



# The Influence of Zn on Superconducting Properties of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$

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## Abstract

It was investigated that the influence of Ca substitution by Zn on the specific resistivity, thermal power, and excess conductivity of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ ,  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Zn}_{0.2}\text{Cu}_2\text{O}_x$ , and  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Zn}_{0.6}\text{Cu}_2\text{O}_x$  polycrystalline samples in the 70–300 K temperature interval. The fluctuation-induced conductivity is analyzed using the Aslamasov and Larkin and Lawrence and Doniach models. The microscopic parameters such as dimensional crossover temperature ( $T_{cr}$ ), interlayer coupling strength ( $J$ ), and zero temperature coherence length along c axis ( $\xi_0$ ) are estimated.

**Keywords** Superconductor · Thermal power · Resistivity · Excess conductivity

## 1 Introduction

The temperature dependences of the electrical resistivity and thermal power in the proximity of superconducting transition are the main characteristics of Bi-based high-critical-temperature superconductors (HTSC). It is well known that the superconducting properties of Bi-based compounds are very sensitive to the hole concentration, which depends on the atomic displacement [1–4]. Substitutions into the BSCCO system affect strongly the carrier concentration and, therefore, lead to significant changes both on the electronic and superconducting properties [5].

Reference [5] previously presented the results of an investigation of the effect of zinc on the conductivity and thermoelectric power of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  and  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_2\text{O}_x$ .

In this paper, we investigate the specific resistivity, thermal power, and fluctuation conductivity of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ ,  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Zn}_{0.2}\text{Cu}_2\text{O}_x$ , and  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Zn}_{0.6}\text{Cu}_2\text{O}_x$  polycrystalline samples.

## 2 Experimental Results and Discussion

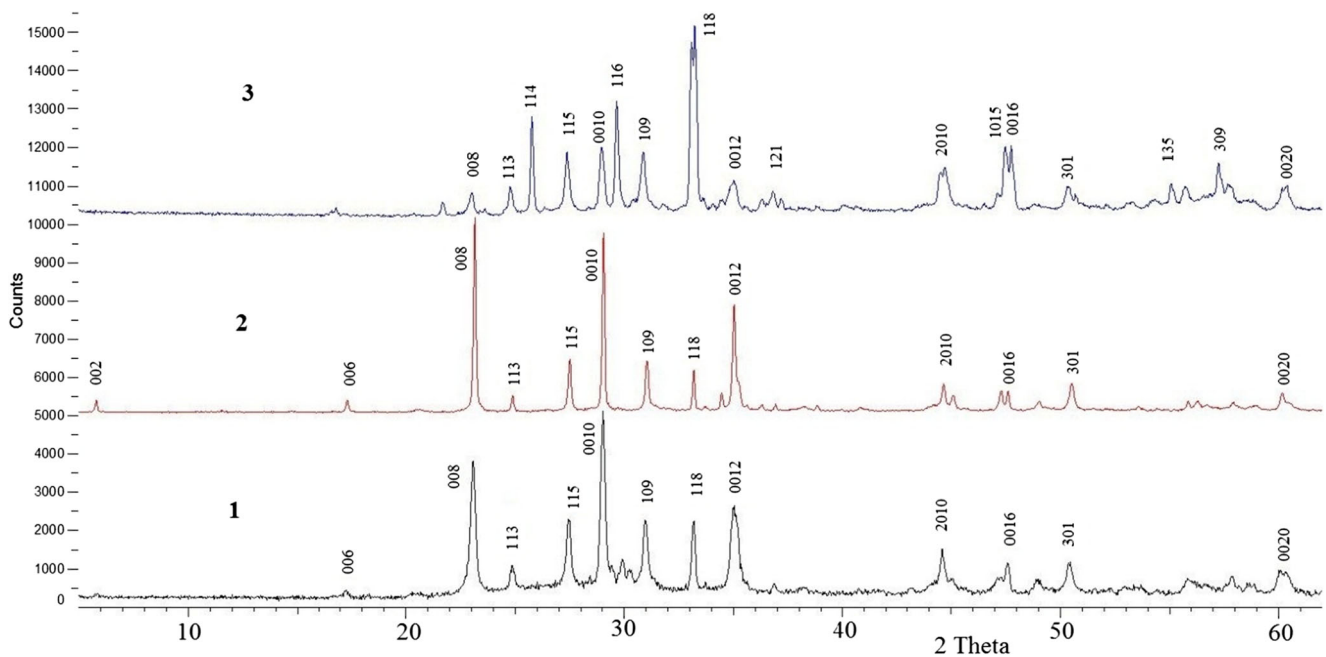
The investigated polycrystalline samples were prepared from stoichiometric amounts of high-purity  $\text{Bi}_2\text{O}_3$ ,  $\text{CaCO}_3$ ,  $\text{SrCO}_3$ ,  $\text{ZnO}$ , and  $\text{CuO}$  powders. First, refractory components ( $\text{CaCO}_3$ ,  $\text{SrCO}_3$ , and  $\text{CuO}$ ) taken in a desired proportion were sintered at 1173–1243 K for 20–50 h and then  $\text{Bi}_2\text{O}_3$  and  $\text{ZnO}$  were added. The solid-state reaction of the mixed and pressed powders was performed at 1100–1135 K in air for 50 h applying intermediate grindings. Cooling was carried out at a rate of 1.5 °C/min.

The phase purity of the obtained samples was investigated by X-ray analyses. The XRD analysis was performed using a Bruker-D8 advance diffractometer at room temperature with scanning mode with a step size  $\Delta(2\theta) = 0.05^\circ$  and  $5^\circ \leq 2\theta \leq 80^\circ$ . One can see from Fig. 1 that the additional peaks are observed for the Zn-doped compound. According to the X-ray data,  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  and  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Zn}_{0.2}\text{Cu}_2\text{O}_x$  can be called single phase. According to the X-ray data, the composition of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  and  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Zn}_{0.2}\text{Cu}_2\text{O}_x$  corresponds to the orthorhombic Pnnn group with lattice parameters,  $a = 5396$ ,  $b = 5395$ ,  $c = 30,643$ , and  $V = 892.06 \text{ \AA}^3$ . The composition of  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Zn}_{0.6}\text{Cu}_2\text{O}_x$  consists of a mixture of two phases: the orthorhombic Pnnn group with lattice parameters,  $a = 5429$ ,  $b = 5431$ ,  $c = 30,840$ ,  $V = 909.31 \text{ \AA}^3$  and tetragonal I4/mmm with lattice parameters,  $a = 3.8097$ ,  $c = 24.607$ , and  $V = 357.14 \text{ \AA}^3$ . According to the intensities of the diffraction peaks, the tetragonal phase over-explodes. This was due to the fact that zinc atoms do not fully occupy

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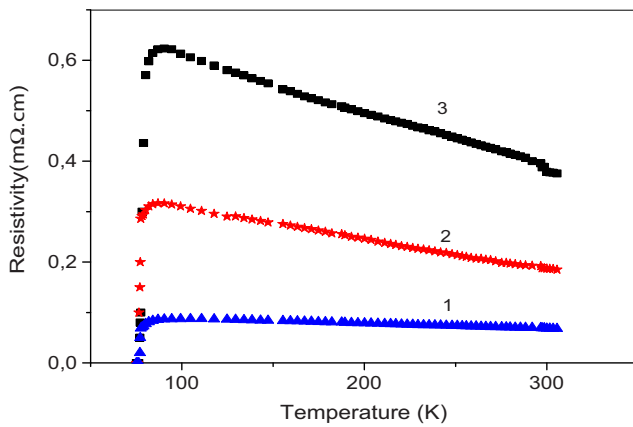
**Fig. 1** The X-ray diffractogram of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ ,  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Zn}_{0.2}\text{Cu}_2\text{O}_x$ , and  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Zn}_{0.6}\text{Cu}_2\text{O}_x$

the corresponding places of the calcium element. Therefore, in the studied  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Zn}_{0.6}\text{Cu}_2\text{O}_x$ , additional diffraction peaks are observed that do not correspond to the initial composition of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ . However, the lattice parameter and the space group of  $\text{Bi}_2\text{Sr}_2\text{ZnCu}_2\text{O}_x$  are  $a = 3797 \text{ \AA}$ ;  $c = 24,577 \text{ \AA}$ , and  $V = 354.42 \text{ \AA}^3$ , system-tetragonal, space group I4 respectively. As can be seen, the lattice parameter decreases from the element calcium to zinc. This is due to the fact that 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.

The resistivity and thermal power were determined by the four-point probe technique. The samples used for the specific resistivity and thermal power (Seebeck) effect measurements had the approximate dimensions 8 mm × 3 mm × 1.2 mm. The obtained results are given in Fig. 2 and Fig. 3. The transition to the superconducting state occurs in a relatively narrow temperature interval between 77 and 82 K. The superconducting critical transition temperature is 78.2 K ( $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ ). In the normal state, the temperature variation in the electrical resistivity is of the semiconductor type decreasing proportionally with the temperature at the mean rate  $-1.1 \mu\Omega\cdot\text{cm}/\text{K}$  ( $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Zn}_{0.6}\text{Cu}_2\text{O}_x$ ),  $-0.6 \mu\Omega\cdot\text{cm}/\text{K}$  ( $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Zn}_{0.2}\text{Cu}_2\text{O}_x$ ), and  $-0.08 \mu\Omega\cdot\text{cm}/\text{K}$  ( $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ ). The normal state electrical resistivity (at 300 K) of the samples studied is of the order of 0.4 mΩ·cm ( $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Zn}_{0.6}\text{Cu}_2\text{O}_x$ ), 0.2 mΩ·cm ( $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Zn}_{0.2}\text{Cu}_2\text{O}_x$ ), and 0.07 mΩ·cm ( $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ ). This value is comparable with that found in other Bi-based HTSC [1].

The temperature dependences of the thermal power for investigated samples are shown in Fig. 3. This shows the behavior characteristic of Bi-based HTSC [1, 6]. In the normal state, the thermal power decreases linearly with increasing temperature. The temperature dependence of thermal power goes through a maximum ( $T \sim 117 \text{ K}$  for  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ ,  $T \sim 120 \text{ K}$  for  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Zn}_{0.2}\text{Cu}_2\text{O}_x$ , and  $T \sim 125 \text{ K}$  for  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Zn}_{0.6}\text{Cu}_2\text{O}_x$ ) and then rapidly falls to zero below  $T_c$ . The maximum value of thermal power is achieved just above  $T_c$  and is  $10 \mu\text{V}\cdot\text{K}^{-1}$  ( $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ ),  $7 \mu\text{V}\cdot\text{K}^{-1}$  ( $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Zn}_{0.2}\text{Cu}_2\text{O}_x$ ), and  $5 \mu\text{V}\cdot\text{K}^{-1}$  ( $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Zn}_{0.6}\text{Cu}_2\text{O}_x$ ). The thermal power sign is positive over the entire measured temperature range. This behavior indicates that the hole carriers are dominant.

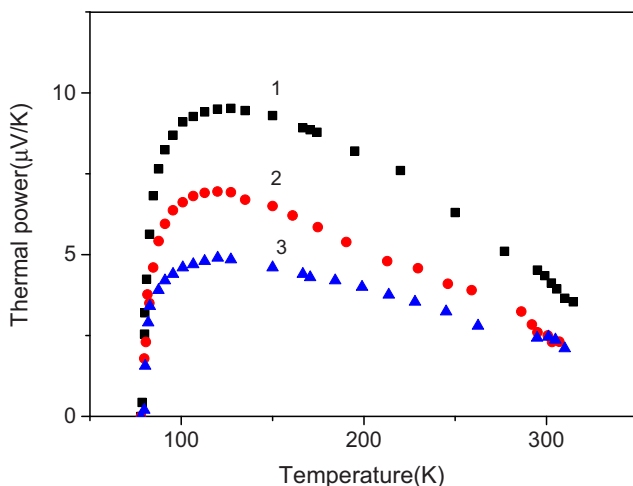
A change in the lattice parameters leads to a significant change in the superconducting parameters due to a change in the distances between the superconducting planes and dielectric blocks, as well as due to the redistribution of the charge between them. As can be seen from the presented experimental data, with an increase in the amount of zinc, the value of resistivity increases, and the thermal power decreases respectively. 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 with Zn leads to the formation of defects in the crystal structure of the sample. As can be seen from Fig. 2, with the partial introduction of Zn, the critical temperature  $T_c$  (78.2 K) does not practically change. This is due to the fact that zinc atoms partially occupy the place of calcium in the CaO planes in the original matrix.



**Fig. 2** The temperature dependences of resistivity of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  (1),  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Zn}_{0.2}\text{Cu}_2\text{O}_x$  (2), and  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Zn}_{0.6}\text{Cu}_2\text{O}_x$  (3)

To interpret the measured data on thermal power, we take into consideration that this compound exhibits multiband superconductivity. The effect of the multibandness of the energy structure on the physical properties of superconductors was theoretically considered in [7]. The two-band model was used by Xin et al. [2, 8] to analyze the experimental data on the measurement of the thermopower in a  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  compound. Thermal power data fitted in the framework of the two-band theory with a linear temperature term. It is shown that the thermal power results obtained experimentally are well described on the basis of the two-band model.

It was investigated that the influence of Ca substitution by Zn on the excess conductivity of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ ,  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Zn}_{0.2}\text{Cu}_2\text{O}_x$ , and  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_2\text{O}_x$  in the phase transition region. Measurement of the fluctuation conductivity is known to be a powerful method of getting reliable information about the normal charge scattering and superconducting coupling mechanisms in HTSC just in the



**Fig. 3** The temperature dependences of thermal power of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  (1),  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Zn}_{0.2}\text{Cu}_2\text{O}_x$  (2), and  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Zn}_{0.6}\text{Cu}_2\text{O}_x$  (3)

pseudogap temperature region [6]. Fluctuation conductivity arises from excess current carried by fluctuation-created Cooper pairs above the superconducting transition temperature  $T_c$ , as has been shown by Aslamasov and Larkin [9]. The obtained experimental results on study of excess conductivity are interpreted using the Aslamasov and Larkin (AL) [9] and Lawrence and Doniach (LD) [10] models. According to the LD model, the excess conductivity  $\Delta\sigma$  due to superconducting fluctuations are expressed by [10].

$$\Delta\sigma = \left(\frac{e^2}{16\hbar d}\right) \left(\frac{T}{T_c} - 1\right)^{-1} \left[1 + J \left(\frac{T}{T_c} - 1\right)^{-1}\right]^{-1/2} \quad (1)$$

Where  $J = (2\xi_c(0)/d)^2$ —interlayer coupling strength,  $\xi_c(0)$ —zero temperature coherence length along the  $c$  axis, and  $d$ —distance between layers. As is seen from (1) at temperatures  $T \gg T_c$  (where  $J \ll \varepsilon$  and  $\varepsilon = (T/T_c - 1)$ ),  $\Delta\sigma$  is proportional  $\varepsilon^{-1}$  (2D—conductivity), and nearly to transition temperature  $T_c$   $\Delta\sigma$  is changed as  $\varepsilon^{-1/2}$  (3D—conductivity). The 2D-3D crossover temperature  $T_{cr}$  is determined from  $\varepsilon = 4\gamma$ , where  $\varepsilon = (T - T_c)/T_c$  and  $\gamma = (\xi_c(0)/d)^2$ ,

$$T_{cr} = T_c \left\{1 + 4(\xi_c(0)/d)^2\right\} \quad (2)$$

Taking into account the experimental data, from dependence  $\ln\Delta\sigma/\sigma$  versus  $\ln(T - T_c)/T_c$  and Expression (2) were calculated 2D-3D crossover temperature for investigated samples ( $T_{cr} = 82$  K,  $J = 0.045$ ,  $\xi_0 = 2.9$  Å, and  $T_c = 77.2$  K) for  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ , ( $T_{cr} = 82.5$  K,  $J = 0.048$ ,  $\xi_0 = 3.1$  Å, and  $T_c = 78.6$  K) for  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Zn}_{0.2}\text{Cu}_2\text{O}_x$ , and ( $T_{cr} = 83.7$  K,  $J = 0.052$ ,  $\xi_0 = 3.2$  Å, and  $T_c = 80$  K) for  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Zn}_{0.6}\text{Cu}_2\text{O}_x$ .

We note that we have previously determined these parameters for this  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.6}\text{Zn}_{0.4}\text{Cu}_2\text{O}_x$  [5]. The data obtained are in good agreement with the previous ones.

### 3 Summary

In this work, we investigate the influence of Ca substitution by Zn on the specific resistivity, thermal power, and excess conductivity of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ ,  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Zn}_{0.2}\text{Cu}_2\text{O}_x$ , and  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Zn}_{0.6}\text{Cu}_2\text{O}_x$  polycrystalline samples in the 70–300 K temperature interval. In all the compositions studied, a superconducting transition was observed. Thermal power data fitted in the framework of the two-band theory with a linear temperature term. The microscopic parameters such as dimensional crossover temperature ( $T_{cr}$ ), interlayer coupling strength ( $J$ ), and zero temperature coherence length along the  $c$  axis ( $\xi_0$ ) are estimated: ( $T_{cr} = 82$  K,  $J = 0.045$ ,  $\xi_0 = 2.9$  Å, and  $T_c = 77.2$  K) for  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ , ( $T_{cr} = 82.5$  K,  $J = 0.048$ ,  $\xi_0 = 3.1$  Å, and  $T_c = 78.6$  K) for  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.8}\text{Zn}_{0.2}\text{Cu}_2\text{O}_x$ , and

( $T_{cr} = 83.7$  K,  $J = 0.052$ ,  $\xi_0 = 3.2$  Å, and  $T_c = 80$  K) for  $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.4}\text{Zn}_{0.6}\text{Cu}_2\text{O}_x$ .

The results are in good agreement with the data obtained by other experimental investigations of similar materials.

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