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Effect of Zn on thermoelectric power in superconducting $Bi_2Sr_2Ca_xZn_{1-x}Cu_2O_{8+y}$ compounds

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For the first time, studies of the temperature dependences of the thermoelectric power for various compositions of $Bi_2Sr_2Ca_xZn_{1-x}Cu2O_{8+y}$ (x = 1; 0.8; 0.4) in the range 77–320 K have been carried out. The obtained experimental results are analyzed within the framework of the Xin's two-band model. The concentration of holes per copper atom and the band gap of the semiconductor type Bi–O layers are determined. It is shown that the replacement of the calcium element with zinc in these proportions does not lead to a change in the electronic band structure of $Bi_2Sr_2CaCu_2O_{8+y}$.

Keywords: electronic band structure, thermoelectric power, two-band model.

Introduction

The study of transport properties is important for understanding the mechanism of superconductivity and the nature of charge carriers in high-temperature superconductors (HTSC). Thermoelectric power S is a sensitive transport property for understanding the mechanism of conduction and the nature of charge carriers. By studying the temperature dependence of the thermoelectric power, one can obtain information about the type of conductivity and the mechanisms of scattering of charge carriers in a superconductor in the normal phase. Besides under certain conditions, with the help of thermoelectric power, it is possible to analyze such issues as the band structure, band gaps, which control the transport properties of the material.

Anomalous temperature and concentration dependences were observed in the study of the thermoelectric power in HTSC cuprates [1–4]. In La- and Y-based cuprates in the normal phase, the thermoelectric power does not depend on the temperature at high temperatures. Near the phase transition to the superconducting (SC) state, a maximum is observed on the $S(T)$ dependence [1, 3, 4]. However, in bismuth superconductors, the temperature dependence of the thermoelectric power is more sharp character [4–6].

Since the discovery of HTSC, several theoretical models have been proposed to analyze the thermoelectric power data, which are: the Phenomenological narrow band model [1], Xin's two-band model [7], a two-band model with a linear temperature coefficient [8], and Hubbard-Hamiltonian model [9]. To explain the features obtained on the temperature dependences of the thermoelectric power (especially a wide maximum above T_c), such models as phonon drag [10], two-band model [11, 12], short-range antiferromagnetic correlation [13] and the Van Hove singularity [14, 15] were proposed. However, a satisfactory interpretation of the experimental results absent.

It is known that impurities have a significant effect on the structure, transport properties, and phase composition of the material. This leads to a change in the basic parameters of superconductors. References 5 and 16–24] are devoted to the influence of various impurities on the transport phenomena of HTSC's. In Y-123, when copper is replaced by both magnetic and nonmagnetic impurities, superconductivity is suppressed [16, 17]. In the case of p-type conductivity, when copper is substituted, the Zn impurities act as electron doping and lead to the formation of deep impurity levels. The presence of such levels leads to strong resonant scattering of charge carriers [18].

It is known that in Bi-based HTSC, there is a weak bond between Bi–O layers. Therefore, to improve the superconducting properties, Bi is replaced with various elements. In this case, the structural properties do not change significantly, however, a change in the concentration of charge carriers affects the critical temperature [20–24].

On the other hand, atomic-crystal defects arising due to distortions of superconducting CuO_2 layers, as well as point defects in layers formed by calcium atoms when they are replaced with various elements, are pinning centers in Bi-based HTSC.

Taking into account the fact that the introduction of various impurities has a significant effect on the structure and conductivity, which leads to a change in the basic superconducting properties, we investigated the Bi-2:2:1:2 system with a partial replacement of Ca by the Zn element. In this article, we investigated the temperature dependence of the thermoelectric power of polycrystalline samples $Bi_2Sr_2CaCu_2O_{8+y}$, $Bi_2Sr_2Ca_{0.8}Zn_{0.2}Cu_2O_{8+y}$, and $Bi_2Sr_2Ca_{0.4}Zn_{0.6}Cu_2O_{8+y}$.

Experimental results and their discussion

The investigated polycrystalline samples of $Bi_2Sr_2CaCu_2O_{8+y}$, $Bi_2Sr_2Ca_{0,8}Zn_{0,2}Cu_2O_{8+y}$, and $Bi_2Sr_2Ca_{0.4}Zn_{0.6}Cu_2O_{8+y}$ were prepared by the solid-state ceramic technique. Powders of $CaCO_3$, $SrCO_3$, and CuO in the desired ratio were mixed and synthesized at 1173–1243 K for 30 h, then Bi_2O_3 and ZnO were added. X-ray diffraction analysis (XRD) of polycrystalline samples was carried out on a Brucker-D8 Advance diffractometer at room temperature in the range of $5° \le 2\theta \le 80°$. The XRD patterns of investigated samples are shown in Fig. 1.

According to x-ray data, the samples of $Bi_2Sr_2CaCu_2O_{8+y}$ and $Bi_2Sr_2Ca_{0.8}Zn_{0.2}Cu_2O_{8+y}$ can be considered monophase and correspond to the orthorhombic *Pnnn* group with lattice parameters $a = 5.396$, $b = 5.395$, $c =3\ 0.643$ Å. However, $Bi_2Sr_2Ca_{0,4}Zn_{0.6}Cu_2O_{8+y}$ consists of two phases. The main phase corresponds to the orthorhombic *Pnnn* group with lattice parameters $a = 5.429$, $b = 5.431$, $c = 30.840$ Å. The other phase is the tetragonal *I*4/*mmm* group with lattice parameters $a = 3.8097$ and $c = 24.607$ Å, respectively.

As can be seen from the data, the parameters of the unit cell change. The reason for this change is the inclusion of zinc ions in the intermediate regions of the unit cell. This leads to a distortion of the crystal structure and, consequently, to a change in the size of the unit cell. Analysis of the data obtained shows that zinc atoms cannot completely take the place of the element calcium. This is because of the fact that the ionic radii of these elements differ: Ca (1.04 Å) and Zn (0.83 Å). As a result, additional pressure arises, and the crystal structure is deformed, and the lattice parameters change [25].

The thermoelectric power measurements were carried out in the temperature range 80–560 K by the four-probe method. Samples for measurement were made in the form of a rectangular bar with dimensions of 8×3×1.2 mm. The obtained experimental results are shown in Fig. 2.

As can be seen, the character of the temperature dependence of the thermoelectric power is the same for all samples and has the form observed for other Bi-based HTSC's. The thermoelectric power has a positive sign corresponding to the hole type of conductivity in all investigated temperature intervals. In the normal state, the thermoelectric power for all investigated compositions decreases with increasing temperature. At temperatures above the maximum, the thermoelectric power has a negative slope, dS/dT, with values of $-\ 0.033\ \mu V/K^2$ ($Bi_2Sr_2CaCu_2O_{8+y}$), $-\ 0.021\ \mu V/K^2$ ($Bi_2Sr_2Ca_{0.8}Zn_{0.2}Cu_2O_{8+y}$), and $-\ 0.015\ \mu V/K^2$ ($Bi_2Sr_2Ca_{0.4}Zn_{0.6}Cu_2O_{8+y}$), respectively. $S(T)$ dependences pass through a maximum before the phase transition and sharply decreases to zero with decreasing temperature. The temperatures of the maximum thermoelectric power of the investigated compositions are $T \sim 125$ K ($Bi_2Sr_2CaCu_2O_{8+y}$), $T \sim 120$ K ($Bi_2Sr_2Ca_{0.8}Zn_{0.2}Cu_2O_{8+y}$), and $T \sim 117$ K ($Bi_2Sr_2Ca_{0.4}Zn_{0.6}Cu_2O_{8+y}$). This takes place both in Bi- and Tl-based superconductors, regardless of the number of layers n in the unit cell [26, 27].

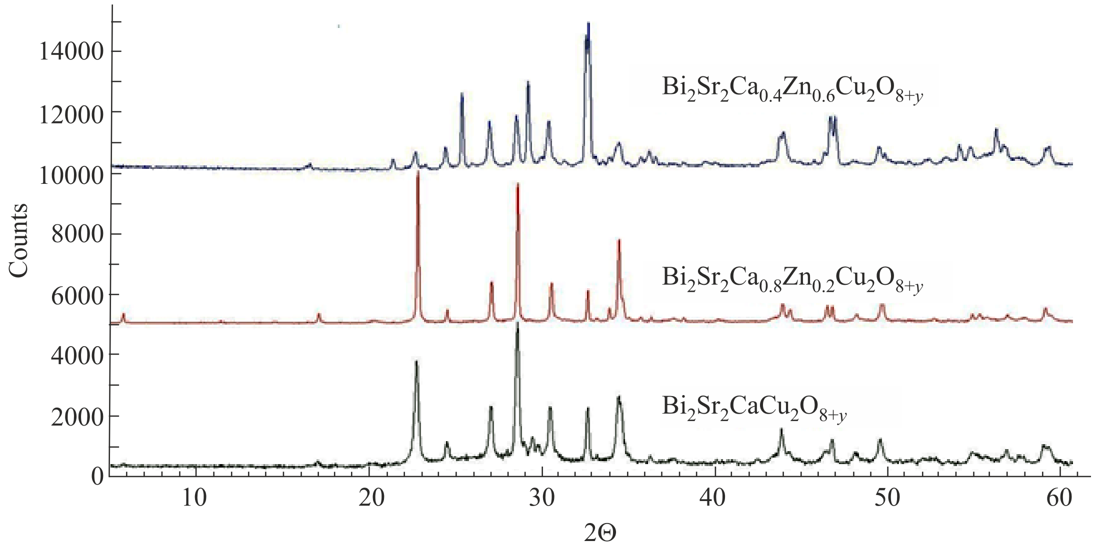

Fig. 1. X-ray diffractograms of the investigated samples.

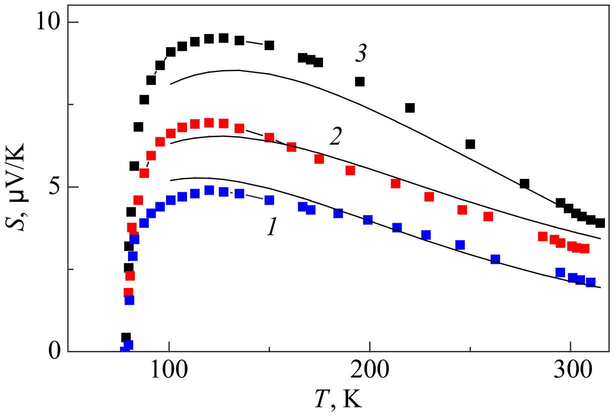

Fig. 2. Temperature dependences of the thermoelectric power of the studied samples: $Bi_2Sr_2CaCu_2O_{8+y}$ (*1*), $Bi_2Sr_2Ca_{0.8}Zn_{0.2}Cu_2O_{8+y}$.(*2*), $Bi_2Sr_2Ca_{0.4}Zn_{0.6}Cu_2O_{8+y}$ (*3*).

Note that phase transformations are not observed in Bi-2212 up to the melting point. Therefore, along with a relatively simple method for obtaining a single-phase state, this composition is also a convenient model object for analyzing the obtained experimental data.

The temperature dependence of the thermoelectric power of investigated samples cannot be analyzed taking into account one type of charge carriers. Hole type of conductivity and negative temperature coefficient of thermoelectric power indicates the participation of electrons in conductivity at the same time. Therefore, it is reasonable to apply a two-band model to analyze the obtained results. The total value of thermoelectric power is given by contributions from both bands and is expressed by

$$S=\frac{\sigma_p}{\sigma_n+\sigma_p}S_p+\frac{\sigma_n}{\sigma_n+\sigma_p}S_n, \tag{1}$$

where S_p and S_n are thermoelectric power, σ_p and σ_n are conductivity due to holes and electrons, respectively. In this case, S and $\sigma_n+\sigma_p$ are the experimental values of the total thermoelectric power and conductivity.

Analysis of the experimental data on the thermoelectric power of Bi-based HTSC's shows the participation of electrons in conduction. However, the question arises about the nature of the energy bands for electrons and holes. This issue was analyzed in [4, 6, 28], where it was suggested that in Bi-2:2:1:2, electronic conductivity dominates in Bi–O layers, and hole conductivity prevails in Cu–O one. A decrease in the valence state of Bi ($Bi^{3+}\rightarrow Bi^{3-x}$) leads to an increase in the electronic conductivity in the Bi–O layers, and an increase in the valence of copper ($Cu^{2+}\rightarrow Cu^{2+x}$) leads to a hole conductivity in the Cu–O layers.

Xin *et al*. developed a two-band model to analyze the thermoelectric data, where one zone is formed by Cu–O and the other by Tl–O planes (in our case Bi–O planes) [7]. According to [7], the thermoelectric power is expressed by

$$S=-g^2\pi^2\left[\frac{d\ln\sigma^+(E)}{d\ln E}\right]T+\left[\frac{E_c}{e}+\frac{k}{e}\frac{d\ln\tau(E)}{d\ln E}T\right]e^{-E_a/kT}. \tag{2}$$

Taking into account the linear and exponential parts, expression (2) can be represented by

$$S=AT+(B\lambda+CT)\exp(-\lambda/T), \tag{3}$$

where A, B, and C are constants for a particular material, T is the temperature, $\lambda=E_c/k_B$, $E_c=E_g/2$ is the energy gap between the bottom of the conduction band and the middle of the band gap, k_B is the Boltzmann constant. As can be seen from (3), the value of the constant A determines the contribution of holes in the Cu–O planes. Note that the hole concentration p depends on the synthesis conditions. It decreases with increasing temperature and sintering time.

It is known that the hole concentration p per each copper atom in HTSC materials can be calculated by using the relation [26]:

$$\frac{T_c}{T_c^{\max}}=1-82.6\left(p-0.16\right)^2. \tag{4}$$

It was calculated the hole concentration per copper atom for each of the studied samples. The calculation took into account $T_c^{\max}$ = 90 K for Bi-2221. For the hole concentration, the values p = 0.1997 ($Bi_2Sr_2CaCu_2O_{8+y}$), p = 0.1979 ($Bi_2Sr_2Ca_{0.8}Zn_{0.2}Cu_2O_{8+y}$), and p = 0.1957 ($Bi_2Sr_2Ca_{0.4}Zn_{0.6}Cu_2O_{8+y}$) were obtained, respectively. A decrease in the concentration of holes with an increase in the content of the element zinc is observed. This, in turn, leads to an increase in S. At the same time, a shift of the maximum on the temperature dependence to higher temperatures is also observed. However, a simple conclusion cannot be drawn that a decrease in the hole concentration should lead to a decrease in thermoelectric power. The change in the thermoelectric power on the temperature of the investigated samples (Fig. 2) implies a gradual change in the electronic part. This contribution is highly dependent on doping, or the oxygen content. These factors lead to a change in the valence state of bismuth, which in turn affects the spectrum of the energy gap of Bi–O.

The obtained value of λ was used to calculate the band gap of the semiconductor type Bi–O layers. The parameter λ, which is included in the exponent depends on the band gap between the Bi–O band and the conduction band. By using the relations $\lambda=E_c/k_B$, and $E_c=E_g/2$, the energy gap values of the investigated compositions are estimated. The fitting parameters A, B, C, as well as the calculated values of E_g are given in Table 1.

Note that the obtained E_g values are consistent with the literature data [5, 28]. In Bi-2212 the gap width depends upon the extent of intercalation of excess oxygen in the Bi–O layers. For the near absence of excess oxygen, the gap

Table 1. The fitting parameters A, B, C, and calculated values of E_g

Compounds	Parameters							
	T_c, K	dS/dT, μV/K^2	A, μV/K^2	B, μV/K^2	C, μV/K^2	p	λ, K	E_g, eV
$Bi_2Sr_2CaCu_2O_{8+y}$	80.5	–0.015	0.1	–0.15	–0.1	0.1997	349	0.06
$Bi_2Sr_2Ca_{0.8}Zn_{0.2}Cu_2O_{8+y}$	79.3	–0.021	0.0798	–0.137	–0.056	0.1979	345	0.0595
$Bi_2Sr_2Ca_{0.4}Zn_{0.6}Cu_2O_{8+y}$	78.2	–0.033	0.068	–0.13435	–0.03746	0.1957	343.2	0.059

approaches zero. Calculations have shown that a strong change in the band gap is not observed. This indicates the constancy of the amount of additional oxygen in the Bi–O layers. Thus, the replacement of the calcium element with zinc in these proportions does not lead to a change in the electronic band structure of $Bi_2Sr_2CaCu_2O_{8+y}$.

Conclusions

XRD analyzes have shown that $Bi_2Sr_2CaCu_2O_{8+y}$ and $Bi_2Sr_2Ca_{0.8}Zn_{0.2}Cu_2O_{8+y}$ are monophase with lattice parameters a = 5.396 Å, b = 5.395 Å, c = 30.643 Å (orthorhombic *Pnnn*). With an increase in the amount of zinc, namely in $Bi_2Sr_2Ca_{0.4}Zn_{0.6}Cu_2O_{8+y}$, in addition to the main phase with lattice parameters, a = 5.429 Å, b = 5.431 Å, c = 30.840 Å, a second tetragonal (*I*4/*mmm*) phase is formed with lattice parameters a = 3.8097 Å, c = 24.607 Å.

The temperature dependences of the thermoelectric power of $Bi_2Sr_2CaCu_2O_{8+y}$, $Bi_2Sr_2Ca_{0.8}Zn_{0.2}Cu_2O_{8+y}$, and $Bi_2Sr_2Ca_{0.4}Zn_{0.6}Cu_2O_{8+y}$ are analyzed within Xin's two-band model. The hole concentration and the energy gap of the semiconductor-like band structure of Bi–O layers are determined. It was shown that, due to different values of ionic radii, zinc atoms cannot completely occupy the place of the element calcium, and are located in intermediate sections of the unit cell. It was found that the partial replacement of the calcium element with zinc in $Bi_2Sr_2Ca_xZn_{1-x}Cu_2O_{8+y}$ (x = 0.8; 0.4) does not change the structure of Bi–O layers, and, therefore, does not lead to a change in the electronic band structure of $Bi_2Sr_2CaCu_2O_{8+y}$.

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Вплив Zn на термоелектрорушільну силу у надпровідних $Bi_2Sr_2Ca_xZn_{1-x}Cu_2O_{8+y}$ сполуках

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Вперше проведено дослідження температурних залежностей термоерс щодо різних складів $Bi_2Sr_2Ca_xZn_{1-x}Cu_2O_{8+y}$ (x = 1; 0,8; 0,4) в інтервалі температур 77–320 K. Отримані експериментальні результати проаналізовано за допомогою двозонної моделі Хіна. Визначено концентрацію дірок на кожен атом міді та ширину забороненої зони шарів напівпровідникового типу Bi–O. Показано, що заміна елемента кальцію цинком в певних пропорціях не призводить до зміни електронної зонної структури $Bi_2Sr_2CaCu_2O_{8+y}$.

Ключові слова: електронна зонна структура, термоерс, двозонна модель.