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Synthesis and superconducting properties of $Tl_{2-x}Bi_xSr_2Ca_{n-1}Cu_nO_y$

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In the system $Tl_{2-x}Bi_xSr_2Ca_{n-1}Cu_nO_y$ (n = 2, 3, $0 \le x \le 0.5$) the effect of initial composition on the ceramics phase composition was investigated. X-ray analysis and resistive measurements of the samples with different composition were carried out. The homogeneity region and change of the unit cell parameters were defined. Size and shape of the particles that form the ceramics were studied using scanning electron microscopy. The electrophysical properties of the superconductors with addition of bismuth deteriorate, reducing the critical temperature in the superconducting transition.
Keywords: doping, thallium ceramics, strontium, high-temperature superconductivity.

В системе $Tl_{2-x}Bi_xSr_2Ca_{n-1}Cu_nO_y$ (n = 2, 3, $0 \le x \le 0.5$) исследовано влияние выходного состава на фазовый состав керамики. Проведены рентгенофазный анализ и резистивные измерения образцов с разным составом. Определена область гомогенности, исследовано изменение параметров элементарной ячейки. Размер и форму частиц, которые входят в состав керамики, исследовали с помощью сканирующей электронной микроскопии. Электрофизические свойства сверхпроводников с добавлением висмута ухудшаются, уменьшая температуру сверхпроводяшего перехода.

Синтез та вивчення надпровідних властивостей ВТНП кераміки $Tl_{2-x}Bi_xSr_2Ca_{n-1}Cu_nO_y$. *І.О.Корбут, С.А.Недiлько.*

В системі $Tl_{2-x}Bi_xSr_2Ca_{n-1}Cu_nO_y$ (n = 2, 3; $0 \le x \le 0,5$) досліджено вплив вихідного складу на фазовий склад кераміки. Проведено рентгенофазовий аналіз та резистивні вимірювання зразків з різним складом. Визначено область гомогенності, досліджено зміну параметрів елементарної комірки. Розмір та форму частинок, що входять до складу кераміки, досліджено за допомогою скануючої електронної мікроскопії. Електрофізичні властивості надпровідників з додаванням бісмуту погіршуються, зменшуючи температуру надпровідного переходу.

1. Introduction

The important feature of discovery of the high-temperature superconductivity (HTSC) is that superconductivity was discovered not in traditional intermetallic compounds, organic or polymeric structures, but in oxide ceramics which usually detects insulating or semiconducting properties. In 1987 the first reports on synthesis of superconductors in the system Bi–Sr(Ca)–Cu–O appeared. At first it was tetragonal $Bi_2Sr_2CuO_6$ with the critical temperature of 12 K, then by addition of calcium in January 1988 Maeda et al. synthesized the series of compounds $Bi_2Sr_2CaCu_2O_8$ and $Bi_2Sr_2Ca_2Cu_3O_{10}$ with the temperature value of 90 and 110 K. The structure of the new compounds was layered and it gave grounds for suggestions and prediction of the ways improving of the critical temperature.

In 1988 Sheng and Herman received superconductor $Tl_2Ba_2Ca_2Cu_3O_{10}$ with the critical temperature of 125 K. The systems based on thallium with the layered structure show higher value of the critical temperature than bismuth-containing.

The bismuth- and thallium-based ceramics have very high value of critical temperature in superconducting transition. The thallium-based HTSC are studied insufficiently because of difficulties of preparation and investigation of samples associated with the thallium toxicity. The results of the research of physical properties of superconductors based on thallium are often conflicting [1–8], that may be related to multiphase structure, heterogeneity of the samples and impurities influence. Further systematic study of the physical properties of Tl systems is important.

The aim of the current work was to study the impact of substitution of Tl^{3+}/Bi^{3+} and Ba^{2+}/Sr^{2+} on structural parameters and electrical properties of the HTSC materials of composition Tl2212 and Tl2223.

2. Materials and methods

Preparation of oxide ceramic high-temperature superconductors includes the following steps: weighing of the initial components, their homogenization, calcination (at the temperatures >800°C), which includes intermediate grinding and forming (pressing) of ceramic materials.

The factor complicating synthesis of bismuth- and thallium-based phases is the volatility of bismuth and thallium oxides. To prevent it the calcination in atmospheres of gases (including oxygen), which creates back pressure and keep thallium in the samples, and the introduction of bismuth and thallium oxides excess are used [9].

In this paper we synthesized the compounds which have excess of two components (thallium and bismuth) 10 % of their stoichiometric composition as they are volatile at the sintering temperature.

Change in the composition of individual components of investigated oxide systems has little effect on the critical temperature value (including variations of thallium oxide composition, which is the most volatile component and forms volatile double or triple compounds).

Synthesis of the thallium ceramics of composition 2212 and 2223 was carried out by the following procedure. To prepare the mixture as starting components were used carbonates of Sr, Ca and copper oxide, which were carefully mixed up. The mixture was heated 24 h at the temperature of 900°C to achieve the oxides mixture instead of carbonates. Monitoring of oscillations of CO_3^{2-}-groups was carried out by recording the infrared (IR) absorption spectra of the mixture. In the obtained mixture the calculated amounts of Tl_2O_3 and Bi_2O_3 oxides were added. After their input the mixture was again thoroughly grinded and pressed in tablets with diameter of ~10 mm and thickness of ~2 mm. The annealing was carried out in oxygen atmosphere. It was investigated that the critical temperature depends on the sintering time weakly and has optimal value of 5 min. The tablets were placed in a tube furnace preheated to 800–810°C for 5 min, then they were quenched in air.

The experiments with repeated heat treatment of the samples of thallium ceramics were conducted. The repeated heat treatment does not increase the critical temperature in the superconducting transition.

The IR absorption spectra of thermolysis products were recorded by spectrophotometer Spectrum BX FT-IR (Perkin Elmer) in 1200–1800 cm^{-1} using the pressing tablets with KBr.

The phase composition and crystal lattice parameters were determined by X-ray diffraction using DRON-3M, CuK_α radiation and Ni-filter. Recording was conducted at the speed of 1–4°/min. Further calculations of the obtained spectra (referring diffractograms, calculation and refinement of the crystal lattice parameters) were performed by PC using the programs Origin, Match, X-ray and Difwin.

3. Results and discussion

Phase composition of the polycrystalline samples in the system $Tl_{2-x}Bi_xSr_2CaCu_2O_y$ ($0 \le x \le 0.5$) was determined using X-ray diffraction analysis (XRD). It was found that the area of isomorphic substitution is within $0 \le x \le 0.3$.

The samples with $x = 0.4$ and 0.5 contain the impurity phases. Fig. 1 shows the X-ray diffraction analysis results of the pure sample Tl2212 and sample with the degree of substitution $x = 0.5$, which show that additional peaks corresponding to the impurity phase $CaSrCu_2BiO_x$ with increasing x (2Θ = 41.86; 51.94) are present, and also some characteristic reflexes of thallium phase disappeared. The quantity of bismuth oxide of the sample with $x = 0.5$ was one third of the required quantity of thallium oxide therefore the phase is not formed.

Table. The unit cell parameters for the systems of composition $Tl_{2-x}Bi_xSr_2CaCu_2O_y$ and $Tl_{2-x}Bi_xSr_2Ca_2Cu_3O_y$ ($0 \le x \le 0.5$)

The composition	a, Å	c, Å
$Tl_2Sr_2CaCu_2O_8$	3.874(1)	29.29(6)
$Tl_{1.95}Bi_{0.05}Sr_2CaCu_2O_y$	3.866(1)	29.33(1)
$Tl_{1.9}Bi_{0.1}Sr_2CaCu_2O_y$	3.857(1)	29.38(1)
$Tl_{1.8}Bi_{0.2}Sr_2CaCu_2O_y$	3.859(2)	29.42(9)
$Tl_{1.7}Bi_{0.3}Sr_2CaCu_2O_y$	3.853(8)	29.32(8)
$Tl_{1.6}Bi_{0.4}Sr_2CaCu_2O_y$	3.841(1)	29.13(6)
$Tl_{1.5}Bi_{0.5}Sr_2CaCu_2O_y$	3.855(8)	29.23(7)
$Tl_2Sr_2Ca_2Cu_3O_y$	3.845(9)	35.54(2)
$Tl_{1.95}Bi_{0.05}Sr_2Ca_2Cu_3O_y$	3.851(7)	35.55(1)
$Tl_{1.9}Bi_{0.1}Sr_2Ca_2Cu_3O_y$	3.858(2)	35.42(2)
$Tl_{1.8}Bi_{0.2}Sr_2Ca_2Cu_3O_y$	3.855(4)	35.33(3)
$Tl_{1.7}Bi_{0.3}Sr_2Ca_2Cu_3O_y$	3.898(5)	35.28(2)
$Tl_{1.6}Bi_{0.4}Sr_2Ca_2Cu_3O_y$	3.798(5)	35.86(4)
$Tl_{1.5}Bi_{0.5}Sr_2Ca_2Cu_3O_y$	3.844(5)	35.44(3)

The samples $Tl_{2-x}Bi_xSr_2CaCu_2O_y$ with partial substitution of thallium for bismuth according to the X-Ray analysis have tetragonal symmetry; with the increase of x the parameter a and unit cell volume V decrease and the parameter c enhances (Table).

In the system $Tl_{2-x}Bi_xSr_2Ca_2Cu_3O_y$ ($0 \le x \le 0.5$) using XRD it was determined that formation of the single-phase products is in the concentration range of $0 \le x \le 0.3$. The following regularity is established: the parameter a and unit cell volume V increase and the parameter c decreases in the homogeneity region (Table).

The results of XRD for the samples of composition $Tl_2Sr_2Ca_2Cu_3O_y$ and $Tl_{1.5}Bi_{0.5}Sr_2Ca_2Cu_3O_y$ are shown in Fig. 2. It can be seen that the majority of the characteristic peaks of pure phase Tl–Sr–Ca–Cu–O without adding bismuth is not revealed on the diffractogram for the sample with $x = 0.5$. However, there are reflections of the impurity phases $2\Theta = 27.2$ (bismuth oxide, unreacted) and $2\Theta = 33.82$; 48.58; 57.86 (oxide of thallium (III)). The quantity of Tl_2O_3 was insufficient to form the thallium phase for $x = 0.4$ and 0.5 because of its decreasing.

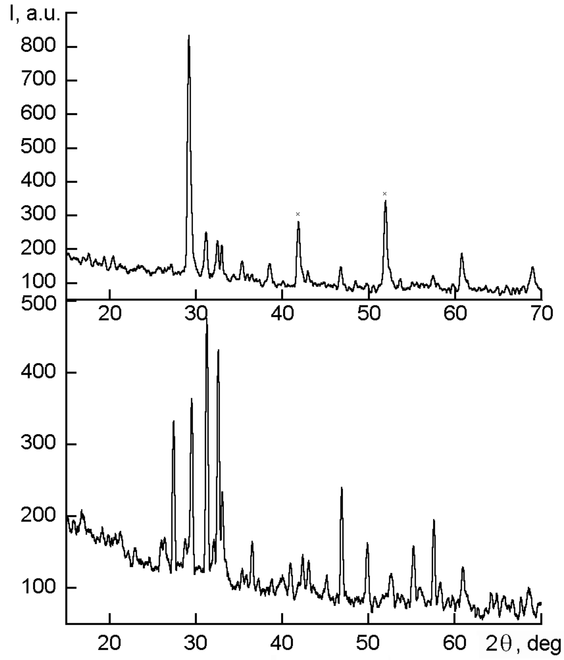

Fig. 1. X-ray diagrams of the samples of composition $Tl_2Sr_2CaCu_2O_y$ (below) and $Tl_{1.5}Bi_{0.5}Sr_2CaCu_2O_y$ (above); x — $CaSrCu_2BiO_x$.

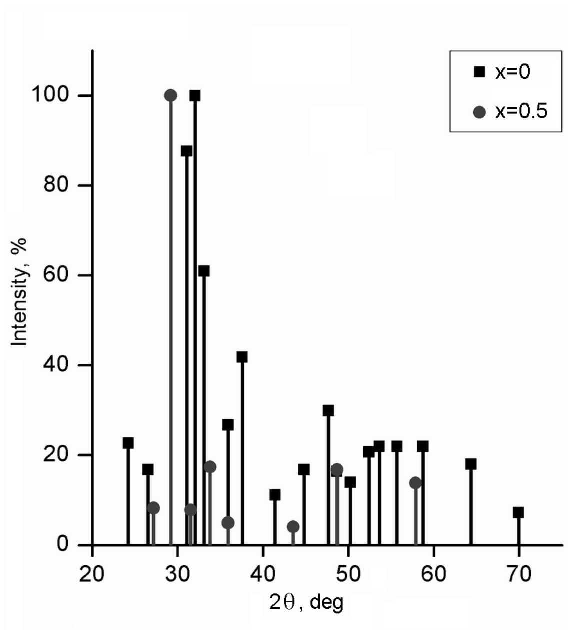

Fig. 2. Diffractograms of the samples of composition $Tl_2Sr_2Ca_2Cu_3O_y$ ($x = 0$) and $Tl_{1.5}Bi_{0.5}Sr_2Ca_2Cu_3O_y$ ($x = 0.5$).

The morphological characteristics of oxides were studied using scanning electron microscopy (SEM). Microstructural analysis of the data showed that the particles are structural agglomerates (Fig. 3). The vast majority of the material is large enough grains of size about 50 μm. However, significantly smaller particles, indicating the ability to sintering, are noticeable; only the small number of particles is not included in the agglomerates. Also from the picture it is clear that the ceramics is characterized by homogeneity.

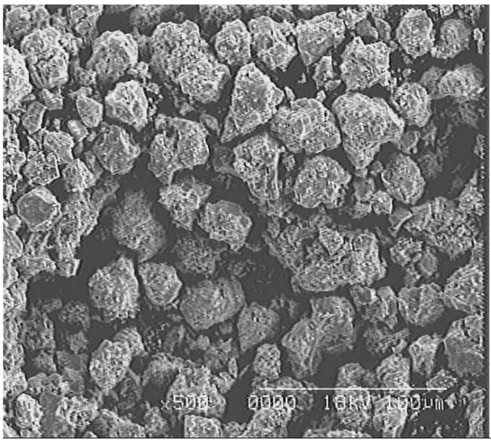

Fig. 3. SEM-photo of the sample $Tl_2Sr_2CaCu_2O_y$.

For the samples of $Tl_{2-x}Bi_xSr_2CaCu_2O_y$ transition to the superconducting state above 77 K was observed (T_c of the pure TlSr–2212 sample is ~ 78 K). The electrophysical measurements in the system $Tl_{2-x}Bi_xSr_2Ca_2Cu_3O_y$ showed that the critical temperature in the superconducting transition for all homogeneous samples (x = 0; 0.05; 0.1; 0.2 and 0.3) is reduced below the boiling point of liquid nitrogen. At the same time it is shown by the authors of [10] that the presence of strontium in thallium superconductors degrades superconductivity not significantly, and in some cases improves [11]. It is possible for the system Tl–1223, for partial replacement of barium by strontium or complete substitution of Ca for Sr (barium in the system remains).

4. Conclusions

The high-temperature superconductors of composition $Tl_{2-x}Bi_xSr_2CaCu_2O_y$ and $Tl_{2-x}Bi_xSr_2Ca_2Cu_3O_y$ ($0 \le x \le 0.5$) were synthesized and investigated. The homogeneity region and change of the unit cell parameters were determined according by X-ray analysis. It is shown that by varying of degree of substitution x there is a change of the parameters a, c, and unit cell volume V. Dependence of temperature in the superconducting transition on the degree of substitution was studied.

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