Thermogravimetric method for determination of oxygen stoichiometry in superconducting 1:2:3 and metal-substituted 1:2:3 compounds

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Abstract. The paper presents a modified thermogravimetric method for determination of oxygen stoichiometry of the oxide superconductors $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and metal-substituted compounds of the type $\text{YBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7+\delta}$ and $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-\delta}$ ($\text{M} = \text{Mg/Zn}$) between 25° and 930°C.

Keywords. Thermogravimetry; stoichiometry.

1. Introduction

The role of copper and oxygen is of considerable importance in the 1:2:3 oxide superconductor. It is generally accepted that deviation of oxygen stoichiometry from an ideal value of 7 either way adversely affects the superconductivity of the material (Mazumder *et al* 1988). Efforts have been made earlier (Mazumder *et al* 1988; Segre *et al* 1987; Sunshine *et al* 1987) to raise the oxygen stoichiometry beyond 7 by partially replacing the bivalent Ba with trivalent La. Similarly, partial substitution of Cu by bivalent metals like Mg/Zn or trivalent metals like Al/Ga has also been investigated (Maeno *et al* 1987; Xiao *et al* 1988a, b; Singh *et al* 1988; Kajitani *et al* 1988). A precise knowledge of oxygen stoichiometry of these oxides is of considerable importance in understanding the superconducting behaviour.

Thermogravimetric analysis (TGA) involving hydrogen reduction has been commonly employed for determination of oxygen stoichiometry. These oxides, however, invariably absorb gases (mainly moisture and CO_2) and contain residual volatile impurities which cause errors in TGA. In this paper a modified method of TGA is presented.

2. Experimental

The superconducting oxide compounds of the type $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, $\text{YBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7+\delta}$ and $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-\delta}$ ($\text{M} = \text{Mg/Zn}$) were prepared following the solid-state reaction route (Mazumder *et al* 1988; Garg *et al* 1989). The sample (~400 mg) was charged in a Mettler's thermoanalyser. The charge was heated under a flow (200 ml/min) of pure oxygen, at 10°C/min up to 930°C for a sufficiently long period (~1.5 h) until a constant mass of the sample was attained. The charge was then slowly cooled, at 1°C/min, to 25°C. A typical thermogram for $\text{YBa}_2\text{Cu}_{2.82}\text{Zn}_{0.18}\text{O}_{7-\delta}$ is shown in figure 1.

The above mentioned treatment removed all absorbed gases, moisture, volatile impurities and undecomposed carbonates and gave an oxide sample well characterized with respect to T_c , crystal structure and oxygen stoichiometry. The sample

Figure 1. Change in weight of oxide $\text{YBa}_2\text{Cu}_{2.82}\text{Zn}_{0.18}\text{O}_{7-\delta}$ during heating under flow of oxygen.

Figure 2. Change in weight of oxide, $\text{YBa}_2\text{Cu}_{2.82}\text{Zn}_{0.18}\text{O}_{7-\delta}$ during reduction under $(\text{Ar} + 8\% \text{H}_2)$ flow.

was then reduced by hydrogen without exposing the charge to atmosphere by replacing oxygen with $\text{Ar} + 8\% \text{H}_2$ gas mixture in the thermoanalyser. The use of this gas mixture minimizes errors due to buoyancy effect. The temperature of the sample was increased, under a flow (200 ml/min) of $\text{Ar} + \text{H}_2$ gas mixture, at $10^\circ\text{C}/\text{min}$ up to 930°C and kept at this temperature for sufficient time till a constant weight was attained. The Cu contents reduced to metallic state at about 900°C in all these oxide compounds. However, in the case of Zn-substituted oxide compound, the sample continued to lose weight even after holding for more than 4 h at 920°C due to vaporization loss of Zn (Zn contents also reduced to the metallic state). The reduction temperature in such cases was raised to 980°C to enhance the rate of vaporization loss. The temperature was limited to 980°C to avoid melting of the reduced product. The sample attained a constant weight at 980°C within 1.5 h (figure 2) indicating complete removal of Zn from the charge. This was confirmed by spectrographic

analysis of the reduced product which gave Zn content as < 50 ppm. It is, therefore, possible to establish composition of the reduced product by this approach.

3. Results and discussion

The overall reduction reactions for 1:2:3 superconducting oxide and metal-substituted compounds are given below:

The mass balance during these reactions gives the following equations:

$$\text{For reac. 1: } (7 - \delta) = 3.5 + L/(W - L) \times Mp/16, \quad (5)$$

$$\text{For reac. 2: } (7 + \delta) = (3.5 + x/2) + L/(W - L) \times Mp/16, \quad (6)$$

$$\text{For reac. 3: } (7 - \delta) = (3.5 + 3x) + L/(W - L) \times Mp/16, \quad (7)$$

$$\text{For reac. 4: } (7 - \delta) = 3.5 - 12.26x + L/(W - L) \times Mp/16, \quad (8)$$

where W , L and Mp are respectively the weight of the characterized sample at 25°C, overall weight loss during the reduction and molecular weight of the reduced product. Equations (5)–(8) were used to calculate the $(7 - \delta)$ or $(7 + \delta)$ values at 25°C for the different oxides.

The oxygen stoichiometry at different temperatures was determined from the oxide composition at 25°C and the thermogram obtained during cooling of the sample from 930°C to 25°C at 1°C/min in pure oxygen (figure 1). The rate of cooling (1°C/min) 930° to 25°C keeps the oxide sample always under equilibrium with oxygen. The weight of the sample at any temperature during cooling, therefore, corresponds to the equilibrium $(7 - \delta)$ or $(7 + \delta)_T$ value. These values were calculated using the following equation:

$$(7 - \delta \text{ or } 7 + \delta)_T = (7 - \delta \text{ or } 7 + \delta)_{25} - (Mw/16W), \quad (9)$$

where $(7 - \delta)$ or $(7 + \delta)_T$, $(7 - \delta)$ or $(7 + \delta)_{25}$, M , w and W are respectively the oxygen stoichiometry at T , oxygen stoichiometry at 25°C, molecular weight of the characterized oxide at 25°C, weight loss at temperature t and weight of the characterized oxide at 25°C. The measured $(7 - \delta)$ or $(7 + \delta)_T$ values for different oxides are shown in figure 3. The correlation between the oxygen stoichiometry, structural and superconducting properties of these oxides has been discussed elsewhere (Segre *et al* 1987; Sunshine *et al* 1987; Maeno *et al* 1987; Xiao *et al* 1988a, b; Mazumder *et al* 1988; Singh *et al* 1988; Kajitani *et al* 1988).

Figure 3. Oxygen stoichiometry ($7 \pm \delta$) determined as a function of temperature ($^{\circ}\text{C}$) in oxide superconductors.

4. Conclusion

A simple but reliable thermogravimetric method has been established for determination of oxygen stoichiometry in 1:2:3 and metal substituted 1:2:3 oxide superconductors.

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