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NMR and EPR spectroscopic studies of fluorinated Bi-2212 HTSC

S.A. NEDILKO[1]*, A.A. ASHUEV[1], V.V. TRACHEVSKY[2], E.G. ZENKOVICH[1]

[1] *Department of Inorganic Chemistry, Taras Shevchenko National University of Kyiv,*
Voloymyrska St. 62a, 01033 Kyiv, Ukraine
[2] *G.V. Kurdyumov Institute for Metal Physics, National Academy of Sciences of Ukraine,*
Akad. Vernadskoho Bld. 36, 03680 Kyiv, Ukraine
* *Corresponding author. Tel.: +390-44-2393306; e-mail: snedilko@ukr.net*

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NMR and EPR spectroscopy were used to analyse the structural changes caused by fluorination in Bi-2212 HTSC compounds. Synthesis of the fluorinated HTSC was carried out by a solid state method, using different fluorinating agents. The dependence of structural and superconducting properties on the nature and concentration of the fluorinating agent was explored. It was shown that substitution of fluorine for oxygen takes place in different preferred positions of the Bi-2212 lattice for different fluorinating agents; substitution in the {CuO_2} layers, with formation of {CuO_3F} and {CuO_2F_2} structural blocks, occurs in the best way when using PbF_2, CuF_2, BiOF and SrF_2 as fluorinating agents. An increase of T_c was observed for the same fluorinating agents when added in optimal amounts.

HTSC / Bi-2212 / Fluorination / Fluorinating agents / NMR / EPR

Introduction

Bismuth-based $Bi_2Sr_2Ca_{n-1}Cu_nO_{4+2n}$ compounds (BSCCO), for example $Bi_2Sr_2CaCu_2O_8$ (Bi-2212), are promising HTSC materials and have already found applications in industry. From the very moment of discovering high-temperature superconductivity in the Bi–Sr–Ca–Cu–O system [1], attempts to improve the superconducting properties have been made by substitution in the anionic or cationic sublattices in the Bi-2212 structure. The greatest attention is nowadays directed to the substitution of fluorine for oxygen.

The research on the influence of fluorination on the properties of Bi-containing HTSC has not given clear results. Some authors [2-4] claim that fluorination of the Bi–Sr–Ca–Cu–O system causes an increase of the critical temperature by 5-10 K. Other researchers [5-7] say that the critical temperature of the obtained superconducting samples does not change, because the fluorine atoms do not occupy positions in the $\{CuO_2\}_n$ chains, which are responsible for carrying the superconductive current. The authors of [8] report that the critical temperature of the (Bi-2223)F phase falls down to 71-75 K.

The disagreement between the reports is related to the serious dependence of the properties of the samples on the way of preparation (method of synthesis, fluorinating agents, starting materials, *etc.*):

- in [8] a low-temperature fluorinating method with NH_4F as fluorinating agent was used;
- in [3,4] a high-temperature solid state synthesis with fluorinating agents such as CuF_2 and PbF_2 was used.

It is possible that the substitution of fluorine for oxygen takes place in different positions of the Bi-2212 lattice when different fluorine agents are used.

Solid state NMR spectroscopy was used to investigate fluorinated Bi-containing HTSC ceramics by the authors of [9]. The presence of at least two types of fluorine atom in different positions of the elemental lattice was detected. An NMR investigation of fluorinated Y-123 ceramics was carried out in [10]; the signal in the NMR spectrum was decomposed into two Lorentzians, which were correlated to fluorine atoms in the $\{CuO_2\}_n$ layers and in positions apical to these layers.

EPR spectroscopy was used for the investigation of structural changes in HTSC in [11,12]. It was assumed [11] that EPR signals in Bi-containing HTSC appear due to the presence of point defects in the $\{CuO_2\}$ structural units. The auhors of [12] observed the superhyperfine structure of two fluorine atoms located in the coordination sphere of copper in the structure of the superconducting compound $Sr_2CuO_2F_{2.4}$.

Aim of work

The aim of this work was to investigate, by NMR and EPR spectroscopy, fluorinated HTSC Bi-2212 ceramics obtained by adding fluorides of the metals present in the Bi-2212 structure (PbF_2, CuF_2, EuF_3, BiOF, CaF_2, and SrF_2) and ammonium fluoride NH_4F, and to study the changes in the superconducting properties of the samples as a function of their structure and composition [13].

Experimental

The samples were obtained by a two-stage high-temperature solid-state synthesis. At the first stage the initial compounds – strontium carbonate, calcium carbonate and copper oxide – were homogenized by grinding in an agate mortar, and calcined for 24 h at 900ºC for complete decomposition of the carbonates. The concentration of carbonates in the powder was checked by IR spectroscopy. At the second stage, bismuth(III) oxide and the selected fluorinating agent were added. The mixture was homogenized, pressed into pellets and calcined for 50 h at 820ºC with intermediate grindings. Samples with the following compositions were synthesized: $Bi_{2-x}Pb_xSr_2CaCu_2O_{8-x}F_{2x}$ ($0 \le x \le 0.4$, PbF_2), $Bi_{2-x}Eu_xSr_2CaCu_2O_{8-1.5x}F_{3x}$ ($0 \le x \le 0.2$, EuF_3), $Bi_2Sr_2CaCu_2O_{8-x}F_{2x}$ ($0 \le x \le 0.2$, NH_4F, CaF_2, BiOF and SrF_2; $0 \le x \le 0.3$, CuF_2).

X-ray diffraction experiments were performed with a powder diffractometer Shimadzu using Ni-filtered Cu *K*α radiation. Phase analysis and calculations were performed with the Match! and FullProf software packages; the PDF-2 database was also used for the phase analysis. NMR studies were performed with a Bruker Avance 400 spectrometer; the MestReNova software package was used for analysis and deconvolution of the NMR spectra. EPR studies were performed with a CMS 8400 EPR Spectrometer. Resistivity measurements were performed by the standard four-contact method in the temperature range 77-298 K.

Phase analysis

According to the XRD patterns, all of the samples are single-phase and isostructural to the Bi-2212 phase (space group *P4/mmm*), except for the samples with a large amount of fluorine, where the formation of small amounts of SrF_2 phase was observed (Fig. 1). For the samples with low fluorine concentration ($x < 0.3$)

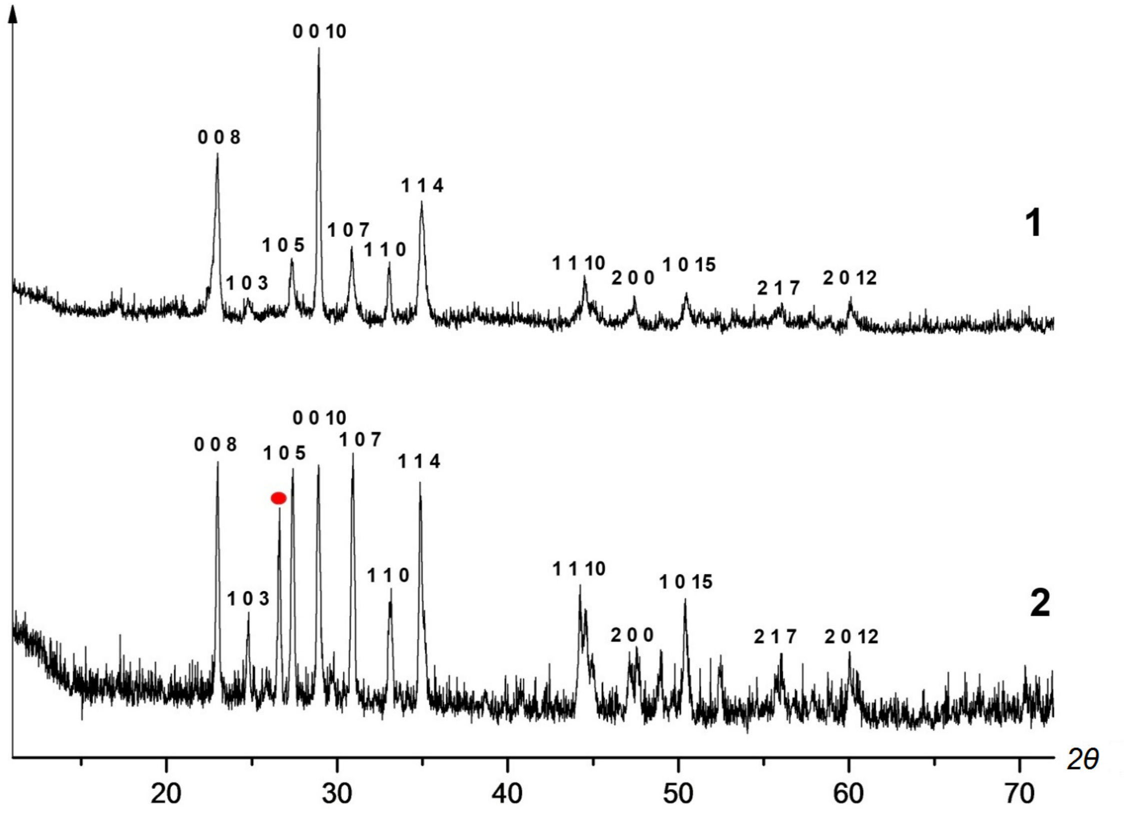

Fig. 1 X-ray diffraction patterns of the samples $Bi_2Sr_2CaCu_2O_{7.8}F_{0.4}$ (CuF_2) (1) and $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{7.4}F_{0.8}$ (2). The line from the impurity phase SrF_2 is marked with a red dot.

the XRD patterns are similar to the XRD patterns of the unsubstituted Bi-2212 phase. With increasing fluorine concentration ($x \geq 0.3$) a redistribution of the intensities of the (1 0 5), (1 0 7) and (0 0 10) peaks was observed for the samples obtained with PbF_2 ($x = 0.3$ and $x = 0.4$). This points to a redistribution of the electron density between structural units, which may facilitate the formation of Cooper pairs and lead to the appearance of the Meissner effect directly after the synthesis, without additional calcination.

The cell parameters were refined for all of the samples (Table 1). The volume of the unit cell decreases with increasing fluorine concentration for the series of samples that were obtained with EuF_3 and CaF_2, but remains almost unchanged in the case of NH_4F and CuF_2. The changes of the volume of the unit cell correlate well with the values of the ionic radii of the cations.

NMR studies

NMR ^{19}F spectra were used for the investigation of structural changes caused by the substitution of fluorine for oxygen in the structure of Bi-2212. An unsplit signal was observed in the spectra of the samples obtained with PbF_2, CuF_2, EuF_3, NH_4F, and CaF_2 as fluorinating agents; this signal appeared to be a superposition of several signals that had not been separated due to both dipole-dipole interactions and the influence of paramagnetic copper-containing structural units (Fig. 2). In the case of the systems obtained with BiOF and SrF_2, another type of spectrum was observed – well separated signals with different chemical shifts, which correspond to fluorine atoms in different chemical surroundings (Fig. 3).

The NMR ^{19}F signals were correlated with the fluorine nuclei in different chemical surroundings in the Bi-2212 lattice by comparison with the spectra of model compounds. Pure fluorides of the metals that form the cationic sublattice of Bi-2212 were used as model compounds (Table 2). The comparison of the values of the chemical shift and integrated intensities of the NMR ^{19}F signals showed that the fluorine atoms concentrate in different positions of the Bi-2212 lattice when different fluorinating agents are used. The structure of Bi-2212 is shown on the drawing in Fig. 4. Substitution of fluorine for oxygen takes place in the {BiO}, {SrO} and $\{CuO_2\}$ layers (where Cu appears to be either in Cu^{2+} or Cu^{3+} form) depending on the fluorinating agent; fluorine atoms also occupy positions in the {Ca} layer and between {BiO} and {SrO} layers. The values of the NMR integrated intensities correlate with the relative content of fluorine in the above-mentioned positions (Table 3).

Table 1 Unit cell parameters of fluorinated Bi-2212 HTSC.

Composition (fluorinating agent indicated in brackets)	Unit cell parameters		
	a, nm	*c*, nm	*V*, nm^3
$Bi_2Sr_2CaCu_2O_8$	0.3835(4)	3.082(3)	0.453(1)
$Bi_{1.95}Pb_{0.05}Sr_2CaCu_2O_{7.95}F_{0.1}$	0.3845(4)	3.091(4)	0.457(1)
$Bi_{1.9}Pb_{0.1}Sr_2CaCu_2O_{7.9}F_{0.2}$	0.3855(5)	3.102(5)	0.461(2)
$Bi_{1.8}Pb_{0.2}Sr_2CaCu_2O_{7.8}F_{0.4}$	0.3858(4)	3.091(4)	0.460(1)
$Bi_{1.7}Pb_{0.3}Sr_2CaCu_2O_{7.7}F_{0.6}$	0.3839(4)	3.089(6)	0.455(2)
$Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_{7.6}F_{0.8}$	0.3839(5)	3.090(6)	0.456(2)
$Bi_{1.95}Eu_{0.05}Sr_2CaCu_2O_{7.925}F_{0.15}$	0.3825(4)	3.075(4)	0.450(2)
$Bi_{1.9}Eu_{0.1}Sr_2CaCu_2O_{7.85}F_{0.3}$	0.3823(7)	3.068(6)	0.449(3)
$Bi_{1.8}Eu_{0.2}Sr_2CaCu_2O_{7.7}F_{0.45}$	0.3818(4)	3.023(3)	0.449(1)
$Bi_2Sr_2CaCu_2O_{7.95}F_{0.1}$ (BiOF)	0.3848(7)	3.096(7)	0.458(3)
$Bi_2Sr_2CaCu_2O_{7.9}F_{0.2}$ (BiOF)	0.3841(6)	3.095(6)	0.457(2)
$Bi_2Sr_2CaCu_2O_{7.8}F_{0.4}$ (BiOF)	0.3839(6)	3.088(6)	0.455(2)
$Bi_2Sr_2CaCu_2O_{7.95}F_{0.1}$ (NH_4F)	0.3829(3)	3.086(3)	0.453(1)
$Bi_2Sr_2CaCu_2O_{7.9}F_{0.2}$ (NH_4F)	0.3829(2)	3.083(2)	0.452(1)
$Bi_2Sr_2CaCu_2O_{7.8}F_{0.4}$ (NH_4F)	0.3826(3)	3.080(4)	0.451(1)
$Bi_2Sr_2CaCu_2O_{7.95}F_{0.1}$ (CaF_2)	0.3838(5)	3.086(3)	0.455(2)
$Bi_2Sr_2CaCu_2O_{7.9}F_{0.2}$ (CaF_2)	0.3823(4)	3.078(3)	0.450(1)
$Bi_2Sr_2CaCu_2O_{7.8}F_{0.4}$ (CaF_2)	0.3809(4)	3.069(3)	0.445(1)
$Bi_2Sr_2CaCu_2O_{7.95}F_{0.1}$ (SrF_2)	0.3857(9)	3.108(9)	0.462(3)
$Bi_2Sr_2CaCu_2O_{7.9}F_{0.2}$ (SrF_2)	0.3842(6)	3.093(6)	0.457(2)
$Bi_2Sr_2CaCu_2O_{7.8}F_{0.4}$ (SrF_2)	0.3840(7)	3.092(7)	0.456(3)
$Bi_2Sr_2CaCu_2O_{7.95}F_{0.1}$ (CuF_2)	0.3843(3)	3.086(3)	0.456(1)
$Bi_2Sr_2CaCu_2O_{7.9}F_{0.2}$ (CuF_2)	0.3845(3)	3.086(3)	0.456(1)
$Bi_2Sr_2CaCu_2O_{7.8}F_{0.4}$ (CuF_2)	0.3848(5)	3.084(5)	0.455(3)
$Bi_2Sr_2CaCu_2O_{7.7}F_{0.6}$ (CuF_2)	0.3844(4)	3.088(4)	0.456(2)

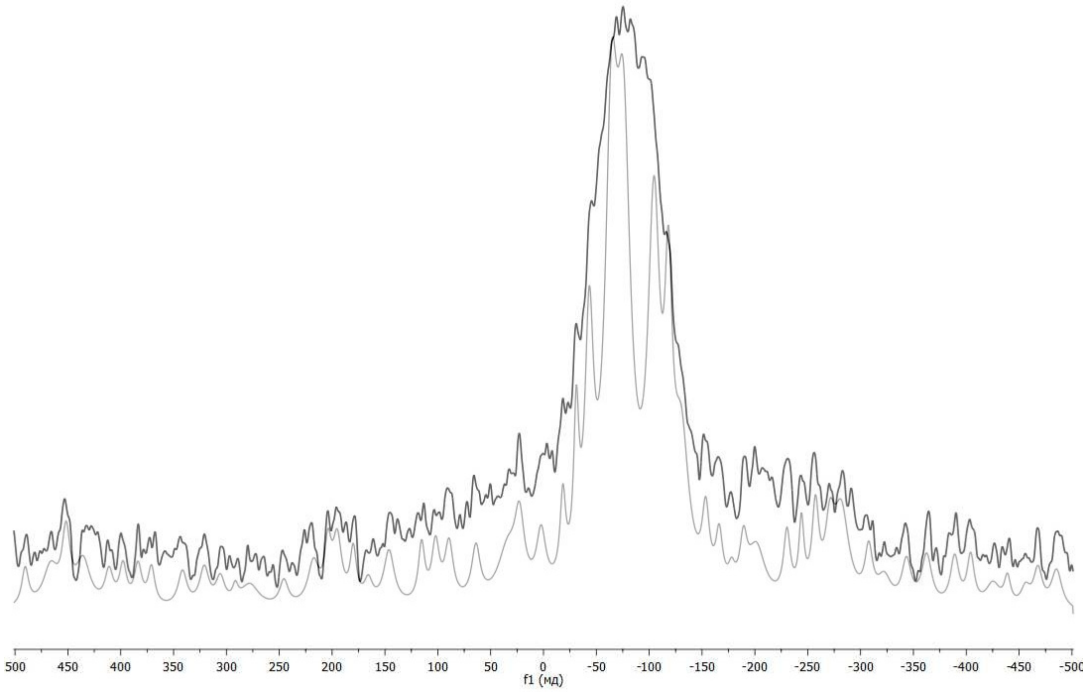

Fig. 2 ^{19}F NMR spectrum of the sample $Bi_2Sr_2CaCu_2O_{7.8}F_{0.4}$ (NH_4F) and computer simulation of the signal.

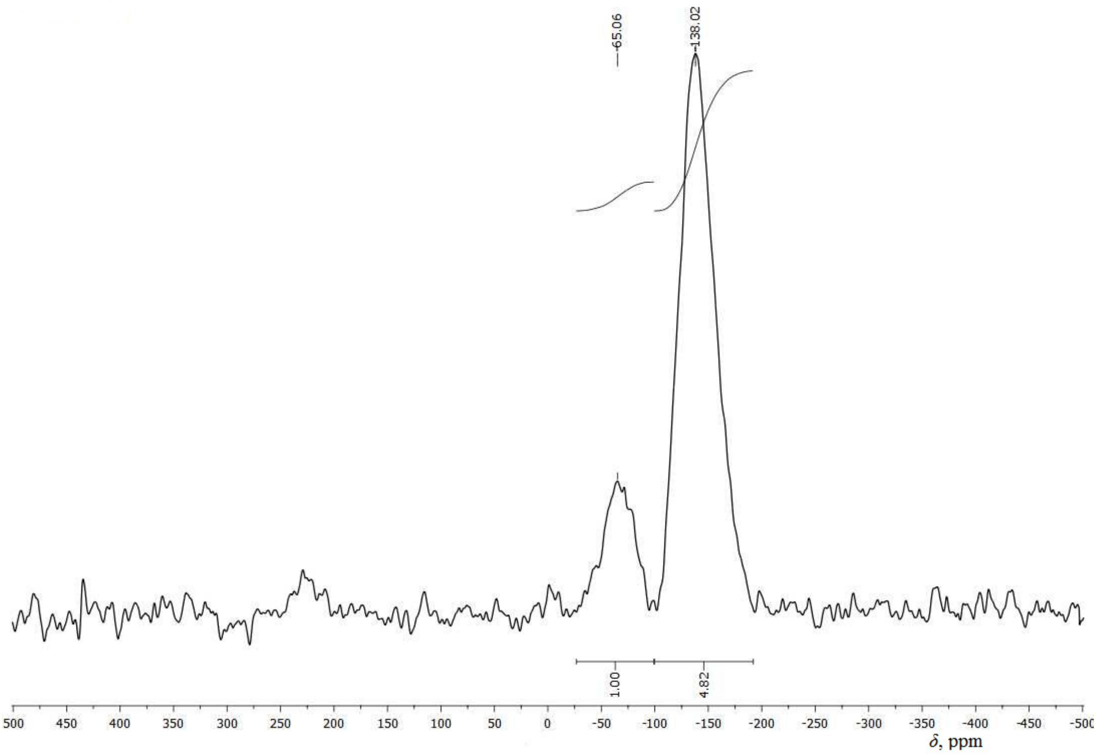

Fig. 3 ^{19}F NMR spectrum of the sample $Bi_2Sr_2CaCu_2O_{7.8}F_{0.4}$ (SrF_2).

Table 2 ^{19}F NMR chemical shifts (δ, ppm) for model compounds.

Compound	δ ^{19}F, ppm
BiOF	-43
SrF_2	-83
CaF_2	-105
PbF_2	-18
	-61
CuF_2	-135
Cu^{3+}	-111

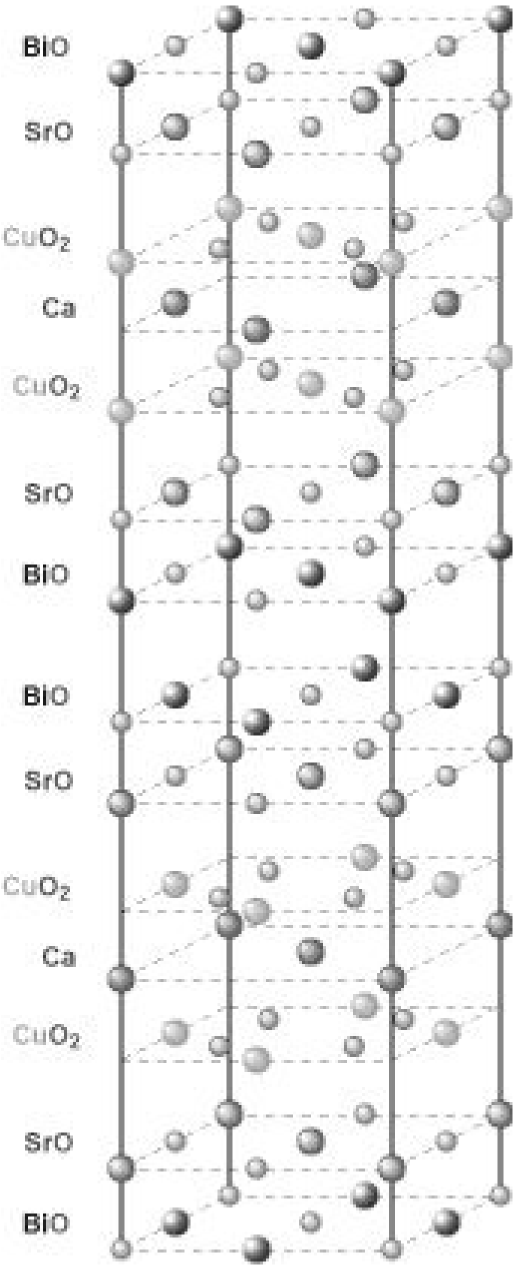

Fig. 4 Unit cell content of the structure of Bi-2212; {BiO}, {SrO}, {Ca} and {CuO_2} structural layers are indicated.

The results show that the fluorine atoms mostly occupy positions between {BiO} and {SrO} layers when NH_4F is added, which correlates with the results reported in [8]. With other fluorinating agents it is possible to increase the relative amount of fluorine that substitutes for oxygen in the $\{CuO_2\}_n$ layers, which may lead to an improvement of the superconducting properties of Bi-2212 after fluorination. The relative content of fluorine in these positions increases in the order CuF_2, PbF_2, BiOF, and SrF_2. Consequently we propose to use these fluorinating agents for the synthesis of fluorinated Bi-2212 HTSC.

EPR studies

For the purpose of exploration of structural changes in the $\{CuO_2\}_n$ chains after fluorination, EPR data were used (Fig. 5). The ratio of the intensities of the spectral components correlates with the fluorine concentration in the samples. The EPR spectrum of the unsubstituted compound Bi-2212 has an isotropic signal with $g = 2.05$ and an axially symmetric signal with $g_{\perp} = 2.05$ and $g_{||} = 2.27$ [11], while the EPR spectra of samples obtained by fluorination of Bi-2212 have at least 3 signals with $g_1 = 2.189\pm0.005$, $g_2 = 2.041\pm0.095$, and $g_3 = 2.400\pm0.082$, where the change of g_2 and g_3 correlates with the fluorine concentration of the samples.

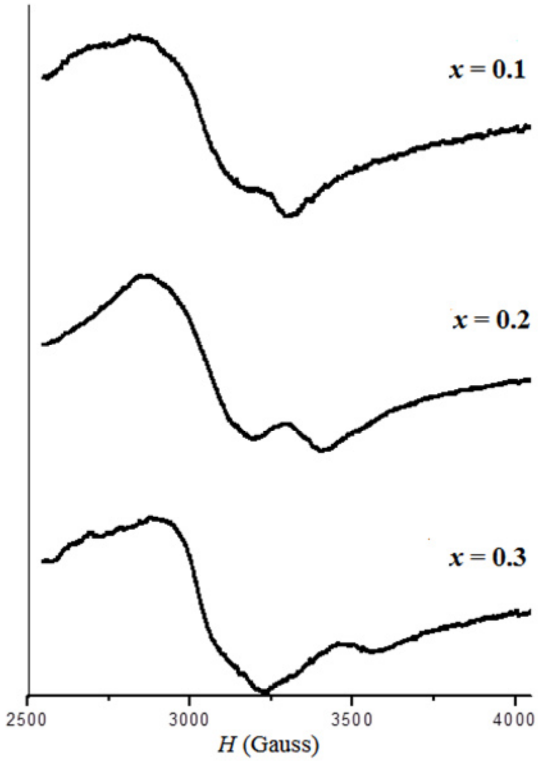

Fig. 5 EPR spectra of samples obtained with PbF_2 as fluorinating agent ($x = 0.1, 0.2, 0.3$).

The EPR spectra of the obtained samples originate from the exchange interaction of local magnetic moments of unpaired Cu^{2+} electrons, which are of variable effectiveness, and their interaction with the nuclear spins of copper and fluorine. The signal with $g_1 = 2.189 \pm 0.005$ is attributed to the presence of point defects in the $\{CuO_2\}_n$ layers [11,12]. The signal with $g_3 = 2.400 \pm 0.082$ is attributed to the asymmetric structural block, namely $\{CuO_3F\}$, which forms after substitution of fluorine atoms for oxygen in the $\{CuO_2\}$ chains.

The intensity of the signal with $g_2 = 2.041 \pm 0.095$ correlates with the x value for the compounds $Bi_{2-x}Pb_xSr_2CaCu_2O_{8-x}F_{2x}$ and $Bi_2Sr_2CaCu_2O_{8-x}F_{2x}$. Most probably this signal corresponds to the symmetric structural block, namely $\{CuO_2F_2\}$ with oxygen and fluorine bridging atoms.

Superconductivity

An increase of T_c to 82-85 K from 77 K for the pure Bi-2212 compound was observed for the samples obtained with such fluorinating agents as BiOF ($x = 0.2$), SrF_2 ($x = 0.2$), PbF_2 and CuF_2 ($0 \leq x \leq 0.2$). The temperature dependence of the resistance for the sample $Bi_2Sr_2CaCu_2O_{7.8}F_{0.4}$ (SrF_2, $x = 0.2$) is shown on Fig. 6. It may be noted that the mentioned fluorinating agents are those that mostly provide substitution in the $\{CuO_2\}$ layers according to the NMR studies, so the increase of T_c correlates with substitution of fluorine for oxygen in the Cu surrounding.

Table 3 ^{19}F NMR chemical shifts (δ, ppm) and chemical surroundings of ^{19}F in the Bi-2212 lattice. Integrated intensities of each component are shown in brackets below the values of the chemical shift.

Compound	δ_1 (Bi^{3+}, Sr^{2+})	δ_2 (Sr^{2+})	δ_3 (Ca^{2+})	δ_4 (Cu^{3+})	δ_5 (Cu^{2+})
$Bi_{1.8}Pb_{0.2}Sr_2CaCu_2O_{7.8}F_{0.4}$ (PbF_2)	-65 **(1.00)**	-81 **(0.86)**	-101 **(1.56)**	-116 (trace amounts)	-130 **(3.06)**
$Bi_{1.8}Eu_{0.2}Sr_2CaCu_2O_{7.7}F_{0.6}$ (EuF_3)	-63 **(1.00)**	-78 **(1.59)**	-95 **(1.55)**	-113 **(0.96)**	-131 **(0.77)**
$Bi_2Sr_2CaCu_2O_{7.8}F_{0.4}$ (BiOF)	-58 **(1.00)**	–	–	–	-141 **(1.09)**
$Bi_2Sr_2CaCu_2O_{7.8}F_{0.4}$ (NH_4F)	-44 (Bi^{3+}) **(1.00)** -66 (Bi^{3+}, Sr^{2+}) **(3.88)**	–	-105 **(1.77)**	-118 **(1.74)**	–
$Bi_2Sr_2CaCu_2O_{7.8}F_{0.4}$ (SrF_2)	-65 **(1.00)**	-80 **(1.19)**	–	–	-138 **(9.14)**
$Bi_2Sr_2CaCu_2O_{7.8}F_{0.4}$ (CuF_2)	–	-89 **(1.00)**	–	-112 **(1.55)**	-137 **(0.88)**

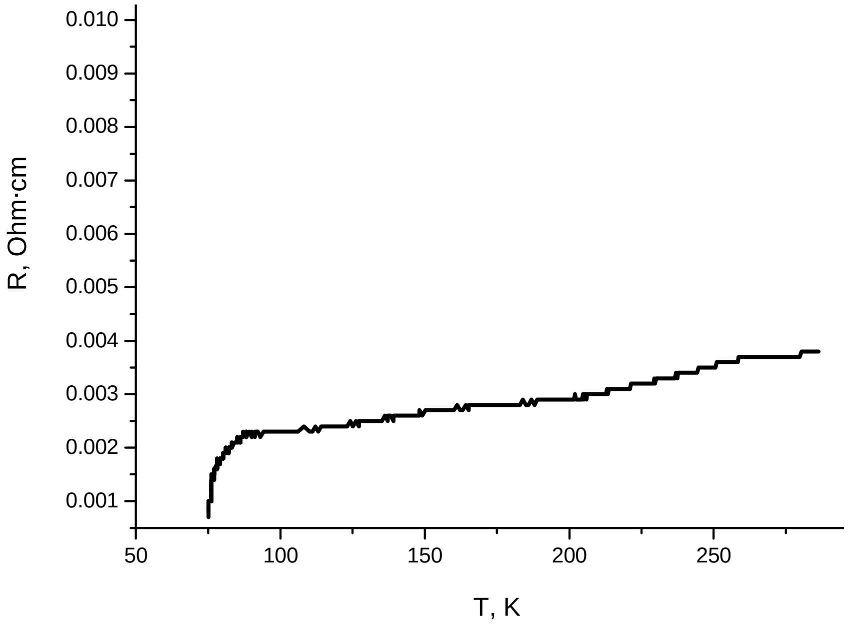

Fig. 6 Temperature dependence of resistance for $Bi_2Sr_2CaCu_2O_{7.8}F_{0.4}$ (SrF_2, $x = 0.2$); T_c (onset) = 82 K.

When increasing the x value to $x = 0.3$, the critical temperature decreases again. It means that there exists an optimal concentration of fluorine, for which the maximum T_c value is reached. We suppose that this optimal concentration is achieved for $x = 0.2$, but this value may change, depending on the fluorinating agent. It is possible that the formation of symmetric $\{CuO_2F_2\}$ units with large x values starts to prevent the superconducting current from passing through the $\{CuO_2\}$ chains, while the formation of $\{CuO_3F\}$ with smaller x values, on the contrary, improves the superconducting properties by increasing the concentration of charge carriers.

Conclusions

Samples of fluorinated Bi-2212 HTSC were synthesized by the method of high-temperature solid state synthesis with different fluorinating agents. It was shown that the substitution of fluorine for oxygen takes place in the $\{CuO_2\}$ layers with the formation of $\{CuO_2F_2\}$ and $\{CuO_3F\}$ structural units, as well as in other positions of the Bi-2212 lattice, in particular, in the {SrO} layers and between {BiO} and {SrO} layers. Fluorinating agents such as PbF_2, CuF_2, BiOF and SrF_2 appeared to be the best for substitution in the $\{CuO_2\}$ layers.

The samples of fluorinated Bi-2212 HTSC showed, in general, higher critical temperatures than unsubstituted 2212 samples; the increase of T_c was, however, limited to low concentrations of fluorinating agent.

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