T_c superconducting ceramics with the compositions $Tl_2Ba_2CaCu_2O_{8-x/2}$ ($0 \le x \le 0.3$), $Tl_2Ba_2(Ca_{1-y}Ce_y)Cu_2O_x$ ($0 \le y \le 0.2$), and $Tl_2Ba_2(Ca_{0.9}Ce_{0.1})(Cu_{1.98}Fe_{0.02})F_{0.2}O_{8.01}$ are synthesized. Partial fluorine substitution for oxygen in $Tl_2Ba_2CaCu_2O_{8-x/2}$ ($0 \le x \le 0.1$) alters the carrier density in the Cu–O planes of the material, raising its superconducting transition temperature from 106 to 110 K. Partial cerium substitution for calcium in $Tl_2Ba_2(Ca_{1-y}Ce_y)Cu_2O_x$ ($0 \le y \le 0.2$) reduces T_c. The combined substitution in $Tl_2Ba_2(Ca_{0.9}Ce_{0.1})(Cu_{1.98}Fe_{0.02})F_{0.2}O_{8.01}$ has an insignificant effect on T_c.

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INTRODUCTION

There is considerable interest in fluorine-substituted high-T_c cuprate superconductors [1–13] because partial fluorine substitution for oxygen may alter the carrier concentration in the Cu–O planes of the material and, accordingly, its superconducting properties. Fluorine substitution raises the superconducting transition temperature of most cuprate superconductors. Table 1 summarizes the relevant experimental data available in the literature.

The effect of fluorine substitution on the structure and transport properties of Tl-based high-T_c superconductors is essentially unexplored. Partial fluorine substitution for oxygen might be expected to change the carrier concentration in their Cu–O planes and, accordingly, their T_c. In connection with this, the objectives of this work were to synthesize the two-layer Tl-based superconductor $Tl_2Ba_2CaCu_2O_8$ (Tl-2212) and to study the effect of partial substitution of fluorine for oxygen and cerium for calcium on the superconducting properties of $Tl_2Ba_2CaCu_2O_8$.

EXPERIMENTAL

Samples for this investigation were synthesized from barium peroxide; barium difluoride; thallium, copper, calcium, and cerium oxides; and enriched iron oxide.

In view of the increased volatility of thallium, the starting mixtures contained an excess of Tl_2O_3 (10 wt %) [13, 14]. Their compositions are listed in Table 2.

Substitution of 2 at % Fe for Cu usually has little effect on the formation of the Tl-based superconductors but slightly reduces their T_c [15–18]. Mössbauer results for the samples studied here will be presented in a subsequent communication.

The starting chemicals used in our preparations were pure-grade Tl_2O_3, extrapure-grade BaO_2, reagent-grade BaF_2, analytical-grade CaO, extrapure-grade CuO, analytical-grade CeO_2, and extrapure-grade Fe_2O_3. CaO was calcined at 1000°C for 1 h in order to

Table 1. Fluorine-substituted cuprate superconductors

Cuprate	T_c, K	Reference
$(Tl_{0.5}Pb_{0.5})Sr_{1.73}Ba_{0.43}Ca_{2.16}Cu_3O_yF_x$	128 ($x = 1$)	[1]
$(Tl_{0.5}Pb_{0.5})Sr_{1.6}Ba_{0.4}Ca_3Cu_4O_yF_2$	128	[2]
$(Tl_{0.6}Pb_{0.5})Sr_{1.8}Ba_{0.2}Ca_{1.9}Cu_3O_yF_{0.6}$	116	[3]
$Tl_{1.9}Sn_{0.1}Ba_2CuO_yF_{1.2}$	97	[4]
$Tl_2Ba_2Ca_2Cu_3O_yF_2$	119	[5]
$Tl_2Ba_2CaCu_2O_yF_2$	115	[5]
$Bi_{2.2}Sr_2CaCu_2O_y$ + 2 wt % NH_4HF_2	105	[3]
$Bi_2Sr_2Ca_2Cu_3O_8F_4$	105	[6]
$Bi_2Sr_2CaCu_2O_6F_4$	75	[6]
$HgBa_2Ca_2Cu_3O_xF_{0.4}$	131.1	[7]
$Hg_{0.8}Re_{0.2}Ba_2Ca_2Cu_3O_yF_{0.08}$	132	[8]
$YBa_2Cu_3O_yF_{1.2}$	90	[9]
$SrBaYCu_3F_2O_6$	105	[10]
$YBa_2Cu_3O_yF_2$	155	[11]
$Sr_2Ca_2Cu_3O_6F_2$	111	[12]

Table 2. Starting-mixture compositions

Molar ratio							Composition
Tl_2O_3	BaF_2	BaO_2	CaO	CuO	Fe_2O_3	CeO_2	
1.1	0.0	2	1.0	1.98	0.01	–	$Tl_{2.2}Ba_2Ca(Cu_{1.98}Fe_{0.02})O_x$
1.1	0.05	1.95	1.0	1.98	0.01	–	$Tl_{2.2}Ba_2Ca(Cu_{1.98}Fe_{0.02})F_{0.1}O_x$
1.1	0.1	1.9	1.0	1.98	0.01	–	$Tl_{2.2}Ba_2Ca(Cu_{1.98}Fe_{0.02})F_{0.2}O_x$
1.1	0.15	1.85	1.0	1.98	0.01	–	$Tl_{2.2}Ba_2Ca(Cu_{1.98}Fe_{0.02})F_{0.3}O_x$
1.1	0.0	2	0.9	1.98	0.01	0.1	$Tl_{2.2}Ba_2(Ca_{0.9}Ce_{0.1})(Cu_{1.98}Fe_{0.02})O_x$
1.1	0.1	1.9	0.9	1.98	0.01	0.1	$Tl_{2.2}Ba_2(Ca_{0.9}Ce_{0.1})(Cu_{1.98}Fe_{0.02})F_{0.2}O_x$
1.1	0.0	2	0.9	–	–	0.1	$Tl_{2.2}Ba_2(Ca_{0.9}Ce_{0.1})Cu_2O_x$
1.1	0.0	2	0.8	–	–	0.2	$Tl_{2.2}Ba_2(Ca_{0.8}Ce_{0.2})Cu_2O_x$
1.1	0.0	2	0.7	–	–	0.3	$Tl_{2.2}Ba_2(Ca_{0.7}Ce_{0.3})Cu_2O_x$
1.1	0.0	2	0.6	–	–	0.4	$Tl_{2.2}Ba_2(Ca_{0.6}Ce_{0.4})Cu_2O_x$

Table 3. Compositions and T_c's of synthesized materials

Sample no.	Nominal composition	Phase composition (x-ray diffraction data)	T_c, K (resistive transition)	T_{c0}, K (inductive transition)
1	$Tl_2Ba_2Ca(Cu_{1.98}Fe_{0.02})O_{8.01}$	Tl-2212	106	107
2	$Tl_2Ba_2Ca(Cu_{1.98}Fe_{0.02})F_{0.1}O_{7.96}$	Tl-2212	110	111
3	$Tl_2Ba_2Ca(Cu_{1.98}Fe_{0.02})F_{0.2}O_{7.91}$	Tl-2212, CuO, $BaCO_3$	109	111
4	$Tl_2Ba_2Ca(Cu_{1.98}Fe_{0.02})F_{0.3}O_{7.86}$	Tl-2212, CuO, $BaCO_3$, $BaCuO_2$, BaF_2	101	106
5	$Tl_2Ba_2(Ca_{0.9}Ce_{0.1})(Cu_{1.98}Fe_{0.02})O_{8.11}$	Tl-2212	99	103
6	$Tl_2Ba_2(Ca_{0.9}Ce_{0.1})(Cu_{1.98}Fe_{0.02})F_{0.2}O_{8.01}$	Tl-2212	103	106
7	$Tl_2Ba_2(Ca_{0.9}Ce_{0.1})Cu_2O_{7.1}$	Tl-2212, $BaCO_3$	100	102
8	$Tl_2Ba_2(Ca_{0.8}Ce_{0.2})Cu_2O_{7.2}$	Tl-2212, $BaCO_3$	103	103
9	$Tl_2Ba_2(Ca_{0.7}Ce_{0.3})Cu_2O_{7.3}$	Tl-2212, $BaCO_3$, $BaCuO_2$	–	
10	$Tl_2Ba_2(Ca_{0.6}Ce_{0.4})Cu_2O_{7.4}$	Tl-2212, $BaCO_3$, $BaCuO_2$	–	

Note: T_{c0} is the superconducting onset temperature.

remove calcium hydroxide (trace amounts). CeO_2 was also calcined at 1000°C for 1 h. Appropriate mixtures were thoroughly mixed by grinding with ethanol in jasper mortars, then loaded in a 12-mm-diameter die, and pressed at 100 MPa. The fluorine-containing green compacts were heated to 840°C at a rate of 2.8°C/min in alundum crucibles with tightly fitting lids and then sintered isothermally for 4 h. The synthesis temperature of the cerium-containing samples was 820°C (the samples prepared at higher temperatures were mixed-phase). The compositions and T_c's of the materials thus synthesized are listed in Table 3.

Phase composition of the samples was determined on a DRON-4 powder x-ray diffractometer (monochromatized CuK_α radiation, $2\theta = 20°–60°$, step-scan mode with a step size of 0.05° and a counting time of 2 s per data point).

The resistive superconducting transition temperature of all the samples was determined by a standard four-probe dc technique. The sensitivity of the null comparator was 5×10^{-9} V. Electrical contacts were made with ACHESON ELECTRODAG 1415M silver paste.

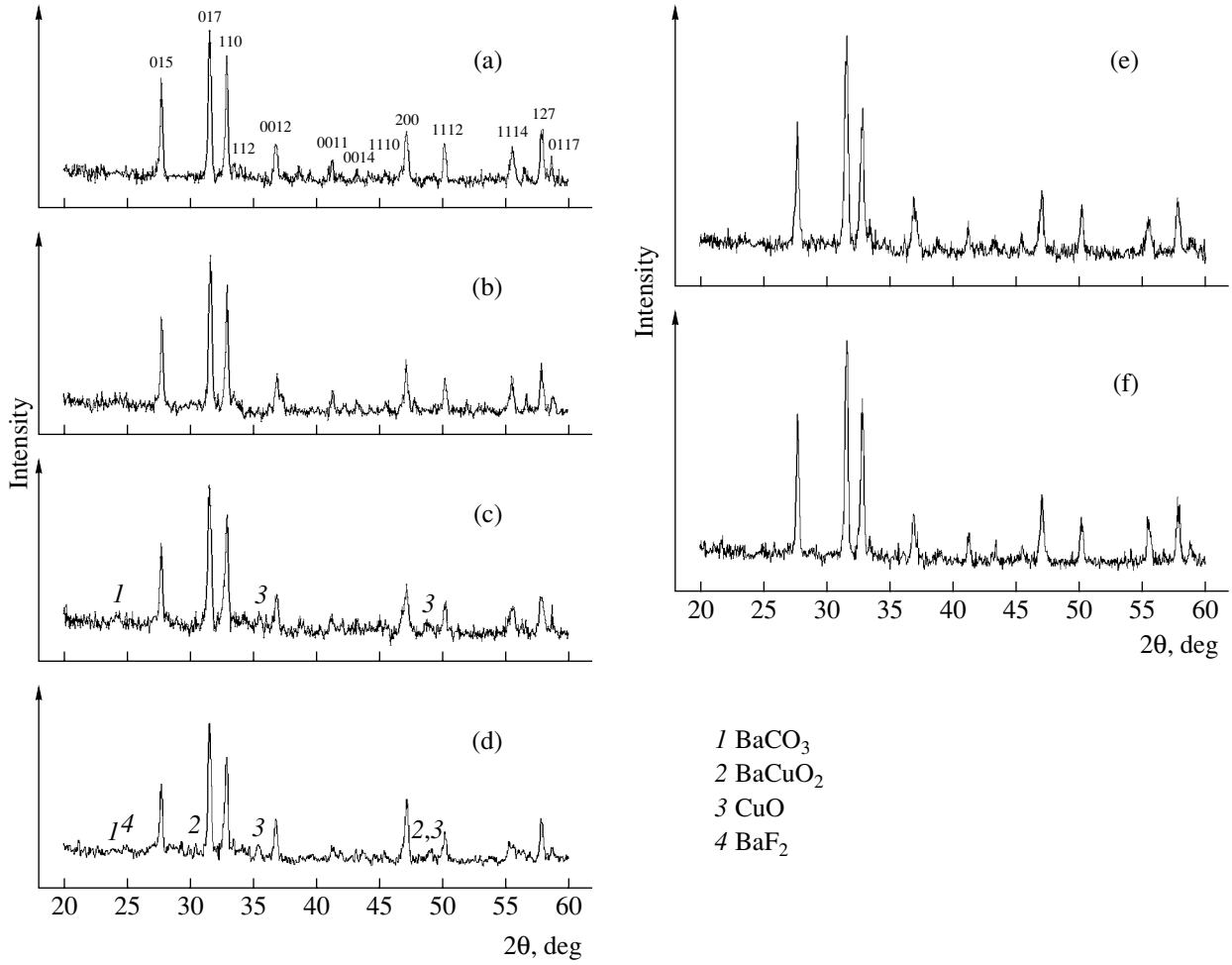

Fig. 1. X-ray diffraction patterns of samples (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, and (f) 6.

Electrical resistance and magnetic susceptibility were measured in the temperature range 77–300 K. The temperature was monitored with an accuracy of ±0.2 K using a TSMF-D1 temperature measuring element. The inductive transition temperature was determined by measuring the inductance of a coil into which the superconducting material was introduced. In this way, we determined the temperature-dependent ac (6.7 kHz) susceptibility of our samples. The uncertainty in both the resistive and inductive transition temperatures was ±1 K.

RESULTS AND DISCUSSION

The samples had a tetragonal structure over the entire composition range studied. The only phase in samples 1 and 2 (Table 3) was Tl-2212 (based on $Tl_2Ba_2CaCu_2O_8$, sp. gr. $I4/mmm$). Samples 3 and 4 wee mixed-phase. The impurity phases included BaF_2 ($Fm\bar{3}m$, a = 6.196 Å), α-$BaCO_3$ ($Pmcn$, a = 5.314 Å, b = 8.904 Å, c = 6.43 Å; product of reaction between BaO_2 and atmospheric CO_2 in the range 320–785°C), $BaCuO_2$ (bcc, $Im3m$, a = 18.26 Å) and unreacted CuO ($C2/c$, a = 5.129 Å, b = 4.684 Å, c = 3.425 Å, γ = 99.44°) (Table 3, Fig. 1). The presence of reflections from BaF_2 in the x-ray diffraction pattern of sample 4 (Fig. 1) points to a limited degree of fluorine substitution for oxygen.

Figure 2a shows the temperature dependences of the R/R_{293} resistance ratio for samples 1–4 (resistive T_c measurements). The four samples undergo a superconducting transition, with a zero-resistance temperature above 100 K. The highest T_c is offered by samples 2 and 3: 110 and 109 K, respectively. The broadening of the superconducting transition in samples 3 and 4 is consistent with the presence of impurity phases revealed by x-ray diffraction. The temperature dependences of magnetic susceptibility for samples 1–4 are displayed in Fig. 2b.

The temperature dependences of R/R_{293} and susceptibility for samples 5 and 6 are shown in Figs. 2c and 2d, respectively. These data demonstrate that cerium doping reduces T_c.

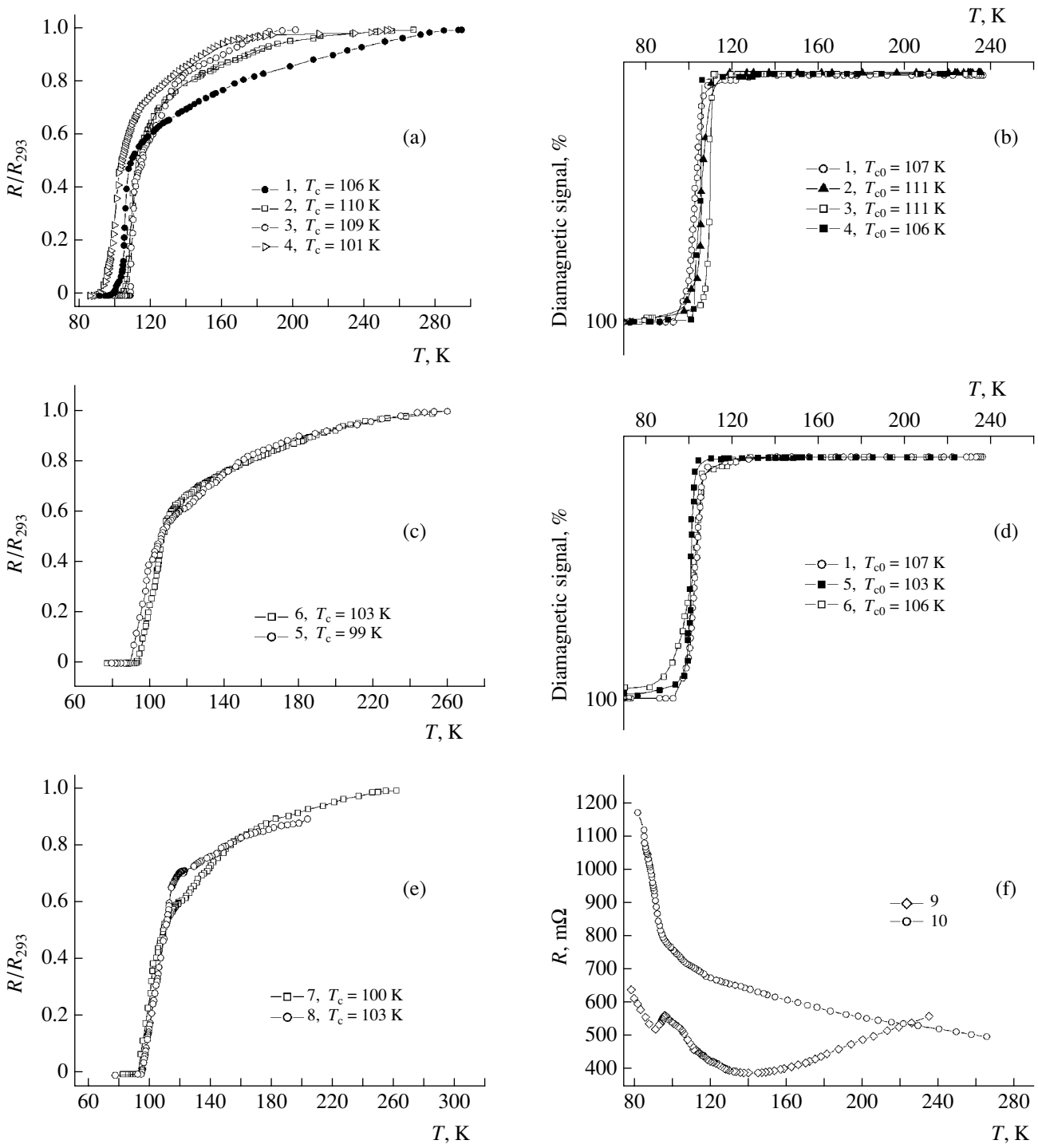

Fig. 2. (a, c, e, f) Electrical resistance and (b, d) diamagnetic signal as functions of temperature: samples (a, b) 1–4, (c) 5, 6, (d) 1, 5, 6, (e) 7, 8, (f) 9, 10.

Figures 2e and 2f display temperature-dependent resistance data for samples 7–10. Samples 7 and 8 undergo a superconducting transition at 100 and 103 K, respectively (Fig. 2e). Substitution of 2 at % Fe for Cu has a weak effect on T_c, reducing it by 1–2 K (Fig. 2). The temperature dependence of resistance for sample 9 shows a kink at 96 K, attesting to the presence of a superconducting phase (Fig. 2f). The curve for sample 10 exhibits typical semiconducting behavior over the entire temperature range studied (Fig. 2f). The reduction in T_c with increasing cerium content is attributable to magnetic scattering.

CONCLUSIONS

We synthesized high-T_c superconducting ceramics with the compositions $Tl_2Ba_2CaCu_2O_{8-x/2}F_x$ ($0 \le x \le 0.3$), $Tl_2Ba_2(Ca_{1-y}Ce_y)Cu_2O_x$ ($0 \le y \le 0.2$), and $Tl_2Ba_2(Ca_{0.9}Ce_{0.1})(Cu_{1.98}Fe_{0.02})F_{0.2}O_{8.01}$.

Partial fluorine substitution for oxygen in $Tl_2Ba_2CaCu_2O_{8-x/2}F_x$ alters the carrier density in the Cu–O planes of the material, raising its superconducting transition temperature from 106 to 110 K as x increases from 0 to 0.1.

The T_c of $Tl_2Ba_2(Ca_{1-y}Ce_y)Cu_2O_x$ ($0 \le y \le 0.2$) is lower than that of cerium-free materials, indicating that cerium substitution is of no utility.

Partial substitution of fluorine for oxygen in combination with cerium substitution for calcium ($Tl_2Ba_2(Ca_{0.9}Ce_{0.1})(Cu_{1.98}Fe_{0.02})F_{0.2}O_{8.01}$) provides no significant enhancement in the superconducting properties of Tl-2212 (only a slight increase in T_c).

REFERENCES

1. Hamdan, N.M., Ziq, Kh.A., and Al-Harthi, A.S., Effect of Fluorine on the Phase Formation and Superconducting Properties of Tl-1223 Superconductors, *Physica C* (Amsterdam), 1999, vol. 314, pp. 125–132.
2. Hamdan, N.M., The Role of Charge Carrier Concentration in Tl-1234, *Physica B* (Amsterdam), 2000, vols. 284–288, pp. 1093–1094.
3. Bellingeri, E., Grasso, G., Gladyshevskii, R., *et al.*, Fluorine Substitution in High Temperature Superconductors, *Int. J. Mod. Phys. B*, 1999, vol. 13, no. 9, pp. 973–978.
4. Sun, C.F., Xin, Y., Lu, D.F., *et al.*, Effects of Fluorine Substitution in Superconducting $Tl_2Ba_2CuO_{6+\delta}$, *Solid State Commun.*, 1997, vol. 101, no. 11, pp. 849–853.
5. Kikuchi, A., Inoue, K., and Tachikawa, K., Structure and Irreversibility Field of the Tl-1223 Phase Synthesized through the Substitution of TlF for Tl_2O_3, *Physica C* (Amsterdam), 2000, vol. 337, pp. 180–186.
6. Bellingeri, E., Grasso, G., Gladyshevskii, R.E., *et al.*, New Bi-Based High-T_c Superconducting Phases Obtained by Low-Temperature Fluorination, *Physica C* (Amsterdam), 2000, vol. 329, pp. 267–278.
7. Wang, X.-G., Huang, Z., and Yuan, L., Effect of F-Doping in the Hg–Ba–Ca–Cu–O System, *Physica C* (Amsterdam), 1995, vol. 253, pp. 254–258.
8. Hamdan, N.M., Sastry, P.V.S.S., and Schwatrz, J., Enhancement of the Phase Formation and Superconducting Properties of HgRe1223 through Fluorine Addition, *Physica C* (Amsterdam), 2000, vols. 341–348, pp. 513–514.
9. Fukami, J., Kido, H., Otaki, H., and Hoshikawa, T., Electrical and Magnetic Properties of Y–Ba–Cu–F–O System Superconductor, *J. Ceram. Soc. Jpn.*, 1988, vol. 96, no. 4, pp. 1483–1485.
10. Zhang, H., Zhao, Y., Zhang, M., *et al.*, Phase and Superconductivity of Sr–Ba–Y–Cu–F–O System, *Solid State Commun.*, 1988, vol. 66, no. 3, pp. 291–294.
11. Ovshinsky, S.R., Young, R.T., Allred, D.D., *et al.*, Superconductivity at 155 K, *Phys. Rev. Lett.*, 1987, vol. 58, no. 24, pp. 2579–2581.
12. Kawashima, T., Matsui, Y., and Takayama-Muromachi, E., High Pressure Synthesis and Superconductivity Properties of $Sr_2Ca_{n-1}Cu_nO_y$ (n = 1–4) and $Sr_2Ca_{n-1}Cu_nO_{2n\pm\delta}F_{2\pm y}$ (n = 2–5), *Physica C* (Amsterdam), 1997, vols. 282–287, pp. 513–514.
13. Akimov, A.I., Boiko, B.B., Karpei, A.L., *et al.*, Phase Analysis of Tl-based High-T_c Ceramics, *Zavod. Lab.*, 1990, no. 8, pp. 68–71.
14. Akimov, A.I., Savchuk, G.K., and Lebedev, S.A., *Mezhdunarodnaya konferentsiya "Peredovaya keramika—tret'emu tysyacheletiyu," CERAM 2001* (Advanced Ceramics for the Third Millennium Int. Conf., CERAM 2001), Kiev, 2001, p. 381.
15. Wang, Y.-Bo, Li, Y., Ju, X., *et al.*, Study of the Fe-Doping Effect of Tl-System Superconductor, *Physica C* (Amsterdam), 1997, vols. 282–287, pp. 975–976.
16. Wang, Y.-Bo, Cao, G.-H., Li, Y., *et al.*, Study of Phonon Anomalies in Tl-System Superconductor near T_c, *Physica C* (Amsterdam), 1997, vols. 282–287, pp. 1087–1088.
17. Yiwei, Z., Xiaohua, Y., Minzhu, L., *et al.*, Mossbauer Observation near the Superconducting Transition Temperature in $TlBaCa_3Cu_3O_{8.5}$ Superconductor, *Phys. Rev. B* (Condens. Matter), 1991, vol. 44, no. 2, pp. 867–870.
18. Kuzmann, E., Mair, M., Klenesar, Z., *et al.*, ^{57}Fe, ^{119}Sn, and ^{151}Eu Mossbauer Studies of $(Tl,Pb)(Ba_{0.2}Sr_{0.8})_2Ca_2Cu_3O_y$ Superconductors, *Physica C* (Amsterdam), 1999, vol. 319, pp. 12–20.