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Superconducting properties of $K_{0.2}Ba_{0.5}Y_{0.3}CuO_x$ powder compacts

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Measurements of the electrical resistivity and thermoelectric power for sintered samples of $K_{0.2}Ba_{0.5}Y_{0.3}CuO_x$ system were carried out. Two sets of the samples were prepared, the first set was sintered in air and the second set was sintered during flowing oxygen. The temperature dependence of the resistivity was found to be similar to that of metals. Further, the zero resistance was attained at 91-95 K depending on the sintering time. The author believes that, the prolonged sintering time caused oxygen vacancies (which may reside either along central-cage Cu-O chains) to become positively charged on trapping the hole, and thus enhance the superconductivity. The thermoelectric power of all samples was found to possess plus sign and decreases slightly with decreasing temperature, and then it falls down to zero, at the critical temperature (T_c).

[Keywords: Electrical resistivity, Critical temperature, Thermoelectric power]

1 Introduction

In a series of investigations of the effect of elemental substitutional changes on the superconducting properties of $RBa_2Cu_3O_7$[1,2], they had studied the influence of potassium substitution. The ionic radii of Ba^{++} and K^+ are similar (1.35 and 1.33 Å, respectively). In most cases, the introduction of impurity atoms, other than rare earth's, into the $YBa_2Cu_3O_7$ lattice, drastically reduces the onset of T_c and shifts the crystal symmetry from orthorhombic to tetragonal[3]. In another paper[2] they reported that, for $YBa_{2-x}K_xCu_3O_{7-\delta}$, ($x$=0.1 and 0.2), T_c is not affected by the substitution. Felner *et al.*[4] studied the crystal structure and magnetic susceptibility of high T_c single phase $YBa_{2-x}K_xCu_3O_{7-\delta}$, and concluded that, the high T_c is not affected by introducing K^+, and the crystal structure remains orthorhombic. Khan[5] measured the resistivity for $K_{0.2}Ba_{0.5}Y_{0.3}CuO_{3-x}$, and found that, the superconducting transition temperature T_c can be changed in the range 91-99 K by changing the conditions of sintering. Furthermore, from the lattice parameter changes, he observed for the K-substituted Ba-Y-Cu-O compounds. It could be inferred that, the solubility of K in the structure of $Ba_{2/3}Y_{1/3}CuO_x$ is very small. Akihiro Oka *et al.*[6] noted that, superconducting materials such as, Y-123 crystals form twin during the heat treatment in an oxygen gas flow, which accompany the phase transition from tetragonal phase to an orthorhombic phase. On the other side, they found that, the J_c-H curves with H // c axis at 70 K and below showed a large dependence on the heat treatment process. These J_c-H curves also showed a peak effect in a high magnetic field (H> $3T$). The peak was significant for the single crystal annealed at 600 °C and subsequently at 500 °C. Ram[7] reported that, the effect of thermal annealing at higher annealing temperature in $YBa_2Cu_3O_{7-\delta}$ superconductors is of little effect. In another paper[8] they improved the critical temperature from 91 to 94 K by preparing the sample without additives.

Many studies[9-12] have been reported that, the sign of the thermoelectric power of Y-Ba-Cu-O is positive. These results indicate that, holes are responsible for electronic conduction in these materials. The aim of this study is to investigate the effect of the atmosphere of sintering and the time of sintering on the temperature dependence of both the resistivity and thermoelectric power of the nominal composition $K_{0.2}Ba_{0.5}Y_{0.3}CuO_x$.

2 Experimental Procedure

Appropriate amounts of Y_2O_3, $BaCO_3$, CuO and K_2CO_3 were well mixed and calcined at 800 °C in air for 4 hr. The calcined product was ground thoroughly and re-calcined at 900 °C for 4 hr in air. Re-calcination at 900 °C for 4hr in air was repeated three times. So, the total calcination time at this temperature was equal to 12 hr. The final product of calcination at 900 °C was ground thoroughly and then pressed under unidirectional hydraulic pressure

7 ton/cm^2 to form powder compacts in the form of discs. The green powder compacts were classified into two sets. One set was sintered at 900 °C for different fixed periods of time in air. Among those powder compacts, the data for those sintered for 48, 64 and 80 hr were only taken into consideration, since shorter periods of time were not found to result in good quality samples. The second set of compacts was sintered at the same temperature 900 °C for different fixed periods of time, during flowing oxygen gas. Also, among the compacts of this set, the data for those sintered for 32, 40 and 48 hr were only taken into consideration. The electrical resistivity was measured by using the standard van-der Pauw method. The environmental temperature during measurements was monitored by a calibrated copper-constantan thermocouple, within an accuracy of ±1K. The differential thermoelectric power (S) of the samples was measured, using the standard differential technique as in Ref. 13.

3 Results

As shown in Fig. 1(a,b), whether the samples were sintered in normal atmosphere (air) or during flowing oxygen, superconducting transition could be held. For samples sintered in air, prolonged sintering time reduces the normal state resistivity much and elevates the critical temperature T_c, since ρ_{300} was equal to 0.085, 0.072 and 0.054 Ωcm and T_c was equal to 91, 92 and 94 K, for the times of sintering, t, 48, 64 and 80 hr, respectively. The semi-metals behaviour of resistivity with a continuous decrease in the value of ρ with decreasing T, characterized the range above T^{ons} (the temperature at which the values of ρ or S fall down) for both samples. Despite, within this range, the ρ–T dependence deviated a little from linearity, which is the characteristic of metals, which is usually observed in one of single-phase superconducting samples. Sintering during flowing oxygen, resulted as shown in Fig. 1(b), in elevating the room temperature-resistivity, since ρ_{300} was equal to 0.204, 0.14 and 0.076 Ωcm and T_c was equal to 92, 93 and 95 K at t equals to 32, 40 and 48 hr. Prolongation of the time of sintering was characterized by relatively lower values of ρ over the whole range of T for the two sets. The influence of the treatment on the properties of Y-123 is similar to many researches[14-18]. It is noteworthy that, T_c was increased with increasing t whether sintering was performed in normal atmosphere or in oxygen. Prolongation of the time of sintering populates the oxygen vacancies on O(1) sites along the side Cu-O chains (for the orthorhombic crystal unit cell structure of Y-123), and become positively charged on trapping holes, and thus, enhances the superconductivity properties, because the carriers in $YBa_2Cu_3O_{7-\delta}$ superconductors are identified as holes[19].

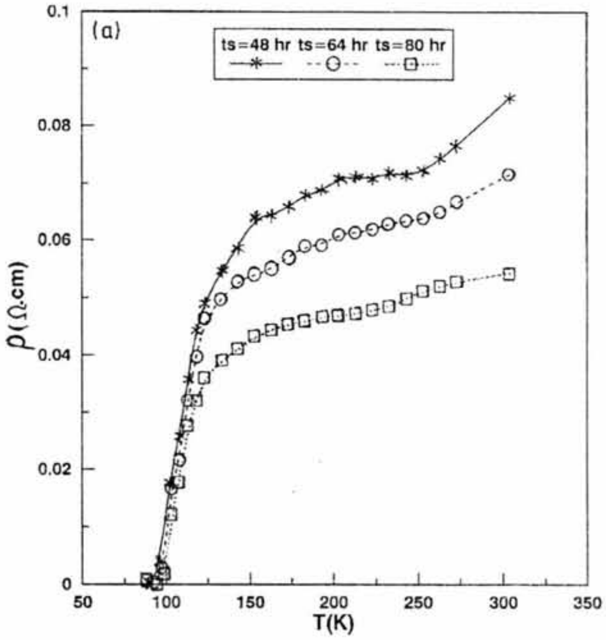

Fig. 1(a) — The relation between resistivity and temperature for the first set

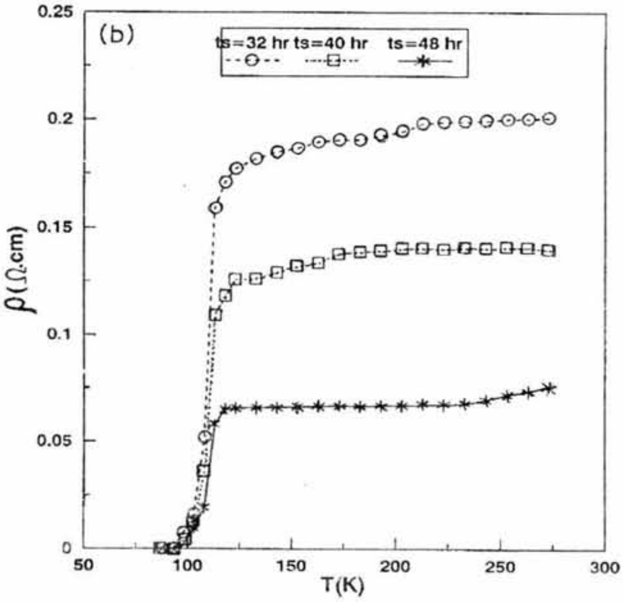

Fig. 1(b) — The relation between resistivity and temperature for the second set

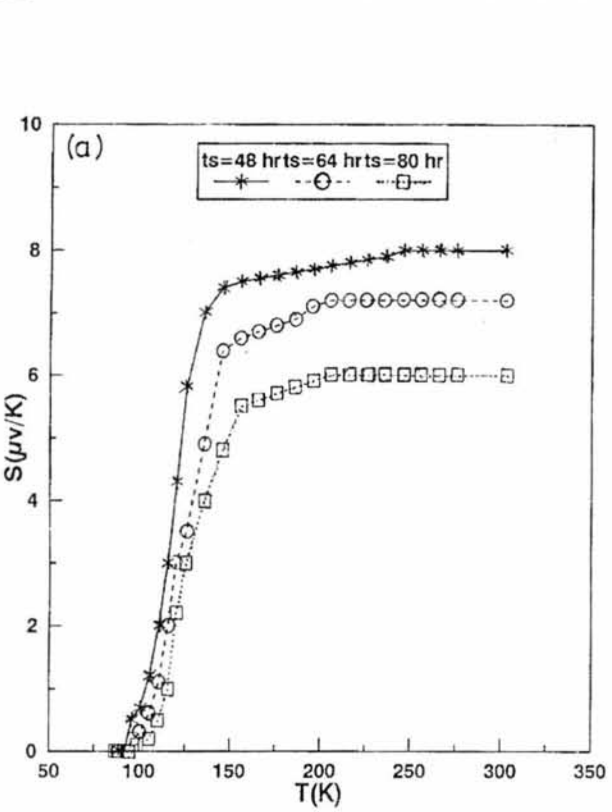

Fig. 2(a) — The relation between TEP and temperature for the first set

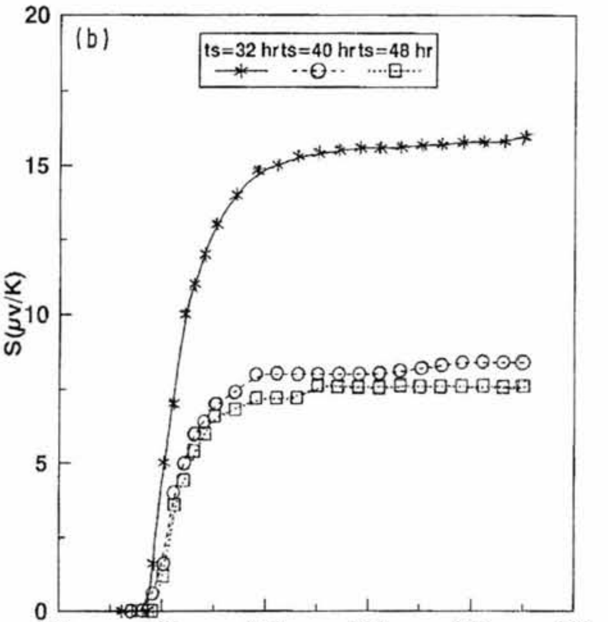

Fig. 2(b) — The relation between TEP and temperature for the second set

Whether the samples were sintered in air or in oxygen atmosphere, the thermoelectric power exhibited positive sign over the whole range considered for *T*. As shown in Fig. 2(a,b), the temperature dependence of Seebeck coefficient was similar. Each of the *S-T* plots can be divided into two main parts. The high temperature part extends from room temperature down to a certain temperature T^{ons} which was equal to 143 and 133 K of t =48 and 64 and t = 80 hr for samples sintered in air and equals to 133 K for the all values of *t*, for samples sintered in oxygen atmosphere. This region is characterized by weak dependence of *S* on *T* and the former decreased slightly by decreasing the latter. For the two sets, the effect of prolonged sintering time seems significant. However, within most of the range of *T*, prolonged *t* seemed associated with a decrease in the values of the plus sign Seebeck coefficient, *S*.

In contrast to the oxygenated samples as shown in Fig. 2(b), the role of sintering was significant, since prolonging the time of sintering resulted in a significant decrease in the value of the plus sign *S*. The second part of the *S-T* dependence was characterized by a fast decrease in the value of the plus sign *S* by decreasing *T* down to a certain temperature T_c at which, *S* equals zero. Within this region, as for the former region, the coefficient *dS/dT* possessed positive sign and its value depends on *t* in case of the two sets. This may reveal that, the value obtained for T_c is characteristic for the YBCO compounds even these compounds are doped with a light element like potassium. However, it is worth mentioning that, as for metals and superconducting oxides, the absolute values obtained for Seebeck coefficient are small, even at room temperature, since S_{275} was equal to 8, 7.2 and 6 μv/K at *t* 48, 64 and 80 hr, in case of air sintered, and 16, 8.4 and 7.6 μv/K at *t* 32, 40 and 48 hr, for the oxygenated samples, respectively. Then, the heat treatment in air or oxygen decreased the magnitude of *S* above T_c, indicating the heat treatment plays a role of releasing the over-doped holes[20]. On the other side, the heat treatment for two sets increased the value of T_c[21] ,as tabulated in Table 1.

Table 1 — T_c values for the two sets calculated from ρ and *S* data

T(K)	The first set			The second set		
	48hr	64hr	80hr	32hr	40hr	48hr
ρ data	91	92	94	92	93	95
S data	91	93	94	92	94	95

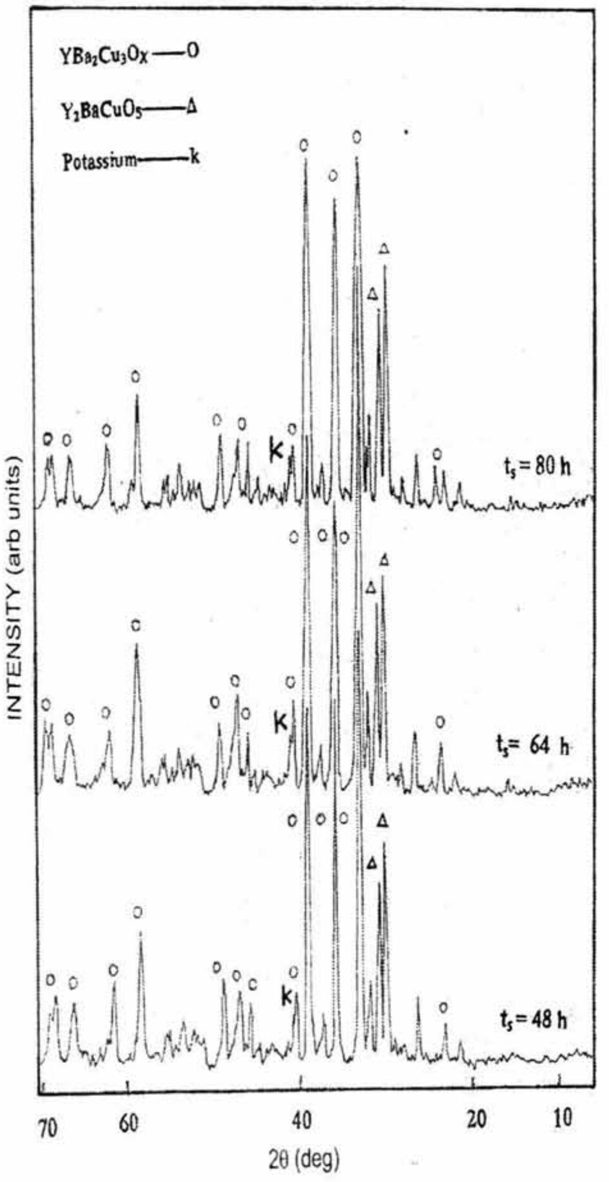

Fig. 3 — X-ray diffraction patterns for the first set

The observed thermoelectric power is a resultant of two components namely, diffusion component S_d and phonon drag component S_g. Based on the conclusion of Grader *et al.*[22], the diffusion component of the thermoelectric power is given by:

$$S_d=\pi^2k^2T/3eE_f \qquad \ldots(1)$$

where k is the Boltzmann's constant, e is the electron charge and E_f is the Fermi energy. On the other side, in degenerate conductors, the Fermi energy is related to both the concentration n and the effective mass m^* of the carriers by the relation:

$$E_f= h^2/2m^*(3n/8\pi)^{2/3} \qquad \ldots(2)$$

where h is Planck's constant. On the other hand, the phonon drag thermo-power is given by:

$$S_g= C_g/3ne \qquad \ldots(3)$$

where C_g is the lattice specific heat and n is the electron density. Eq. (3) indicates that, the main parameter contributes to S_g is C_g. Far below Debye temperature θ_D, C_g follows the Debye T^3 law. Therefore, at temperatures below $\theta_D/20$, it is expected that, the phonon drag thermo-power is proportional to the energy density of thermal phonons, and so, S_g varies as T^3 law. At high temperatures, the dominant scattering mechanism is the enharmonic phonon-phonon scattering and the phonon drag thermo-power follows the $1/T$ law. The Debye temperatures of oxide superconductors are in general higher than 400 K[23]. Since, for all the considered samples $91 \leq T^o_c \leq 95$ K and all measurements of thermoelectric power are carried in the range above 80 K, the conclusion that the phonon drag component of the thermoelectric power is negligible is accepted. This conclusion is consistent with that published in literature for superconducting oxides in normal region[24,25].

The XRD diffractograms shown in Fig. 3 for the samples sintered for 48, 64 and 80 hr of the first set confirm that most of the diffraction peaks are corresponding to the 123 phase. In addition, for each of the three samples, two peaks were observed, corresponding to the Y_2BaCuO_5 phase.

On the other side, potassium could be identified as a separated elemental phase, which confirms that its solubility in the structure of YBCO is very small. However, this result agrees with that reported by Khan[5].

4 Conclusion

In the light of the most significant results obtained from different studies, it may be said that: (i) the dependence of the resistivity on the temperature of the $K_{0.2}Ba_{0.5}Y_{0.3}CuO_x$ is similar to that of metals; (ii) the thermoelectric power of all samples exhibited plus sign over the range considered for T; (iii) the critical temperature T_c, whether obtained from resistivity or thermoelectric power temperature dependence, was near values and increased with prolonging the time of sintering of two sets; (iv) the values of both ρ and S above T_c for the two sets decreased with increasing t; and (v) the solubility of potassium in the structure of YBCO is small.

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