Mat. Res. Bull., Vol. 24, pp. 803-807, 1989. Printed in the USA. 0025-5408/89 \$3.00 + .00 Copyright (c) 1989 Maxwell Pergamon Macmillan plc.

THE OXYGEN STOICHIOMETRY OF YBa₂Cu_{2.82}^{Zn}0.18^O7-**5** BETWEEN 25 AND 930°C

S.P.Garg, R.Venkataramani and S.Mazumder* Physical Metallurgy Division, BARC, Bombay-400085, INDIA *Neutron Physics Division, BARC, Bombay-400085, INDIA

(Received February 16, 1989; Refereed)

ABSTRACT

The paper presents a new methodology for determination of oxygen stoichiometry of YBa₂(Cu₁ Zn₂)₃O₇ type of compounds taking x=0.06 as an example. The method involves heating of the sample upto 930 °C and slow cooling (1 °C/min) under pure oxygen upto 25°C followed by hydrogen reduction in a thermobalance. Both copper and zinc contents of the oxide reduced to metallic state under hydrogen at about 900°C. In the present method the sample was kept at 980°C for sufficiently long period such that zinc was completely removed by volatilisation. This helped in establishing the composition of the reduced product and thereby oxygen stoichiometry of the oxide. The oxygen stoichiometry for the oxide. The oxygen at 1.0 atm was found to vary from 6.84 \pm 0.03 to 6.27 \pm 0.03 from 25 to 930°C

MATERIALS INDEX: copper, zinc, oxides, superconductors

Introduction

The role of copper and oxygen is of considerable importance in the 1:2:3 oxide superconductor. It is generally accepted that the deviation of oxygen stoichiometry from an ideal 7.00 either way adversely of affects the value in superconductivity of the material /1/. For understanding the critical role played by copper towards superconducting nature of material, partial substitution of copper by bivalent metals like Mg/Zn or trivalent metals like Al/Ga, would be of immense importance. Superconducting oxides of the type $YBa_2(Cu_{1-x}Zn_x)_3O_7$ (where M=Mg, Zn, Al, Ga,etc) have been investigated by several workers /2-6/ with emphasis to understand the relative importance of oxidation state of copper at the two sites, Cu(1) and Cu(2). In

S.P. GARG, et al.

Vol. 24, No. 7

this context, an important observation made for the compound with M=Zn, is that the structural symmetry remains invariant over a considerable extent of substitution, but critical temperature (Tc) falls vary sharply /3,4/. As far as the occupancy of zinc is concerned, there exists some confusion. Xiao et al /3,4/ claim that zinc occupies Cu(2) sites, whereas Kejitani et al /6/ conclude that majority (about 66.6%) of zinc goes to Cu(1) sites. Question remains as to whether the sharp fall in Tc is primarily because of substitutional effects or due to change in oxygen stoichiometry arising out of substitution.

A precise knowledge of oxygen stoichiometry of these oxides at different temperatures is, therefore, of considerable importance. Thermogravimetric analysis involving hydrogen reduction has been commonly employed for determination of oxygen stoichiometry. The compounds of the type $YBa_2(Cu_{1-x}Zn_x)_3O_7$, however, poses some special problems because of simultaenous reduction of both copper and zinc contents of these oxides and volatilisation loss of zinc. The paper presents a new thermogravimetric methodology for determination of oxygen stoichiometry of such oxides taking $YBa_2Cu_{2.82}Zn_{0.18}O_7-\delta$ as an example.

Experimental Details and Discussions

The YBa₂Cu_{2.82}Zn_{0.18}O_{7- δ} oxide was prepared by calcining mixture of the component oxides and barium carbonate, of analytical grade, in proper proportion at 930°C for 12 h to get desired bulk composition of the metal constituents. After thorough grinding and mixing, the powder was pressed into 10 mm dia pellets at 0.5 GPa and sintered at 930°C for 12 h. Oxygenation was carried out in flowing stream of high purity oxygen at 500°C for 10 h.

A small piece (about 350 mg) of the oxide sample was charged in a Mettler Thermoanalyser. The charge was heated, under a flow (200 ml/min) of pure oxygen, at 10° C/min upto 930°C and held at this temperature for sufficiently long period (about 1.5 h) till a constant weight of sample was attained. The charge was then slowly cooled, at 1° C/min, to 25° C. The thermogram is shown in Fig. 1.

The above mentioned treatment removed all absorbed gases, moisture, volatile impurities and undecomposed carbonates and gave an oxide sample well characterised with respect to Tc, crystal struture and oxygen stoichiometry. The sample was then reduced by hydrogen without exposing the charge to atmosphere by replacing oxygen with Ar+8% H₂ gas mixture in the thermoanalyser. The use of Ar+H₂ mixture minimises errors due to buoyancy effect. The temperature of the sample was increased, under a flow (200 ml/min) of Ar+H₂ gas mixture, at 10°C/min upto 930°C. The charge was kept at this temperature for about 4 h, even then a constant weight of the sample was not attained as shown in Fig.2. This was mainly due to volatilisation loss of zinc as the hydrogen reduction of other similar oxides (without containing zinc oxide) gets completed within 2 h at 930°C in order to enhance the rate of vaporisation

804





Change in weight of oxide, $\rm YBa_2Cu_{2.82}Zn_{0.18}O_{7-\delta},$ during heating under flow of oxygen.





Change in weight of oxide, $YBa_2Cu_{2.82}Zn_{0.18}O_{7-\delta}$, during reduction under (Ar + 8%H₂) flow.

S.P. GARG, et al.

Vol. 24, No. 7

----(1)

loss of zinc. The temperature was limited to 980 °C to avoid melting of the reduced product. The sample attained constant weight at 980 °C within 1.5 h (Fig.2) indicating complete removal of zinc from the charge. This was confirmed by spectrographic analysis of the reduced product which gave zinc content as less than 50 ppm.

The overall reduction reaction can, thus, be written as,

The mass balance of reaction (1), considering complete removal of zinc, gives

 $(7-\delta) = (2.765 \text{ W} + 34.66 \text{ L})/(\text{W} - \text{L})$ -----(2)

where W and L are respectively the initial weight of the characterised sample and overall weight loss during the reduction. The $(7-\delta)$ value at 25°C for this oxide was, thus, found to be 6.84 \pm 0.03.

The oxygen stoichiometry at different temperatures were determined from the composition at $25^{\circ}C$ (i.e. YBa₂Cu_{2 82}Zn_{0 18}°_{6 84}) and thermogram obtained during cooling of the sample from 930⁴ to $25^{\circ}C$ at the rate of $1^{\circ}C/min$ in pure oxygen



FIG. 3

 $(7-\delta)$ in YBa₂Cu_{2.82}Zn_{0.18}O_{7- δ} at different temperatures measured thermogravimetrically.

806

Vol. 24, No. 7

(Fig.2) using following equation,

 $(7-\delta)_{m} = (7-\delta)_{25} - (M \le 16 \le)$ -----(3)

where $(7-\delta)_{TT}$, $(7-\delta)_{25}$, M, w and W are respectively the oxygen stoichiometry at T, oxygen stoichiometry at 25° C, molecular weight of the characterised oxide at 25° C (i.e.YBa₂Cu₂ ₈₂Zn₀ ₁₈O₆ ₈₄), weight loss at temperature T and weight of the characterised oxide at 25° C. It may be noted from Fig.2 that W in this particular case was equal to (0.34804 - 0.00045 = 0.34759 g) where 0.00045 g is the overall weight loss of the oxide during heating and cooling of the sample under pure oxygen.

The measured values of $(7-6)_{\rm T}$ are shown in Fig.3. The maximum oxygen content (i.e. 6.86) in the oxide was attained at about 375 °C which has been a common feature of these type of oxides. The smooth variation of the oxygen stoichiometry with temperature indicates that the oxide is of single phase as also suggested by the XRD and EDX studies /5/.

Investigations on variation of $(7-\delta)$ with x in YBa₂(Cu_{1-x}^{Zn}x)₃O_{7- δ} and its effect on superconducting properties are in progress and shall be presented elsewhere .

Conclusion

A simple but reliable thermogravimetric method has been established for the determination of oxygen stoichiometry of the $YBa_2(Cu_{1-x}Zn_x)_3O_{7-x}$ type of compounds.

References

- S. Mazumder, H. Rajagopal, A. Sequeira, R. Venkataramani, S.P. Garg, A. K. Rajarajan, L. C. Gupta and R. Vijayaraghavan, J. Phys. (C), 21, 5967 (1988).
- Y. Maeno, T. Tomita, M. Kyogoku, S. Awaji, Y. Aoki, K. Hoshino, A. Minomi and J. Fujita, Nature, 320, 512 (1987).
- 3. G. Xiao, M. Z. Cieplak, D. Musser, A. Gavrin, C. L. Chien, J.J. Rhyne, and J.A. Gotass, Nature, 332, 238 (1988).
- 4. G. Xiao, M.Z. Cieplak, A. Gavrin, F.H. Streitz, A. Bakhshai and C.L. Chien, Phys. Rev. Lett., 60, 1446 (1988).
- 5. J. Singh, A.K. Rajarajan, L. C. Gupta and R. Vijayaraghavan, Proc. Symp. 'Solid state Physics', Bhopal, India, 172 (1988).
- T. Kajitani, K. Kusaba, M. Kikuchi, Y. Syono and M.Hirabayashi, Jap. J. App. Phys., 27, L 354 (1988).

807