ELSEVIER

Oxygen determination from cell dimensions in YBCO superconductors

Paola Benzi[a,b,*], Elena Bottizzo[a], Nicoletta Rizzi[a]

[a] *Dipartimento di Chimica Generale ed Organica Applicata, Universitá degli Studi di Torino, Corso Massimo d'Azeglio 48, 10125 Torino, Italy*
[b] *Istituto Nazionale di Fisica della Materia, Villa Brignole, Corso Perrone 24, 16152 Genova, Italy*

Communicated by R. Kern

Abstract

A rapid and simple procedure for the determination of non-stoichiometric oxygen in $YBa_2Cu_3O_{7-\delta}$ (YBCO) superconductors is described, based on the relationship between oxygen content and c-axis parameter of the YBCO structure. To test the proposed method the oxygen content of samples sinterised starting from different precursors has been calculated from X-ray powder diffraction analysis and compared with the oxygen content obtained by iodometric titration with satisfactory correspondence.
© 2004 Elsevier B.V. All rights reserved.

1. Introduction

The problem of oxygen non-stoichiometry is common for all high-temperature superconductors and is connected with the mixed valence of the metallic atoms (namely Cu(II)/Cu(III), Bi(III)/ Bi(V), Tl(I)/Tl(III) and Pb(IV)/Pb(II)), particularly with that of copper, which has a prominent role for the superconducting properties of these materials [1–4].

For $YBa_2Cu_3O_{7-\delta}$ (YBCO) [5–7], in which only copper has a variable oxidation state, the relation between oxygen content and cell dimensions or annealing temperature has been pointed out in many works [1,8–14].

The δ-value acts as a regulating factor of the structural and electrical properties of the material (when δ decreases T_c increases). The YBCO

*Corresponding author. Dipartimento di Chimica Generale ed Organica Applicata, Universitá degli Studi di Torino, Corso Massimo d'Azeglio 48, 10125 Torino, Italy. Tel.: +39-011-6707583; fax: +39-011-6707591.

E-mail address: paola.benzi@unito.it (P. Benzi).

structure gradually varies when δ varies in the range $1 \leqslant \delta \leqslant 0$: an increase of oxygen content up from 6 to 6.5 ($\delta = 1-0.5$) makes it possible to obtain the tetragonal-semiconducting phase; for $\delta = 0.5$ the phase transition from tetragonal to orthorhombic occurs, over $\delta = 0.2$ the superconductive properties appear and for $\delta = 0$ the structure is completely orthorhombic-superconductive with T_c above 90 K.

Therefore the δ-value of interest for YBCO as superconductor varies in the range from 0.2 to 0; it is necessary to control δ-value within a narrow range in order to obtain higher T_c samples.

In the orthorhombic phase a- and c-parameters decrease with the increase of oxygen content, while b-parameter increases. The c-axis parameter has been observed in literature to change in the range from 11.8391 Å for $YBa_2Cu_3O_6$ (tetragonal) to 11.660 Å for $YBa_2Cu_3O_7$ (orthorhombic) [15].

Many experimental methods have been used to evaluate the oxygen content in the high-T_c superconductors samples:, iodometric titration [16–19], coulometric titration [17,20], thermogravimetric analysis [16,18,21], micro-Raman spectroscopy [22], spectrophotometric method [23–25], volumetric method [26] but all these measurements are destructive, so one knows the characteristics of the sample when it is no more useful. From these considerations the importance of a non-destructive method for the oxygen evaluation in high-T_c superconductors become obvious.

A quantitatively correlation of the c-axis dimension with the oxygen content has been tried by Ono, in a paper of 1987, on the basis of the weight variations of annealed samples but assuming 6.89 as the maximum oxygen content [27].

Because the superconductivity in oxygen deficient perovskites is closely related to the crystal structure, we think that a non-destructive method for the oxygen quantitative evaluation in high-T_c superconductors could be drawn from experimental data of the cell dimensions [1,28]. The aim of this study is looking for a general mathematical relation between the oxygen content and the cell parameters in YBCO samples allowing a non-destructive determination.

2. Experimental procedure

Samples has been prepared both from inorganic and organic salts. In the first case we started from grinded powders of a stoichiometric mixture of Y_2O_3, CuO and of a different barium compound ($BaCO_3$ or $Ba(NO_3)_2$ or BaO_2) [29]. In the second case the neodecanoates of copper, barium and yttrium were dissolved in xylene/pyridina solvent mixture always taking in account the exact stoichiometry. The solution was then dried and the obtained intimate powders were pressed. The resulting pellets were annealed at $T > 900°C$, with a further thermal treatment at 450°C in oxygen flow.

To obtain the unit cell dimensions, each sample was analysed with X-ray powder diffraction analysis using a D5000-Siemens diffractometer equipped with Göbel mirrors, using Ni-filtered Cu K_α radiation. The diffraction intensities in 2θ-range 20–40° were collected in a $2\theta - \theta$ scan mode, with 0.02° steps. In the chosen 2θ-range there is the most of the stronger reflections (JCPDS 39-1496; 40-0159). The sample unit cell parameters have been refined using a least-square method. Using this program, it is possible to obtain the values of the a, b, c crystallographic parameters with the estimated standard deviations.

Experimental oxygen content was obtained using the standard iodometric titration, following the suggestion of Harris [18].

A LakeShore7225 susceptometer was used for the magnetic measurements ($v = 1000$ Hz; $H_c = 100$ A/m^2). A home-made four probes apparatus was used for the resistive measurements.

3. Results and discussion

The non-superconductive phase has the oxygen atoms randomly distributed among the sites O(1) and O(5), so that the structure is a disordered tetragonal one. The space group is P4/mmm and the sites O(1) and O(5) are equally occupied (Fig. 1).

On the contrary, the YBCO superconducting phase at the higher critical temperature ($0 \leqslant \delta \leqslant 0.2$) is orthorhombic with the space group
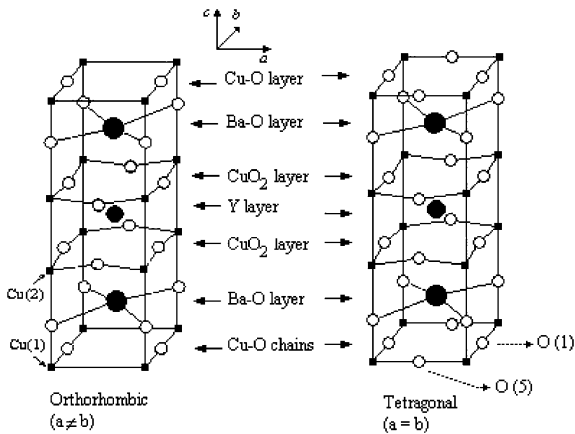
Fig. 1. Orthorhombic and tetragonal structures of $YBa_2Cu_3O_{7-\delta}$ material.
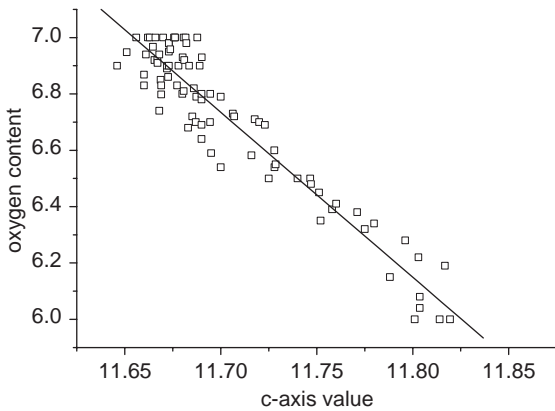

Fig. 2. $(7-\delta)$ values as a function of the c-axis values obtained from ICSD Database. The solid line is the fit of the points.

Pmmm. The crystal structure [28] is an oxygen deficient perovskite with ordered vacancies consisting of three unit cell stacked as $-CuO_x-BaO-CuO_2-Y-CuO_2-BaO-CuO_x-$. In the CuO_x layer, each Cu is coordinated by four oxygen atoms while in the CuO_2 layer each Cu is surrounded by five oxygen atoms.

In the inorganic Crystal structure database (ICSD) about 240 $YBa_2Cu_3O_{7-\delta}$ structures have been found, refined by different techniques, namely X-ray diffraction from a powder (XPD), neutron diffraction from a powder (NPD), synchrotron radiation of single crystal (SNS), structure theoretically calculated (THE). Because this is our intention to perform an experimental test on the applicability of the method reported in this paper using the results of XPD analyses (see below), among the ICSD YBCO structures we have chosen only the Pmmm spatial group structures refined using the results of XPD and NPD analyses obtained in the same our conditions.

ICSD Database reports for each chosen structure both the δ and the c-axis values. The $(7-\delta)$ values have been plotted as a function of the c-axis values, as shown in Fig. 2. The fit of the points give the following equations:

$$(7 - \delta) = 75.250 - 5.856c, \tag{1}$$

where $(7-\delta)$ is the oxygen content and c is the c-axis value).

In order to verify the possibility to use the above equation to calculate the oxygen content of a new YBCO sample from the c-axis value obtained from

Table 1
Chemical precursors used to obtain YBCO bulk samples and lattice parameters obtained from XRD analysis

Sample	Starting compounds	Lattice parameters		
		a-Axis (Å)	b-Axis (Å)	c-Axis (Å)
1	$Y_2O_3 + CuO + BaCO_3$	3.81	3.87	11.690
2	Y, Ba, Cu neodecanoates	3.82	3.88	11.660
3	$Y_2O_3 + CuO + Ba(NO_3)_2$	3.81	3.88	11.669
4	$Y_2O_3 + CuO + BaCO_3$	3.82	3.87	11.662
5	$Y_2O_3 + CuO + BaCO_3$	3.81	3.87	11.687
6	$Y_2O_3 + CuO + BaO$ in acetic acid	3.84	3.91	11.659
7	$Y_2O_3 + CuO + BaO$ in nitric acid	3.82	3.90	11.698
8	$Y_2O_3 + CuO + BaO_2$	3.82	3.87	11.662

XPD analysis, eight $Y_1Ba_2Cu_3O_{7-\delta}$ bulk samples have been prepared using sintering method and starting from the different mixtures of precursors collected in Table 1.

In Table 1 are also reported the unit cell dimensions of the YBCO samples obtained from XPD analyses data. From the *c*-axis values reported in Table 1 and using Eq. (1) the samples oxygen content values have been calculated. For comparison, the oxygen content has been also experimentally determined using iodometric titration [18].

The values obtained are reported in Table 2 whereas Fig. 3 shows the calculated and experimental oxygen content as a function of *c*-axis value with the respective fit lines. It is possible to observe that the oxygen content value obtained by Eq. (1) in each case is higher than the value obtained by iodometric titration. Moreover, the two fit lines are almost parallel.
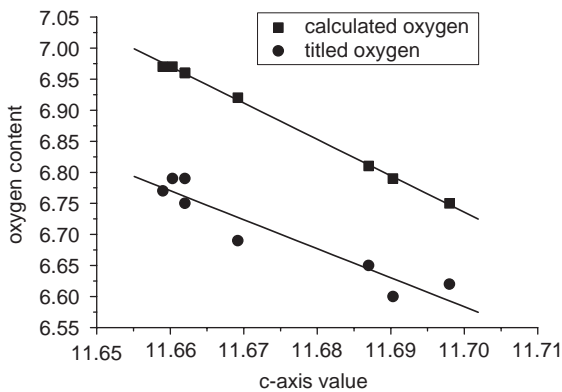

Fig. 3. Calculated and experimental oxygen content as a function of *c*-axis value. The solid lines are the fits of the points.

It is known that the oxygen content influences the YBCO structure and hence the superconductive properties. Considering the oxygen content calculated with Eq. (1), the critical temperature (T_c) values listed in Table 2 can be predicted for our samples [1,30].

The performed magnetic and resistive measurements give T_c values (also reported in Table 2) lower than the predicted ones suggesting that the proposed method overestimates the oxygen content, nevertheless the experimental T_c values are in better agreement with the calculated oxygen content values with respect the ones obtained from iodometric titration. Therefore, it is reasonably to suppose that the real values are between the values obtained with the two methods.

4. Conclusions

The proposed method allows to calculate the oxygen content of YBCO samples starting from the *c*-axis value. It offers some advantages with respect the conventional methods of oxygen determination: it is simple and rapid and hence can be used as a toll for a quick preliminary screening of the samples having superconductive properties. Moreover, no chemical compounds must be added and the method does not destroys or damages the sample which is therefore available for further characterisation or applications.

The calculated oxygen content values are consistent with those obtained from iodometric titration and even if the experimental results

Table 2
Experimental and calculated oxygen content and transition temperature of the YBCO samples

Sample	Calculated oxygen value	Experimental oxygen value	T_c (K) (predicted)	T_c (K) (experimental)
1	6.79	6.60	81	78
2	6.97	6.79	91.5	90
3	6.92	6.69	91.5	89.5
4	6.96	6.75	91.5	90
5	6.81	6.65	82	80
6	6.97	6.77	91.5	91
7	6.75	6.62	72	Non-superconductive in liquid N_2
8	6.96	6.79	91.5	90

indicate that the proposed method overestimates the oxygen content, the experimental T_c values are in better agreement with the calculated oxygen content values with respect the ones obtained from iodometric titration indicating that reliable oxygen content values are obtained from Eq (1).

References

[1] J.D. Jorgensen, D.G. Hinks, P.G. Radaelli, S. Pie, P. Lightoot, B. Dabrowski, C.U. Segre, B.A. Hunter, Physica C 185–189 (1991) 184.

[2] A. Fukuoka, M. Karppinen, M. Itoh, K. Hamada, H. Yamauchi, J. Supercond. 8 (1995) 31.

[3] J.T.S. Irvine, C. Namgung, J. Solid State Chem. 87 (1990) 29.

[4] M. Namiki, K. Hirokawa, Fresenius J. Anal. Chem. 344 (1992) 265.

[5] T. Nedeltcheva, A. Stoyanova-Ivanova, L. Kostadinova, I. Ivanova, Fresenius J. Anal. Chem. 342 (1992) 196.

[6] P. Lanza, A. Marzocchi, Anal. Chem. Acta 304 (1995) 223.

[7] Z. Dankhazi, A. Szasz, J. Kojnok, H. Kirchmayr, H. Müller, L. Watson, M. Gal, K. Torkos, K. Solymos, J. Supercond. 4 (1991) 219.

[8] S.C. Tidrow, D.M. Pierce, A. Tauber, W.D. Wilber, R.D. Finnegan, D.W. Eckart, J. Supercond. 11 (1998) 29.

[9] J.-M. Tarascon, B.G. Bagley, MRS Bulletin, January 1989, p. 53.

[10] J.D. Jorgensen, M.A. Beno, D.G. Hinks, L. Soderholm, K.J. Volin, R.L. Hitterman, J.D. Grace, I.K. Schuller, C.U. Segre, K. Zhang, M.S. Kleefisch, Phys. Rev. B 36 (1987) 3608.

[11] S. Degoy, J. Jimenez, P. Martin, O. Martinez, A.C. Prieto, D. Chambonnet, C. Audry, C. Belouet, J. Perriere, Physica C 256 (1996) 291.

[12] C. Namgung, J.T.S. Irvine, J.H. Binks, A.R. West, Supercond. Sci. Technol. 1 (1988) 169.

[13] J. Ye, K. Nakamura, Phys. Rev. B 48 (1993) 7554.

[14] Kh.A. Ziq, Supercond. Sci. Technol. 14 (2001) 30.

[15] 399-1496 and 40-0159-JCPDS-International Centre for Diffraction Data.

[16] M. Karppinen, L. Niinistö, Supercond. Sci. Technol. 4 (1991) 334.

[17] A. Fukuoka, M. Karppinen, N. Seiji, J. Valo, A. Kareiva, L. Niinistö, M. Leskelä, N. Koshizuka, H. Yamauchi, Supercond. Sci. Technol. 8 (1995) 673.

[18] D.C. Harris, T.A. Hewston, J. Solid State Chem. 69 (1987) 182.

[19] W.M. Chen, X.S. Wu, J.F. Geng, J. Chen, D.B. Chen, X. Jin, S.S. Jiang, J. Supercond. 10 (1997) 41.

[20] R. Chavdarova, T. Nedeltcheva, L. Vladimirova, Anal. Chim. Acta 353 (1997) 325.

[21] I.S. Shaplygin, I.A. Konovalova, E.A. Tishchenko, V.B. Lazarev, Russ. J. Inorg. Chem. 33 (1988) 1098.

[22] P.V. Huong, A.L. Verma, J.P. Chaminade, L. Nganga, J.C. Frison, Mater. Sci. Eng. B 5 (1990) 255.

[23] T. Nedeltcheva, L. Costadinova, P. Simeonova, V. Lovchinov, Anal. Chim. Acta 336 (1996) 223.

[24] Z. Málcová, J. Novák, V. Hamplová, Z. Pokorná, Fresenius J. Anal. Chem. 347 (1993) 478.

[25] T. Nedeltcheva, Anal. Chim. Acta 437 (2001) 25.

[26] L. Liu, C. Dong, J. Zhang, H. Chen, L. Chen, Physica C 383 (2002) 17.

[27] A. Ono, Jpn. J. Appl. Phys. 26 (1987) L1223.

[28] P. Burlet, P. Bourges, J. Bossy, E. Elkaim, J.Y. Henry, J.P. Lauriat, V.P. Plakhty, L.P. Regnault, J. Schweizer, Y. Sidis, C. Vettier, F. Yakhou, J. Supercond. 9 (1996) 357.

[29] A. Agostino, P. Benzi, N. Rizzi, P. Volpe, Supercond. Sci. Technol. 15 (2002) 902.

[30] R.J. Cava, A.W. Hewat, E.A. Hewat, B. Batlogg, M. Marezio, K.M. Rabe, J.J. Krajewski, W.F. Peck Jr., L.W. Rupp Jr., Physica C 165 (1990) 419.