Journal of Thermal Analysis, Vol. 41 (1994) 1417-1424

THERMAL PROPERTIES OF SOME PRECURSOR OXIDES OF YBCO SUPERCONDUCTOR

G. A. Costa and E. Kaiser

Istituto di Chimica Fisica, Università di Genova, Corso Europa 26, Palazzo delle Scienze, 16132 Genova, Italy

Abstract

The lattice parameters of $BaCuO_2$ and CuO were measured as a function of temperature from 10 to 300 K. The fitting of the parameters led to the thermal expansion coefficients and the anisotropy characteristics of the polycrystalline materials. The accuracy of these measurements is discussed, as is the use of thermal expansion measurements, even if not particularly accurate, with a view to calculation of C_v from C_p.

Keywords: heat capacity, superconducting oxides, thermal expansion

Introduction

A knowledge of the temperature dependence of the thermal parameters, specific heat and thermal expansion is of fundamental significance for an understanding of physical systems.

The specific heat C_p is the key thermal property of solids. It reflects the overall energetic state of the energy levels of the system, and therefore expresses the density of states of electrons, phonons, magnons, etc. Specific heat data allow direct determination of the thermodynamic standard functions and the characterization of phase transitions.

The thermal expansion α is closely related to other thermal parameters; in particular, its temperature dependence is similar to that of the specific heat. The fundamental information conveyed about the vibrational behaviour of solids by studying thermal expansion is rather poor, but thermal dilatation experiments are a helpful, and sometimes necessary tool for the interpretation of measurements of elastic constants and specific heat.

The thermal expansion coefficient $\alpha=1/V\ (\partial V/\partial T)_P= -\ 1/V\ (\partial S/\partial P)_T$ can be directly measured macroscopically by capacitive or optical techniques, or microscopically by means of X-ray experiments. Generally, the less sensitive [1] diffractometric technique becomes necessary with sintered materials that are sometimes slightly polyphasic.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

From elementary thermodynamics, one may show that α is directly related to C_p by the Grüneisen law: $\Gamma=\alpha V K_s/C_p$, where Γ, V and K_s denote, to a first approximation, the Grüneisen parameter, the crystal volume and the isentropic bulk modulus of elasticity, respectively. Thus, α is proportional to C_p. Similarly, the thermal dependence of C_p–C_v can be easily calculated.

In the applications, a knowledge of lattice constants and thermal expansion coefficients is needed for the development of epitaxy processes. The thermal expansion coefficients of materials and substrate should be similar in order to prevent cracking and strain problems during cooling of the epitaxial structure from the deposition temperature to ambient and to low temperature.

This paper deals with the thermal expansion properties of two very important precursors ($BaCuO_2$ and CuO) in the preparation of the superconducting materials of the Yttrium Barium Copper Oxides (YBCO) family [2] and of the intriguing superconducting compounds derived from $HgBa_2CuO_x$ [3]. In many respects, $BaCuO_2$ and CuO are the key compounds in the overall process of synthesis. They are found in many cases among the impurities of the final materials. The presence of $BaCuO_2$ is probably more considerable and more frequent than usually reported for the lower capability of detection of XRD, as already observed by Ito *et al.* [4].

Experimental and discussion

$BaCuO_2$ was prepared by a solid-state reaction based on the thermal decomposition of BaO_2 (2N, Material Research), instead of $BaCO_3$ [5], and CuO (2N, Merck). Details are reported elsewhere [6, 7]. Batches of about 30 g were prepared by the usual dry powder method, with thorough mixing of the starting oxides in a rotating mixer. The sample was first reacted in air at about 1170 K for 12 h (heating rate: 10 deg·min^{-1}), and then slowly cooled to room temperature. The compound was weighed to determine the reaction weight loss and then finely powdered, dry-sieved and structurally characterized.

The crystal structures of $BaCuO_2$ and CuO samples were investigated by the X-ray powder method, using CuK_α radiation. The intensity calculations for the powder patterns were performed with the Lazy Pulverix program [8]. $BaCuO_2$ analysis indicated a single-phase sample of cubic Im3m structure-type, with a lattice parameter (a=18.307 Å) in agreement with the literature data [9]. The CuO lattice parameters reported in the literature differ somewhat, but our values are in good agreement with those reported by Pearson [10] (a=4.689 Å, b=3.425 Å, c=5.127 Å and beta=99.56°). The reason for the difference could be a deviation from stoichiometry, already pointed out for Cu_2O by King [11], which is to be expected for all copper oxides.

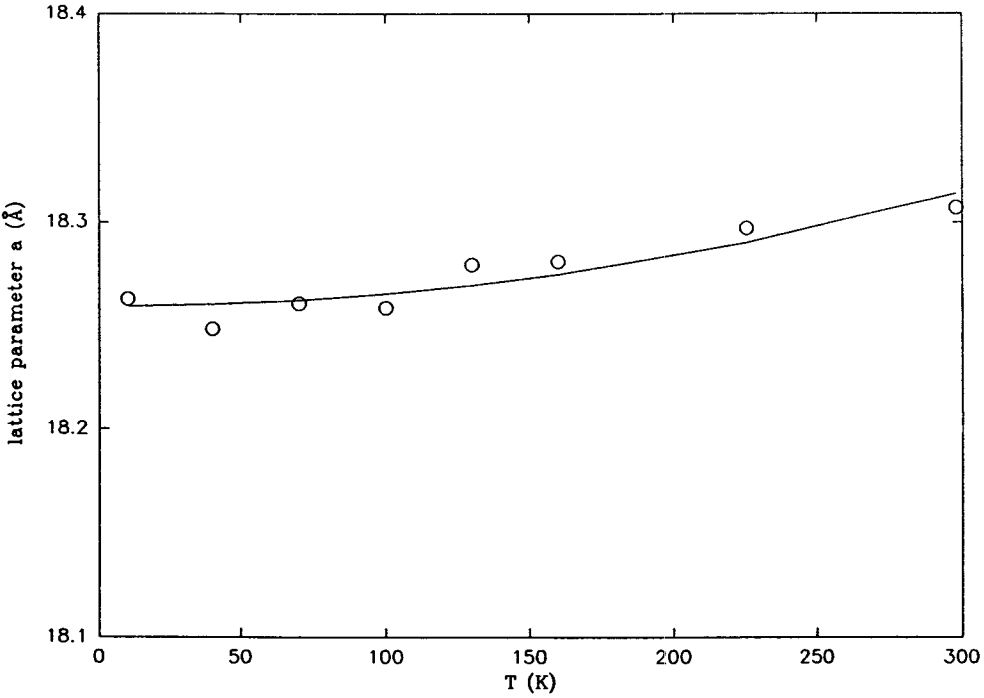

Fig. 1 Temperature dependence of $BaCuO_2$ lattice parameter

The oxygen content of the sample was determined by using a modification of the standard iodometric titration technique [12], with potentiometric detection of the end-point. Analysis gave compositions $CuO_{0.99}$ and $BaCuO_{2.08}$. As this method is very reproducible and accurate, study of the dependence of the lattice parameter on the oxygen content is in progress.

Low-temperature measurements of reticular parameters were carried out with a Hüber low-temperature computer-controlled Guinier camera. The measurements were performed by adding silicon to the powders in order to refine the reticular parameters with an internal standard whose thermal expansion at low temperatures is well known [13]. In this case an accuracy of better than $\Delta a/a=10^{-4}$ can be easily obtained, although Batchelder and Simmons [14] and Schuele and Smith [15] have achieved a resolution of about $5 \cdot 10^{-6}$ with oscillating back-reflection techniques. Clearly, this is not sensitive enough for determining α at temperatures $T < \Theta_D/10$. The three-crystal spectrometer, which makes use of dislocation-free perfect crystals such as silicon, does have a much higher sensitivity ($\Delta a/a=10^{-8}$), but it is applicable only to crystals with a "perfect" lattice.

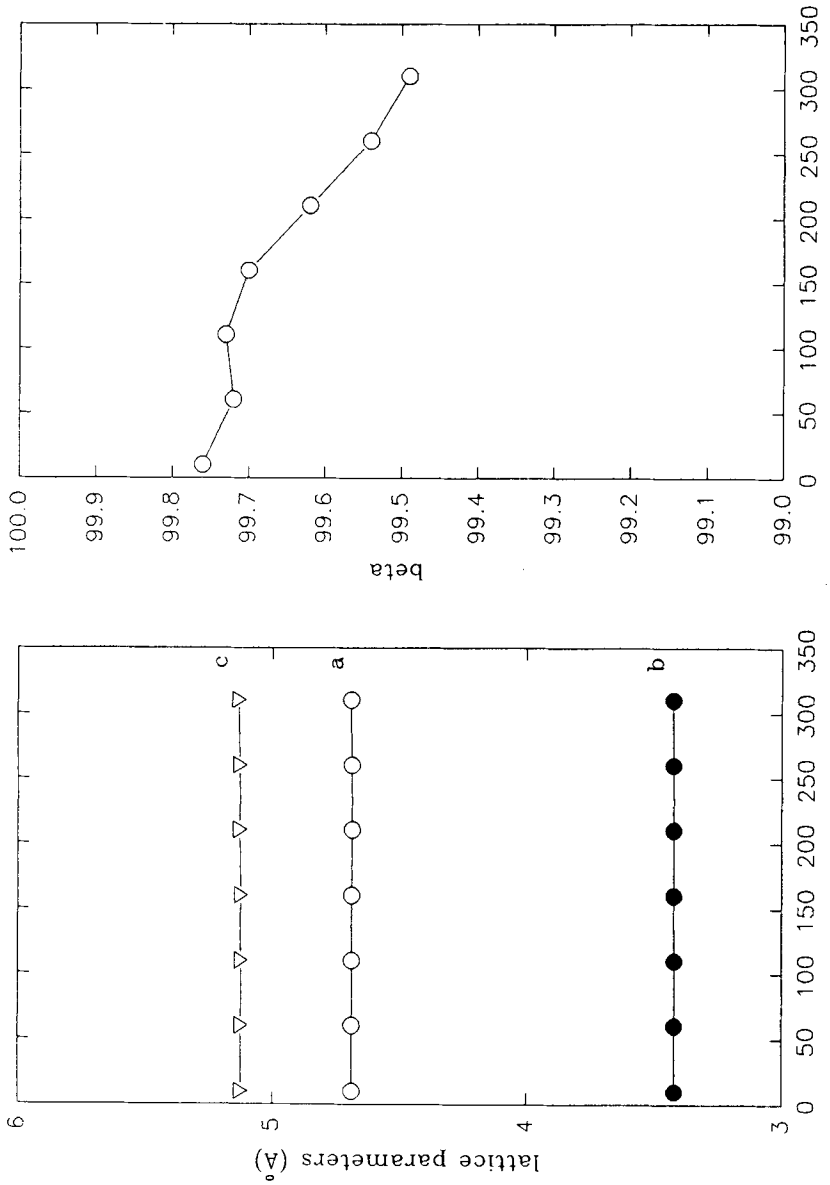

Fig. 2 Dependence from the temperature of lattice parameters and β of the monoclinic CuO

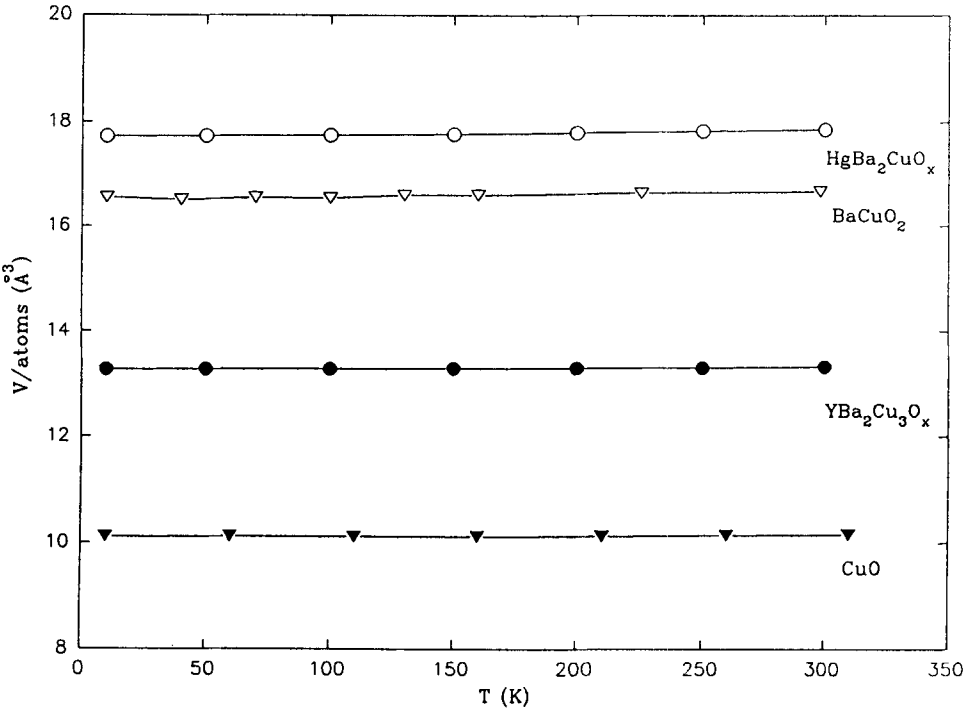

Fig. 3 Comparison of the thermal dependence of the mean atomic volume for several oxides (triangles: this work; o from [20] and • from [17])

Figure 1 presents structural results for $BaCuO_2$ as a function of temperature from 10 to 300 K. The *a vs. T* behaviour is nearly linear in the range starting from 150 K, it becomes flat at lower temperature. The value of α at room temperature, calculated from fitting to the quadratic polynomial equation $a(T) = 18.26 + 6.1 \cdot 10^{-7} \cdot T^2$ (Å), is reported in Table 1, together with the anisotropic thermal expansion coefficients of CuO and some superconducting oxides.

Table 1 Thermal expansion coefficients

Composition	$\alpha(a)$ / 10^{-6} K^{-1}	$\alpha(b)$ / 10^{-6} K^{-1}	$\alpha(c)$ / 10^{-6} K^{-1}
CuO	2	6	4
$BaCuO_2$	20		
$La_{1.8}Sr_{0.2}CuO_x$ [18]	7		17
$YBa_2Cu_3O_x$ [17]	11		25
$Bi_2CaSr_2Cu_2O_x$ [19]	15	15	22
$HgBa_2CuO_4$ [20]	16		19

The scattering of the data is relatively high, due to instrumental problems connected with the $BaCuO_2$ absorption factor.

The structural results on CuO are reported in Fig. 2. The temperature dependence of the lattice parameters becomes very low below 200 K, whereas β changes continuously, even at low temperature. The values of the anisotropic thermal expansion coefficients are also listed in Table 1. We have taken into account the high-temperature structural data quoted by Pearson [10] to report the thermal behaviour of the cell volume, fitted in the range from 10 to 1100 K. We obtained

$$V(T) = 80.95 + 2.69 \cdot 10^{-6} \cdot T^2 - 9.88 \cdot 10^{-10} \cdot T^3 \text{ (Å)}^3$$

Figure 3 compares the mean atomic volumes for several oxides, superconducting or not. The overall dependence is quite similar, even if a different slope must be expected for the superconducting oxides (Ehrenfast's relation) in the thermal dependence below and above the critical superconducting temperature.

Due to the smallness of the jump, in a first approximation calculation, α can be considered not to vary through out the transition. If this is done, and the

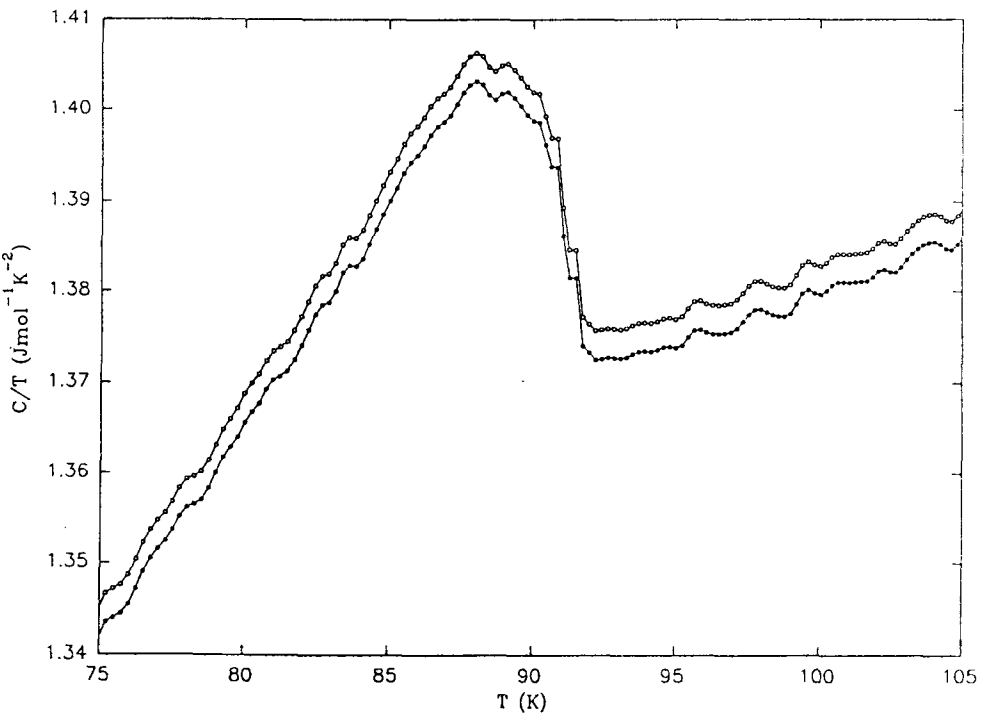

Fig. 4 Molar C/T values at constant pressure (o) and volume (•). Data from [6, 16, 17]

compressibility is also considered as independent of temperature, a good calculation of C_v from C_p can be obtained as:

$$C_v = C_p - \alpha^2 VTK$$

where K is the bulk modulus and V the molar volume. Since the thermal expansivities α of liquids and solids are small, it is tempting to deduce from the above expression that $C_p \approx C_v$. However, this is not always so because the isothermal compressibility might also be small, so that $\alpha^2 K$ might be large and the two heat capacities could differ by several per cent. The difference is small, but appreciable, as can be observed in Fig. 4 for the 123 superconductor. C_p data were taken from [5], and K and α from [16] and [17], respectively.

As the term $\alpha^2 VTK$ acts as a small connection in the calculation of C_v, the accuracy of this calculation remains substantially that of the measurement of C_p, even for not particularly accurate values of α such as those obtained by X-ray method. Thus, thermal expansion measurements by means of X-ray techniques are suitable for calorimetric measurements.

* * *

This work was supported by the Italian Consiglio Nazionale delle Ricerche.

References

1 T. H. K. Barron, J. G. Collins and G. K. White, Advances in Physics, 29 (1980) 609.
2 M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang and C. W. Chu, Phys. Rev. Lett., 58 (1987) 908.
3 S. N. Putilin, E. V. Antipov, O. Chmaissem and M. Marezio, Nature, 362 (1993) 226.
4 T. Ito, M. Uzawa and H. Uchikawa, J. Am. Ceram. Soc., 71 (1988) C188.
5 G. A. Costa, M. Ferretti and E. Kaiser, Thermochim. Acta, 162 (1990) 69.
6 G. A. Costa, M. Ferretti and G. L. Olcese, J. Crystal Growth, 91 (1988) 392.
7 G. A. Costa and M. Ferretti, J. Less Comm. Met., 157 (1990) 77.
8 K. Yvon, W. Jeitschko and E. Parthè, J. Appl. Crystallogr., 10 (1977) 73.
9 R. Kipka and H. Muller-Buschbaum, Z. Naturforsch., 32B (1977) 121.
10 P. Villars and L. D. Calvert, Pearson's Handbook of Crystallographic Data for Intermetallic Phases, A.S.M. International, USA 1991, II Ed., vol. 3. p. 2959.
11 R. M. King, J. Am. Cer. Soc., 54 (1971) 361.
12 D. C. Harris, M. E. Hills and T. A. Hewston, J. Chem. Education, 64 (1987) 847.
13 J. S. Shah and M. E. Straumanis, Sol. St. Comm., 10 (1972) 159.
14 D. N. Batchelder and R. O. Simmons, J. Appl. Phys., 36 (1965) 2864.
15 D. Schuele and C. S. Smith, J. Phys. Chem. Solids, 25 (1964) 801.
16 J. D. Jorgensen, Shiyou Pei, P. Lightfoot, D. G. Hinks, B. W. Veal, B. Dabrowski, A. P. Paulikas and R. Kleb, Physica C, 171 (1990) 93.
17 E. du Tremolet de Lacheisserie, B. Barbara and J. H. Henry, J. Magn. Mag. Mat., 71 (1988) L125.

18 E. Gmelin in Studies of High Temperature Superconductors, A. Narlikar (Ed.), Nova Science Publishers, USA, 1989, vol. 2, p. 95.
19 R. H. Arendt, M. F. Garbauskas, C. A. Meyer, F. J. Rotella, J. D. Jorgensen and R. L. Hitterman, Physica C, 182 (1991) 73.
20 J. L. Wagner, P. G. Radaelli, D. G. Hinks, J. D. Jorgensen, J. F. Mitchell, B. Dabrowski, G. S. Knapp and M. A. Beno, Physica C, 210 (1993) 447.

Zusammenfassung — Die Gitterparameter von $BaCuO_2$ und CuO wurden als eine Funktion der Temperatur zwischen 10 und 300 K bestimmt. Das Fitting der Parameter führte zu den thermischen Ausdehnungskoeffizienten und der Anisotropieeigenschaften dieser polykristallinen Substanzen. Die Genauigkeit der Messungen und die Verwendung von – wenn auch nicht genauen – thermischen experimentellen Messungen zur Berechnung von C_v aus C_p wird diskutiert.