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The decomposition of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ doped into Ba_2YRuO_6

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One of the persistent criticisms of claims for observation of superconductivity in $\text{Ba}_2\text{YRu}_{1-u}\text{Cu}_u\text{O}_6$ (O6) is that the diamagnetism is actually due to the decomposition of the material into $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and other phases. We report a series of experiments in which $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ is doped into Ba_2YRuO_6 and carried through a series of sintering steps which were followed by magnetization, neutron diffraction, and scanning electron microscopy/microprobe measurements. It was found that the dopant $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ decomposed and failed to reform with cooling. It is concluded that the O6 phase is the stable high-temperature phase. The Cu released from the Y123 decomposition doped the host Ba_2YRuO_6 , in partial substitution for Ru. This doping resulted in a small diamagnetic response with an onset temperature of ~ 84 K. © 2008 American Institute of Physics.

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I. INTRODUCTION

It has been argued that the superconductivity¹ observed in $\text{Ba}_2\text{YRu}_{1-u}\text{Cu}_u\text{O}_6$ (Cu doped O6) arises from an undetected level of impurity phase $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Y123), since all of the constituents of that compound are present in the starting composition. This claim has been made despite the fact that Y123 undergoes a peritectic decomposition² at ~ 1000 °C and the resulting products undergo a second decomposition³ at ~ 1270 °C, while the sintering temperature employed for the synthesis of $\text{Ba}_2\text{YRu}_{1-u}\text{Cu}_u\text{O}_6$ is 1450 °C. Since the O6 phase is stable to much higher temperatures, on thermodynamic grounds one would not expect it to decompose upon cooling through the lower peritectic temperature of the Y123 or Y211 phases. To confirm this expectation, we have carried out a number of experiments, (i) to look for any evidence for such a decomposition, that were not limited to searching for evidence of the presence of Y123, including examining the effect of BaO on polycrystalline $\text{Ba}_2\text{YRu}_{1-u}\text{Cu}_u\text{O}_6$ and (ii) to examine the stability of Y123 at low concentrations in mixtures of Ba_2YRuO_6 when subjected to the processing conditions appropriate to the synthesis of the O6 phase. These experiments show that any Y123 initially present is converted into the thermodynamically stable Cu-doped O6 phase.

II. METHODOLOGY

The preparation of polycrystalline samples of $\text{Ba}_2\text{YRu}_{1-u}\text{Cu}_u\text{O}_6$ follows closely the procedure given by Wu *et al.*⁴ Oxides of Y, Cu, and Ru were mixed with Ba carbon-

ate in stoichiometric proportions from materials dried at temperatures of 300–500 °C. The powders were hand-ground in agate mortars for several hours and calcined at 970 °C for 48 h. Low-energy ball milling alone was found to be ineffective, failing in a number of attempts to produce superconducting material. The calcined powders were reground and pressed at 10 000 psi into thin pellets of approximately 1.5 g. Two or three pellets were stacked on the remaining calcined powder, to avoid contamination from the crucible, and sintered in a reactant gas mixture of 70% Ar and 30% O for 12 h at 1450 °C. Multiple calcinations for long times at lower temperatures were found to be ineffective for producing the desired product phase, as Ru is known to volatilize at temperatures as low as 800 °C. Pellet densification is important; the same procedure with 3–4 g less dense pellets fails to yield superconducting material, presumably due to component volatility. The sintered pellets are very much harder than those of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Samples consisting of initial mixtures of Ba_2YRuO_6 and Y123 were prepared and subjected to the same heat treatment schedule as employed for the syntheses described earlier. The samples were characterized by neutron diffraction and by superconducting quantum interference device (SQUID) magnetometry, using zero-field cooling (ZFC), field-cooling (FC), and field-cooled-warming (FCW) in low magnetic fields (0–10 Oe). Scanning electron microscopy (SEM) and electron microprobe techniques were employed to study the final material.

III. TESTS OF DECOMPOSITION-PHASE SEPARATION

In the following we describe several experiments designed to test the possibility that decomposition products could produce the observed superconductivity (diamagne-

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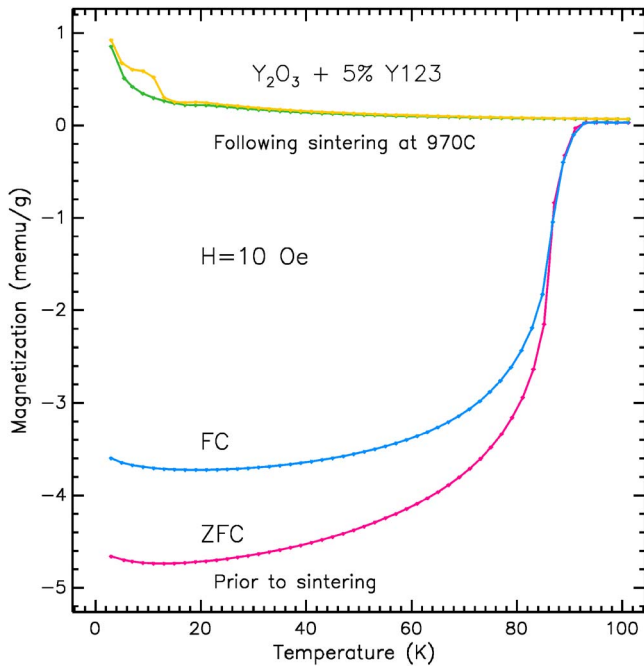


FIG. 1. (Color online) Magnetization measurements on $\text{Y}_2\text{O}_3 + 5\%$ Y123 in the form of mixed powder and following sintering at 970°C for 12 h. Prior to sintering, a diamagnetic response is observed. Following sintering, evidence for diamagnetism vanishes; the dopant Y123 has decomposed and the material is an insulator.

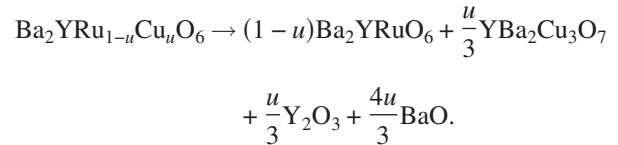
tism resistivity) and to consider the decomposition products and their effects on the (potential) diffraction patterns as well as the mechanical stability of the resulting pellets.

A. Y123– Y_2O_3 mixtures

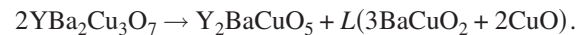
The effects of mixing Y123 with an insulator (Ba_2YRuO_6 is also a charge-balanced insulator) have been examined by thoroughly mixing 5% Y123 by weight with Y_2O_3 powder. Here we test the suggestion that a small content of a superconductor dispersed in an insulator would exhibit superconductivity and a vanishing resistivity.⁵ The temperature-dependent ZFC and field-cooled magnetizations were measured (Fig. 1). Since no thermal processing had been carried out, the diamagnetic response of a powder sample was expected and observed. After sintering the densified Y_2O_3 –Y123 mixture at 970°C , for 12 h (the standard calcination parameters for the O6 material), the magnetization and resistivity were measured. The material is found to be an insulator with no diamagnetic response. The paramagnetic response appearing at low temperature is likely due to BaCuO_x or to Y_2BaCuO_5 reaction products. The color of the sample was pale gray-green, consistent with the formation of dispersed, nonsuperconducting Y_2BaCuO_5 . Even at a temperature below the peritectic, Y123 has decomposed (as expected from the equilibrium phase diagram) and no superconductivity was found. These results, therefore, clearly establish that superconducting filaments do not emerge in an insulating host.

B. Decomposition of $\text{Ba}_2\text{YRu}_{1-u}\text{Cu}_u\text{O}_6$

The conceivable decomposition of $\text{Ba}_2\text{YRu}_{1-u}\text{Cu}_u\text{O}_6$ to produce Y123 and undoped Ba_2YRuO_6 is



For the typical dopant content of $u=0.15$, complete decomposition would result in 5% (mol) Y_2O_3 and Y123, with 20% BaO. This potential decomposition would be of interest only if the products were stable at 1450°C , which they are not. At $\sim 1020^\circ\text{C}$, Y123 undergoes a peritectic decomposition as follows:



Here Y_2BaCuO_5 (Y211) is the nonsuperconducting green phase and L indicates the liquid phase. Heating Y211 to 1270°C results in a further decomposition,



Thus, the proposed products are not thermodynamically stable at the sintering temperature. We confirmed this by heating Y123 to $\sim 1200^\circ\text{C}$ for several hours; the resulting slag had no x-ray diffraction lines characteristic of Y123. During the O6 calcination process, a large fraction of the desired product, $\text{Ba}_2\text{YRu}_{1-u}\text{Cu}_u\text{O}_6$, is seen to form, without the presence of identifiable Y123, Y_2O_3 , or BaO. The disposition of Y123 potentially formed during calcination will be discussed in Sec. III D.

Some have argued that Y123 could form epitaxially on the surface of O6 grains, due to the presence of similar BaO planes in both structures and that these thin epitaxial layers would be invisible to neutron or x-ray diffraction. In fact, the cell parameters of the O6 (8.339 \AA) are substantially larger than twice the basal axes of Y123, and phase separation, rather than epitaxy, is more likely if Y123 were to appear. In any case, no similar cloak of invisibility can be invoked to hide the 20% BaO product which would accompany the needed 5% Y123. The BaO concentration is more than an order of magnitude above the detectability limit for the neutron diffraction experiments. The $\sim 7\%$ mismatch between the BaO ($a \sim 5.5323 \text{ \AA}$) (Ref. 6) and the O6 lattice parameters⁷ most likely precludes epitaxial growth. Instead it should appear as a granular second phase. Its absence in the diffraction experiments rules out phase separation of the Cu from the O6 phase and therefore excludes Y123 as a decomposition product. Moreover, we have shown that excess BaO would make its presence known through air instability of the product.

C. Consequences of excess BaO

Although the tell-tale BaO has never been detected in the diffraction measurements, a test was conducted to determine its potential consequences. A sample of undoped Ba_2YRuO_6 was ground with 20 (mol)% of Ba (in the form of the carbonate) and sintered at 1450°C for 12 h. Although

the fired pellet was dense, it was found that this doping produced material that was not even air stable; it crumbled into very small grains in 10 h exposure to air. X-ray diffraction of the resulting powder showed that BaCO_3 had reformed. It is concluded that if BaO were released as a necessary consequence of the formation of Y123, the most obvious consequence would be that the resulting material would not be air stable. This is in striking contrast to experience in which samples have changed little in either appearance or properties with more than a year's exposure to ambient air. Of course, this behavior also contrasts sharply with Y123, which deteriorates rapidly when exposed to ambient air.

D. Stability of Y123 in the presence of Ba_2YRuO_6 at high temperatures

To explore the disposition of small or even (x-ray) undetectable contents of Y123, we have constructed several experiments⁸ operating in a reverse sense, by doping (undoped) O6 with Y123, and following the temperature processing steps with magnetization measurements and diffraction experiments. If Y123 were to form as a decomposition product of Cu-doped O6, it would have to overcome the chemical pressure to remain single phase; i.e., the decomposition products would have to be more stable than the starting host. On the other hand, doping undoped O6 with Y123 presents quite a different situation; the Y123 is free to coat O6 grains without competition to reform the starting (O6) material. Stated another way, if Y123 doped into the undoped O6 fails to form as a grain-boundary wrapper, under optimal circumstances, such formation can be dismissed. Doping⁹ Gd123 into $\text{Ba}_2\text{GdRuO}_6$ enables a test of this grain boundary conjecture. The result of such experiments is that no superconductivity or trace of Gd123 remains following intimate mixing and high temperature sintering; $\text{Ba}_2\text{GdRu}_{1-n}\text{Cu}_n\text{O}_6$ is not a superconductor.¹⁰

E. Doping of Ba_2YRuO_6 with Y123

To reinforce the earlier findings, additional experiments were carried out in which previously processed undoped Ba_2YRuO_6 was mixed with 5% by weight of superconducting Y123. Since Y123 undergoes complete decomposition near 1270 °C into Y_2O_3 , CuO , and BaCuO_x , based on the earlier results, the expectation is that formation of additional O6 phase will be accompanied by the Cu doping of the host O6, resulting in an 84 K superconductor. Additional nonconducting impurity phases will likely form on grain boundaries. Accordingly, previously processed (undoped) O6 material was ground and 5% by weight of ground Y123 was added and thoroughly mixed. The composite powder was examined by neutron diffraction to confirm the presence of Y123 (and our ability to detect it), and then the powder was densified and sintered at a temperature appropriate (~900 °C) to Y123 processing to yield a solid that could be cut into bars suitable for resistivity and magnetization measurements. This material was not annealed in oxygen to restore superconductivity to the included Y123. In a final step, the doped material was once again ground, pressed into a pellet and sintered at ~1450 °C in an Ar–O gas mixture, the normal processing

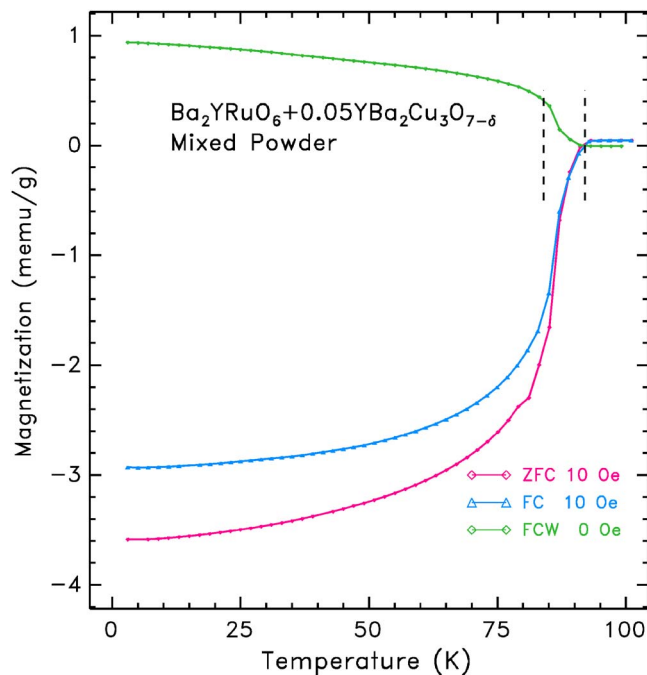
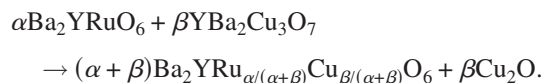


FIG. 2. (Color online) Magnetization as a function of temperature for the composite mixed powder sample consisting of O6 and 5% Y123 by weight. The sample exhibits a transition temperature near 92 K; the vertical dashed lines indicate 92 and 84 K. The shape of the temperature-dependent magnetic response is characteristic of Y123. The data include ZFC, FC, and FCW scans.

procedure for the O6 material. With the molar fractions α and β , the equation describing the decomposition of the dopant Y123, and its subsequent redistribution is



Unless there has been substantial loss of Ru due to sublimation (which the Cu could replace), this equation describes very light Cu hole doping with substantial unincorporated Cu. The disposition of the excess Cu is not known; one possibility is that it forms insulating CuO on grain boundaries. It does not form BaCuO_2 , since such formation would give rise to a detectable paramagnetic response; no paramagnetic BaCuO_2 resonance was observed following high temperature sintering in the Gd doping exercises.⁹ The results of experiments on this composite material are described later.

The magnetization of the mixed powdered material was examined using a commercial SQUID, the results are given in Fig. 2. As we expected, the magnetism is a superposition of the paramagnetic/antiferromagnetic Ba_2YRuO_6 and the superconducting Y123. The vertical dashed lines mark 92 and 84 K here and in Figs. 4 and 6. The data of Fig. 2 also show the response characteristic of Y123, while the Ru antiferromagnetic ordering transition is too small to be seen against the diamagnetic response. In Fig. 3, the neutron data for the unprocessed mixed powder is given; the two phases are readily identified. Refinement for Y123 found 4.1(mol)% Y123. Since the sample was still in powder form, no resistance measurements were possible.

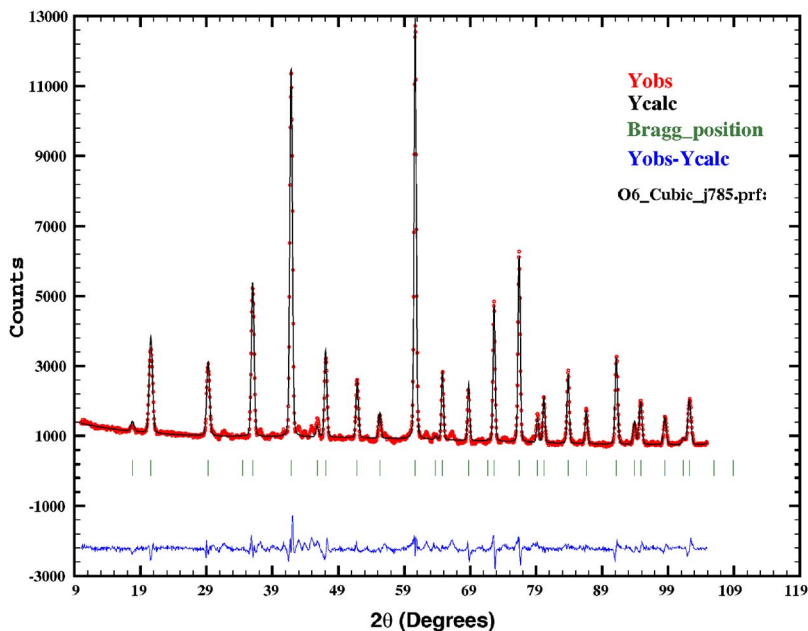


FIG. 3. (Color online) Room temperature neutron diffraction of a composite mixed powder sample. The tick marks indicate the positions of the O6 diffraction peaks, while the diffraction peaks due to Y123 are readily identified in the residual. Since the Ru orders at a much lower temperature, no peaks due to the magnetic unit cell are seen.

Sintering a pressed pellet of the mixed powder at 970 °C yielded a material that exhibited a reduced (by approximately a factor of 5) diamagnetic response (see Fig. 4), as compared to the data in Fig. 2, but was an insulator, as expected. Thus, we have again demonstrated that direct doping by 5% Y123 fails to yield even a conductor. The sintering temperature was below the peritectic decomposition temperature of the Y123. Nevertheless, the shape of the transition has changed, the transition temperature has fallen slightly, and a paramagnetic impurity is clearly seen in the

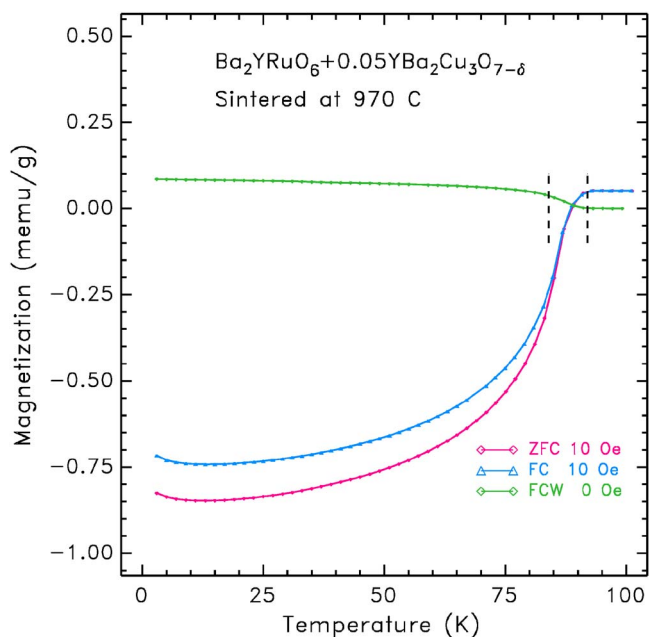


FIG. 4. (Color online) Magnetization as a function of temperature for the composite mixed powder sample consisting of O6 and 5% Y123 by weight following sintering at 970 °C and no oxygen annealing. The vertical dashed lines indicate 92 and 84 K. The previous diamagnetic response has been reduced by nearly a factor of 5. In addition, the upturn at low temperatures indicates the presence of BaCuO_x. The Y123 has partially doped the host O6, and partially decomposed into BaCuO_x. The sample is an insulator.

low-temperature upturn of the magnetization. This paramagnetic impurity is almost certainly BaCuO_x. Part of the sample was ground for neutron diffraction measurement. These (Fig. 5), which was easily able to detect the multiphase composition, finding ~2% of Y123. It is evident that the dopant Y123 has been partially decomposed by the sintering process, partially doping the O6, and also forming BaCuO_x. The small doping from the partially dispersed Cu was insufficient to produce a conductor with a resistivity small enough to measure.

The final step in this sequence was to regrind the composite material and sinter it at ~1450 °C in an Ar–O mixture. The resulting material was converted to a (high resistivity) semiconductor at room temperature, with increased flux expulsion, see Fig. 6. In addition, the paramagnetic impurity has nearly vanished. The transition temperature is characteristic of Ba₂YRu_{1-u}Cu_uO₆ (84 K) and the temperature-dependent shape of the transition is that of the O6. Our experience has been that the low temperature (~400 °C) anneal typically required of Y123 actually reduces the diamagnetism in the O6 material. Neutron diffraction, see Fig. 7, showed that the Y123 had been decomposed, yielding a material with substantial impurity content due to additional breakdown phases. Refinement for Y123 found less than 1%. The processing led to the incorporation of the constituents of Y123 into the O6 phase, with the added Cu located on the Ru sublattice, partially hole doping the structure. The point here is that the decomposed Y123 did not reform; small contents of impurity phases were left. By virtue of the experiments with the Gd homologs, it is not even possible to argue that Y123 could have formed on grain boundaries.

IV. MICROPROBE STUDIES

SEM and energy dispersive x-ray analysis (EDXA) studies were carried out on the Y123 doped O6 material following the final 1400 °C sintering. The sample selected for ex-

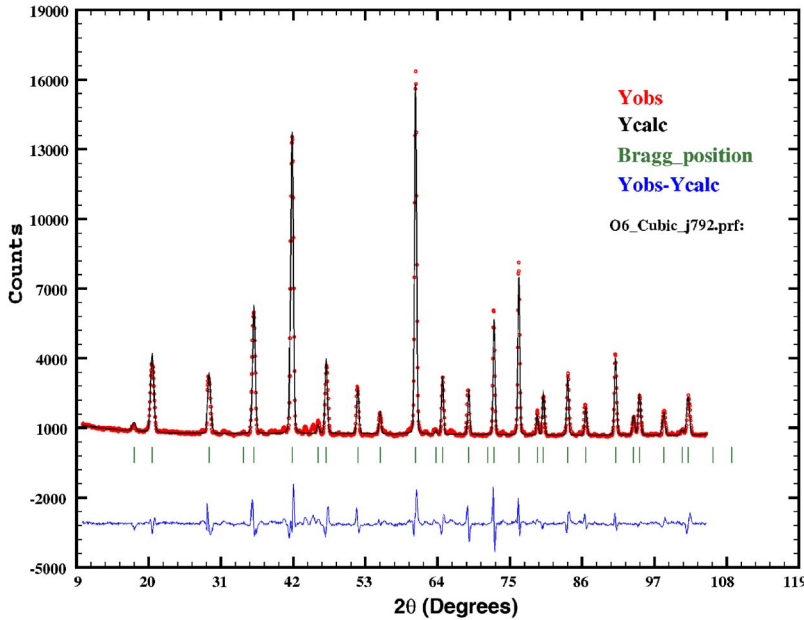


FIG. 5. (Color online) Room temperature neutron diffraction of the composite mixed powder sample following 900 °C sintering and oxygen annealing. The diffraction peaks due to the Y123 in the residual are reduced in intensity as compared to the data of Fig. 3; the Y123 has partially reacted with the host. Since the Ru orders at a much lower temperature, no peaks due to the magnetic unit cell are seen.

amination was cut from the center of the pellet and was immediately adjacent to the piece measured by SQUID, which yielded the data shown in Fig. 6. Figure 8 shows a typical region, consisting of a large number of grains with cubic morphology and a few much smaller grains with a different morphology. The large grains are easily identified as Cu-doped Ba_2YRuO_6 . A number of grains (31) were selected for EDXA measurements. The instrument was not calibrated using an undoped Ba_2YRuO_6 sample; as a result,

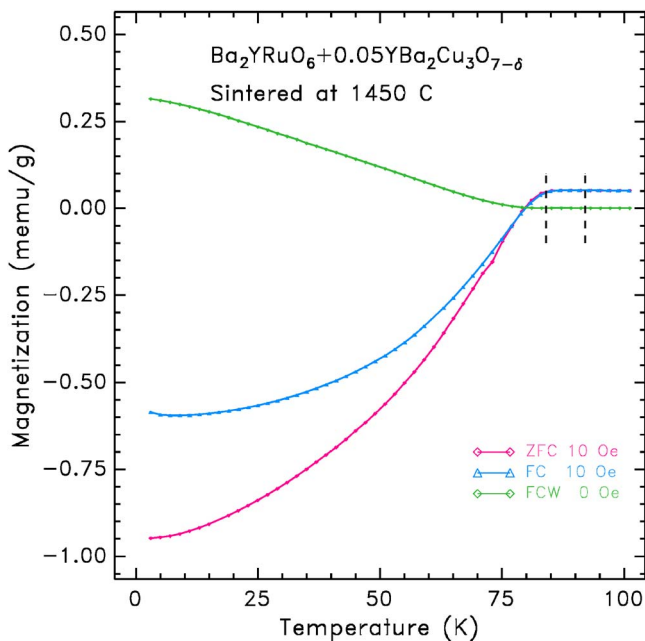


FIG. 6. (Color online) Magnetization as a function of temperature for the composite pelletized sample consisting of O6 and 5% Y123 following sintering at 1450 °C and no oxygen annealing. The sample exhibits increased net diamagnetism due to the decomposition of Y123 resulting in partial Cu doping of the host O6 and the transition temperature has dropped to 84 K. Although the diamagnetic response is a fraction of that of O6 material which has been properly prepared, the Ru antiferromagnetic response has been screened. There is no clear evidence for remaining unincorporated paramagnetic BaCuO_x .

the systematic errors are somewhat larger than optimal. All but one of the 31 sampled grains were consistent with O6 phase chemistry; one small grain had a Cu content three times higher than the average (1.19%) for the remaining 30. This single point came from an atypical speck located on the surface of a large O6 grain, as shown in Fig. 8. It is estimated that the total volume of such grains represents less than 0.1% of the volume of the O6 phase. Only one other sampled point had a Cu content more than 50% of the concentration of that single atypical grain. Excluding the atypical grain from the averaging resulted in the following concentration ratios: $\text{Ba}/\text{Y}=2.17$, $\text{Ba}/(\text{Cu}+\text{Ru})=1.91$, $\text{Y}/(\text{Cu}+\text{Ru})=0.88$, and $\text{Cu}/(\text{Ru}+\text{Cu})=0.16$. The Cu content of the grains lies within the reported solubility range for the phase, while the Cu content of the atypical grain is a factor of 3.5 lower than required for the formation of Y123. Although there are systematic errors of a few percent, it is clear that no Y123 remains (or reforms) after the 1450 °C sintering step. These results indicate clearly that most of the Cu provided by the Y123 source was incorporated into the O6 phase. Because of the different atomic ratios of the two phases, this requires that some Ru must leave the phase to “make room” for the Cu. These atoms presumably are lost to volatilization. This tendency to lose Ru may explain the difficulty in producing superconducting Cu-doped Ba_2YRuO_6 from a stoichiometric mixture of oxide and carbonate precursors. These studies showed that Cu doped the O6 phase, without forming Y123 (which has 23.1% Cu) from the decomposition products, even though substantial excess Cu was provided.

V. SUMMARY AND DISCUSSION

Cubic Ba_2YRuO_6 is a magnetically ordered insulating material with a Néel temperature of 37–39 K. Electron microprobe studies of Y123 doped material following sintering at 1450 °C demonstrated that the dopant Cu is present in grains of the O6, without finding Y123, confirming the results of the neutron diffraction, which also failed to find

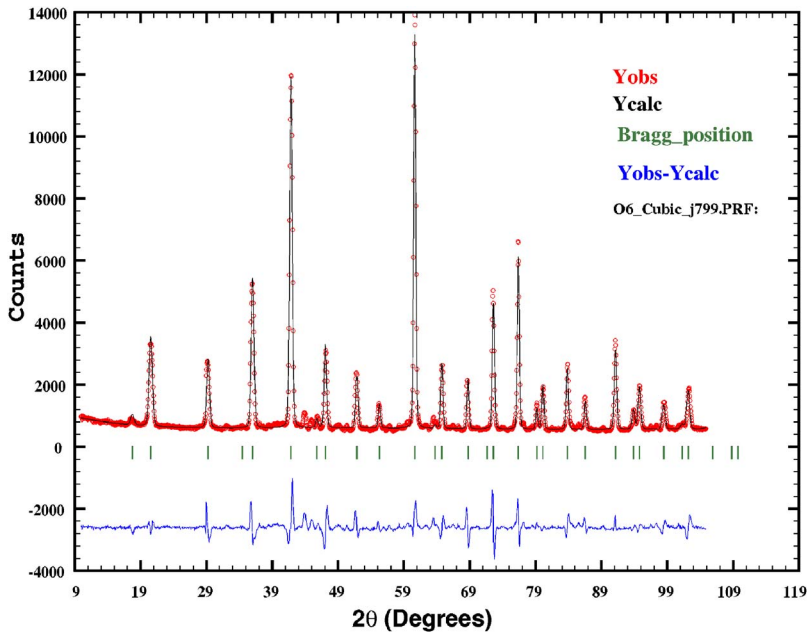


FIG. 7. (Color online) Room temperature neutron diffraction of the composite material following pelletizing and 1450 °C sintering in an Ar–O gas mixture. Examination of the residual indicates that the diffraction peaks due to the Y123 have nearly vanished, as compared to the data of Figs. 3 and 5. There remain small unaccounted for residual responses, due to an unknown phase.

Y123. Hole doping by partial replacement of Ru by lower valence Cu, as confirmed by the microprobe analysis, yielded a superconductor, $\text{Ba}_2\text{YRu}_{1-u}\text{Cu}_u\text{O}_6$, with a transition temperature of ~ 84 K. In accord with thermodynamic expectations, our experiments demonstrate that the 123 phase does not phase separate from Cu doped O6 compositions; the O6 phase is the stable high temperature phase. Were such a separation to occur, a larger content of BaO would necessarily result, while none is detected. The neutron diffraction failed to detect Y123 and the EDXA studies confirmed that the composition was not that of Y123. Furthermore, the EDXA studies showed that Cu-doped the O6 phase, without forming Y123 from the decomposition products. Hence, the observed diamagnetism and vanishing resistivity must be attributed to the O6 material.

In a recent paper,¹¹ it was argued that the observed superconductivity in the homolog $\text{Sr}_2\text{YRu}_{1-u}\text{Cu}_u\text{O}_6$ (Sr-O6) was due to inclusions of $\text{YSr}_2\text{Cu}_3\text{O}_{7-\delta}$ (YSCO). It was fur-

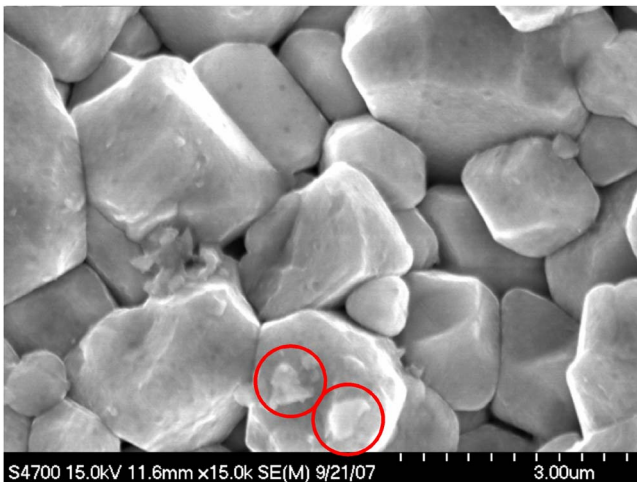


FIG. 8. (Color online) Scanning electron micrograph of the Y123-doped O6 following sintering at 1450 °C. The cubic grains are of relatively uniform size, typically 3–4 μm . Two circled grains of ~ 0.5 μm size are seen; these have a higher Cu content, but not that of Y123.

ther argued that the YSCO was formed as a consequence of pressure provided by surrounding grains, which resulted from partial melting. The superconducting onset transition temperature (64 K) observed is not that of Sr-O6; it was associated with YSCO. However, examination of Fig. 5 of Galstyan *et al.*¹¹ reveals two diamagnetic transitions: The first, a weak transition, occurs at ~ 64 K, while a second larger transition occurs at ~ 30 K, simultaneously (or very nearly so) with the magnetic ordering of the YRuO_4 layers in the Sr-O6. The transition at ~ 30 K, is typical of the superconducting transition temperature expected for the Sr-O6. Since there are no reports of multiple superconducting transitions in YSCO, the 30 K transition is logically attributed to $\text{Sr}_2\text{YRu}_{1-u}\text{Cu}_u\text{O}_6$.^{12,13} Further, it is very difficult to understand how the onset of ferromagnetic order in the YRuO_4 planes could enhance the superconductivity of the granular YSCO. Galstyan *et al.*¹¹ also showed that any YSCO appears in a granular phase. It is therefore not possible that resistive zeros, reported for $\text{Sr}_2\text{YRu}_{1-u}\text{Cu}_u\text{O}_6$, could be attributed to this impurity. This obtains because the maximum concentration of this impurity is 5% for $u=0.15$ in $\text{Sr}_2\text{YRu}_{1-u}\text{Cu}_u\text{O}_6$, well below the 3– d percolation limit of $\sim 16\%$ required for a granular phase. The preparation procedures exercised, based on our experience, would not be expected to produce quality superconducting O6. However, it is no surprise that the Cu-rich phases could emerge from those procedures, since the Cu concentration (50%) was well above the reported Cu solubility limit ($\sim 20\%$) in the O6 phases. With lower ($\sim 10\%$) doping, Galstyan *et al.*¹¹ found that the Cu was incorporated in the Sr-O6 phase. In Ref. 11, the superconducting volume fraction exceeded that possible if all of the dopant Cu were incorporated into perfect YSCO, producing a sharp diamagnetic transition at ~ 30 K, a temperature anomalously low for YSCO (roughly 1/2 of its characteristic T_c). If the arguments of Ref. 11 were to be applied to the appearance of superconductivity in $\text{Ba}_2\text{YRu}_{1-u}\text{Cu}_u\text{O}_6$, a superconducting T_c well above 92 K would be expected, since the positive pressure dependence of the T_c of Y123 is well

known. This is in contrast to the characteristic 84 K T_c seen for this material. While Galstyan *et al.*¹¹ claim to have disposed of arguments for superconductivity in Sr-O6, careful analysis suggests that their work actually supports it.

While the doping strategy discussed produced only a small diamagnetic response, it is evident that the Ru loss issue is paramount to successful production of higher quality material. Cu doping with CuO and one sintering step yields material with a diamagnetic response 4–5× larger.

The magnetic configuration of the O6 materials has been reported by numerous groups and consists of ferromagnetic YRuO₄ planes, which are stacked antiferromagnetically. For the Ba material, the ordering temperature is ~39 K, and the Ru moments are found to lie in the basal plane. It has recently been shown that the CuO₂ layers in (superconducting) YSr₂Cu_{2.1}Nb_{0.9}O₈ (Ref. 14) and in Y_{1.5}Ce_{0.5}Sr₂Cu₂NbO₁₀ (Ref. 15) are magnetically ordered and exhibit the same magnetic (antiferromagnetic) configuration as exhibited by the O₆ materials. In addition, the homologs of these two materials including YSr₂Cu₂RuO₈ (Refs. 16 and 17) and Y_{1.5}Ce_{0.5}Sr₂Cu₂RuO₁₀ (Ref. 18) exhibit the same magnetic and magnetic resonance behavior and have the same cuprate plane configuration. These examples may suggest a possible common coupling between magnetism and superconductivity, rather than the generally expected antagonism. From this perspective, Ba₂YRu_{1-u}Cu_uO₆ can be viewed as a structurally limiting form, having only two chemically distinct layers. Ba₂YRu_{1-u}Cu_uO₆, because of its simplicity, its lanthanide homologs, its variable Cu content, and its relatively high (84 K) transition temperature, may become a laboratory for the study of the high temperature superconductivity (HTSC), perhaps helping to isolate the elusive HTSC pairing mechanism.

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- ¹D. Y. Chen, F. Z. Chien, D. C. Ling, J. L. Tseng, S. R. Sheen, M. J. Wang, and M. K. Wu, *Physica C* **282–287**, 73 (1997).
- ²S.-J. Kim, *J. Ceram. Proc. Res.* **7**, 230 (2006).
- ³M. Nakamura, Y. Yamada, and Y. Shiohara, *J. Mater. Res.* **9**, 1946 (1994).
- ⁴M. K. Wu, D. Y. Chen, F. Z. Chien, S. R. Sheen, D. C. Ling, C. Y. Tai, G. Y. Tseng, D. H. Chen, and F. C. Zhang, *Z. Phys. B* **102**, 37 (1996).
- ⁵Here we are concerned with materials which consist of less than the percolation limit (~16%) of Y123 (or one of its homologues) dispersed in an insulating host such as Y₂O₃ and sintered at high temperatures into solid form.
- ⁶The BaO face diagonal distance $a^{1/2}=7.82$ Å.
- ⁷N. G. Parkinson, P. D. Hatton, J. A. K. Howard, C. Riter, F. Z. Chien, and M. K. Wu, *J. Mater. Chem.* **13**, 1468 (2003).
- ⁸By “doping” with a material such as Y123, we mean that we may expect a mixed phase to be formed. Decomposition of the “dopant” material may also result in hole doping by partial replacement of Ru⁵⁺ by Cu³⁺ or possibly even Cu⁴⁺.
- ⁹H. A. Blackstead, M. Kornecki, M. P. Smylie, P. J. McGinn, W. B. Yelon, and Q. Cai, *J. Alloys Compd.* (in press).
- ¹⁰H. A. Blackstead, J. D. Dow, D. R. Harshman, W. B. Yelon, M. X. Chen, M. K. Wu, D. Y. Chen, and D. B. Pulling, *Phys. Rev. B* **63**, 214412 (2001).
- ¹¹E. Galstyan, Y. Xue, M. Iliev, Y. Sun, and C.-W. Chu, *Phys. Rev. B* **76**, 014501 (2007).
- ¹²H. A. Blackstead, J. D. Dow, D. R. Harshman, M. J. DeMarco, M. K. Wu, D. Y. Chen, F. Z. Chien, D. B. Pulling, W. J. Kossler, A. J. Greer, C. E. Stronach, E. Koster, B. Hitti, M. Haka, and S. Tooronigan, *Eur. Phys. J. B* **15**, 649 (2000).
- ¹³H. A. Blackstead, J. D. Dow, P. J. McGinn, and D. B. Pulling, *J. Supercond.* **13**, 977 (2000).
- ¹⁴H. A. Blackstead, W. B. Yelon, M. Kornecki, M. P. Smylie, Q. Cai, J. Lamsal, V. P. S. Awana, H. Kishan, S. Balamurugan, and E. Takayama-Muromachi, *Phys. Rev. B* **75**, 140514(R) (2007).
- ¹⁵H. A. Blackstead, W. B. Yelon, M. P. Smylie, Q. Cai, J. Lamsal, V. P. S. Awana, S. Balamurugan, and E. Takayama-Muromachi (unpublished).
- ¹⁶W. B. Yelon, Q. Cai, J. Lamsal, H. A. Blackstead, M. Kornecki, V. P. S. Awana, H. Kishan, S. Balamurugan, E. Takayama-Muromachi, *J. Appl. Phys.* **101**, 09G104 (2007).
- ¹⁷H. A. Blackstead, W. B. Yelon, M. Kornecki, M. P. Smylie, Q. Cai, J. Lamsal, V. P. S. Awana, H. Kishan, S. Balamurugan, and E. Takayama-Muromachi, *Phys. Rev. B* **76**, 094507 (2007).
- ¹⁸H. A. Blackstead, W. B. Yelon, M. P. Smylie, M. Kornecki, Q. Cai, J. Lamsal, V. P. S. Awana, S. Balamurugan, and E. Takayama-Muromachi (unpublished).