

## The Oxygen Content of the High-Temperature Superconducting Compound $\text{Bi}_{2+x}\text{Sr}_{3-y}\text{Ca}_y\text{Cu}_2\text{O}_{8+d}$ with Respect to Varying Ca and Bi Contents

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### Abstract

The oxygen content of  $\text{Bi}_{2+x}\text{Sr}_{3-y}\text{Ca}_y\text{Cu}_2\text{O}_{8+d}$  (2212 phase) has been determined as a function of its cation concentration. With increasing Ca and Bi content the oxygen content increases and  $T_C$  decreases. The oxygen content of Ca rich 2212 phase increases with decreasing annealing temperatures. The study shows that the  $T_C$  of the 2212 phase primarily is controlled by its cation concentration.

### 1. Introduction

The oxygen content of the 2212 phase with respect to varying cation concentrations of the phase has not yet been determined in detail, although the phase exhibits an extended single phase region which allows considerable deviations from the ideal formula  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$  [1,2]. In addition, the  $T_C$  of the phase obviously is a function of the Sr, Ca and Bi content [1,3]. The question arises, whether the  $T_C$  is controlled by the oxygen content directly or by the cation concentration which of course influence the oxygen content of the phase.

### 2. Experimental

Samples were prepared along the concentration range  $\text{Bi}_{2.18}\text{Sr}_{3-y}\text{Ca}_y\text{Cu}_2\text{O}_z$  with  $y = 0.8, 0.9, 1.1, 1.3, 1.45, 1.5$  and  $1.7$ . A second batch of samples were prepared

with varying Bi contents referring  $\text{Bi}_{2+x}\text{Sr}_2\text{CaCu}_2\text{O}_z$  with  $x = 0.125, 0.18, 0.2$  and  $0.3$ . The samples were sintered for 24 hours at  $820\text{ }^\circ\text{C}$  in air. Subsequently, the samples were regrinded, pressed, sintered at the same temperature for 60 hours and furnace cooled. Finally, the samples were annealed at  $670\text{ }^\circ\text{C}$  in flowing nitrogen for 15 hours in order to reach high  $T_c$  values. Phase identification has been performed using a Scanning Electron Microscope with EDX (Cambridge Instruments S 200), X-ray diffraction (Philips PW 1050,  $\text{CuK}$  ) and optical microscopy (Zeiss Axiomat) using polarized light. The oxygen content has been measured by carrier gas hot extrusion using the Leco Inst. N/O-analysator TC 436. The  $\text{CO}_2$  content of the prepared samples were measured using the Rosemount carbon/hydrogen analysator 5003. The critical temperatures have been determined by AC susceptibility measurements. The standard deviation of the  $\text{CO}_2$  analysis is about 0.005 weight percent and that of the  $T_c$  measurements  $\pm 1\text{ K}$ .

### 3. Results

The prepared samples consist at least of about 95 volume percent 2212 phase. Second phases are  $\text{Ca}_2\text{CuO}_3$ ,  $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41-x}$  and  $\text{CuO}$ . The oxygen content of the prepared samples increases with increasing Ca and Bi content (Fig. 1 and 2). The accuracy of the d-value obviously depends on the second phase content of the samples. The samples having a great deviation of the d-value (e.g. samples with the y-value of 0.9 and 1.7 in Fig. 1) have a second phase content of about 5 percent. Whereas single phase samples (e.g. y-value 1.1 in Fig. 1) exhibit a very narrow deviation of the d-value. However, even with respect to the deviation of the d-value the trend of the d-value with increasing Ca and Bi content of the 2212 phase is clearly seen.

In agreement with the literature data, the  $T_c$  of the prepared samples decreases with increasing Ca and Bi content. The  $\text{CO}_2$  content of a Sr rich ( $\text{Bi}_{2.18}\text{Sr}_{2.1}\text{Ca}_{0.9}\text{Cu}_2\text{O}_{8+d}$ ) and a Ca rich ( $\text{Bi}_{2.18}\text{Sr}_{1.5}\text{Ca}_{1.5}\text{Cu}_2\text{O}_{8+d}$ ) sample have been determined to be 0.06 weight percent. The thermogravimetry measurements reveal that the oxygen content of the 2212 phase increases with

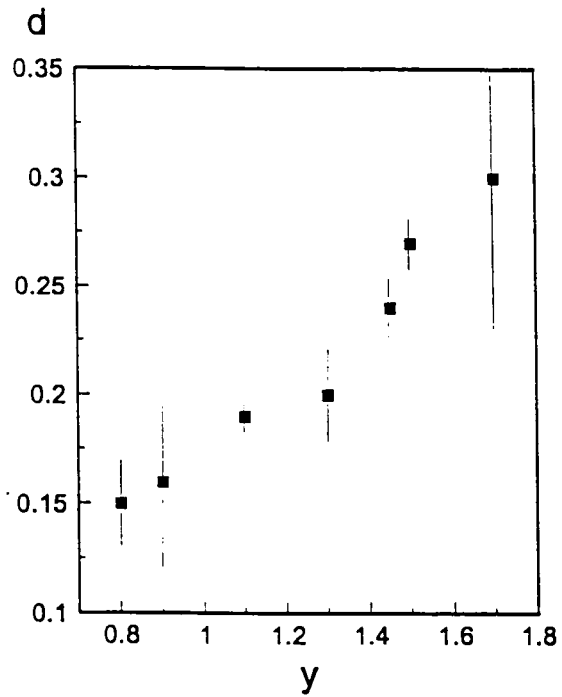


Fig. 1: The oxygen index  $d$  vs. the Ca content.  $y$ -values ref.  $\text{Bi}_{2.18}\text{Sr}_{3-y}\text{Ca}_y\text{Cu}_2\text{O}_{8+d}$ .

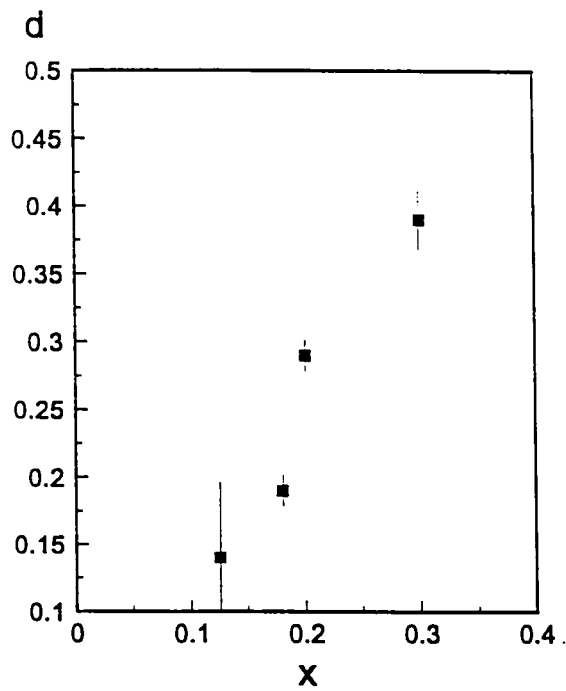


Fig. 2: The oxygen index  $d$  vs. the Bi content.  $x$ -values ref.  $\text{Bi}_{2+x}\text{Sr}_2\text{CaCu}_2\text{O}_{8+d}$ .

decreasing temperature (Fig. 3), which agrees with the results of [4]. In addition, Fig. 3 clearly shows that this increase is a function of the Ca content of the phase and reaches highest values at Ca rich compositions. Simultaneously, with decreasing annealing temperature the  $T_c$  of the 2212 phase decreases (Fig. 4). However, the decrease of  $T_c$  of Ca rich ( $\Delta T_c \approx 10$  K) 2212 phase is much more pronounced than that of Sr rich one ( $\Delta T_c \approx 2$  K).

#### 4. Discussion

With respect to the deviation of the d-value due to the second phase content of the samples, the observed increase of the oxygen content of the 2212 phase is obviously caused by an increased oxygen solubility of the Ca and Bi rich 2212 phase compared to  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+d}$ . The identical  $\text{CO}_2$  contents of the Sr and Ca rich samples give evidence that the observed increase of the oxygen content is not an artefact, i.e. due to unreacted  $\text{CaCO}_3$  in the Ca rich samples.

The enhanced oxygen content of the Bi rich samples is possibly due to the fact, that the Bi ions, which substitute the  $\text{Ca}^{2+}$  and  $\text{Sr}^{2+}$  ions, are three valent. The resulting excess of the positiv charge supposedly is totaly or partly balanced by the observed increase of the oxygen content of the phase. However, the increase of the oxygen content with increasing Ca content of the phase can not be explained by that model, because both Ca and Sr are two valent.

Fig. 5 shows the  $T_c$  values vs. the oxygen index d, published by [5] and the  $T_c$  values and oxygen indices d of the prepared samples with varying Sr:Ca ratios. It is clearly seen that the samples with intermediate Sr:Ca ratios (Sr:Ca  $\approx$  1.7:1.3 to 1.5:1.5) exhibit moderate  $T_c$  values of about 80 K, although they have oxygen contents, which should yield high  $T_c$  values of about 90 K. The reason for this discrepancy supposedly is that the  $T_c$  of the phase is primarily controlled by the cation concentration, especially by the Ca content of the phase. However, considering the prepared samples with enhanced Bi content this effect is not or less pronounced compared to the samples with varying Sr:Ca ratios (Fig. 6). At decreasing temperatures the oxygen content of the 2212 phase was found to

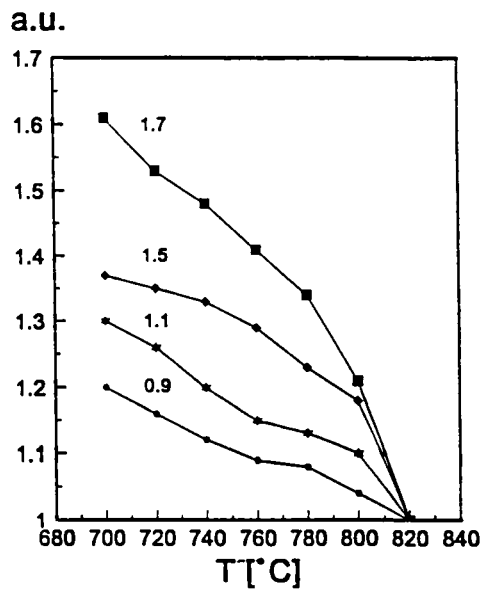


Fig. 3: Oxygen content of the 2212 phase determined by thermo gravimetry measurements vs. temperature. Values are y-values ref.  $\text{Bi}_{2.18}\text{Sr}_{3-y}\text{Ca}_y\text{Cu}_2\text{O}_{8+d}$ .

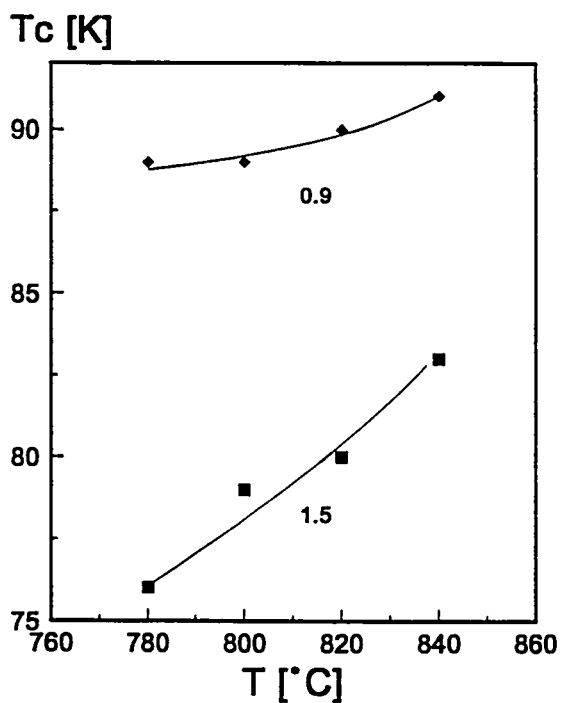


Fig. 4: The  $T_c$  of the 2212 phase vs. temperature. The values are y-values ref.  $\text{Bi}_{2.18}\text{Sr}_{3-y}\text{Ca}_y\text{Cu}_2\text{O}_{8+d}$ .

increase and  $T_c$  was found to decrease which agrees with the results of [4]. Considering Ca rich 2212 phase, the increase of the oxygen content and the corresponding decrease of  $T_c$  is much more pronounced than that of the Sr rich 2212 phase which clearly shows that at constant cation concentration the oxygen content of the 2212 phase significantly influences the  $T_c$ .

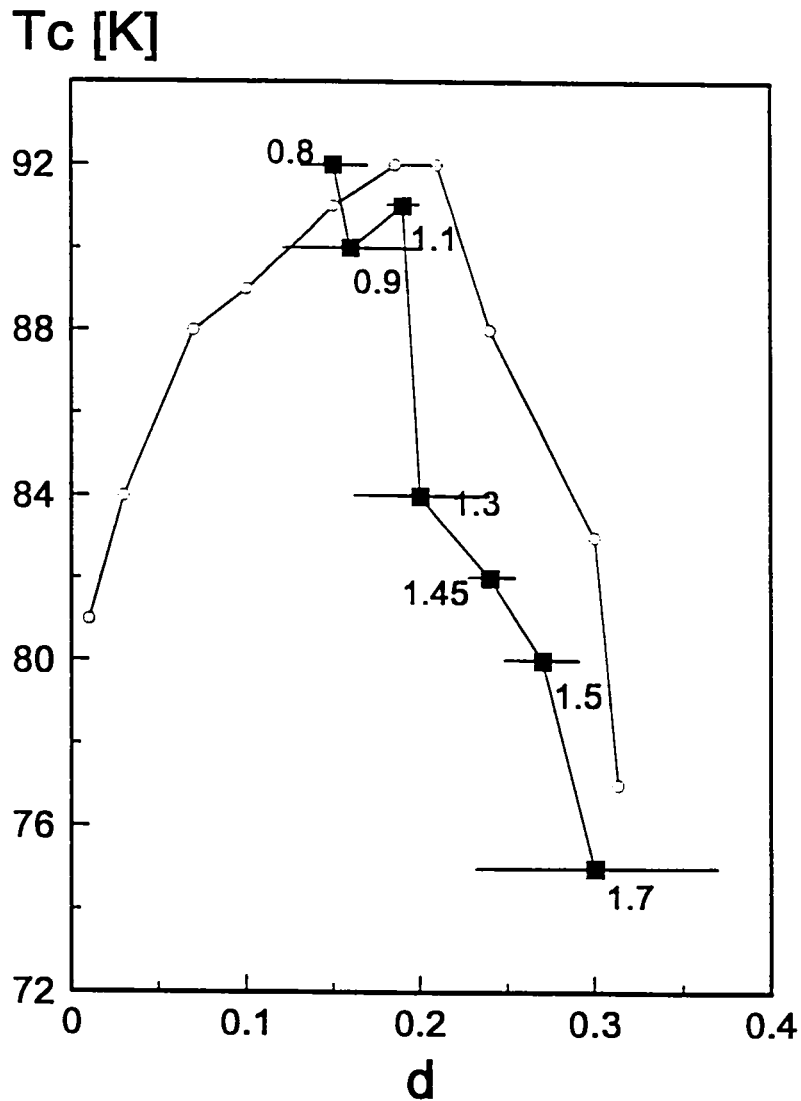


Fig. 5: The  $T_c$  vs. the oxygen index  $d$  of samples with varying Sr:Ca ratios (black squares: this work; grey points: [5]). The values at the squares are the  $y$ -values referring  $\text{Bi}_{2.18}\text{Sr}_{3-y}\text{Ca}_y\text{Cu}_2\text{O}_{8+d}$ .

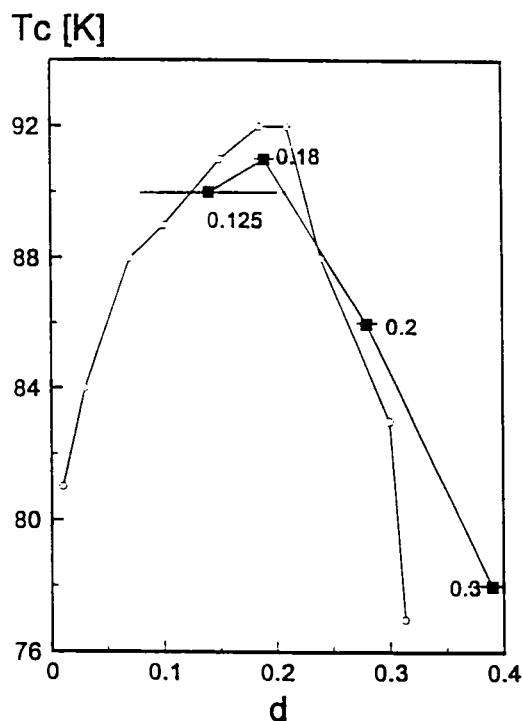


Fig. 6: The  $T_c$  vs. the oxygen index  $d$  of samples with varying Bi contents (black squares: this work; grey points: [5]). The values at the squares are the  $x$ -values referring  $\text{Bi}_{2+x}\text{Sr}_2\text{CaCu}_2\text{O}_{8+d}$ .

## 6. References

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