

Defect Chemistry of “BaCuO₂”

II. Transport Properties and Nature of Defects

G. Chiodelli, U. Anselmi-Tamburini, M. Arimondi, G. Spinolo, and G. Flor

Department of Physical Chemistry and C.S.T.E./CNR, University of Pavia, viale Taramelli, 16, I-27100 Pavia, Italy

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The charge transport properties of “BaCuO₂” with 88:90 (Ba:Cu) cation ratio were characterized by thermopower, electrical conductivity and ionic transport number measurements in a wide range of temperature and oxygen partial pressure conditions.

The nature of carriers is always represented by small polarons due to self-trapping of the electronic holes generated by the oxygen non-stoichiometry equilibrium.

Some anomalies in carrier mobility as a function of temperature are shown not to be related to incomplete ionization of oxygen atoms on interstitial sites

Key words: BaCuO₂, Superconductors, Small polarons, Oxygen non-stoichiometry.

1. Introduction

In spite of its critical role in the solid state synthesis of YBa₂Cu₃O_{7- δ} [1, 2], a complete understanding of the defect chemistry of BaCuO₂ is still lacking.

In part I of this work [3], the oxygen non-stoichiometry of “BaCuO₂” was investigated under a wide range of temperature (300 ÷ 820 °C) and oxygen partial pressure conditions (1 ÷ 10⁻³ atm). It was shown that the material with 88:90 \cong 0.98 (Ba:Cu) composition is monophasic, and oxygen over-stoichiometry exists [i.e. $\delta > 0$ in Ba_{0.98}CuO_{1.98+ δ}] over the whole investigated *T* and *P*(O₂) ranges. The behavior of non-stoichiometry is consistent with the presence of oxygen interstitials with a limiting value of available sites, and with the possibility of different interstitial sites.

The present work aims at clarifying the nature of defects that are responsible for the transport properties of the material by using thermopower, electrical conductivity and ionic transport number determinations in the same ranges of external conditions investigated in part I.

2. Experimental

2.1. Materials

Barium cuprate “BaCuO₂” was obtained from BaO₂ and CuO (Fluka *puriss.*) [3]. The powders of the

two reactants, in the molar ratio 88:90 \cong 0.98, were thoroughly mixed in a mortar and then pressed uniaxially using a compacting load of 4 · 10² kg, in order to obtain small pellets 1.2 cm in diameter and weighting a few grams. The pellets were then placed in alumina crucibles and submitted to a first thermal treatment at 830 ± 5 °C for 24 h under a pure oxygen flux (\cong 4 l/h). After cooling, the samples were again ground, pressed, and heated at (900 ± 5) °C for 100 h in pure oxygen. The final cooling was performed in two steps of 4 h each at 600 and 400 °C.

2.2. Methods

Impedance spectroscopy analysis was performed with a SOLARTRON 1255 FRA operating in the frequency range 10⁻⁴ Hz ÷ 20 MHz. The apparatus was equipped with an impedance adapter to extend the measuring range (1 Ω ÷ 10¹² Ω).

d.c. conductivity measurements were performed with a SOLARTRON 1286 potentiostat using the four probe technique. Using a diamond saw and abrasive paper, the sample was shaped into a parallelepiped 3 × 3 × 10 mm in size. The smaller faces of the specimen were made conductive with silver paint and used as working electrodes, while the measuring electrodes were two small silver wires wound around the sample near to the end faces. The resistance of the sample was determined through the potential drop across the two measuring electrodes. The current applied to the working electrodes varied between 0.1 and 10 mA, depending on sample conductivity. The sample

Reprint requests to Prof. G. Spinolo.

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was enclosed in a quartz tube placed in an horizontal furnace, equipped with an EUROTHERM 822 temperature controller/programmer (temperature stability $\pm 1^\circ\text{C}$ up to 900°C). A thin type-K thermocouple placed very close to the sample was used to measure its temperature, while the atmosphere was controlled by a flow of a certified mixture of oxygen in nitrogen.

The transport number and thermoelectric power were measured in the same experimental apparatus [4], which was composed of two half-cells divided by the disk-shaped sample. The atmosphere and temperature of the two halves of the apparatus were controlled independently, and a temperature gradient inside the sample could be obtained through a small additional heating element placed on one half-cell.

The transport number was determined by setting two different oxygen partial pressures at the two sides of the sample, without any temperature gradient. In this configuration, if any solid state oxygen conduction is possible through the sample, a potential difference ΔE_{exp} builds up, and the ionic transport number is directly obtained from the ratio: $\Delta E_{\text{exp}}/\Delta E_{\text{theor}}$, where ΔE_{theor} is given by the Nernst relation

$$\Delta E_{\text{theor}} = \frac{RT}{4F} \ln \left[\frac{P'(\text{O}_2)}{P''(\text{O}_2)} \right], \quad (1)$$

and $P'(\text{O}_2)$ and $P''(\text{O}_2)$ indicate the oxygen partial pressures at the two sides of the sample.

For thermoelectric power measurements, the atmospheres at the two sides of the sample were kept equal, while a temperature gradient was established through the sample using the additional heating element. The thermopower was obtained from the slope of the linear function $\Delta E = f(\Delta T)$.

3. Results

3.1. a.c. and d.c. Conductivity

It is well known that the significance of d.c. measurements largely depends on the characteristics of the experimental setup and sample microstructure. Electrode polarization and grain boundary resistance are the main experimental drawbacks that make it difficult to obtain meaningful bulk conductivity data. Therefore, preliminary a.c. conductivity measurements at various frequencies (impedance spectroscopy) were performed. Figure 1 shows a typical complex impedance (Cole and Cole) plot obtained for one sample at room temperature. In this kind of plots, the

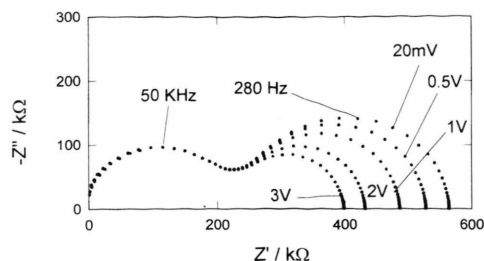


Fig. 1. Impedance spectroscopy of a “BaCuO₂” sample at room temperature under air.

semicircles identify different contributions to the total sample conductivity, each contribution being characterized by its own relaxation time. The semicircle on the right shows a strong dependence on the polarization voltage superimposed to the a.c. frequency, a typical feature of an electrodic interface. The other semicircle, on the contrary, can be safely identified with the contribution of bulk conductivity. The absence of any other semicircle suggests that other phenomena, such as grain boundary conduction, are negligibly low or totally absent. As further evidence the value of the sample bulk resistivity, as calculated on the basis of the left semicircle, results to be identical with the value from the four probe d.c. measurements. This clearly supports the indication that the d.c. measurements truly represent the bulk conductivity, and rules out the possibility that they can be due to some spurious process.

The d.c. conductivity of barium cuprate under different conditions is shown in Fig. 2, where two different regions can be observed. In the first one, between 200 and 400°C , the conductivity increases regularly with temperature, while at each temperature there is a slight increase with increasing oxygen partial pressure. Such a trend is qualitatively similar to the typical behavior of a semiconductor material with predominant hole conductivity, where the equilibrium of defects is described by the equation



In order to confirm the nature of predominant carriers, the ionic transport number was determined in this temperature range: the measurements were performed at 400°C with $P'(\text{O}_2)/P''(\text{O}_2)$ ratios of 10 and 10^5 ($P'(\text{O}_2) = 1 \text{ atm}$), and always gave values below 10^{-3} , thus confirming the presence of a totally electronic conductivity.

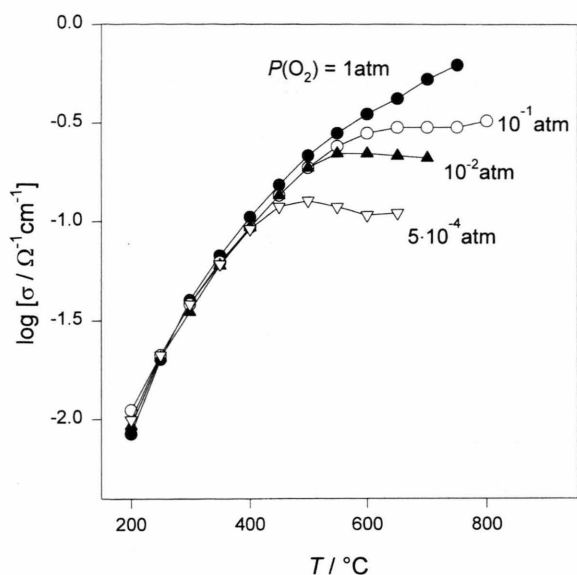


Fig. 2. d.c. conductivity of "BaCuO₂" as a function of temperature.

In the second temperature region (between 400° and 800°C), the conductivity data show a remarkable different behavior under different oxygen partial pressures. In fact, while for $P(\text{O}_2) > 10^{-2}$ atm the conductivity grows monotonously with temperature, for the lowest value of $P(\text{O}_2)$ a decrease with increasing temperature is first observed, followed by a new increase above 600°C, where the gravimetric measurements [3] showed a large variation in oxygen stoichiometry. Moreover, the experimental observation of a fast oxygen content response to changes of external variables indicates a high oxygen mobility. Despite that, the ionic transport number is extremely low also in this temperature range: this indicates that oxygen does not take part in the conduction process, that remains totally electronic. However, the large change in oxygen stoichiometry is responsible for the observed large dependence of the conductivity on the oxygen partial pressure, as required by the classical oxide defect equilibrium (2).

3.2. Thermoelectric Power

The thermoelectric power data for the temperature range 200÷800°C and the oxygen partial pressure range ($1 \div 10^{-4}$) atm are shown in Figure 3. The See-

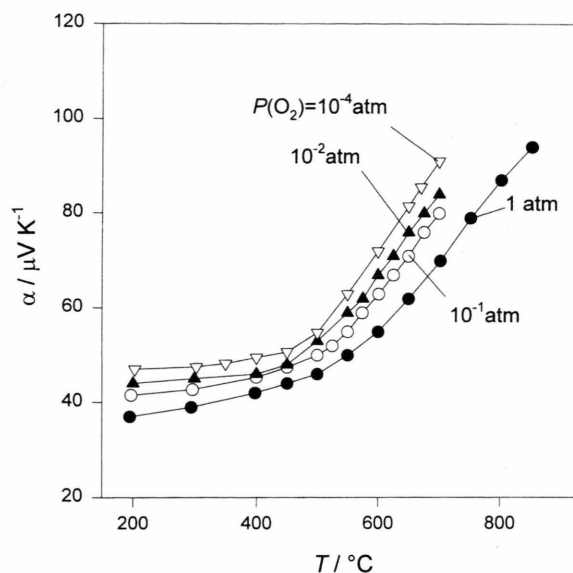


Fig. 3. Thermopower of "BaCuO₂" as a function of temperature.

beck coefficient is here defined as

$$\alpha = - \frac{V_h - V_c}{T_h - T_c}, \quad (3)$$

where $V_h - V_c$ indicates the potential difference between the hotter and the colder side of the sample, and $T_h - T_c$ the corresponding temperature difference. With this definition, the Seebeck coefficient has the same sign as the carriers.

It must be first noted that the data of Fig. 3 remain positive over the entire range of temperatures and oxygen partial pressures considered in this work. This indicates the presence of positively charged carriers and (coupled with ionic transport number data) confirms that holes are the majority carriers, as shown by (2). Figure 3 shows that the thermoelectric power follows two different trends with temperature, in analogy with the conductivity. Below 400÷500°C, in fact, the Seebeck coefficient slightly changes with temperature for all oxygen partial pressures, while a much stronger dependence is observed at higher temperatures.

Figure 4 shows the dependence of α on $\log P(\text{O}_2)$ under isothermal conditions. For each temperature, decreasing oxygen partial pressure drives an increase of the thermoelectric power, which can be understood as a the reduction of the number of carriers.

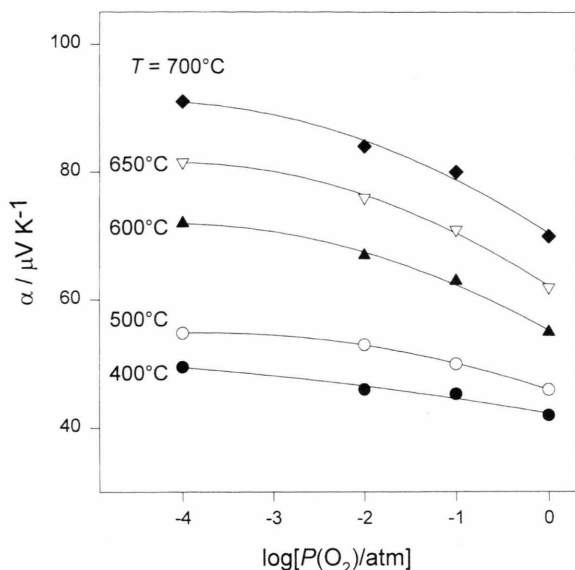


Fig. 4. Thermopower of "BaCuO₂" as a function of oxygen partial pressure.

4. Discussion

The above results show a quite complex behavior that can only partially be understood on the basis of the interpretative scheme traditionally used for conductive oxides. In some way, Ba_{0.98}CuO_{1.98+δ} shows the typical characteristics of a semiconducting, oxygen over-stoichiometric oxide, with the defect equilibrium described by (2). However, the agreement is more qualitative than quantitative and applies to a reduced range of temperatures and oxygen partial pressures. It must be reminded that the phase shows several unusual aspects, and the analogy with other oxides must be used with great care. This compound, in fact, can lose up to 10% of its oxygen content without any change in crystallographic structure [3]. This prevents to apply the most common theoretical treatment of defects in solids, which is based on a high dilution approximation. Apparently this assumption cannot be accepted for Ba_{0.98}CuO_{1.98+δ}, as shown both by the non-stoichiometry data [3] and the present data. In fact, in a [log σ] vs. [log P(O₂)] plot, (2) would require a linear dependence with slope 1/6. The experimental data, reported in Fig. 5 show instead a more complex behavior, thus indicating that (2) does not hold quantitatively in our case.

In the previous part of this work, the behavior of oxygen non-stoichiometry with *T* and *P*(O₂) was

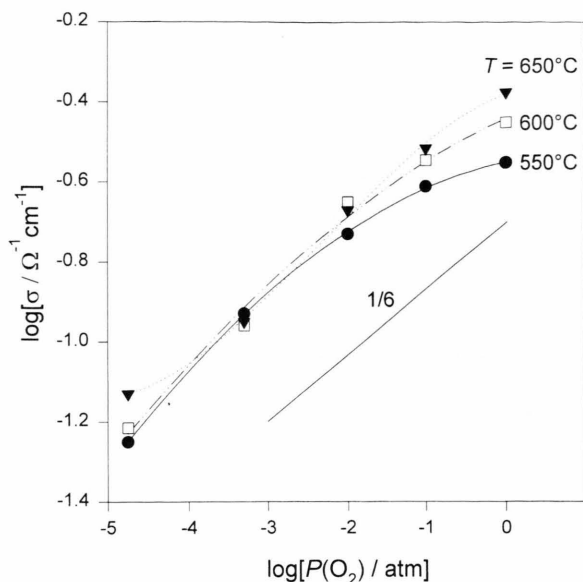
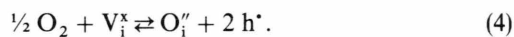


Fig. 5. d.c. conductivity of "BaCuO₂" as a function of oxygen partial pressure.

qualitatively explained by explicitly taking into account the saturation of the available interstitial sites, which corresponds to a modified form of (2):



The experimental trend of δ vs. *P*(O₂) at different temperatures also suggested that a number of different interstitial sites are involved. The non-stoichiometry data, however, did not allow to specify the nature (neutral or ionized) of the interstitials. This point can be clarified here.

All this being taken into account, the experimental results can be analyzed in some detail. Let us first consider the conductivity data (Figure 2). The unusual feature of these data is the non-monotonous trend of σ vs. *T* at the lowest oxygen partial pressures and highest temperatures. Actually the conductivity data contain two different contributions, because the temperature not only changes (or can change) the mobility of carriers but also their amount. On the basis of the experimental evidence described in the previous section it can be assumed that only holes are responsible for the conductivity. Then we can write

$$\sigma_{\text{tot}} = \sigma_h = |e| [h^\cdot] \mu, \quad (5)$$

where [h[·]] is the hole concentration, *e* the electronic charge, and μ the hole mobility. The latter can be obtained from (5) if the hole concentration for each set

of experimental conditions is known. This can be done with our previous gravimetric data [3] and the relation

$$[h^*] = \frac{2\delta}{V_c} 90, \quad (6)$$

where V_c indicates the volume of the elementary cell [$6128.5 \cdot 10^{-24} \text{ cm}^3$ [3]] containing 90 Ba_{0.98}CuO_{1.98+δ} formula units and δ the oxygen over-stoichiometry. It is worth noting that (6) does not imply that (2) holds, but simply implies that

$$[h^*] = 2[O_i^*], \quad (7)$$

i.e. that each oxygen interstitial is completely ionized. For instance, (6) is in agreement with (4), and with the presence of different interstitial sites, i.e. with a number of simultaneous equilibria of the kind described by (4).

Thus, the values of μ obtained for four different oxygen partial pressures are shown in Figure 6. Also in this case, a regular increase with temperature is observed only when the oxygen partial pressure is 1 atm. At lower partial pressures, in fact, a deviation from a common increasing initial trend is observed when the temperature reaches 500 °C. For this reason the 1 atm data will be discussed more deeply.

It is well known that the dependence of the mobility on temperature is characteristic of each conduction mechanism. In the case of barium cuprate the absolute value of the mobility (around $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and its strong increase with temperature suggest two possible mechanisms: a semiconductor band conductivity and a small polaron hopping conduction. Both these mechanism, in fact, show an increase of mobility with temperature, although characterized by a different functional dependence. A broad band semiconductor is expected to show a dependence of the mobility on temperature of the kind

$$\mu \propto T^{3/2}. \quad (8)$$

A more complex situation holds for small polarons. Here the movement of the carriers requires a coupling between electronic states and phonon modes. Two limiting cases are generally identified: in the first one (adiabatic hopping), the movement of the electron is slower than the movement of the lattice polarization around it; in the other case (non-adiabatic hopping) the limiting process is represented by the movement of the lattice polarization. Several theoretical approaches have been proposed for the two cases, and the resulting expression for the dependence of the mobility on

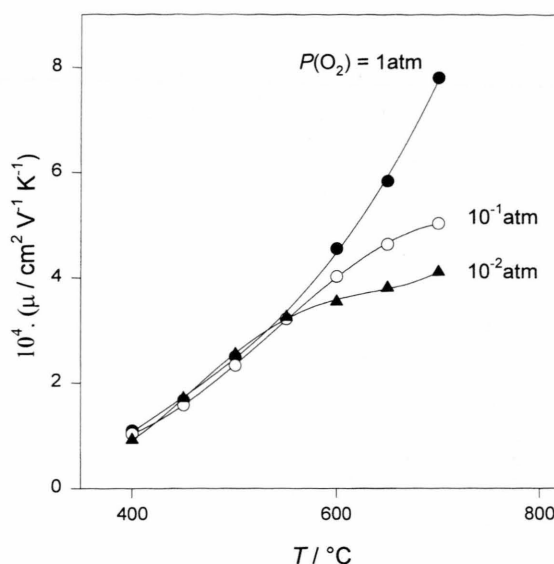


Fig. 6. Carrier mobility in "BaCuO₂".

temperature significantly differs from Author to Author. However, for the experimental characterization of transport properties some simplified equations are generally used, which can be summarized by the form

$$\mu \propto A P \exp\left(-\frac{W_h}{kT}\right), \quad (9)$$

where W_h is the activation energy for the hopping process, P is the probability for the electron to follow the movement of the lattice polarization, and A is a term that shows a different behavior in the case of adiabatic ($A \propto T^{-1}$) and non-adiabatic hopping ($A \propto T^{3/2}$). Also, $P \approx 1$ in the case of adiabatic hopping and $P \ll 1$ for non-adiabatic hopping. These equations are considered generally satisfactory at least in the case of low defect concentration and high temperatures [5–7].

The choice between the two different conduction mechanisms, broad band semiconductor or polaron hopping, can in principle be made on the basis of the previous equations. In Fig. 7 the two plots μ vs. $T^{3/2}$, (8) and $\log \mu$ vs. $1/T$, (9) are shown for the data obtained at $P(\text{O}_2) = 1 \text{ atm}$. The straight line of the latter case gives a strong evidence of small polarons as the majority carriers in barium cuprate. Furthermore, the activation energy obtained from the slope of this line is about 0.38 eV, a value quite typical for small polarons in ionic solids [5].

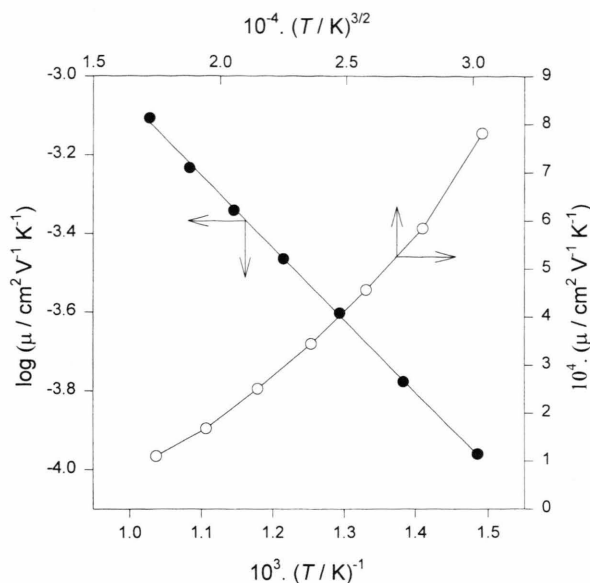


Fig. 7. Test of (8) and (9) (see text).

Independent evidence of the presence of small polarons can be obtained by considering the thermoelectric power data. Several relations have been obtained theoretically [8] for the thermoelectric power in the case of small polarons conduction. Generally, they can be reduced to the form

$$\alpha = \frac{k}{|e|} \left[\ln \beta \left(\frac{1-c}{c} \right) + \frac{S_h}{k} \right], \quad (10)$$

where c is the fraction of structural sites where the carrier is self-trapped, S_h is the vibrational entropy of lattice relaxation around the carrier and β is an additional parameter that takes values 1 or 2 depending on the spin degeneration of the carriers [5, 9, 10]. Equation (10) shows that the thermoelectric power does not depend on temperature in the case of small polarons, contrary to the typical behavior of broad band conductors. Regarding the numerical value of S_h , some theoretical calculations give very small values ($\approx 10 \mu\text{eV/K}$ for simple structures).

In the case of barium cuprate, (10) can be written in the form

$$\alpha = \frac{k}{|e|} \left\{ \ln \beta \frac{[\text{Cu}^{2+}]}{[\text{h}^+]} + \frac{S_h}{k} \right\} \quad (11)$$

if we assume that holes are trapped on Cu^{2+} sites. Equation (11) can be used to evaluate α if the values of $[\text{Cu}^{2+}]/[\text{h}^+]$ are known, the only uncertainties being

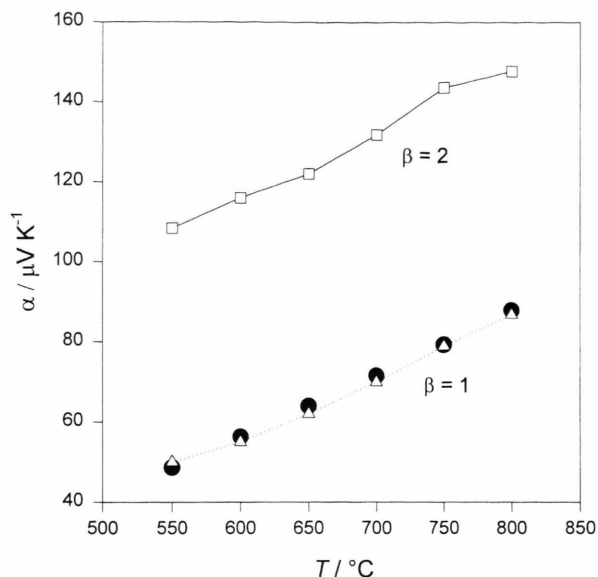


Fig. 8. Comparison of the experimental thermopower (filled circles) with the values calculated from non-stoichiometry data and from (11), with $\beta=1$ and $\beta=2$ (open symbols); the lines are guides to the eye.

the values of S_h and β . In Fig. 8 the values of α , calculated from (11) with the above value of S_h and with the $[\text{Cu}^{2+}]/[\text{h}^+]$ data of our previous oxygen non-stoichiometry determinations, are compared with thermopower measurements in the T range ($550 \div 800$)°C and at $P(\text{O}_2)=1$ atm. A remarkable agreement between calculated and experimental data exists for $\beta=1$. This is both a strong support to our conclusions and an indication that all Cu^{2+} ions are actually available as hole trapping sites, even though they are not crystallographically equivalent.

As a further argument, Chen et al. [11] have shown how thermopower data can be combined with d.c. conductivity measurements in order to obtain reliable indications of the presence of small polarons. In fact, in the case of an activated hopping mechanism it can easily be shown that

$$\left(\frac{\partial \ln \sigma}{\partial 1/T} \right)_\alpha = \left(\frac{\partial \ln \mu}{\partial 1/T} \right)_\alpha = \left(\frac{\partial \ln \mu}{\partial 1/T} \right)_q = T - \frac{E_H}{k}, \quad (12)$$

where E_H is the activation energy for the hopping process, and the subscripts α and q mean that the derivatives must be made at constant thermopower or at constant carrier concentration, respectively. Equa-

tion (12) states that in the case of an activated hopping mechanism a plot $[\log \sigma]$ vs. $[1/T]$ at constant α must be a straight line with a generally negative slope (unless $E_H \leq kT$), while in the case of band conductor the derivative $[\partial \ln \sigma / \partial (1/T)]$ must always be null. Equation (12) is fulfilled by many small polaron conductors and is considered one of the most probing tests for the presence of these carriers. It must be realized, however, that this kind of analysis is extremely demanding from the experimental point of view: the required quantities, $\log \sigma$ at constant α , are not directly accessible experimentally, and their determination requires a large number of experimental measurements of conductivity and thermoelectric power in a wide range of temperature and compound stoichiometry.

Figure 9 shows the results for two different values of the thermoelectric power: 50 and 60 $\mu\text{V/K}$. The data actually lie on straight lines with a negative slope, and the activation energy obtained from these slopes agrees quite well with those from the temperature dependence of mobility (Figure 6).

The above results are a further evidence for a small polaron conduction model in barium cuprate. In this model, the carriers are holes generated by oxygen non-stoichiometry equilibria such as (2) or (4), which undergo some sort of localization or self-trapping near one or more structural sites. It is impossible to unveil the microscopic details of the self-trapping process from our experimental data. However, our data allow to draw a few more considerations regarding the defect equilibria.

As already said, the unusually high level of oxygen non-stoichiometry of "BaCuO₂" makes questionable the validity of (2). It is a well known fact that high defect concentrations are usually related with association or other forms of defect interaction. Beside that, it is possible to imagine a change in oxygen content without formation of the corresponding electronic defect: in this perspective, oxygen atoms can get in and out of the compound in a sort of chemical absorption process without any ionization. This may be seen as a strong defect interaction between ionized oxygen interstitials and electronic defects. In all these cases, the correspondence between oxygen over-stoichiometry

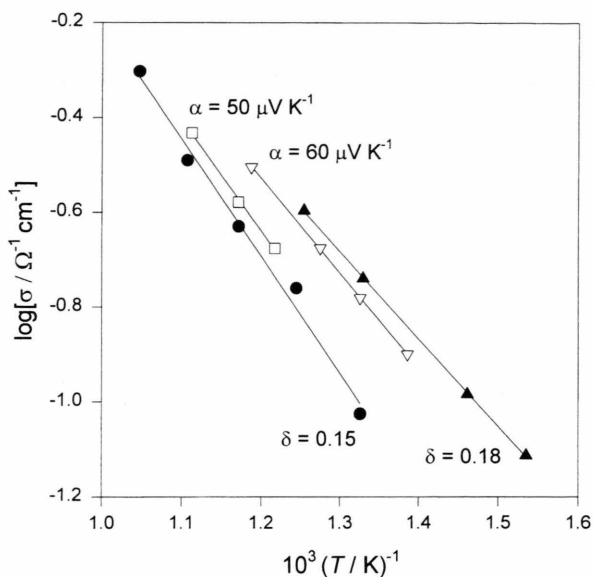


Fig. 9. d.c. conductivity vs. $1/T$ at constant non-stoichiometry (filled symbols) or at constant thermopower (open symbols).

and amount of holes, as defined by (7), is lost. A simple and effective test for this possibility is reported in Fig. 9, where the plot of $\log \sigma$ vs. $1/T$ at constant thermopower (open symbols) is compared with the corresponding plot at constant stoichiometry (filled symbols). For these plots, only the experimental data corresponding to temperatures between 400 and 700 °C and oxygen partial pressures between 1 and 10^{-3} atm have been used. The remarkable agreement between the trends observed at constant thermopower and at constant oxygen stoichiometry means that in spite of the large defect concentration, (7) holds, and the number of carriers is always proportional to the number of oxygen exchanged by the compound.

Acknowledgements

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