Available online at www.sciencedirect.com

SCIENCE DIRECT

Physica C 443 (2006) 29–32

PHYSICA C

www.elsevier.com/locate/physc

Effect of fluorine and cerium substitutions on the properties of the $Tl_2Ba_2CaCu_{1.98}Fe_{0.02}O_8$ superconductor

A.I. Akimov [a], V. Ksenofontov [a], S.A. Lebedev [b,*], T.M. Tkachenka [a]

[a] Institute of Solid State and Semiconductor Physics, National Academy of Sciences of Belarus P, Brovki 19, Minsk 220072, Belarus
[b] Johannes Gutenberg-Universitaet, Staudinger Weg 9, D-55099 Mainz, Germany

Received 6 February 2006; received in revised form 23 March 2006; accepted 13 April 2006
Available online 21 June 2006

Abstract

Fluorine and cerium substituted Tl-2212 high-T_c superconductors were produced. X-ray diffraction, Mossbauer effect method, temperature measuring of the resistances and a.c. susceptibilities for all $Tl_2Ba_2Ca_{1-y}Ce_yCu_{1.98}Fe_{0.02}O_{8-x/2}F_x (0 \leqslant x \leqslant 0.2$ and $0 \leqslant y \leqslant 0.1)$ were applied. It was found that the cerium admixture does not affect significantly the Tl-2212 superconductor properties. Fluorine admixture alone appreciably affects the value of superconducting transition temperature. The biggest increase in T_c is 10 K and is realised for $x = 0.10$–0.20. Substituting admixtures are not clearly exhibited in Mossbauer parameters, i.e. do not influence Fe–O bonding tangibly.

PACS: 61.18.Fs; 74.62.Bf; 74.72.Jt

Keywords: High-T_c superconductor; $Tl_2Ba_2CaCu_2O_8$; 2212 structure; Mossbauer effect

1. Introduction

A relatively large number of superconducting phases can exist in the Tl–Ba–Ca–Cu–O system [1]. They can be divided into 2 groups depending on the Tl–O layer structure (one- or two-layer). For the first time, high temperature superconducting thallium oxides with the structure derived from $Bi_4Ti_3O_{12}$ and chemical formula $Tl_2(BaSr)_2Ca_{n-1}Cu_nO_{2n+4}$, have been produced in [2]. In [3], two-layer phase 2212 in the $Tl_2Ba_2CaCu_2O_8$ system with a superconducting transition temperature of 98 K degrees has been obtained. It is common knowledge that the change of current carrier density in Cu–O planes results in changing the electrical physical properties including the superconducting transition temperature [4]. It was supposed that the substitutions of oxygen by fluorine and calcium by cerium in the Tl-2212 superconductor could change hole density in Cu–O planes. It was a purpose of this work to synthesize $Tl_2Ba_2Ca_{1-y}Ce_yCu_{1.98}Fe_{0.02}O_{8-x/2}F_x$ (2212), initially with $x = 0$ and $y = 0$, and to increase the substituting admixture amounts up to the limit of the homogeneity range, thus studying the influence of substitutions on the properties of the superconductor.

2. Samples

Calcium in $Tl_2Ba_2CaCu_{1.98}Fe_{0.02}O_8$ was partly substituted by cerium and oxygen by fluorine. The essentialities of synthesising process have been described by the authors elsewhere [5]. The concentrations of the substituting admixtures in $Tl_2Ba_2Ca_{1-y}Ce_yCu_{1.98}Fe_{0.02}O_{8-x/2}F_x$ initially were taken in the concentration range of $0 \leqslant x \leqslant 0.3$ and $0 \leqslant y \leqslant 0.3$.

X-ray analysis shows the single 2212 phase formation in the samples (1) for the fluorine concentration of $x \leqslant 0.1$; (2) for the cerium concentration of $y \leqslant 0.1$. (3) As either x or y exceed 0.1 (each of x or y increases above 0.1), additional phases (CuO, $BaCO_3$ etc.) appear in the samples.

* Corresponding author. Tel.: +375 17 284 12 54; fax: +375 17 284 09 41.
E-mail address: lebedev@ifttp.bas-net.by (S.A. Lebedev).

0921-4534/$ - see front matter
doi:10.1016/j.physc.2006.04.091

However, the presence of a Ce content in the superconductor allows increase the fluorine concentration while remaining within the 2212-phase range. When both cerium and fluorine were substituted, their simultaneous solubilities were $0 \leqslant y \leqslant 0.1$, $0 \leqslant x \leqslant 0.2$. When sintering, 2% at. Cu atoms were substituted by Fe enriched with ^{57}Fe isotope to allow for the Mossbauer investigating of the samples. Addition of 2% of Fe into superconducting samples usually does not influence the phase formation appreciably but leads to small decrease (a few degrees) in the T_c value [6–9].

3. Results and discussion

The temperatures of superconductor transitions of the samples obtained were measured in two different ways, i.e. using the resistive method on constant current (i) and a.c. susceptibility measurements in the temperature region 77–300 K (±0.2 K) (ii). The resistance of the samples was measured by the standard four-probe technique and a.c. susceptibility was measured using the standard inductance technique. The accuracy of T_c determination was ±1 K. The results are summarised in Table 1.

It was found, that the two of the samples $Tl_2Ba_2Ca(Cu_{1.98}Fe_{0.02})F_{0.1}O_{7.95}$ and $Tl_2Ba_2Ca(Cu_{1.98}Fe_{0.02})F_{0.2}O_{7.9}$ have the temperatures of superconducting transition higher than that of the known unsubstituted Tl-2212.

The $Tl_2Ba_2Ca_{1-y}Ce_yCu_{1.98}Fe_{0.02}O_{8-x/2}F_x$ system, $0 \leqslant x \leqslant 0.2$ and $0 \leqslant y \leqslant 0.1$ with 2212 type of crystal structure was studied by Mossbauer effect method. The usual transition geometry and constant acceleration regime were applied.

The results of the Mossbauer study at room temperature are close to those for Bi-2212 [10–12]. The $Tl_2Ba_2CaCu_{1.98}Fe_{0.02}O_8$ spectrum at room temperature was approximated by two quadruple doublets (see Fig. 1) with the same value of the isomer shift (0.275 mm/s relative to α-Fe) and the quadruple splitting values: $QS_1 = 1.245$ mm/s and $QS_2 = 0.882$ mm/s. These results are not surprising once the microstructure of superconductors under investigation (Fig. 2) and crystallographic peculiarities of 2212 superconducting phase (Fig. 3) are taken into account. In fact, the Fe/Cu atoms inside the superconducting phase grains have only one possible type of the nearest neighbouring. Each Fe/Cu atom is placed at the centre of a strongly distorted oxygen pyramid. The distance between Cu and O(1) atom in Cu-containing plane is 1.92 Å, the Cu–O(2) distance is equal to 2.70 Å. The electric field gradient appears at Fe atom sites. It leads to the quadrupole splitting of the Mossbauer spectrum and the doublet 1 is responsible for those Fe atoms occupying the Cu

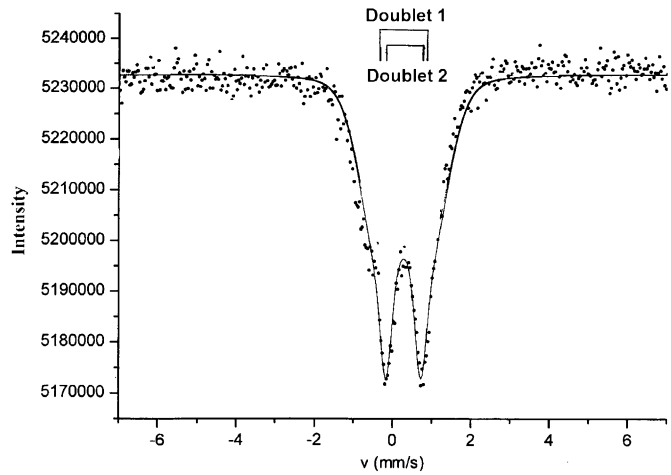

Fig. 1. $Tl_2Ba_2CaCu_{1.98}Fe_{0.02}O_8$ spectrum ($T = 293$ K).

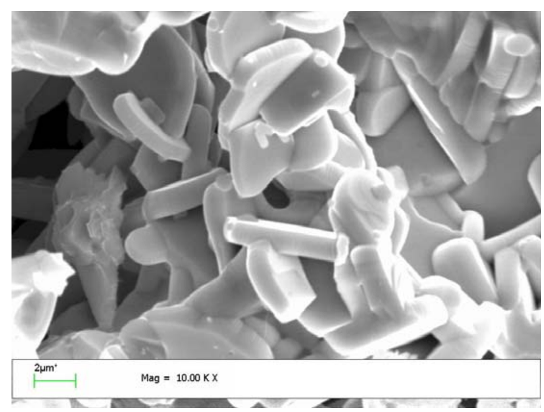

Fig. 2. Microstructure of Tl-2212 superconductor.

Table 1
Superconducting transition temperatures of $Tl_2Ba_2Ca_{1-y}Ce_y(Cu_{1.98}Fe_{0.02})O_{8-x/2}F_x$

N	Composition (estimated chemical formula)	Phase composition (X-ray analysis data)	T_C, K	
			Resistive measurements	Magnetic measurements
1	$Tl_2Ba_2Ca(Cu_{1.98}Fe_{0.02})O_8$	Tl-2212	106	107
2	$Tl_2Ba_2Ca(Cu_{1.98}Fe_{0.02})F_{0.1}O_{7.95}$	Tl-2212	110	111
3	$Tl_2Ba_2Ca(Cu_{1.98}Fe_{0.02})F_{0.2}O_{7.9}$	Tl-2212, negligible CuO, $BaCO_3$	109	111
4	$Tl_2Ba_2Ca(Cu_{1.98}Fe_{0.02})F_{0.3}O_{7.85}$	Tl-2212, CuO, $BaCO_3$, $BaCuO_2$, BaF_2	101	106
5	$Tl_2Ba_2(Ca_{0.9}Ce_{0.1})(Cu_{1.98}Fe_{0.02})O_8$	Tl-2212	99	103
6	$Tl_2Ba_2(Ca_{0.9}Ce_{0.1})(Cu_{1.98}Fe_{0.02})F_{0.2}O_{7.9}$	Tl-2212	103	106
7	$Tl_2Ba_2(Ca_{0.9}Ce_{0.1})Cu_2O_8$	Tl-2212, $BaCO_3$	100	102
8	$Tl_2Ba_2(Ca_{0.8}Ce_{0.2})Cu_2O_8$	Tl-2212, $BaCO_3$	103	103
9	$Tl_2Ba_2(Ca_{0.7}Ce_{0.3})Cu_2O_8$	Tl-2212, $BaCO_3$, $BaCuO_2$	Not superconducting	
10	$Tl_2Ba_2(Ca_{0.6}Ce_{0.4})Cu_2O_8$	Tl-2212, $BaCO_3$, $BaCuO_2$	Not superconducting	