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Effect of Oxygen Stoichiometry on the Critical Temperature and Thermal Expansion of Two-Layer BiSrCaCu Oxide Superconductors

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Single-phase $Bi_2(Sr,Ca)_3Cu_2O_{8+\delta}$ has been prepared from an initial batching formulation of Bi_2O_3, $1.5SrCO_3$, $1.5CaCO_3$, and 2CuO by solid-state reaction. Oxygen stoichiometry of the compound has been defined by thermogravimetric analysis, and it can be varied by thermal history. Thermal expansions and critical temperatures (T_c) have been obtained for different oxygen stoichiometries. At 500 °C changes of $\Delta\delta = 0.04$, ΔT_c (onset) = −22 K and $\Delta L/L = -0.06\%$ are obtained for an oxygen anneal vs a nitrogen anneal. The stoichiometry effects for $Bi_2(SrCa)_3Cu_2O_{8+\delta}$ are more like $Ba_2YCu_3O_{7-\delta}$ than $Pb_2Sr_2(YCa)Cu_3O_{8+\delta}$.

Introduction

Since the discovery by Maeda[1] et al. that the rare-earth-element-free BiSrCaCu oxide system yields compounds with attractively high T_c's, much work has been directed at obtaining compositions that yield a single-phase ceramic and have a well-defined T_c. It has been found that the kinetics of reaction are slow, and many special schemes have been suggested to increase the rate of formation of the superconducting phase. Among these, a low P_{O_2} atmosphere[2] and the addition of Pb[3,4] and other cations have shown success in yielding large amounts of the three-layer (107 K) phase. Obtaining the single phase has been more difficult, and the compositions, which correspond to the simple cation ratios 2212 or 2223, are not single phase even after extended reaction times.

The effects of oxygen stoichiometry on T_c, lattice parameter, and thermal expansion of the two-layer Pb-free $Bi_2[SrCa]_3Cu_2O_{8-\delta}$ compound have been reported. Buckley[5] found as much as a 16 K shift in T_c with increasing quench temperature for samples annealed in air, while Morris[6] noted a 13 K increase with decreasing P_{O_2} for a 600 °C anneal. This latter shift did not depend on cooling rate. Groen[7] used a larger P_{O_2} range at 600 °C and obtained a 40 K shift for a compound with 10% Y substituted for Ca. All reported a 0.1-Å increase in the *c* lattice parameter for samples equilibrated at the lower P_{O_2}. Buckley calculated an oxygen stoichiometry variation of $\Delta\delta = 0.4$ while the maximum that Groen could measure was $\Delta\delta \sim 0.04$. Groen reported an expansion of +0.06% at 600 °C as the P_{O_2} is decreased. A small peak in the thermal expansion near 300 °C was seen only during the initial heating. A phase transition was suggested as the cause of this anomaly. Other workers have not found significant effects of oxygen stoichiometry in the two-layer (~85 K) superconductor.

Experimental Section

Bi_2O_3, $SrCO_3$, $CaCO_3$, and CuO were mixed by ball milling to yield various formulations near the 2212 composition. After mixing, each composition was prereacted in oxygen at 800 °C for 12 h. Zirconia containers were used to hold the powders during prereaction. After a second ball milling with ZrO_2 media under water, pressed shapes were sintered in oxygen for 100 h at a temperature between 840 and 880 °C. An Ag sheet was used to support the ceramic during firing. X-ray diffraction (XRD) was used to establish whether reaction was complete and whether the formulation yielded single phase. Fully reacted samples were annealed for 4 h at 500 °C in nitrogen, 0.2% oxygen, 5% oxygen, air, or oxygen and furnace cooled. Afterwards, T_c was determined by ac susceptibility. The $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_8$ composition was characterized with respect to thermal expansion in oxygen and nitrogen as well as the compositional expansion while the atmosphere was switched during isothermal heating. Thermogravimetric (TGA) and evolved gas (EGA) analyses on this same composition completed the analyses. Lattice constants for different oxygen stoichiometries were determined from room-temperature and high-temperature XRD measurements.

Table I. Phase Distribution[a] after 860 °C for 100 h in O_2

	batching compn cation content					
	Bi	Sr	Ca	Cu	major phase	minor phase
A	1	1	1	2	A	U
B	2	1	2	2	A	Ca_2CuO_3 U
C	2	1.5	1.5	2	A	
D	2	2	1	2	A	U
E	2	1.2	2	3	A	CuO, Ca_2CuO_3, U
F	2	1.6	2	3	A	U
G	2	2	2	3	A	U

[a] A: pseudotetragonal Aurivillius phase $a/b \sim 5.4$ Å, $c \sim 30.6$ Å, $b^{\#} \sim 4.7$. U: unknown(s) with strong lines at $d = 3.41$, 3.17, 2.96, 2.77, 2.46, and 2.35 Å.

Results and Discussion

Phase Distribution. Table I shows the phase distributions, obtained for the various compositions sintered at 860 °C in oxygen for 100 h. Sample melting and/or reaction with the Ag sheet became appreciable at 870 °C in air or 880 °C in oxygen for most compositions. The choice of a 100-h sintering time was made because shorter times often did not achieve full reaction as indicated by the changes in the relative phase amounts with time. XRD did not find second phase in composition C, and its indexed pattern is shown in Figure 1. The indexing includes a fourth Miller index, which is used to identify the lines that originate from an incommensurate modulation.[8,9] This structural irregularity occurs along the *b* axis and is caused by the insertion of an extra oxygen atom in the Bi layer once every ~4.8 unit cells.[10] The lines are generally

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(1) Maeda, H.; et al. *Jpn. J. Appl. Phys.* **1988**, *27*, L209.
(2) Endo, U.; et al. *Jpn. J. Appl. Phys.* **1988**, *27*, L1476.
(3) Takano, M.; et al. *Jpn. J. Appl. Phys.* **1988**, *27*, L1041.
(4) Cava, R. J.; et al. *Phys. Lett.* **1988**, *153*, 560.
(5) Buckley, R. G.; et al. *Physica C* **1988**, *156*, 629.
(6) Morris, D. E.; et al. *Phys. Rev. B* **1989**, *39*, 6612.
(7) Groen, W. A.; deLeeuw, D. M. *Physica C* **1989**, *159*, 417.
(8) Onoda, M.; et al. *Jpn. J. Appl. Phys.* **1988**, *27*, L833.
(9) Shaw, T. M.; et al. *Phys. Rev. B* **1988**, *37*, 9856.

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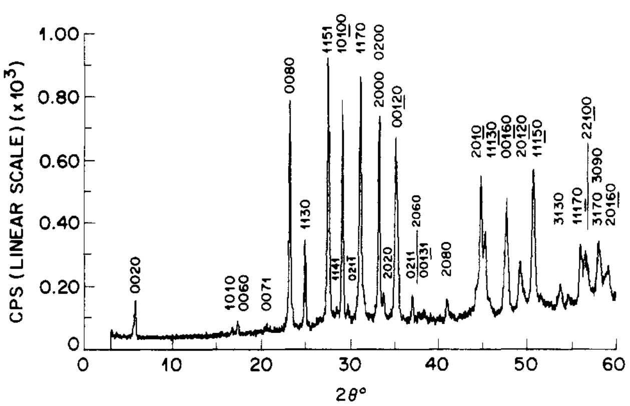

Figure 1. XRD diffraction pattern for $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_{8+\delta}$ heated 860 °C for 100 h in O_2 and slow cooled. Indexing follows Onoda.[8]

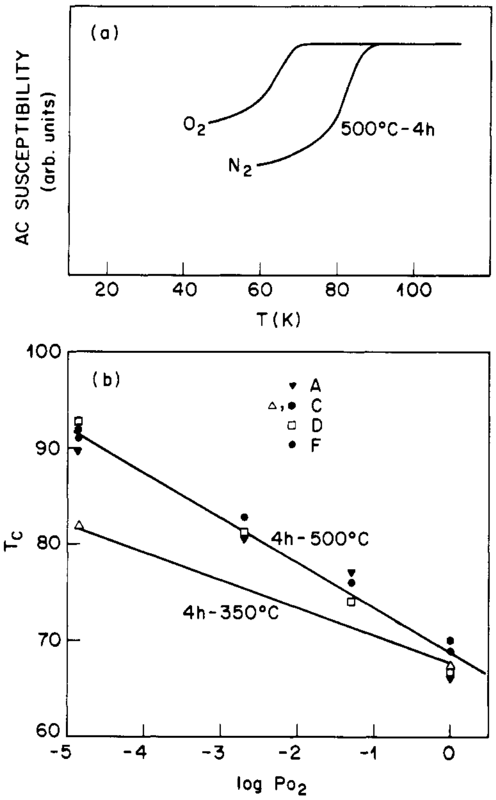

Figure 2. Effect of annealing atmosphere on T_c (onset): (A) $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_8$ annealed at 500 °C; (B) T_c (onset) as a function of P_{O_2}. Sample designation from Table I.

weak [the strongest being (0211) at $I/I_{max} \sim 8\%$ and $2\theta \simeq 37.0°$] and are often misidentified as second phase or ignored. For all compositions the major phase could be indexed with a pseudotetragonal unit cell having the average dimensions $a = 5.4$, $b = 5.4$, and $c \simeq 30.7$ Å and the $b^{\#} \sim 4.7$ modulation factor. The identification of single-phase composition as $Bi_2Sr_{1.5}Ca_{1.5}Cu_3O_8$ has also been reported by Tarascon et al.[11] and Roth et al.[12]

Critical Temperature. As prepared, the T_c(onset) was 70–78 K for the various compositions. After equilibration at 500 °C for 4 h in atmospheres with P_{O_2}'s between 1 atm and 10^{-5} atm (nitrogen), susceptibility curves similar to Figure 2a were obtained. Figure 2b summarizes the onset T_c's for several compositions. Quenching or longer annealing times did not affect the T_c. However a strong effect of P_{O_2} on T_c is noted, and low P_{O_2} raises T_c. XRD measurement on these samples did not disclose that annealing produced any phase change or alteration of the incommensurate lines, but a small increase (+0.1 Å) was obtained in the c axis for nitrogen vs oxygen. The fact that for similar heat treatments both the two-phase and single-phase samples have the same T_c (onset) suggests that either the superconducting phase has no solid solution region or there is no effect of cation stoichiometry on T_c.

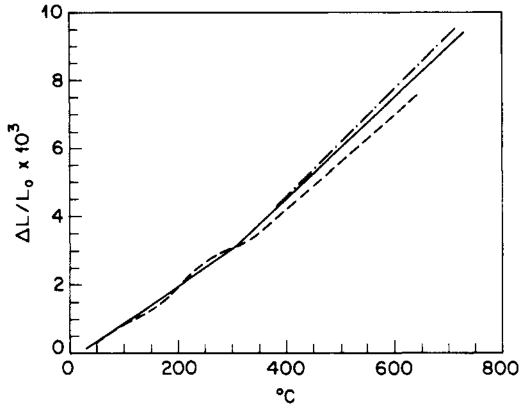

Figure 3. Expansions of $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_x$ in oxygen and nitrogen. Heating rate 4 °C/min: initial heating in oxygen (- - -); reheating oxygen (—); reheating in nitrogen (-·-).

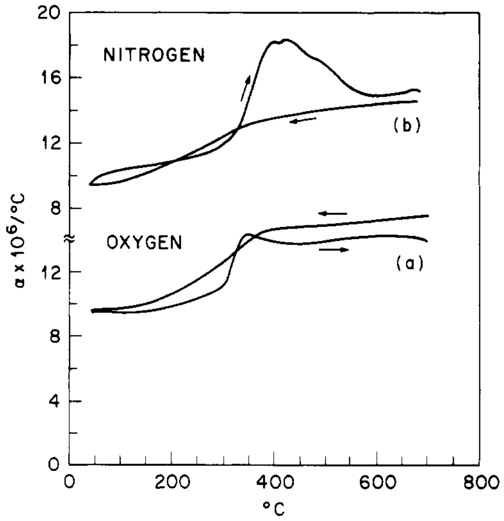

Figure 4. CTE of $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_x$. Heating rate 4 °C/h: (a) oxygen; (b) nitrogen.

Thermal Analyses. Dilatometric data for a ceramic sample with the single-phase composition, $Bi_2Sr_{1.5}Ca_{1.5}Cu_3O_{8+\delta}$, showed that its expansion depends strongly on the oxygen partial pressure in the atmosphere. For a sample that had been furnace cooled from 860 °C after a 100 h in oxygen, the initial expansion curve (Figure 3) shows an increased rate of expansion near 200 °C. Reheating oxidized samples in either oxygen or nitrogen did not reproduce this low-temperature anomaly, but changes in slope near 350 °C were seen. An increase in the coefficient of thermal expansion (CTE) from 9×10^{-6} to $\sim 14 \times 10^{-6}$ (°C)$^{-1}$ near 350 °C is shown in Figure 4a. The more pronounced change in CTE during heating suggests an oxygen stoichiometry change that occurs quickly with increasing temperatures and slowly with falling temperature. When a sample cooled in oxygen is reheated in nitrogen, the thermal expansion again increases near 325 °C, and the CTE reaches 18×10^{-6} (°C)$^{-1}$ before falling to 14×10^{-6} (°C)$^{-1}$ (Figure 4b). On cooling in ni-

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(10) LaPage, Y.; et al. *Phys. Rev. B* **1989**, *40*, 6810.

(11) Tarascon, J. M.; *Phys. Rev. B* **1988**, *37*, 9382.

(12) Roth, R. S.; et al. Paper 6 SIII-90 92th Annual Meeting, American Ceramic Society Dallas, April 23, 1990.

(13) O'Bryan, H. M.; Gallagher, P. K. MRS Symposium M, 1989.

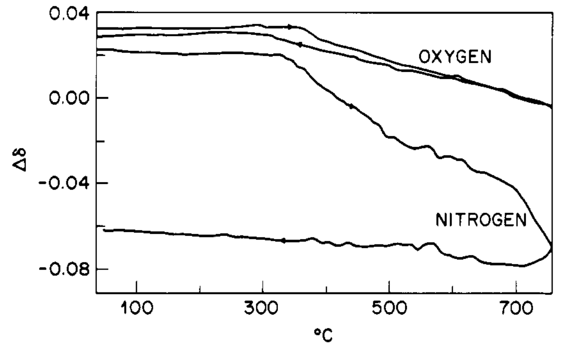

Figure 5. TGA of $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_x$ in nitrogen and oxygen. Heating rate 4 °C/min. Sample previously sintered in oxygen at 860 °C. Weight changes have been converted to oxygen stoichiometry factor δ.

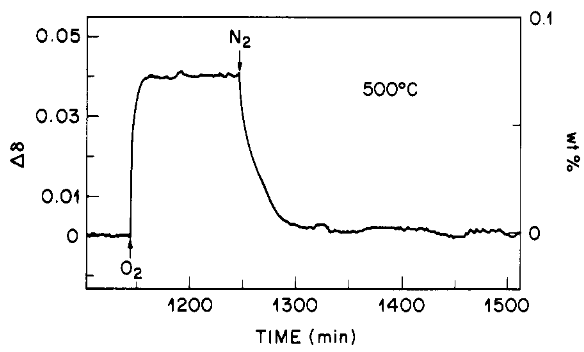

Figure 6. Change in oxygen stoichiometry of $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_x$ as atmosphere is switched at 500 °C.

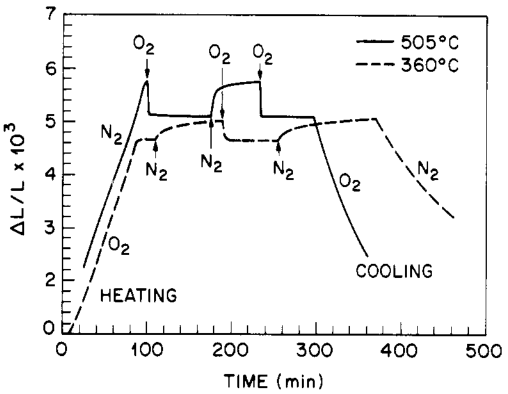

Figure 7. Expansions of $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_x$ at 505 and 360 °C as atmosphere is switched.

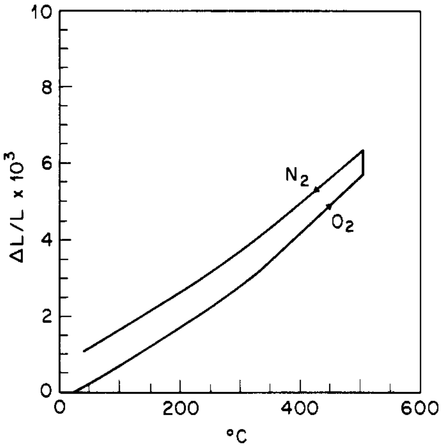

Figure 8. Expansion of $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_x$ during heating in oxygen to 500 °C, equilibration with nitrogen at 500 °C for 4 h, and cooling in nitrogen.

Table II. Lattice Constants and Expansions for Samples Annealed for 4 h at 500 °C

	Lattice Constant					
XRD	oxygen			nitrogen		
temp, °C	*a*	*c*	$b^{\#}$	*a*	*c*	$b^{\#}$
25	5.4059	30.668	4.67 ± 0.1	5.4113	30.773	4.74 ± 0.1
500	5.423	30.928		5.425	30.963	

Thermal Expansion (%), 25 → 500°C		
av $\Delta L/L$(XRD)	0.63	0.53%
Δ/L (D)	0.58	0.53

compositional expansion, Oxygen → Nitrogen		
av $\Delta L/L$ (XRD)	25 °C	0.18%
	500 °C	0.06%
$\Delta L/L$(D)	500 °C	0.065%

trogen, no change in expansion rate near 350 °C is observed because oxygen is not available for recovery.

TGA measurements on a powder obtained by crushing a sintered sample are shown in Figure 5. During heating weight loss begins for both atmospheres near 350 and 500 °C the oxygen content has decreased by $\Delta\delta = 0.02$ in oxygen and $\Delta\delta = 0.06$ in nitrogen. Upon cooling the lost oxygen is regained only in the oxygen atmosphere. An anomalous effect was noted for a sample been exposed to the laboratory atmosphere. For this sample the initial heating produced a weight loss of 0.3% or $\Delta\delta = 0.16$ below 400 °C, and EGA has identified the evolved material as water. Subsequent heating and cooling in oxygen or nitrogen did not show this weight change. This water evolution must also be the source of the anomalous expansion noted in dilatometry for the initial heating (Figure 3, curve 1).

Isothermal TGA and dilatometry confirm that changes in oxygen stoichiometry produce the expansion differences noted. Figure 6 shows that at 500 °C a sample equilibrated in nitrogen gains weight rapidly when the atmosphere is switched to oxygen. The gain of 0.075 wt % corresponds to a change in oxygen stoichiometry $\Delta\delta = +0.04$. When the atmosphere is switched back to nitrogen the weight loss is also 0.075% ($\Delta\delta = -0.04$) but an hour is required to reach a stable weight. At 600 °C, $\Delta\delta = 0.043$ and the kinetics are faster. Isothermal dilatometry (Figure 7) shows that the addition of oxygen produces linear shrinkages of 0.65×10^{-3} and 0.40×10^{-3} at 505 and 360 °C, respectively. These shrinkages are reversed when the atmosphere is switched to nitrogen. The kinetics of oxidation are considerably faster than those for reduction in agreement with the TGA results.

Table II shows the lattice constants and expansions obtained by XRD at 25 and 500 °C for the different oxygen contents. The dilatometric expansions (*D*) are included for comparison. Agreement between the thermal expansions, measured by XRD and dilatometry, is good. Also in good agreement are compositional expansions for measurements made at 500 °C. The larger compositional expansion calculated from the 25 °C constants is partially explained by the increased thermal expansion of the oxygen-loaded $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_{8+\delta}$. This is shown graphically in Figure 8, where the length difference between nitrogen and oxygen is seen to be 50% larger at 25 °C that at 500 °C.

At temperatures ≥700 °C, the TGA data show a slow weight loss during a nitrogen anneal (Figure 9). Upon a switch to oxygen, there is a rapid recovery of oxygen followed by a slower recovery. The weight changes are fully reversible. Dilatometry at 700 °C shows a slow shrinkage in both oxygen and nitrogen that is not recoverable. The length change is caused by either a deformation of the

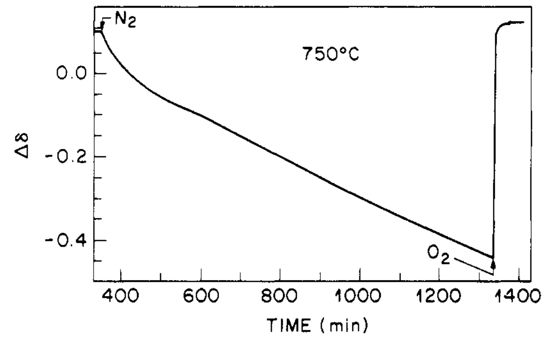

Figure 9. TGA of $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_x$ as atm is switched at 750 °C.

Table III. Effect of Oxygen Stoichiometry

	this study	Groen[7]
single-phase composition	$Bi_2Sr_{1.5}Ca_{1.5}$-$Cu_2O_{8+\delta}$	$Bi_2Sr_2Ca_{0.9}Y_{0.1}Cu_2O_{8+\delta}$
P_{O_2} range	10^{-5} to 1 atm at 500 °C	10^{-7} to $10^{-0.7}$ atm at 600 °C
T_c ac susceptibility, K	90 to 66 (onset)	88 to 61 (midpoint)
c axis, Å	30.792 to 30.668	30.890 to 30.823
Δc axis	−0.12	−0.07
$\Delta\delta$	+0.040	+0.04 (P_{O_2} $10^{-3.7}$ to 1 atm)
isothermal $\Delta L/L$	−0.065	−0.06
expansion 25 to 600 °C, %	0.66 (p_{O_2} = 1 atm)	0.21 (p_{O_2} = $10^{-0.7}$ atm)

sample under the weight of the dilatometer probe or a reaction between the silica holder and the cuprate and is not related to the slow weight change observed by TGA. At lower temperature all expansion changes were reversible. The weight change noted by TGA appears to be caused by a phase decomposition, although no second phase appears in the XRD pattern. It is suggested that 750 °C is too low a temperature for the formation of the second-phase regions of the size necessary to produce an XRD pattern.

In summarizing the results of this study, it is instructive to compare our data with those of Groen. Although the compositions that yield a single-phase two-layer ceramic are different, the effects of annealing in oxygen and nitrogen are quite similar. Table III compares those results. With regard to the thermal expansion, the value obtained by Groen for air seems too low and probably has been reduced by a small peak that he observed near 300 °C during initial heating and attributed to a phase transition. It is probable that this anomaly was caused by the evolution of moisture as was observed in our study. We note a substantial difference in thermal expansion for different δ but observe similar compositional expansion.

It has been suggested that in the 2212 structure the extra oxygen (i.e., δ) required for superconductivity is accommodated by the insertion of oxygen in the Bi layers. The result is a corrugation of these layers.[10] For a incommensurate factor $b^{\#} \sim 4.7$ there is ~0.2 atom extra per unit cell. If the oxygen removed during annealing is taken from the Bi layers, then a change in $b^{\#}$ is expected. The fact that the present data (Table II) show that the incommensurate factor is not affected by the $\Delta\delta = 0.04$ suggests another source. However, since it is difficult to measure $b^{\#}$ and only 20% of the inserted oxygen has been removed, the data are not conclusive.

In both the $Ba_2YCu_3O_{7-\delta}$ and $Pb_2Sr_2YCu_3O_{8+\delta}$ compounds a change in oxygen stoichiometry is seen to affect the c-axis expansion.[12] In both structures the removable oxygen is located near Cu, which has 2-fold or 4-fold coordination. However only in $Ba_2YCu_3O_{7-\delta}$ does a lower oxygen content increase the lattice constant and lower T_c. Since all the copper ions in the Aurivillius structure (2212) have 5-fold coordination, it is difficult to find the removable oxygen in a position where Cu coordination can be increased. The relatively larger effect of composition on expansion for $Bi_2Sr_{1.5}Ca_{1.5}Cu_3O_{8+\delta}$ vs $Ba_2YCu_3O_{7-\delta}$ ($\Delta L/L\Delta\delta$ = 1.5%/atom vs 0.35%/atom) also suggests a site not closely connected to copper, and perhaps the removable oxygen is positioned between the puckered Bi layers.

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