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OXYGEN STOICHIOMETRY AND ITS INFLUENCE ON SUPERCONDUCTIVITY IN $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$

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Abstract:

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ (2212) was synthesized from freeze-dried precursors. The oxygen content of 2212 was determined as a function of temperature and oxygen partial pressure and the variation of T_c with oxygen content was determined. It was found that 2212 without excess oxygen ($x=0$) is superconducting. This points to the role of the $(\text{Bi-O})_\infty$ layers as a source for holes in 2212. Four probe resistivity measurements were also performed on 2212. The nature of oxygen intercalation and oxygen removal in 2212 was studied by thermogravimetry and resistivity. It was also found that samples of 2212 with the same oxygen content had different T_c 's depending on thermal history. This difference in T_c is thought to arise from oxygen occupying different sites in the lattice while maintaining the same total oxygen content.

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1. Introduction:

Oxygen stoichiometry is known to have an important effect on the properties of high T_c cuprate superconductors. The effect of oxygen stoichiometry has been extensively studied in $\text{YBa}_2\text{Cu}_3\text{O}_x$ ¹⁻⁵ as well as in the $\text{La}_{2-x}(\text{AE})_x\text{CuO}_{4+z}$ ⁶⁻⁸ systems (where AE is an alkaline earth such as Sr or Ba). For these cuprates it has been demonstrated that T_c goes through a maximum for a particular value of oxygen content, corresponding to an optimum hole concentration.

The oxygen stoichiometry of superconductors in the Bi-Sr-Ca-Cu-O system, however, has not been as extensively studied due to the difficulty of synthesizing pure phases with known stoichiometry. In addition, oxygen content analysis by thermogravimetry is complicated by the presence of volatile species such as Bi and Pb. Though carefully controlled titration experiments on $\text{Bi}_2\text{Sr}_{1.88}\text{Ca}_{1.00}\text{Cu}_{2.14}\text{O}_y$ have yielded the valences of Bi and Cu,⁹ the presence of two redox couples makes the determination of oxygen content from such experiments difficult. There remains much divergence in the data concerning $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$; some reports indicate that the oxygen nonstoichiometry is small, with the oxygen content being very close to 8.0,¹⁰ whereas others indicate that the oxygen content is about 8.2 and relatively insensitive to oxygen partial pressure and temperature.¹¹ Recently, thermogravimetry has been shown to be effective in determining the oxygen content of 2212 in the absence of Pb.¹² Previously¹³, we had reported the successful synthesis of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ (2212) with the exact cation stoichiometry of Bi:Sr:Ca:Cu = 2:2:1:2. The oxygen content of 2212 as a function of oxygen partial pressure (P_{O_2}) and temperature (T) was investigated. In this paper we report high temperature resistivity measurements carried out as a function of T and P_{O_2} . The kinetics of oxygenation and deoxygenation of 2212 were studied by thermogravimetry and resistivity. The variation of T_c with oxygen nonstoichiometry and oxygen ordering was also studied.

2.0 Experimental:

Samples with the stoichiometry Bi:Sr:Ca:Cu = 2:2:1:2 were synthesized from freeze dried nitrate precursors as reported earlier.¹⁴ The phase purity of the powders was determined from X-ray diffraction (XRD), scanning electron microscopy (SEM) and scanning/transmission electron microscopy (STEM) coupled with electron microprobe and energy dispersive spectroscopy (EDS). Magnetic susceptibility measurements were made

on a SQUID magnetometer to determine the T_c as well as the presence of any secondary superconducting phases.

The oxygen content of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ was determined by thermogravimetry as described previously.¹³ Standard four probe resistivity measurements were carried out on bar shaped 2212 sintered samples. The kinetics of oxygen intercalation and deoxygenation in 2212 were studied out by thermogravimetry and resistivity.

It should be noted here that all the following results for oxygen content and T_c refer to the precise stoichiometry of $\text{Bi}:\text{Sr}:\text{Ca}:\text{Cu} = 2:2:1:2$. It is difficult to synthesize 2212 with exact cation stoichiometry by conventional ceramic techniques. These techniques¹⁵ usually yield samples with $\text{Bi}:\text{Sr}$ ratio > 1 which can be expected to result in values for oxygen content and T_c at variance with those reported in this paper.

3.0 Results:

3.1 MEASUREMENT OF OXYGEN CONTENT

The oxygen content of the samples was measured by reducing the sample in a 10% H_2 - 90% N_2 mixture and calculating the weight change based on the following reaction:

The error in the measurement (for the thermogravimetric system used in these experiments) is approx. 0.2% of the oxygen content. The results of the experiments on the oxygen content at different temperatures and oxygen partial pressures are summarized in the graph shown in Figure 1. There appear to be two regimes of behavior for 2212. Below 800°C the oxygen content of 2212 is relatively insensitive to Po_2 and is determined only by temperature. Above 800°C the oxygen content depends on both temperature and Po_2 .

Figure 1: Oxygen content as a function of temperature (T) and oxygen partial pressure (Po₂) in Bi₂Sr₂CaCu₂O_{8+x}. Above 800° C the oxygen content of 2212 depends on T and Po₂. Below 800° C the oxygen content is independent of Po₂.

3.2 RESISTIVITY MEASUREMENTS AS A FUNCTION OF T AND PO₂

Standard four probe resistivity measurements were carried out on sintered bar shaped samples. The results are summarized in Figure 2. Changes in resistivity with T and Po₂ follow the same trends as changes in oxygen stoichiometry. There is no change in resistivity with Po₂ for temperatures below 800° C while for 800° C resistivity changes with Po₂.

3.3 CHANGES IN LATTICE PARAMETER AND T_C WITH OXYGEN CONTENT

Changes in lattice parameter were studied by X ray diffraction. The variation of lattice parameter with oxygen content is shown in Figure 3a. T_C's of samples with different oxygen contents were determined by magnetization measurements performed on a squid magnetometer. The variation of T_C with oxygen content of 2212 is shown in Figure 3b. It is interesting to note the close relationship between T_C and structure. Both 'c' axis and T_C have similar variations with oxygen content. An important point to note here is that excess

oxygen is not required for 2212 to be superconducting. Samples with the ideal stoichiometry of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8.0}$ are superconducting with a T_C of 84 K.

Figure 2: Conductivity of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ with T and Po_2 . Two distinct regimes are observed. Below 800°C the oxygen content is independent of Po_2 and varies with T. Above 800°C the oxygen content is a function of both T and Po_2 .

3.4 KINETICS OF OXYGEN INTERCALATION AND DEOXYGENATION IN 2212

Both thermogravimetry and resistivity measurements were made as a function of time. The changes in weight with changes in Po_2 (which are attributed to the changes in the oxygen content of the sample) are shown in Figure 4a. It can be seen that the rate of oxygen removal from the sample is much slower than the rate of oxygen intercalation. The process is reversible and can be repeated to give identical weight changes. A further confirmation of this anomaly in the kinetics of oxygen intercalation and deoxygenation is seen from resistivity measurements. The change in resistivity with time as the Po_2 is changed is plotted in Figure 4b. The resistivity shows the same behavior as the weight change. The change in resistivity is much slower as the Po_2 is decreased, as compared to when it is increased, implying that the rate of oxygen removal from the sample is much slower than the rate of oxygen intercalation.

a)

b)

Figure 3: a) Variation of 'c' axis of 2212 with oxygen content.

b) Variation of T_c as a function of oxygen content in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$. T_c goes through a maximum for an oxygen content of 8.13.

a)

b)

Figure 4: a) TGA plot indicating change in weight of the sample associated with changes in the oxygen content of 2212 as the P_{O_2} is changed between 20% and 1%. Oxygen removal from 2212 proceeds at a slower rate than oxygen introduction. This anisotropy could be attributed to the oxygen occupying different sites in the lattice.

b) Resistivity data showing the changes in resistivity of 2212 at 810°C as the P_{O_2} is varied. The resistivity data show the same anisotropy for oxygen intercalation of 2212 as the TGA data. The removal of oxygen from the sample proceeds more slowly than the introduction of oxygen.

4.0 Discussion

Solid state techniques used to synthesize 2212 result in samples which have a cation stoichiometry different from the ideal chemical formula. The use of freeze dried precursors in addition to ensuring high purity, leads to 2212 which has the cation stoichiometry of $\text{Bi}_{2.0}\text{Sr}_{2.0}\text{Ca}_{1.0}\text{Cu}_{2.0}\text{O}_{8+x}$. This allows the study of the oxygen stoichiometry in the absence of effects due to cation nonstoichiometry which can significantly influence parameters such as T_c .

The nature of the change in oxygen content above 800°C is different from that below 800°C . Above 800°C the oxygen content is a function of temperature and Po_2 that is similar to that of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_y$ and $\text{YBa}_2\text{Cu}_3\text{O}_x$. Below 800°C the behavior is quite different, in that the oxygen content is independent of Po_2 . A possible explanation for the behavior below 800°C , advanced by Fueki et al,⁹ is that neutral oxygen is incorporated in the $(\text{Bi-O})_\infty$ layers.

An important result is that $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8.0}$ is superconducting ($T_c = 84\text{ K}$) without the presence of excess oxygen. This behavior is unlike the other cuprate superconductors, where an excess of oxygen (or doping) is necessary for superconductivity. 2212 has an intrinsic carrier concentration that does not arise from oxygen nonstoichiometry. The $(\text{Bi-O})_\infty$ layers in 2212 are thought to act as a source for holes,¹⁶⁻¹⁹ with the total carrier concentration arising from both the $(\text{Bi-O})_\infty$ layers as well as oxygen nonstoichiometry. The charge transfer may be represented by the following reaction:

X-ray absorption near-edge spectroscopy (XANES) measurements have recently confirmed the role of the $(\text{Bi-O})_\infty$ layers as a source for holes.¹⁹ The role of the $(\text{Bi-O})_\infty$ layers is not independent of the oxygen stoichiometry and their effect is more pronounced when the oxygen nonstoichiometry is small. The maximum of $T_c = 87\text{ K}$ occurs for an oxygen content of 8.12 ($x=0.12$) and drops to 76 K for an oxygen content of 8.2 ($x=0.2$).

It is observed, from the combination of conductivity and oxygen nonstoichiometry data, that the conductivity of 2212 is closely related to oxygen content. At lower temperatures (corresponding to higher oxygen contents) the conductivity is higher,

indicating that the holes introduced by the excess oxygen are responsible for the increase in conductivity. The behavior of conductivity with changes in Po_2 mirror those of oxygen content. Below 800°C both conductivity and oxygen content are independent of Po_2 while above 800°C both decrease as the Po_2 is decreased. This illustrates the fact that the anion nonstoichiometry closely controls the hole concentration. Further, it is seen that there is a close relationship between the 'c' axis and T_c (or hole concentration). It has been proposed²¹ that changes in the 'c' axis lead to a redistribution of holes between the $(\text{Bi-O})_\infty$ and Cu-O layers. Oxygen is first removed from the $(\text{Bi-O})_\infty$ layer leading to a slight increase of 'c' and T_c . Further oxygen is then removed from the Cu-O layer causing a decrease in T_c and the 'c' axis.

Another important aspect is the influence of the position of oxygen in the 2212 lattice on superconducting properties. Samples with the same oxygen content but with different thermal histories have very different T_c 's. This is illustrated by the magnetic susceptibility curves shown in Figure 5 for two different samples of 2212, each with an oxygen content of 8.28. Sample A was cooled rapidly in a 22% O_2 atmosphere while Sample B was cooled very slowly to ensure equilibration at each point. It is clear that Sample B, ($T_c = 74\text{ K}$) which was slowly cooled, has a much lower T_c than Sample A ($T_c = 82\text{ K}$). (It should be noted that the T_c of sample B is slightly lower than that expected from Figure 4b. This difference is attributed to the much slower cooling rate of Sample B as compared to the samples used to determine T_c in Figure 3b. These samples were quenched from 810°C to various temperatures and then annealed).

Figure 5. Magnetic Susceptibility curves for two 2212 samples having the same oxygen content (8.28). The slow cooled sample has a T_c of 74 K while the rapidly cooled sample has a T_c of 82 K.

The kinetics of oxygen intercalation and deoxygenation may provide some insight into the cause for these differences in T_C depending on thermal history. As shown in Figures 4a and 4b the rates of oxygenation and deoxygenation are different. This again points to the fact that oxygen occupies two distinct sites in the lattice. The oxygen may first be introduced into the $(\text{Bi-O})_\infty$ layer, and then on equilibration into the Cu-O layer. The position of oxygen controls the hole concentration which in turn affects T_C . Thus the total oxygen content is not sufficient in determining the hole concentration, the position of the excess oxygen in the 2212 lattice plays a significant role in determining T_C .

The effect of thermal history on T_C in 2212 parallels that of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. In the Y-Ba-Cu-O system there exists a *tetragonal* polymorph of the superconducting phase, with an oxygen content of 6.9 (i.e.: $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$), in which the oxygen is disordered on the (Cu-O_2) planes.²² The oxygen content of $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ should clearly place it in the superconducting regime, however, the fully oxygenated tetragonal polymorph is nonsuperconducting. In 2212, however, the effect of differences in the position of oxygen in the lattice is to suppress T_C rather than completely destroy superconductivity. This may be due to the fact that oxygen nonstoichiometry alone is not responsible for superconductivity and the hole carrier concentration arising from the $(\text{Bi-O})_\infty$ layers compensates for this effect.

5.0 Conclusions:

Through the use of freeze-dried precursors, it was possible to synthesize phase pure $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ with ideal cation ratios. The oxygen nonstoichiometry as a function of temperature and oxygen partial pressure indicates two distinct regimes of behavior. Above 800° C the oxygen content is a function of both temperature and P_{O_2} , whereas below 800° C the oxygen content is independent of P_{O_2} . These results are confirmed by resistivity measurements as a function of T and P_{O_2} . High temperature resistivity measurements when viewed in conjunction with the results of oxygen nonstoichiometry point to the fact that the hole concentration is closely linked to the oxygen nonstoichiometry.

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ with the stoichiometric amount of oxygen, 8.0 (i.e. $x=0$), was found to be superconducting with a T_C of 84 K. This demonstrated the fact that oxygen excess is not required for superconductivity in 2212. The $(\text{Bi-O})_\infty$ layers act as a source of holes in this system. It was also found that the total oxygen content in 2212 is not sufficient to determine T_C . Samples with the same oxygen content but different thermal histories had

different T_c 's. The differences in T_c could be a result of the oxygen occupying different sites in the 2212 lattice while maintaining the same total oxygen content. This is also illustrated by the differences in rates of oxygenation and deoxygenation of the 2212 samples.

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