ELSEVIER Thermochimica Acta 269/270 (1995) 591–598

thermochimica
acta

Structural and thermal properties of the alkaline cuprate $KCuO_2$ ☆

Giorgio A. Costa*, Elena Kaiser

Instituto di Chimica Fisica, Università di Genova, Corso Europa 32, 16132 Genova, Italy

Received 22 November 1994; accepted 9 June 1995

Abstract

In this work we have investigated the structural, electric and magnetic properties of $KCuO_2$, along with thermal expansion measurements, from 10 to 420 K. A resistive transition was observed at about 350 K. For comparison, the characteristics and the resistive and magnetic behavior of $RbCuO_2$ and $CsCuO_2$ are also reported. In addition, the importance of substitutional studies on the crystallographic site of K by Cd and Hg is pointed out.

Keywords: Alkaline cuprates; DTA; Electrical resistivity; Magnetic properties; Potassium oxycuprate ($KCuO_2$); Structural properties; Superconductivity; Thermal properties; X-ray diffraction

---

1. Introduction

The study of binary oxycuprates with copper in the trivalent state (Cu^{3+}) could be helpful in the understanding of high temperature superconductivity (HTSC). In some superconducting oxycuprates the presence of Cu^{3+} near divalent copper has been ascertained [1]. The simplest oxide compounds of this kind are of formula $MCuO_2$ with M = alkali metal.

Much of the work on trivalent copper oxides was done by Hoppe and his co-workers. $KCuO_2$ was first prepared by Wahl and Klemm [2] and the structure was determined by Hestermann and Hoppe using data from single crystal X-ray photo-

---

* Corresponding author.

☆ Presented at the 6th European Symposium on Thermal Analysis and Calorimetry, Grado, Italy, 11–16 September 1994.

SSDI 0040-6031(95)02575-8

graphs [3]. Unfortunately it is very difficult to obtain this compound with the stoichiometric oxygen content. In fact it is practically impossible to avoid the formation of defects in the crystal structure, and this leads to the tendency of Cu^{3+} to be reduced to lower valence state. Experimentally this makes it necessary to check the oxygen content accurately after preparation. However the lack of experimental data on these compounds makes reasonable the large effort in preparation and the careful choice of the reaction paths. In this work we have studied the thermal, electric and magnetic behavior of $KCuO_x$ with x very close to two.

Further studies are in progress on compounds with different trivalent copper and oxygen contents, obtained by substitution of potassium with higher valence atoms (for example, Cd and Hg). Moreover the study of isostructural compounds $RbCuO_2$ and $CsCuO_2$ could help the understanding of the effect of a change in the atomic dimension of the alkali metal on the properties of this very interesting oxide family.

2. Experimental

$KCuO_2$ was prepared by solid state reaction of KO_2 (Aldrich, 2N) and Cu (Merck, 4N) powders. Equimolar amounts of the metals were mixed by the usual dry powder method under purified argon atmosphere (to avoid a reaction with wet air). The sample was annealed in oxygen for 18 h in a platinum crucible at about 715 K, to avoid the decomposition of the compound at higher temperatures. The compound was weighed to determine the reaction weight loss and then finely powdered, dry sieved and structurally characterized by X-ray powder diffraction.

$RbCuO_2$ and $CsCuO_2$ were prepared by reaction of Rb_2O (Aldrich, 2N) and Cs_2O (Aldrich, 2N) with CuO (Merck, $2N^+$) powders, respectively, at 675 and 655 K in oxygen.

The crystal structures of the compounds were investigated by the X-ray powder method using CuKα radiation. The theoretical intensities for the powder patterns were calculated using the Lazy Pulverix program [4] on the basis of the structural data of Hestermann and Hoppe [3].

Low temperature measurements of lattice parameters were carried out using a Hüber low-temperature, computer-controlled Guinier camera. The measurements were performed by adding silicon as an internal standard of well known thermal expansion [5]. The absolute accuracy of the reticular parameters ranged from 0.05% to 0.10% depending on the quality of the pattern; the temperature control was within ±1 K.

Resistivity tests, due to the high value of the resistivity, were performed by the conventional two-wire a .c. technique, to avoid polarization, on a cylindrical pellet ($\varnothing = 10$ mm; $h = 5$ mm) with the base surfaces platinized and the electrodes held in place by a clamp. The behavior of resistance versus temperature above room temperature was studied also in variable oxygen partial pressure (from 10 to 10^{-2} atm $p(O_2)$). The measurements were performed introducing pure oxygen through a variable leak operating dynamically.

Differential thermal analysis was performed using platinum crucibles in flowing oxygen in a Netzsch DTA apparatus model 404 S with a heating rate of $10\,\mathrm{K\,min^{-1}}$.

The calorimetric measurement was executed around the resistive transition in a differential scanning Mettler calorimeter model DSC 30 on 12 mg of sample with a heating rate of $10\,\mathrm{K\,min^{-1}}$ and $p(O_2) = 0.2$ atm.

Magnetic measurements were performed in vacuum from 4 to 300 K with a commercial SQUID magnetometer (MPMS by Quantum Design) with variable applied magnetic field.

The bivalent and trivalent copper content of the samples was determined using a modification of standard iodometric titration technique [6] with potentiometric detection of the end-point. In reality, as already observed by Nazzal et al. [7], this method determines the degree of oxidation in terms of the average charge, p, on each $[\mathrm{Cu{-}O}]^{p+}$ species, rather than the formal copper valence $(2 + p)$ or the concentration of Cu^{3+} or O^{1-}. Assuming the K/Cu ratio of the sample is known accurately (and there are no second phases, or other complications), the oxygen content can then be calculated, using charge neutrality. As this method is very reproducible and accurate, the uncertainty in the value of oxygen is within 0.5%.

3. Results and discussion

In Table 1 we present the characteristics of $KCuO_2$ compared with $RbCuO_2$ and $CsCuO_2$. Only $KCuO_2$ is single phase, whereas the presence of second phase CuO is

Table 1
Characteristics of $KCuO_2$ compared with $RbCuO_2$ and $CsCuO_2$

Compounds	$KCuO_2$	$RbCuO_2$	$CsCuO_2$
Preparation	$KO_2 + Cu$	$Rb_2O + CuO$	$Cs_2O + CuO$
Reaction temperature/K	715	675	655
Color	Blue	Blue-black	Black
Shrinkage/%	+1.67	−1.67	−3.33
Reaction in air	Fairly slow	Fast	Very quick
Consistency	Hard	Soft	Very soft
Lattice parameters at room temperature/Å	$a = 4.375(1)$ $b = 11.696(2)$ $c = 5.414(1)$	$a = 4.756(7)$ $b = 11.957(17)$ $c = 5.409(8)$	$a = 5.254(5)$ $b = 12.128(9)$ $c = 5.380(2)$
Presence of CuO determined by X-ray diffraction	No	Yes	Yes
Copper mean valence	2.82	2.41	2.44
Temperature of the resistivity transition/K	350–355	375–400	400–420
Magnetic behavior	Diamagnetic	Paramagnetic	Paramagnetic
Oxygen content per formula unit	1.91	1.71	1.72

always ascertained in Rb and Cs cuprates; the data for these samples are given here only for comparison purposes.

The thermal analysis results are in agreement with the observations of Wahl and Klemm [2]; the start of decomposition is determined to be at 760 K, and the colour changes from blue to a pale green at 975 K. Melting occurs at 1025 K.

The X-ray pattern of the reacted powders shows no impurity phases with the orthogonal Cmcm structure type and lattice parameters in good agreement with those reported in the literature ($a = 4.375(1)$ Å, $b = 11.696(2)$ Å and $c = 5.414(1)$ Å [3]. The structure (Fig. 1) comprises strings of edge-sharing CuO_4 rectangles (above) with the potassium atoms at center of trigonal prisms (below). Such coordination is quite rare in

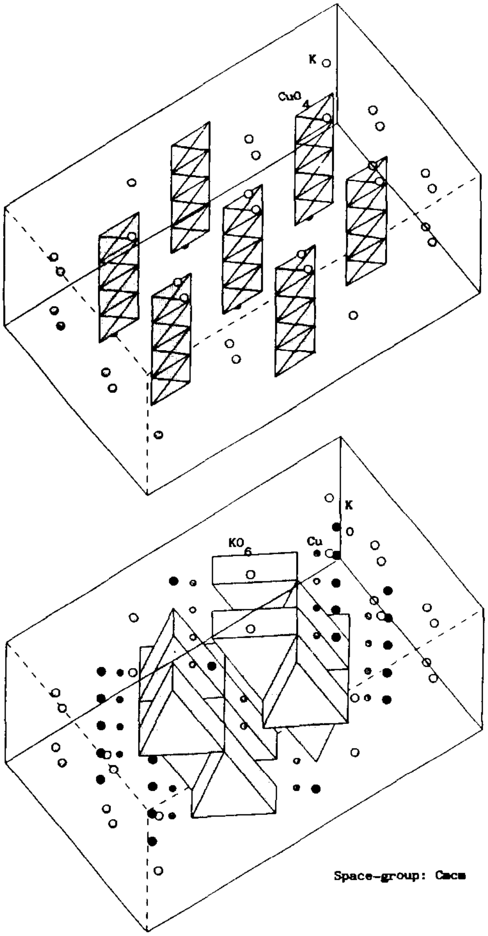

Fig. 1. Structure of $KCuO_2$: the rectangular coordination of Cu is shown above and the trigonal prisms of KO_6 are shown below.

oxides. Suitable substitution could change this structure: in particular, a dream would be to change these CuO_4 strings into CuO_4 planes typical of HTSC [8,9].

We have also performed structural measurements as a function of temperature. No structural transformation was observed in the 20–420 K range. Thermal behavior was obtained from the lattice parameters and smoothed by best fit. The thermal behavior of the $KCuO_2$ unit cell volume (Fig. 2) was found very accurately and could be fitted by the following equation:

$$V(\text{Å}^3) = 2.74 \times 10^2 - 1.45 \times 10^{-2} \times T + 1.76 \times 10^{-4} \times T^2$$
$$- 4.46 \times 10^{-7} \times T^3 + 3.96 \times 10^{-10} \times T^4$$

from which the coefficient of volumic thermal expansion 3α is deduced from the thermodynamic relationship $3\alpha = 1/V \times (\partial V/\partial T)p$. The α value at room temperature (300 K) so calculated is $16.2 \times 10^{-6}\,K^{-1}$ and can be favorably compared with the literature data of some other oxides [10].

At lower temperatures below 60 K, the above expression fails to be accurate for the calculation of the thermal expansion parameter; however it is clear that the thermal expansion becomes negative below 50 K. This could be due to the scattering of the data,

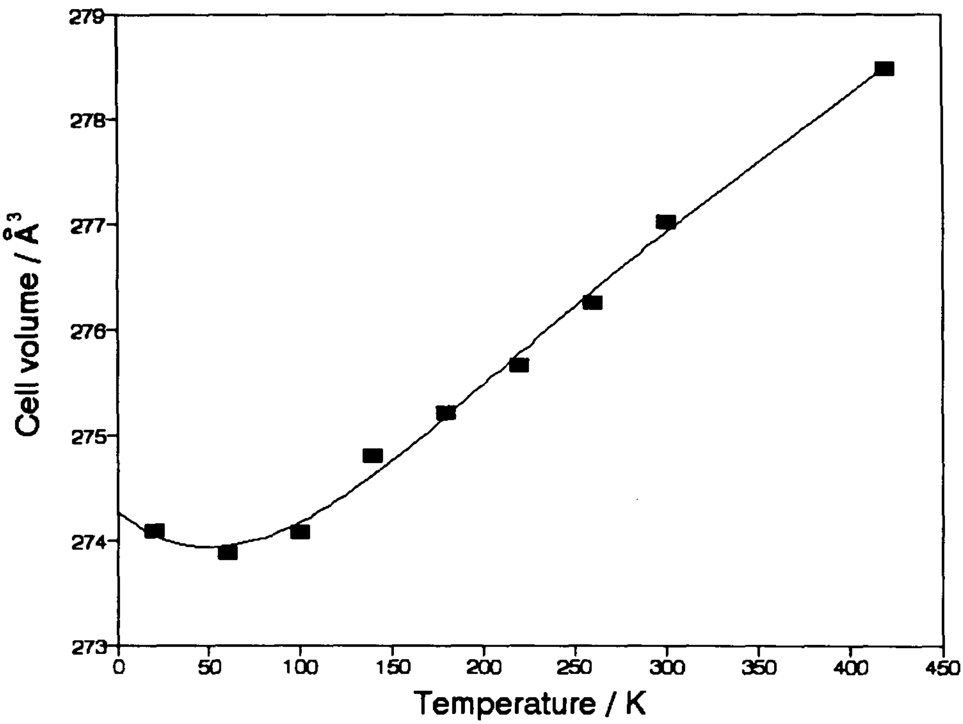

Fig. 2. Thermal behavior of $KCuO_2$ lattice volume.

but this behavior is also known, for example, in silicon [5] and it is not uncommon in loosely packed structures.

The measurement of resistivity at low temperature shows typical semiconducting behavior with resistivity rising to very high values (Fig. 3). Above room temperature a resistivity transition of at least three orders of magnitude was observed at about 355 K, confirmed also be DSC calorimetric measurements (see insert of Fig. 4). A transition-temperature-dependence on oxygen partial pressure is also observed (Fig. 4) and appears not to be linear. The study of the real functional dependence, which could give insight into the mechanism of the transition itself, is in progress. Even though the exact nature of this transition is not yet ascertained, we can exclude structural origin. We have observed that the same transition occurs also in the isostructural compounds $RbCuO_2$ and $CsCuO_2$, where the K atoms are replaced with larger atoms; in fact $RbCuO_2$ and $CsCuO_2$ also show a resistivity transition, with regular dependence of the transition temperature on the cell volume. Lower jumps in these cases are probably due to the presence of secondary phases.

Only $KCuO_2$ displays diamagnetic behavior until very low temperatures (4 K); the other materials are only slightly paramagnetic. In this case also we think that this characteristic is due to the presence of copper oxide in $RbCuO_2$ and $CsCuO_2$.

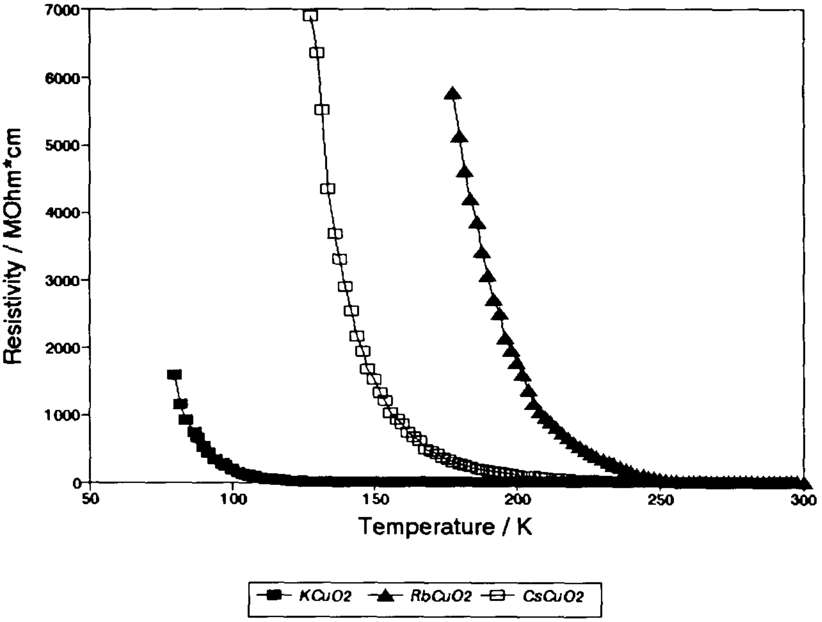

Fig. 3. Low temperature resistivity of $KCuO_2$ compared with $RbCuO_2$ and $CsCuO_2$.

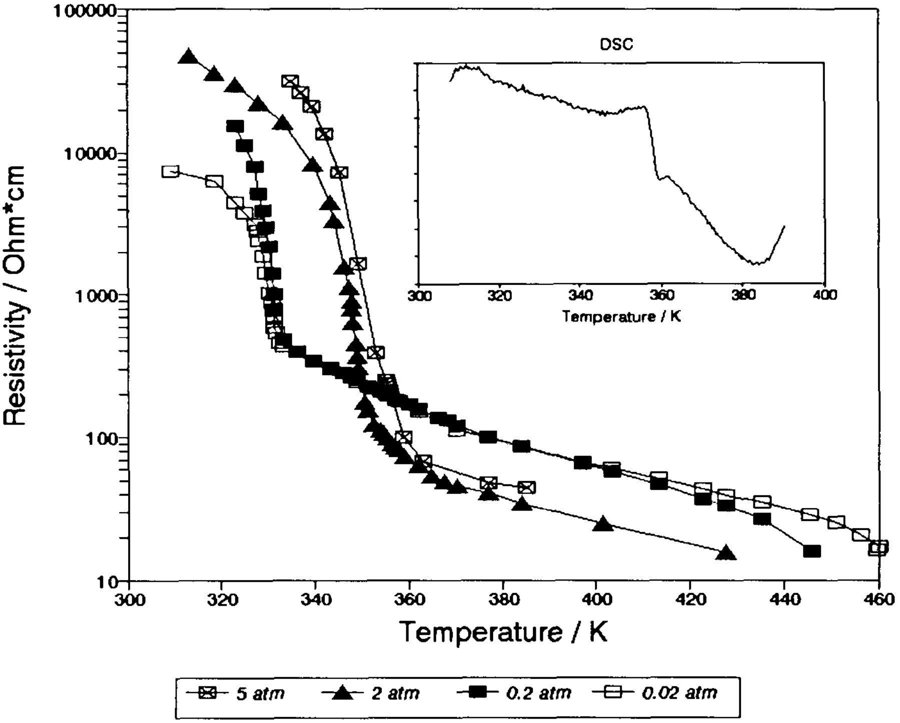

Fig. 4. Electrical transition of $KCuO_2$ at different oxygen partial pressures. The insert shows DSC measurements across the transition.

4. Conclusions

We have studied the structural and thermal properties of $KCuO_2$, considering this compound as a possible material for development of new HTSC. $KCuO_2$, $RbCuO_2$ and $CsCuO_2$ are not superconducting compounds down to 4 K. The behavior of the electrical conductivity is typical of a semiconducting phase. As many superconducting transitions are on the edge of the conductor–insulator region (Mott transition), further studies should be undertaken on the electrical properties, doping the materials with suitable substitutional atoms. On the other hand, the presence of trivalent copper in the compounds, the four coordination of the Cu–O in the structure and the presence of an unknown electrical transition near room temperature suggest that these materials could be tested for superconductivity for further substitutional studies at the alkaline metal and the copper sites.

Acknowledgements

The authors are grateful to Prof. C. Ferdeghini for his help with magnetic measurements. This work was supported by the Italian Consiglio Nazionale delle Ricerche.

References

[1] L.J. De Jongh, Eur. J. Solid State Inorg. Chem., 27 (1990) 222.
[2] K. Wahl and W. Klemm. Z. Anorg. Allg. Chem., 270 (1952) 69.
[3] K. Hestermann and R. Hoppe, Z. Anorg. Allg. Chem., 367 (1969) 249.
[4] K. Yvon, W. Jeitschko and E. Parthè, J. Appl. Crystallogr., 10 (1977) 73.
[5] J.S. Shah and M.E. Straumanis, Solid. State Commun., 10 (1972) 159.
[6] D.C. Harris, M.E. Hills and T.A. Hewston, J. Chem. Educ., 64 (1987) 847.
[7] A.I. Nazzal, V.Y. Lee, E.M. Engler, R.D. Jacowitz, Y. Tokura and J.B. Torrance, Physica C, 153–155 (1988) 1367.
[8] Y.K. Tao, Y.Y. Sun, P.H. Hor and C.W. Chu, J. Solid State Chem., 105 (1993) 171.
[9] B. Raveau and C. Michel, Chemtronics, 2 (1987) 107.
[10] G.A. Costa and E. Kaiser, J. Therm. Anal., 41 (1994) 1417.