Bulk superconducting $Y_2Ba_4Cu_7O_{15-\delta}$ and $YBa_2Cu_4O_8$ prepared in oxygen at 1 atm

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Synthesis of bulk $Y_2Ba_4Cu_7O_{15-\delta}$ and $YBa_2Cu_4O_8$ high- T_c superconductors at atmospheric pressure, without the addition of alkali rate enhancers, is reported. The superconducting transition temperature for $Y_2Ba_4Cu_7O_{15-\delta}$ is shown to depend on oxygen stoichiometry, with the resistive onset observed above 90 K. The $YBa_2Cu_4O_8$ phase has zero resistance T_c close to 80 K. A modified Y-Ba-Cu-O P-T phase diagram is presented.

Synthesis of the n = 1 ("2:4:7") and n = 2 ("2:4:8", usually referred to as "1:2:4") members of the high- T_c superconducting series of compounds $Y_2Ba_4Cu_{6+n}O_{14+n}$ has, until recently, only been achieved at oxygen pressures exceeding 20 MPa.¹⁻³ Morris *et al.*,⁴ however, have formed both compounds at pressures ≤ 3 MPa and Cava *et al.*⁵ have now demonstrated that the 1:2:4 compounds may be made in flowing oxygen at atmospheric pressure. They used weight-for-weight addition of an alkali carbonate to the prereacted stoichiometric mix to catalytically enhance the reaction rate. However, they were unable to prepare the 2:4:7 compound by this process. We report here that both members can be prepared as singlephase material, displaying bulk superconductivity, in 1 atm of oxygen with or without the addition of alkali. The 1:2:4 phase has zero resistance T_c close to 80 K, while that of 2:4:7 depends on the oxygen stoichiometry and, contrary to previous reports, the resistive onset has been observed at temperatures higher than 90 K.

The 2:4:7 phase may be prepared in similar fashion to



FIG. 1. X-ray powder diffraction patterns using Co $K\alpha$ radiation for (a) YBa₂Cu₄O₈ and (b) Er₂Ba₄Cu₇O_{15- δ}. Impurity peaks are indicated by (•) Y₂O₃, (×) BaCuO₂, and (\odot) Er₂BaCuO₅.

YBa₂Cu₃O_{7- δ} (1:2:3), the primary difference being the reaction and/or sintering temperature, in this case between 845 and 870 °C, i.e., at intermediate temperatures between those of 1:2:3 and 1:2:4. Stoichiometric quantities of Y₂O₃, Ba(NO₃)₂, and CuO are mixed and prereacted to decompose the nitrate, then reacted and/or sintered in flowing oxygen over several days at 860-865 °C, preferably with intermediate grinding. We find it necessary to use submicron CuO powder to produce good quality 1:2:4 and 2:4:7 x-ray diffraction (XRD) patterns.

The 1:2:4 phase can also be prepared entirely without the addition of alkali. In this process Y_2O_3 , $BaCuO_2$ and CuO are ground together, die pressed into pellets, and initially reacted at 900 °C. The 1:2:3 phase is formed at this point, with CuO, $BaCuO_2$, and Y_2BaCuO_5 present as impurities. After grinding and repressing, the pellets are sintered at temperatures between 790 °C and 830 °C in flowing oxygen, with good results at 815 °C. X-ray

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diffraction patterns show a substantial proportion of the 1:2:4 phase after a sintering time of 1 day; phase purity again improves with repeated grinding and sintering. The formation of 1:2:4 in this way via 1:2:3 is evidence that 1:2:4 is the stable phase in this temperature and pressure regime. Interestingly, the reaction times are not significantly longer than those quoted for the highpressure method.

Motivated by the observation of 1:2:4 as an impurity phase in alkali-substituted 1:2:3, we find the reaction rate for both 2:4:7 and 1:2:4 compounds is improved by the addition of small quantities of an alkali nitrate to the precursor materials. For instance, nearly single-phase 1:2:4 can be prepared by mixing stoichiometric proportions of Y_2O_3 , Ba(NO₃)₂, and CuO with up to a 0.2 mol fraction of NaNO₃ or KNO₃, prereacting as a loose powder for 30 min, then grinding, die pressing pellets, and reacting for at least 12 h at 800 °C in flowing oxygen. Phase purity is

,	Indices	1	$d_{\rm obs}$	$d_{\rm calc}$	
h	<u>k</u>	l	(A)	(A)	(%)
0	0	2	13.58	13.58	6
0	0	4	6.80	6.80	6
0	0	6	4.531	4.536	3
0	1	1	3.832	3.829	10
1	0	2	3.695	3.695	13
0	1	3	3.561	3.558	4
0	0	8	3.405	3.403	5
1	0	4	3.343	3.344	29
С	1	5	3.158	3.153	3
1	0	6	2.931	2.931	30
0	1	7	2.743	2.743	100
1	1	1	2.711	2.712	100
1	1	3	2.610	2.610	28
1	0	8	2.547	2.547	51
0	1	9	2.383	2.383	10
0	0	12	2.268	2.269	11
1	1	7	2.232	2.232	18
1	1	9	2.025	2.025	6
С	0	14	1.945	1.945	24
0	2	0	1.934	1.935	38
2	0	0	1.920	1.920	33
1	1	11	1.833	1.833	11
1	2	0	1.727	1.728	3
1	2	2	1.715	1.714	3
0	0	16	1.703	1.702	3
2	1	3	1.690	1.690	3
1	2	4	1.675	1.675	7
1	1	13	1.662	1.661	5
0	1	15	1.643	1.644	3
1	2	6	1.615	1.615	9
2	1	7	1.574	1.573	24
1	2	8	1.541	1.541	17
1	1	15	1.511	1.511	20
2	1	9	1.494	1.496	3
0	2	12	1.473	1.473	4

1.409

1.409

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TABLE I. Powder x-ray diffraction data, collected using Co $K\alpha$ radiation for YBa₂Cu₄O₈—fitted on an orthorhombic *a*-centered cell of dimensions a = 3.842 Å, b = 3.871 Å, and c = 27.244 Å.

improved with repeated grinding and sintering. Because of the volatility of the alkali, it is not clear whether it acts in a substitutional role for compounds of the form $YBa_{2-x}Na_xCu_4O_y$, or simply as a catalyzing flux. The attractive feature in the use of alkali nitrates is that by the time the reaction is complete, all Na₂O or K₂O has evaporated from the material, leaving a sintered ceramic product. In contrast, the use of alkali carbonate in the method of Cava *et al.*⁵ requires subsequent washing away of the carbonate with water leaving powdered material only. We find that improved crystallinity is obtained if BaCuO₂ replaces Ba(NO₃)₂ as a precursor. Complete substitution of some rare earths for Y also enhances that rate of formation of 1:2:4 and 2:4:7; for instance, singlephase Er-1:2:4 may be prepared at 815 °C, without alkali.

The x-ray diffraction pattern for Y-1:2:4, shown in Fig. 1(a), reveals an essentially phase-pure material. The pattern for Er-2:4:7 is shown in Fig. 1(b); the main impurities are small amounts of $BaCuO_2$ and Er_2BaCuO_5 . In both compounds there is no evidence of competing superconducting phases. Tables I and II list *d* spacings and intensities for both the 1:2:4 and 2:4:7 patterns, respectively.

Zero resistance T_c for 1:2:4 is recorded at approxi-



FIG. 2. The temperature dependence of the resistance for $YBa_2Cu_3O_{7-\delta}$ (----), $YBa_2Cu_4O_8$ (---), and $Er_2Ba_4Cu_7O_{15-\delta}$ (--) at a number of oxygen stoichiometries as determined by quenching into liquid nitrogen after annealing in oxygen at 1 atm at the temperatures indicated.

mately 78 K, with an onset of 84 K (Fig. 2), in good agreement with earlier results.^{1,2} We find T_c for 2:4:7, however, depends strongly on oxygen stoichiometry in a manner similar to that exhibited by 1:2:3. Shown in Fig.

Indices			$d_{\rm obs}$	$d_{\rm calc}$	I/I_0
h	k	l	(Å)	(Å)	(%)
0	0	2	25.17	25.28	3
0	0	4	12.66	12.65	15
0	0	12	4.215	4.218	6
0	1	1	3.853	3.855	14
1	0	2	3.800	3.794	4
0	1	3	3.772	3.769	4
1	0	4	3.673	3.672	8
0	0	14	3.615	3.615	5
1	0	8	3.279	3.281	5
1	0	12	2.840	2.839	22
0	1	13	2.744	2.744	77
1	1	1	2.720	2.720	100
1	1	3	2.691	2.689	19
1	0	14	2.632	2.632	24
1	0	16	2.439	2.441	7
0	1	17	2.360	2.359	10
0	0	22	2.301	2.301	5
1	1	13	2.232	2.232	22
1	1	17	2.009	2.010	6
0	0	26	1.947	1.947	18
0	2	0	1.934	1.934	30
2	0	0	1.919	1.919	24
1	1	21	1.806	1.805	3
0	0	30	1.688	1.687	3
1	1	25	1.625	1.625	4
1	2	12	1.598	1.598	7
2	1	13	1.573	1.573	20
1	2	14	1.558	1.558	10
1	1	27	1.545	1.544	8

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2 are the resistance traces for 2:4:7 rapidly quenched from three different oxygen anneal temperatures. T_c increases with decreasing anneal temperature, with onset above 90 K and a zero resistance value as high as 80 K being found for the sample quenched from 300 °C, though this has yet to be optimized. We interpret these changes as being due to oxygen loading, since thermogravimetric analysis (TGA) has already established that oxygen stoichiometry in 2:4:7 varies with temperature⁴ and the procedure of rapid quenching from various anneal temperatures and oxygen partial pressures to control the stoichiometry has been used elsewhere.⁶ Moreover, we observe a mass increase with decreasing temperature, consistent with oxygen uptake, and the resistive and diamagnetic transition temperatures cycle reproducibly with anneal temperature.

We suggest, then, that T_c values of approximately 50 K found in earlier work, for samples prepared at high pressure,^{4,7} result from incomplete oxygen loading, especially if the samples are dense. One of these samples⁷ was shown from neutron scattering to be $Y_2Ba_4Cu_7O_{14,3}$, i.e., $\delta = 0.7$. Presumably, since they were prepared at high temperature and pressure, these samples were too dense to load further oxygen due to the low oxygen diffusion coefficient. Our sintered samples were 70-90 % dense and these load and unload readily. A T_c of 80 K compares well with the value of 86 K found in oxidized ribbons of metallic precursors in the Yb-Ba-Cu-Ag system.⁸ The broadness of our resistive transitions is most likely to be caused by the poorly sintered nature of the material, as indicated by scanning electron microscopy (SEM) studies, particularly in 2:4:7. Bulk superconductivity is confirmed in both 1:2:4 and 2:4:7 samples by the ac susceptibilities, shown in Fig. 3. For comparison, the susceptibility for fully loaded Y-1:2:3 is also shown. The change in diamagnetic transition temperature with oxygen loading is evident.

Our syntheses allow us to modify the Y-Ba-Cu-O pressure-temperature phase diagram for compositions in the vicinity of 1:2:3 to 1:2:4 as shown in Fig. 4. The bold lines delineate the regions of stability of the competing phases of 1:2:3, 2:4:7, and 1:2:4, while, for metastable 1:2:3, the dashed line shows the orthorhombic to tetragonal transition and the light lines are contours of constant composition, δ . It is notable that 2:4:7 is stable over a very narrow band, and 1:2:3 is metastable at all except the highest temperatures. Contrary to the proposal of Morris et al.,⁴ the phase boundaries, like the solidus and the O-T line, do not follow lines of constant composition. At this stage it cannot be said with any certainty that the phase boundaries or the O-T line will cut the solidus line at any achievable oxygen partial pressure. The fact that these phases may be reversibly interconverted by changing temperature or oxygen partial pressure offers interesting processing possibilities. By spinodal decomposition of either 2:4:7 or 1:2:4 the dispersion of CuO or Cu₂O in 1:2:3 can be carefully controlled. In this way we have been able to obtain composite materials with interesting magnetic properties.

In summary we have prepared bulk 2:4:7 and 1:2:4 material in 1 atm of oxygen, in much the same way that



FIG. 3. The temperature dependence of the ac susceptibility for the same samples as in Fig. 2. $YBa_2Cu_3O_{7-\delta}$ (----), $YBa_2Cu_4O_8$ (---), and $Er_2Ba_4Cu_7O_{15-\delta}$ (---).

1:2:3 (the n = 0 member) is prepared. The addition of small amounts of alkali is not necessary, merely increasing the rate of formation. Zero-resistance T_c for Y-1:2:4 is near 78 K, while T_c for 2:4:7 depends on oxygen stoichiometry, but values up to 80 K have been observed for Er-2:4:7, though these have yet to be optimized.



FIG. 4. The phase diagram for the Y-Ba-Cu-O system close to the 1:2:3 or 1:2:4 composition showing stability boundaries for 1:2:3, 2:4:7, and 1:2:4 as a function of oxygen partial pressure, PO₂. The dashed line shows the *O*-*T* transition line in metastable 1:2:3 and the solid lines are contours of constant composition for YBa₂Cu₃O_{7- δ} with values of δ shown. The figure is compiled from the present results and those of Ref. 1 and 5. The *O*-*T* line at lower pressure was determined from elastic measurements in Ref. 9.

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