THE STRUCTURAL ANALYSIS AND THERMAL POWER OF $Bi_2Sr_2CaCu_2O_X$ and $Bi_2Sr_2Ca_{0.6}Zn_{0.4}Cu_2O_X$

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The temperature dependences of the thermopower of $Bi_2Sr_2CaCu_2O_X$ and $Bi_2Sr_2Ca_{0.6}Zn_{0.4}Cu_2O_X$ were studied in the temperature range of 77–320 K. It is shown that zinc atoms partially occupy the place of calcium in the CaO planes in the initial matrix. The critical temperature of the transition to the superconducting state for both samples was T_c=78 K. The obtained experimental data on the thermopower are analyzed on the basis of a two-band model. It was shown that a partial replacement of the element Ca by zinc leads to a decrease in the width of the forbidden zone. The calculations performed in the framework of the two-band model are in satisfactory agreement with the experiment.

Keywords: superconducting material, thermal power, two-band model
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1. INTRODUCTION

Despite the many studies on HTSC, the nature of superconducting pairing and the mechanisms of scattering of charge carriers in the normal state are still not completely clear. It is also known that the temperature of the superconducting transition T_c in layered HTSCs significantly depends on the degree of doping and reaches its maximum value at the optimum doping value. The introduction of impurities in HTSC leads to a change in the electron system and, as a consequence, to a change in the microscopic parameters of the superconductor.

The study of the thermal power allows us to directly determine the type of conductivity, identify the mechanisms of scattering of charge carriers, determine the degree of their degeneration, calculate such important band parameters as the band gap ε_g, the effective mass of charge carriers m^*[1]. The magnitude and sign of the thermal power in bismuth-based (including yttrium, mercury, and thallium) HTSC cuprates are mainly determined not by the number of CuO_2 planes, but by the carrier concentration in these planes, which can be changed by replacing the basic substance atoms with different elements or by doping with oxygen [2- 4].

In this work, we investigated the effects of the zinc element on the thermal power of $Bi_2Sr_2CaCu_2O_X$ and $Bi_2Sr_2Ca_{0.6}Zn_{0.4}Cu_2O_X$ in the temperature range 77-320 K.

2. EXPERIMENTAL RESULTS AND THEIR DISCUSSION

The studied samples were prepared by the method of solid-phase synthesis, the stoichiometric proportions mixing highly pure powders Bi_2O_3, $CaCO_3$, $SrCO_3$, ZnO and CuO. Samples were annealed for 10 hours at 840^0 C temperature, and then cooled by 1.5^0 C/min speed up to room temperature.

X -ray diffraction analysis was performed on Brucker -D8 advance at room temperature with a resolution of $\Delta(2\theta) = 0.05^0$ in the $5^0 \le 2\theta \le 80^0$ interval. The obtained results are shown in fig. 1. As can be seen, additional peaks are observed on the diffractogram with the introduction of the zinc element. Some structural parameters of the studied samples were determined from the data of *X* -ray structural analysis. The space group of the lattice parameter and the volume of the unit cell of the sample $Bi_2Sr_2CaCu_2O_x$ are: sp. gr. orthorhombic Pnnn; a =5,396, b =5,395, c =30,643, V =892.06 A^3, respectively.

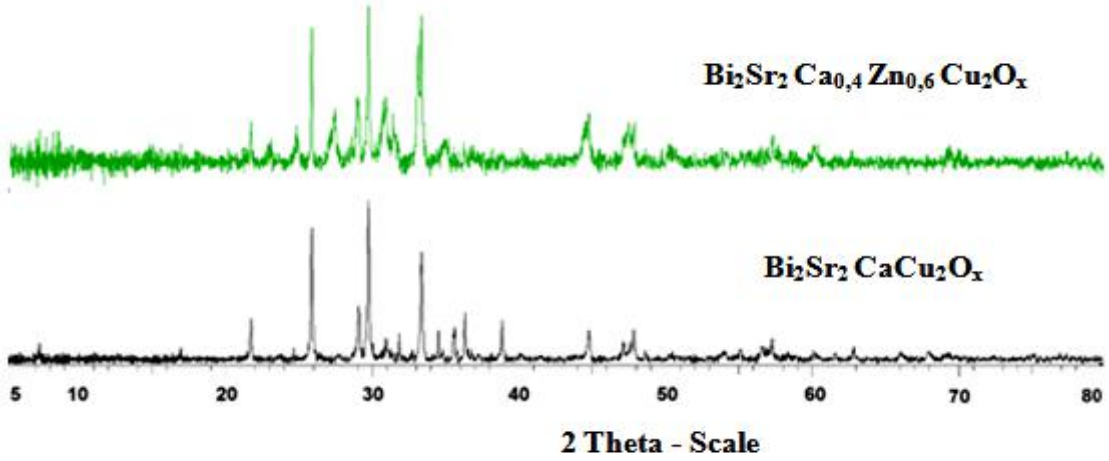

Fig. 1. The *X*-ray diffractogram of $Bi_2Sr_2CaCu_2O_X$ and $Bi_2Sr_2Ca_{0.6}Zn_{0.4}Cu_2O_X$

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The $Bi_2Sr_2Ca_{0.6}Zn_{0.4}Cu_2O_X$ sample consists of two phases: orthorhombic Pnnn with lattice parameters a=5,429, b=5,431, c=30,840, V=909.31 $Å^3$, and tetragonal I4/ mmm with lattice parameters, a =3.8097, c =24.607, V =357.14 $Å^3$. According to the intensities of the diffraction peaks, the tetragonal phase prevails.

If we take into account the data of the lattice parameters $Bi_2Sr_2ZnCu_2O_x$ equal to I4 a =3.797 A; b =24.577 A; V =354.42 A^3 it can be seen that the lattice parameters decrease when the calcium element is replaced with zinc. This is due to the fact that zinc atoms do not fully occupy the corresponding places of the calcium element. Therefore, in the studied compositions, additional diffraction peaks are observed that do not correspond to the initial composition of $Bi_2Sr_2CaCu_2O_x$. On the other hand, zinc has a smaller ionic radius than calcium (1.04 $Å$ and 0.83 $Å$, respectively). When Ca is replaced by Zn, the crystal structure deforms, similar to that arising under external pressure, as a result of which the lattice parameter decreases [5].

The thermal power was measured by the standard four-contact method in a zero magnetic field. Electrical contacts were applied with indium. The fig. 2 shows the results of the temperature dependences of the thermal power of the studied samples. As can be seen, the temperature dependences of the thermal power pass through a maximum before the phase transition. In both cases, the thermal power value decreases with increasing temperature. The character of the $S(T)$ curves for both studied samples is the same and indicates the hole type of conductivity in the studied temperature interval. However, there is a clear tendency to change the sign of conductivity with increasing temperature. This indicates that two types of charge carriers are involved in conduction; both holes and electrons. To explain the temperature dependence, we used the Xin model [6].

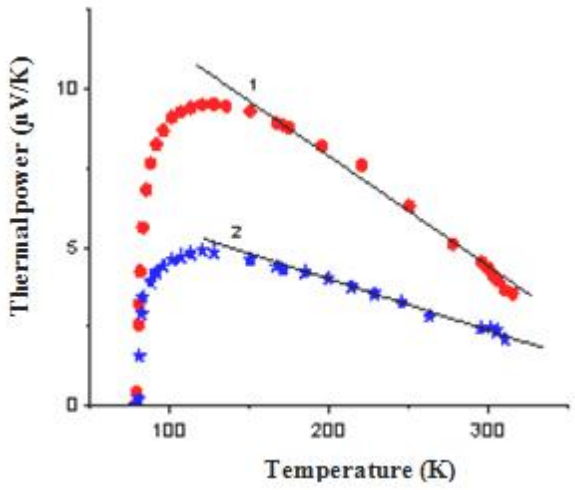

Fig. 2. The temperature dependences of thermal power of $Bi_2Sr_2CaCu_2O_X$ (1) and $Bi_2Sr_2Ca_{0.6}Zn_{0.4}Cu_2O_X$ (2)

The two-band model of Xin is based on structural-zone calculations, which suggest that the metallic conductivity is due to Cu -O planes, and the Bi -O zone (Bi_{6p}-O_{2p}) affects the Fermi energy E_f and the Fermi surface of the HTS material. In the Bi-O planes, electron conductivity takes place, while hole conductivity dominates in the Cu-O plane. A decrease in the valence state of Bi^{3+} to $Bi^{3-\delta}$ leads to an increase in the electron conductivity in the Bi-O plane, while the oxidation of Cu^{2+} to $Cu^{2+\delta}$ increases the hole conductivity of the Cu -O planes.

As is known, in the case of two types of charge carriers, S can be represented as:

$$S = \frac{\sigma_p}{\sigma_n + \sigma_p} S_p + \frac{\sigma_n}{\sigma_n + \sigma_p} S_n \qquad (1)$$

where S_p and S_n are thermal power due to holes and electrons; $\sigma_p = ep\mu_p$, $\sigma_n = en\mu_n$, μ_p, μ_n, p, n – are the conductivity, mobility, and concentration of holes and electrons, respectively. This formula is fairly general and independent of the specifics of the mechanism for the appearance of the thermal power [1].

If we assume that the metallic conductivity of the valence band is inversely proportional to temperature, i.e. σ ~1/T, and the conductivity of electrons in the conduction band is a classical semiconductor type

$$\sigma \sim exp\ (-E_c/kT) \qquad (2)$$

Then the thermal power in some approximation can be expressed as

$$S = AT + (B\lambda + CT)\ exp\ (-\lambda/T) \qquad (3)$$

where the parameter A depends on the contribution of mobile holes from the Cu-O planes, B and C are constant. Note that the increase in the value of the parameter A is due to a decrease in the hole concentration, which in turn depends on the oxygen content in these samples. Regarding the parameter λ, we can say that it depends on the energy gap between the Bi-O and the conduction band.

Calculations of thermal power were carried out on the basis of relation (3). The obtained data are presented in the fig. 2 by solid lines in comparison with the experimental curves $S(T)$. The parameters used in the calculations for these studied samples were respectively equal: for $Bi_2Sr_2CaCu_2O_X$ (A=0,3 мkV/K^2, B= -0,5 mk V/K^2, C=0,2 and λ =545), and for $Bi_2Sr_2Ca_{0.6}Zn_{0.4}Cu_2O_X$ (A = 0,36 mk V/K^2, B= -0,45 mk V/K^2, C =0,2 and λ =520). As can be seen, the value of the parameter A increases in the case of substitution by the element Zn. Note that the parameter A is associated with the contribution of mobile holes in the Cu –O planes. Thus, in this case, an increase in the value of the parameter A in $Bi_2Sr_2Ca_{0.6}Zn_{0.4}Cu_2O_X$ indicates a decrease in the hole concentration. As can be seen from the fig. 2, the calculations performed are in satisfactory agreement with the experiment.

The calculated values of the coefficient λ for the studied samples also differ. Since λ depends on the energy gap, its decrease is due to a decrease in the width of the forbidden band. We believe that this may be due to the presence of $Bi_2Sr_2Ca_{0.6}Zn_{0.4}Cu_2O_X$ in the

sample compared with $Bi_2Sr_2CaCu_2O_X$ slightly greater number of defects, which leads to a decrease in the width of the forbidden zone. Note that the critical temperature of the transition to the superconducting state according to the resistivity data for both samples was T_c =78.2 K. This is due to the fact that Zn atoms partially occupy the place of calcium in the CaO planes in the original matrix.

On the other hand, a change in the lattice parameters leads to a significant change in the SC parameters due to a change in the distances between the superconducting planes and dielectric blocks, as well as due to the redistribution of the charge between them. As can be seen from fig. 2, with inclusion element Zn, the value of thermal power decreases. Note that the resistance of the samples may increase either by increasing the number of defects or by decreasing the density of charge carriers. It is possible that in this case both mechanisms take place. The replacement of Ca by Zn leads to the formation of defects in the crystal structure of the sample.

3. CONCLUSION

The replacement of Ca with Zn leads to the formation of defects in the crystal structure of the superconducting $Bi_2Sr_2Ca_{0.6}Zn_{0.4}Cu_2O_X$. The experimental data on the thermal power are analyzed on the basis of a two -band model and was shown that a partial replacement of the element Ca by Zn leads to a decrease in the width of the forbidden zone.

[1] *L.S. Stilbans*. Semiconductors Physics, M., Soviet radio, p. 452, 1967 (in Russian).

[2] *M. Pekala, K. Kitazava, A. Polaczek* et al. Anisotropy thermoelectric power and thermal conductivity in superconducting single crystals Bi-Ca-Cu-O. Solid State Communations, v. 76, № 3, p. 419 -421, 1990.

[3] *S.S. Ragimov, A.A. Saddinova, V.M. Aliev, R.I. Selim-zade.* The influence of fluctuations on the superconducting properties of $Bi_2Sr_2Ca_{0.6}Zn_{0.4}Cu_2O_X$ and $Bi_2Sr_2Ca_1Cu_2O_X$, Materials Science Forum, v. 845, p. 17-20, 2016.

[4] *E.S.Itskevich, V.F.Kraidenov, I.G.Kuzemskaya* JETG, vol. 118, №.3 (9), p.p. 647-653, 2000.

[5] *S.S. Ragimov, I.N. Askerzade, G.I. Agayeva.* Journal of Superconductivity and Novel Magnetism, N1, doi.org/10.1007/s10948-019-5010-y., 2019.

[6] *Y.Xin, K.Wong, C.Fan* et al. Thermoelectric power of the thallium-based superconductor $Tl_2Ba_2Ca_2Cu_3O_{10-X}$, J. Phys. Rev. B, v.48, №1, p. 557-560, 1993-I.

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