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Thermoelectric power and resistivity of the $Sr_{1-x}K_xBiO_3$ superconductor

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We have measured the temperature dependence of thermoelectric power (TEP) and resistivity for the $Sr_{1-x}K_xBiO_3$ superconductor (x=0.45-0.6). At T=10.2K, the resisitivity starts to increase from zero and a rather broad superconducting phase transition ($\Delta T \sim 2.3K$) is observed. TEP at room temperature has a small negative value ($S=-1.96\mu V/K$), characteristic of metallic-like TEP. The temperature dependence of TEP shows two distinct features. With decreasing temperature from room temperature, the absolute value of TEP decreases and the sign of TEP changes from negative to positive around 200K. Also, the negative slope of TEP(dS/dT) decreases substantially and becomes rather flat at around 160K, which is a feature already noted in $Ba_{1-x}K_xBiO_3$[1].

1. Introduction

Recently, a sample synthesis method using the high-pressure-high-temperature technique has enabled scientists to synthesize many new high T_C compounds, which could not be obtained by the usual solid state reaction method in atmospheric pressure environments. The search for a new high T_C compound using the high-pressure-high-temperature method has mainly focused on the CuO based superconductors, until the synthesis of $Sr_{1-x}K_xBiO_3$ by S. M. Kazakov *et al* [2]. This compound·has intrigued many scientists because it poses a new family of BiO based superconductors which have exotic structural and superconducting properties (Chage-Density-Wave insulator as a parent material and a simple perovskite-based structure), sharing similarities with the high T_C CuO based superconductors (low density of states at the Fermi level and T_C variation with doping) and also with conventional superconductors (well-defined onset of a superconducting gap and BCS-like isotope effect).

In this work we report the results of resitivity and thermoelectric power measurements for $Sr_{1-x}K_xBiO_3$ (SKBO) in the temperature range between 6K and 300K.

2. Experimental

The detailed synthesis procedure of SKBO was well described in Ref. [2]. The brief sample synthesis procedure is as follows. The first step was the preparation of $Sr_2Bi_2O_5$ by annealing the appropriate mixture of $SrCO_3$ and Bi_2O_3 in air at 850°C for 50 hours with two intermediated grindings. Stoichiometric amounts of $Sr_2Bi_2O_5$, Bi_2O_3 and KO_2 were ground and sealed in a Pt capsule for the high pressure synthesis. After placing the Pt capsule in a belt-type high pressure furnace, the pressure was increased to 20kbar and the temperature was raised to 700°C. This was maintained for 1 hour. The X-ray diffraction result shown in Fig. 1. appears as a single perovskite-like phase with lattice parameters a=b=5.941Å and c=8.439Å. The Energy Dispersive Spectroscopy analysis gives a slight variation of K content, x=0.45~0.6 in the sample.

The DC 4-probe method is used for the resistivity measurement with an applied current, I=100μA. The thermoelectric power (TEP) measurement was done by the differential technique [3] after calibration on Cu wires for the thermoelectric voltage reading. A Chromel-Constantan thermocouple was used to measure the small thermal gradient (ΔT= 0.5K) across the sample.

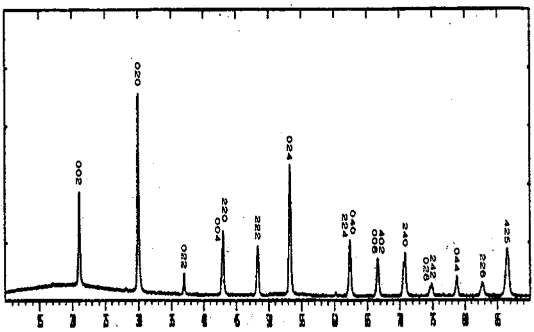

Fig.1. X-ray diffraction pattern of $S_{1-x}K_xBiO_3$ (x=0.45-0.6).

3. Results and discussion

The resistivity of SKBO as a function of temperature is shown in Fig.2. The onset temperature of the superconductivity in the resistivity measurement is T_{Conset}=12.5K and the zero resistivity is obtained at T_{Czero}=10.2K. A shoulder at around 11.3K observed in the superconducting transition (see the inset of Fig.2) could be attributed to impurity phases with different K content in our sample, since the small room temperature conductivity (200S/cm) and a large value of the resistivity ratio (ρ(15K)/ρ(300K)~0.85) indicates a substantial amount of structural scattering sources involving impurities and grain boundaries in our sample. The temperature dependence of the resistivity down to 140K can be described as metallic and below 140K the resistivity shows a T^2 dependence. A similar temperature dependence has already been reported in $Ba_{1-x}K_xBiO3$ and overdoped cuprates [4][5].

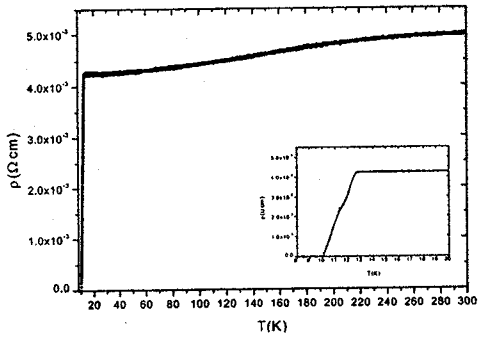

Fig.2. Resistivity of SKBO as a function of temperature. In the inset: resistivity versus temperature below 20K.

We compare Tc of SKBO with the results of D. T. Marx *et al* [6], where they systematically measured the variation of Tc of $Ba_{1-y}K_yPb_xBi_{1-x}O_3$ with changing the dopant ratio x+y. In their report, for dopant concentration x+y=0.45~0.6, Tc was found in the range 14.7K~22K. This result shows at least 2.5K difference with T_{Conset}=12.5K of SKBO with the same dopant concentration, K, in the range x=0.45~0.6. Also we note that SKBO shares many similarities with the $BaPb_{0.8}Bi_{0.2}O_3$ - tetragonal phase, similar lattice parameters: a=b=6.045Å and c=8.607Å for $BaPb_{0.8}Bi_{0.2}O_3$ - with almost the same Tc [6]. This suggests the change of Tc can not be solely attributed to the dopant concentration, and consideration of the structural phase modulation as well as the doping ratio are necessary in connection with the change of Tc of

BiO based superconductors.

Fig.3 shows the temperature dependence of TEP, $S(T)$, of SKBO. The metallic size of the room temperature TEP ($S(300K)=-1.96\mu V/K$) indicates that the possible effects of impurity phases and grain boundaries on TEP of our polycrystalline sample could be negligible, as noted previously [7]. Characteristic features of TEP we have found in SKBO are: at around 200K the type of effective carriers changes from electron-like to hole-like. We also observe a substantial decrease of the absolute value of dS/dT at around 160K, which follows a slight flattening of the $S(T)$ vs T curve below 160K. The change of dS/dT at around 160K was also observed in optimally and overdoped $Ba_{1-x}K_xBiO_3$ [1][8].

Since the BiO based superconductors have been known to be located near the boundary between an electron-like and hole-like Fermi surface [9][10], and it was found that, from optical measurement of $BaPb_xBi_{1-x}O_3$ as the doping ratio increases, a semimetallic band crossing was observed between the semiconducting hole band and the metallic electron band [11]. We now attempt to fit our TEP data of SKBO to a two-band model, which can explain the TEP of $BaPb_{0.25}Bi_{0.75}O_{3-\delta}$ [9].

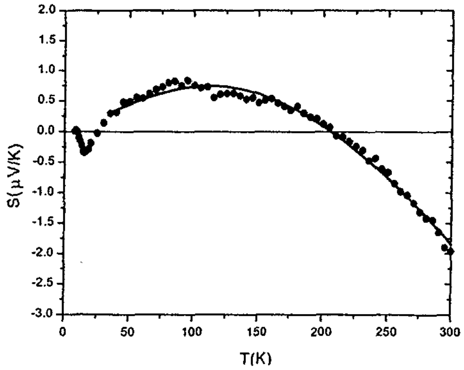

Fig.3. TEP of SKBO as a function of temperature. The solid line represents the fitting curve calculated by using Eq.(2).

In the two-band model, we assume the coexistence of electrons and holes, where electrons give rise to the metallic conduction in the normal state while holes contribute to the semiconducting conduction. The TEP can be described by

$$S=\frac{\sigma_- S_- + \sigma_+ S_+}{\sigma_- + \sigma_+} \tag{1}$$

where σ_- and S_- represent the contribution of metallic electron carriers. The temperature dependence is given as $\sigma_- \propto 1/T$ and $S_- \propto T$. For the semiconducting hole carriers, $\sigma_+ \propto \exp(-1/T)$ and $S_- \propto 1/T+\mathrm{const}$. Assuming that conductivity in the normal state is dominated by the metallic electrons, $\sigma = \sigma_- + \sigma_+ \simeq \sigma_-$, Eq.(1) gives the following equation for $S(T)$.

$$S(T)=\alpha T+(\beta+\gamma T)\exp(-\delta/T) \tag{2}$$

where $\alpha=-(\pi^2/3)(k^2/e)\{1/(E_F-E_c)\}$, $\delta=\Delta E$ and β *and* γ are positive constants. E_c is the energy at the bottom of the electron conduction band and ΔE is the activation energy for the generation of holes. The fitting curve using Eq.(2) is presented in Fig.2. Although Eq.(2) yields a good fitting curve, the fitting parameters of Eq.(2) obtained have unrealistic values. For example, the value of α, which must be negative for metallic diffusive TEP due to electrons, is found to be positive, α =8.79e-9. The failure of the two-band model in our sample suggests that other possible mechanisms should be considered to explain the TEP of SKBO along with other TEP data of BiO based superconductors. It is interesting to note that the general behavior of our measured TEP of SKBO looks similar to that of overdoped cuprates.

4. Conclusions

We have measured the resistivity and TEP of SKBO as a function of temperature. The resistivty data show a superconducting transition with T_{Conset}=12.5K and T_{Czero}=10.2K. We found some difference between the T_C of SKBO and the T_C of $Ba_{1-y}K_yPb_xBi_{1-x}O_3$ with the same dopant concentration, indicating a role of structural phase modulation on T_C of BiO based superconductors. The temperature dependence of TEP shows characteristic features which are also found in $Ba_{1-x}K_xBiO_3$. The application of the two-band model to our TEP data of SKBO results in unrealistic parameters, suggesting the consideration of other mechanisms to explain the general behavior of TEP in BiO based superconductors.

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