

## Nature and Extent of Oxygen Nonstoichiometry in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$

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Oxygen nonstoichiometry in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  has been investigated using a number of thermogravimetric and titrimetric techniques. Apparent discrepancies between the results obtained by different methods have been resolved and can be explained by consideration of the chemical processes involved in the analytical procedures. For samples prepared in air at 850°C and air quenched the total oxygen constant is 8.19 O per formula unit. Titrimetric measurements show that there are two components to the oxygen excess in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ . One, 0.14 O, leads to oxygen evolution on dissolution; the other, 0.05 O, retains its high oxidation state on dissolution. Thermogravimetric measurements also show that the oxygen excess consists of these two components. One part, 0.06 O per formula unit, can be removed by heating in air at temperatures just below melting and is easily reduced by hydrogen. The remainder, 0.13 O, is more difficult to remove, persisting after most of the bismuth and copper oxygens have been removed by hydrogen. © 1990 Academic Press, Inc.

### Introduction

Oxygen nonstoichiometry is a common feature in the high temperature superconducting copper oxides. The degree of nonstoichiometry is an important parameter in determining the superconducting properties. In  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , for example, it is possible to prepare a range of oxygen nonstoichiometries by varying preparation conditions (1, 2). The superconducting critical temperature decreases with  $x$ , although the form of this dependence depends upon the method of preparation (1-3). The magnitudes of the changes in oxygen content obtained by annealing  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  under different conditions are much less than those obtained for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , although the changes in critical temperature are also dramatic (4, 5).

The oxygen content of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  has

been investigated by thermogravimetry (1, 6, 7), iodometric titration (8), citrate modified iodometry (9),  $\text{Fe}^{2+}$  titration (10, 11), and oxygen evolution methods (12, 13). The results obtained are generally in agreement, with, for example, most methods giving an oxygen content of 6.92-7.00 for samples slowly cooled in oxygen. There have also been a number of conflicting reports, for instance, a total oxygen content of 6.71 was obtained for a sample slowly cooled in oxygen by  $\text{Fe}^{2+}$  titration (11). These discrepancies may be due to poor quality samples; however, care is also needed to ensure that the quantity measured corresponds to the total oxygen content; different methods/procedures may measure different quantities.

The oxygen content of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  has not been widely investigated, largely because of the difficulty of preparing single

phase samples. Thermogravimetry is rarely used because of problems associated with volatilization of Bi. Some titrimetric determinations have been made using  $\text{Fe}^{2+}$  titrations (4, 14) and iodometry (15); however, the reported values vary greatly.

In this study we have used a range of thermogravimetric and titrimetric methods to investigate oxygen nonstoichiometry in well-characterized, single phase samples of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ .

## Experimental

Single phase polycrystalline samples of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  were prepared by reacting appropriate amounts of  $\text{Bi}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ , and  $\text{CuO}$  in gold foil boats. Samples were initially fired at 700–800°C for 1 day, ground, and refired at 880°C for 1 day. The samples were then reground, pressed into pellets, and fired at 880°C. After 3 days at 880°C, the pellets were removed from the furnace and air quenched. Completion of reaction was checked by X-ray powder diffraction (Guinier-Hagg), ensuring that the observed pattern contained only the subcell and supercell reflections expected for single phase  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  (16). Transmission electron microscopy indicated the presence of only one crystalline phase and no amorphous phases. As no significant weight loss (<0.1%), other than that due to carbonate decomposition, was observed during the preparation procedure, the composition of the resulting phase must correspond to  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ .

Thermogravimetric analyses were performed on ~75-mg samples of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  in alumina crucibles using a Stanton Redcroft STA 1500 combined TG/DTA. Titrations were performed on ~0.1-g samples, repeating each determination 5–10 times. Four titration techniques were used:

1. *Standard iodometry.* The sample was dissolved, under argon, in 15 ml of 50%

HCl containing 2 g of potassium iodide. After dissolution, the solution was diluted with 25 ml of distilled water and the liberated iodine determined by titration with 0.05 M  $\text{Na}_2\text{S}_2\text{O}_3$ , using a microburette. Starch was used as indicator, adding 1–2 drops of 1% (w/v) starch solution, when the colour due to iodine started to disappear. The oxygen content was calculated assuming that the final oxidation state of copper was +1.

2. *Neutral iodometry.* The sample was dissolved in 15 ml of 50% HCl, Ar gas bubbled through for 5 min and 25 ml distilled water added. The solution was then neutralized with 2 M  $\text{Na}_2\text{CO}_3$  solution and 2 g KI added. The liberated iodine was titrated with 0.05 M  $\text{Na}_2\text{S}_2\text{O}_3$  and the oxygen content calculated assuming that all the copper was converted to  $\text{Cu}^+$ .

3. *Citrate iodometry (9).* The sample was dissolved in 2 ml of ice-cold 4 M HBr, 5 ml of 1 M sodium citrate added, and the solution neutralized with 2 M  $\text{Na}_2\text{CO}_3$ . Twenty milliliters of cold 0.2 M KI was added and the liberated iodine determined with 0.05 M  $\text{Na}_2\text{S}_2\text{O}_3$ . Citrate stabilized  $\text{Cu}^{2+}$  by complex formation, decreasing the redox potential of the  $\text{Cu}^{2+}/\text{Cu}^+$  couple; hence, the final oxidation state of copper was +2.

4.  *$\text{Fe}^{2+}/\text{Fe}^{3+}$  titration.* The sample was dissolved in 25 ml of 0.001 M  $\text{FeSO}_4$  in 50% HCl. The residual  $\text{Fe}^{2+}$  was determined by titration with 0.0002 M  $\text{Na}_2\text{Cr}_2\text{O}_7$  using barium diphenylamine-sulfonate as an indicator. Oxygen content was calculated assuming a final oxidation state for Cu of +2.

## Results

### Thermogravimetry

The thermogravimetry of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  was investigated in air using a stepwise heating program, holding isothermally at each stage, for at least 30 min until constant weight was achieved (Fig. 1). No

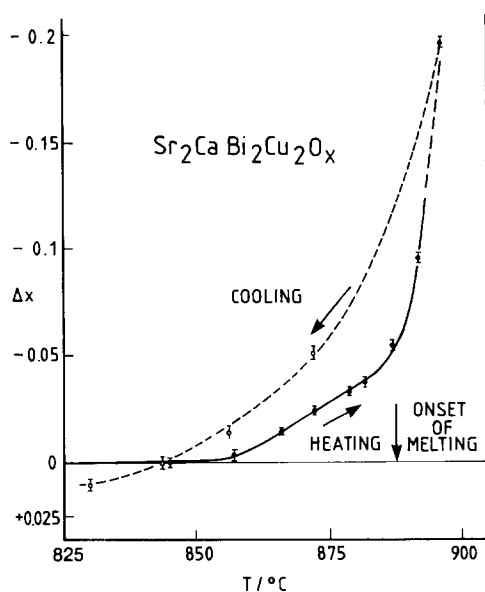


FIG. 1. Thermogravimetric response of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ , heated in a series of isothermal steps in air.

weight change was observed below  $850^\circ\text{C}$ . Between  $850^\circ\text{C}$  and melting temperature ( $888^\circ\text{C}$ ) weight decreased approximately linearly with temperature. The weight loss between  $850^\circ\text{C}$  and melting temperature,

which was reversible, corresponded to a loss of 0.05 oxygens per formula unit. Above the melting point, weight decreased sharply with temperature. On cooling the sample regained more weight than it had lost; however, the recrystallized material consisted largely of a phase with the same X-ray powder diffraction pattern as  $\text{Bi}_{2.1}\text{Sr}_{1.9}\text{CuO}_{6+\delta}$  (17).

The absolute stoichiometry of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  was investigated by temperature-programmed reduction in a 5%  $\text{H}_2$ :95%  $\text{N}_2$  atmosphere. A sample was heated at  $10^\circ\text{C min}^{-1}$  with isothermal holds at  $578^\circ\text{C}$  and  $860^\circ\text{C}$  (Fig. 2). Three stages of weight loss were observed. The first stage occurred between  $350^\circ\text{C}$  and the isothermal hold at  $578^\circ\text{C}$  and corresponded to a loss of  $5.06 \pm 0.01$  oxygens per formula unit. A second, much smaller, step was observed between  $700^\circ\text{C}$  and  $800^\circ\text{C}$ , corresponding to a loss of  $0.13 \pm 0.01$  oxygens per formula unit. The third stage which partially overlapped with the second stage, involved a steady loss of weight as the sample was heated beyond  $800^\circ\text{C}$ . Weight loss continued during the isothermal hold at  $860^\circ\text{C}$ . This final stage is

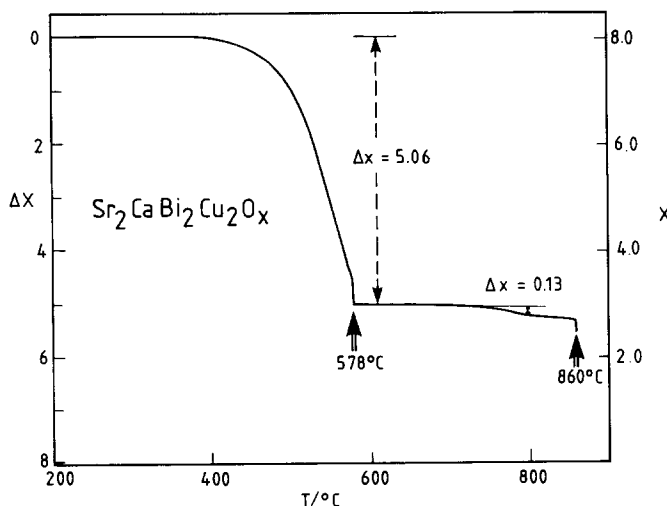
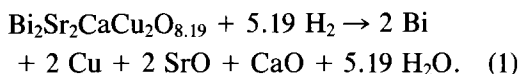


FIG. 2. Thermogravimetric response of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  in 5%  $\text{H}_2$ /95%  $\text{N}_2$ , heated at  $10^\circ\text{C min}^{-1}$  with isothermal holds at  $578^\circ\text{C}$  and  $860^\circ\text{C}$ .

thought to be associated with the loss of bismuth metal, as bismuth contamination of the hangdown in the thermogravimetric balance was observed after cooling.

X-ray powder diffraction of the residue after temperature-programmed reduction showed the presence of Cu, Bi, and (Sr, Ca)O. Thus the overall reduction reaction can be written as



### Titrimetric

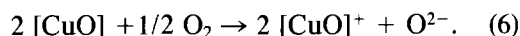
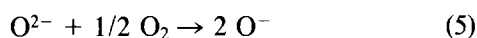
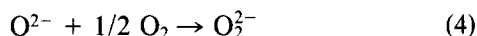
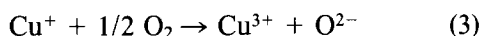
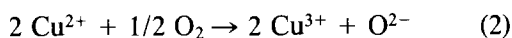
The oxygen content of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  was also investigated using the four different titrimetric procedures; the results of these determinations are given in Table I. Two values were obtained for  $x$ ; one, 8.19, was obtained by standard iodometry and citrate iodometry; the other, 8.05, was obtained by neutral iodometry and  $\text{Fe}^{2+}$  titration. Increasing the concentration of  $\text{Fe}^{2+}$  from 0.001 to 0.005  $M$  did not alter the result obtained, 8.045, although a slightly higher value, 8.06, was obtained by using 0.025  $M$   $\text{Fe}^{2+}$ . Although, there appears to be conflict between the results obtained by the various methods, the values obtained correspond closely to the two components of the oxygen content obtained by thermogravimetry.

TABLE I  
OXYGEN CONTENT OF  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$  OBTAINED BY DIFFERENT TITRIMETRIC PROCEDURES

Procedure	$x$	SD
Standard iodometry	8.2	$\pm 0.1$
Neutral iodometry	8.05	$\pm 0.02$
Citrate iodometry	8.19	$\pm 0.01$
$\text{Fe}^{2+}/\text{Fe}^{3+}$	8.045	$\pm 0.005$

### Discussion

A number of possible mechanisms for incorporation of excess oxygen into the lattice of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  are given in Eqs. (2-6):



It has been a matter of some contention whether the introduced holes occupy Cu  $3d$ ,  $\text{Cu}^{3+}$ , or O  $2p$ ,  $\text{O}_2^{2-}$ , orbitals; however, it is more likely that they occupy bands with both  $\text{Cu}^{3+}$  and  $\text{O}_2^{2-}$  character,  $[\text{CuO}]^+$  in Eq. (6).

In order to analyze the oxygen content of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$  it is necessary to destroy the lattice, either by dissolving in acid or by thermal decomposition. During the disruption processes, the holes will reoxidize the lattice. This will lead to either oxygen evolution or the formation of isolated  $\text{Cu}^{3+}$  and/or  $\text{O}_2^{2-}$  ions.

The apparent discrepancies between the titration results can be explained by considering the chemistry involved in the titrimetric procedures. Standard redox potentials of the species likely to be encountered in the determinations (Fig. 3) show that both  $\text{Cu}^{3+}$  and peroxidic oxygen are strong oxidizing agents and so will oxidize the reducing agents used in the determinations, i.e.,  $\text{I}^-$ ,  $\text{Fe}^{2+}$ . The redox potential for the reduction of oxygen to peroxide is much less than that for reduction of  $\text{Cu}^{3+}$  or  $\text{O}_2^{2-}$ . Indeed, the redox potential for  $\text{O}_2$  reduction is less than that for the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  couple and is only greater than that for the  $\text{I}_3^-/\text{I}^-$  couple if  $\text{pH} < 2$ . Thus, evolved oxygen would not be detected by  $\text{Fe}^{2+}$  titration or by neutral iodometry, explaining the discrepancy be-

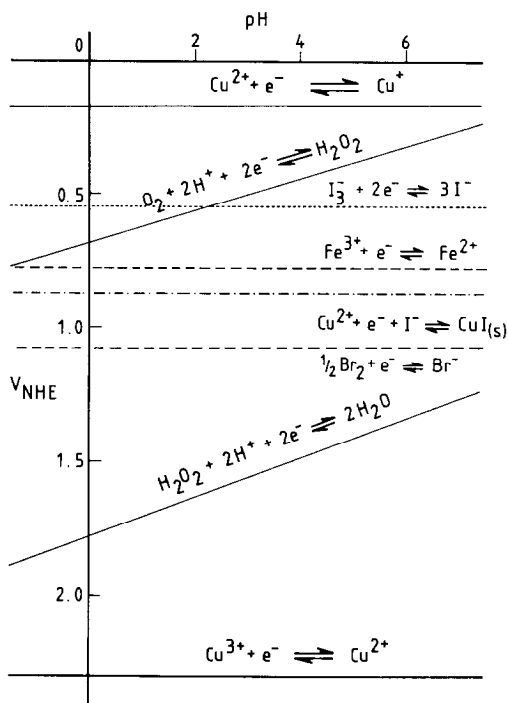


FIG. 3. Standard redox potentials at 25°C.

tween these methods and standard iodometry.

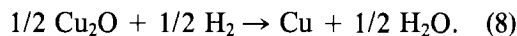
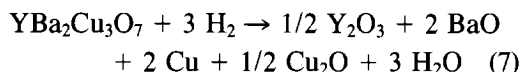
Citrate iodometry would not detect evolved oxygen either, as the redox potential for  $\text{Br}_2/\text{Br}^-$  is too large; however, the large concentration of reducing agent (4 M) present at dissolution prevents oxygen evolution. If a high enough concentration of reducing agent is present, the holes in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  will oxidize the reducing agent rather than the lattice. In neutral iodometry, no iodide is present during dissolution and in the  $\text{Fe}^{2+}$  titration only 0.001 M  $\text{Fe}^{2+}$  was used. Other workers (14), using higher concentrations of  $\text{Fe}^{2+}$ , have obtained larger values for the oxygen content of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ . We also obtained a larger value with high concentrations of  $\text{Fe}^{2+}$ , 0.025 M; however, our results indicate that the concentration of  $\text{Fe}^{2+}$  used in the determinations, 0.001 M, was too low to

compete successfully with oxygen evolution.

Titrimetric measurements show that there are two components to the oxygen excess,  $\delta = 0.19$ , in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ . One, 0.14 O, leads to oxygen evolution on dissolution; the other, 0.05 O, retains its high oxidation state on dissolution. Thermogravimetric measurements also show that the oxygen excess consists of these two components. One part, 0.06 O per formula unit, can be removed by heating in air at temperatures just below melting and is easily reduced by hydrogen. The remainder, 0.13 O, is more difficult to remove, persisting after most of the bismuth and copper oxygens have been removed by hydrogen.

Peroxides form stable species on dissolution and decompose readily on heating; the smaller component of the oxygen excess, 0.06 O, behaves similarly.  $\text{Cu}^{3+}$  does not normally form a stable species on dissolution, instead it reacts with either water or the oxide lattice to release oxygen; thus the larger component, 0.13 O, behaves in a similar manner to  $\text{Cu}^{3+}$  on dissolution.

The two stage loss of oxygen in temperature-programmed reduction is reminiscent of the behavior of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (6, 18).  $\text{YBa}_2\text{Cu}_3\text{O}_7$  loses 3 O per formula unit on heating to 600°C and then 0.5 O between 700 and 900°C. These decomposition processes can be represented by Eqs. (7 and 8):



By analogy, the high temperature loss of oxygen in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  can be attributed to the reduction of  $\text{Cu}_2\text{O}$  to Cu metal. It is unlikely that this  $\text{Cu}_2\text{O}$  arises from the decomposition of peroxidic species; thus, the larger part of the oxygen excess, 0.13 O, again appears to be associated with  $\text{Cu}^{3+}$  character.

## Conclusions

Thermogravimetric and titrimetric investigations of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$  both show that the oxygen excess consists of two components. These are thought to reflect the band in which the superconducting holes are located. In samples, prepared by air quenching from  $880^\circ\text{C}$ , this band contains 0.19 holes per formula unit and appears to have  $2/3 \text{Cu}^{3+}$  character and  $1/3 \text{O}_2^{2-}$  character.

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