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Structural Chemistry of Au(III)-Substituted $Ba_2YCu_3O_{7-\delta}$

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A series of gold-substituted perovskite superconductors $Ba_2Y(Cu_{1-x}Au_x)_3O_{7-\delta}$ ($x = 0$–0.1) was synthesized. For $x = 0.1$ there was no change in the *a* and *b* lattice parameters ($a = 3.826$ Å and $b = 3.889$ Å) but a 0.06 Å *c* axis expansion to 11.75 Å was observed. Substituted gold was found to be trivalent by X-ray photoelectron spectroscopy. Replacing Cu(1) in the copper oxide chain with a slight reordering of oxygen is consistent with *c* axis expansion. The formal charge of the site remains trivalent while remaining Cu in the chains is reduced to Cu(I) resulting in an oxygen stoichiometry <7. Finally, no large effect on T_c is observed ($T_c = 89$ K for $x = 0.10$), in contrast to the effect of a number of other metal ion dopants. These results are discussed relative to the chemistry of Au(III) and to the use of the metal in structures containing gold and ceramic superconductors.

Since reports of the synthesis (*1*) and structure (*2*) of the superconductor $Ba_2YCu_3O_{7-\delta}$ many copper substitution studies have appeared. These efforts have mainly focused on ions of the first-row transition (*3–6*) and Group IIIB (*5–7*) metals. For these metals, it appears that trivalent ions substitute at the Cu(1) site in copper oxide chains and induce an orthorhombic/tetragonal transition while divalent ions substitute in copper oxide planes and do not cause a major structural shift. As oxygen ordering is disrupted by the structural requirements of substituting ions, T_c is lowered, particularly for Cu(2) plane dopants (e.g., Zn^{2+}) (*3*).

An understanding of the structural and superconducting properties of metal-doped perovskite superconductors is critical not only for possible insights into mechanisms of ceramic superconductivity but also because these phases are often formed during synthesis of useful superconducting structures (i.e., thin films (*7*) or composites (*8*)). Recently, the fabrication and characterization of a Au–$Ba_2YCu_3O_7$ composite was described (*8*). In light of this report, we present results on the formation and properties of Au(III)-doped $Ba_2YCu_3O_{7-\delta}$. We discuss these results as they relate to the known chemistry of Au(III) and the use of gold in structures containing ceramic superconductors.

The oxides were synthesized from CuO, BaO_2, Y_2O_3, and Au_2O_3 powders ground together and fired at 950°C for 32 hr. X-ray

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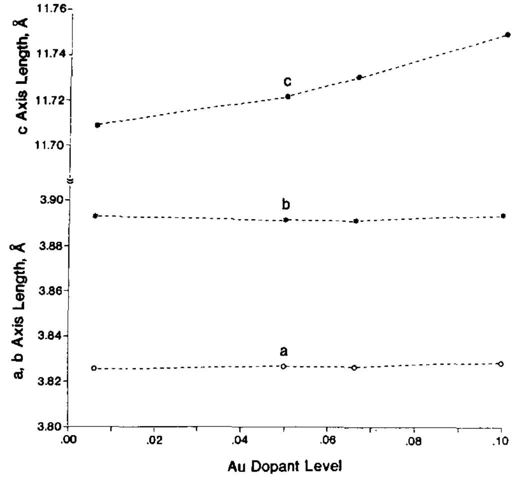

FIG. 1. Lattice parameters of Au(III)-doped $Ba_2Y Cu_3O_{7-x}$ vs Au(III) doping level. Note that *a* and *b* axes remain constant while *c* axis expands 0.06 Å.

photoelectron spectroscopy (XPS) measurements were made on a Perkin–Elmer XPS-AES-SIMS instrument. The ac susceptibility and the dc resistance were used to measure T_c. X-ray diffraction data were collected on a Scintag diffractometer using monochromated Cu$K\alpha$ radiation.

Structural data for a series of $Ba_2Y(Cu_{1-x}Au_x)_3O_{7-\delta}$ superconductors is shown in Fig. 1. The assignment of the trivalent oxidation state is made by virtue of XPS data which shows a shoulder at 87 eV. This 3-eV shift from metallic gold is characteristic of the trivalent state (*9*). Maintainance of the integrity of the *a–b* plane and expansion of the *c* axis is the most striking result of our study. These results stand in stark contrast to earlier results with trivalent metal ion doping which produces a tetragonal structure for Fe (*4–6*), Co (*4–6*), Al (*6, 7*), and Ga (*5*) for $x < 0.10$. An interesting illustration of the lengthening of the *c* axis is shown in Fig. 2. As the mole percentage of Au(III) is increased from $x = 0$ to 0.05 and then to 0.10, the 006 peak in the X-ray pattern shifts to lower 2θ values while the 020 and 200 peaks remain stationary. This destroys the coincidence existing between the 006 and 020 peaks in the X-ray pattern of the native structure.

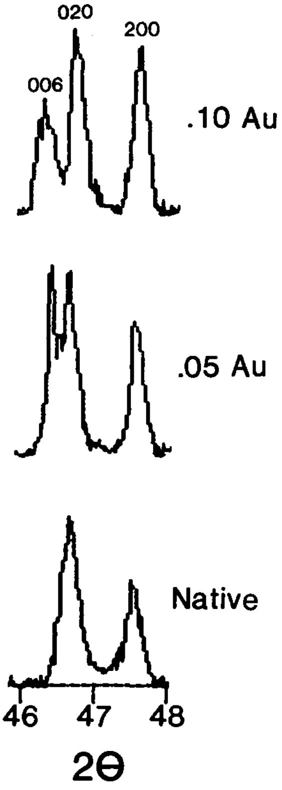

FIG. 2. X-ray patterns for doped $Ba_2YCu_3O_{7-x}$ vs Au(III) level; shows split of 006 from 020 as 020 and 200 remain constant.

A brief summary of structural and electrical data for well-characterized metal-doped $Ba_2YCu_3O_{7-\delta}$ is outlined in Table I and includes data from this study. As noted above, trivalent metal ions predominantly substitute for copper at the Cu(1) site along chains though Fe(III) may also dope at the Cu(2) site (*6*). While no single-crystal data exist for divalent metal-doped species, powder X-ray and thermogravimetric analysis (TGA) data on the effect of metal doping on Cu(1) bound oxygen removal points to doping in the *a–b* plane (*6*).

Structural studies of the perovskite superconductor show that the Cu(1) site can

TABLE I

STRUCTURAL AND ELECTRICAL DATA* OF METAL-DOPED $Ba_2YCu_3O_{7-\delta}$

Dopant	Electronic structure	Dopant level**	Dopant location	Structure	T_c (K)***
Al^{3+}	$2s^22p^6$	0.03	Cu(1) (*7*)[a]	Tetr. (*6, 7*)	92 (*6*)
		0.07	Cu(1) (*7*)[a]	Tetr. (*4, 7*)	<4 (*7*), 85 (*6*)
Fe^{3+}	$3d^5$	0.10	Cu(1,2) (*6*)[b]	Tetr. (*4, 5*)	38 (*3*)
		0.17	Cu(1) (*4*)[a]	Tetr. (*4, 6*)	0 (*4, 6*)
Co^{3+}	$3d^6$	0.10	Cu(1) (*6*)[c]	Tetr. (*4–6*)	21 (*3*)
		0.33	Cu(1) (*4*)[a]	Tetr. (*4, 6*)	0 (*4, 6*)
Ni^{2+}	$3d^8$	0.10	Cu(2) (*6*)[c]	Orth. (*6*)	40 (*6*)
Zn^{2+}	$3d^{10}$	0.15	Cu(2) (*6*)[c]	Orth. (*6*)	0 (*5*)
Ga^{3+}	$3d^{10}$	0.20	Cu(1) (*5*)	Tetr. (*5*)	60 (*5*)
Au^{3+}	$5d^8$	0.01	Cu(1)	Orth.	92[d]
		0.05			89[d]
		0.07			92[d], 90[e]
		0.10			89[d]

* Data obtained from noted references and/or determined by: [a]single-crystal X-ray structure, [b]Mössbauer, [c]TGA, [d]ac susceptibility, or [e]dc resistance.

** Dopant level in mole fraction per Cu atom.

*** Differences may be due to sample inhomogeneity or lack of oxygen annealing; see discussions in Refs. (*6*) and (*7*).

be described as formally Cu(III) in a square planar geometry and the Cu(2) site is five coordinate; Cu(II) sits above the plane of a square pyramid (*2*). Available data indicates that charge considerations determine site selection for copper substitution. This can be contrasted to other metal oxides like spinels, for example, where crystal field stabilization energy influences site selection (*10*). A d^8 ion such as Ni^{2+} tends to substitute at the Cu(1) site.

Structural considerations have been mentioned by several workers as leading to oxygen disordering. For example, substitution of Al^{3+}, which prefers octahedral coordination, eventually drives the structure to tetragonal to achieve a more stable Al coordination environment (*7*); the same argument could also apply to Ga^{3+} (*5*). Fe^{3+} and Co^{3+} which prefer tetrahedral or octahedral and octahedral coordination, respectively, have been noted to cause similar disordering (*4*). The differing effects of Ni^{2+} and Zn^{2+} may be in the increased tolerance of d^8 ions for 5 coordination as opposed to d^{10} Zn^{2+} which tends toward tetrahedral coordination.

With these considerations in mind, the influence of Au(III) is consistent with the observed substitution chemistry of perovskite superconductors and the chemistry of trivalent gold. Au(III) is known to form square planar complexes almost exclusively due to the large difference in energy between the unfilled $d_{x^2-y^2}$ and the filled d_{z^2} orbitals of the $5d^8$ ion. The expansion of the *c* axis can be attributed to the larger size of the Au(III) in the same way that a slight decrease in the *c* axis was noted for Al substitution (*7*). However, we did not observe an increase of the *b* axis which would be expected for simple substitution at the Cu(1) site. We believe there is a slight reordering of oxygen involving the *a–b* plane accompanied by reduction of the other Cu ions to Cu(I). More detailed studies are in progress to elucidate the exact nature of the oxygen ordering at the Au(III) site. We also considered Au(III) doping at the rare-earth site or simply not substituting into the lattice. However, neither result is consistent with a change in oxygen stoichiometry (vide infra) or the lack of a second phase such as $YBaCuO_5$ (*11*) which would be expected based on our reaction stoichiometries.

Reduction of Cu(1) on the chain to Cu(I) has also been observed to increase the *c* lattice parameter (*6*). In fact it has been noted that trivalent doping may be accompanied by either oxygen increase or reduction of Cu on the chain to Cu(I) (*4, 6*). Our crude weight loss results from reaction data indicate that there is a decrease in oxygen stoichiometry. These results can be contrasted to other trivalent substitutions which exhibit oxygen stoichiometries ≥ 7 for Co (*4, 6*), Fe (*4, 6*), Ga (*5*), or Al (*6, 7*). It is interesting to note that Zn doping may actually lead to a slight decrease in oxygen which correlates to Zn concentration ($\delta = 0.3$ when $x = 0.3$) and to the preferred tetrahedral coordination of Zn^{2+} (*6*). The loss of oxygen upon increased gold substitution is consistent with the square planar nature of Au(III) relative to the other trivalent ions. Substitution of Au(III) leads to formation of linear two-coordinate Cu(I) which leads to a loss of oxygen along the chains.

Data from other substitution studies indicate that doping in the *a–b* plane has a greater impact on superconductivity than doping on the chains (*3–7*). The impact of trivalent metal ion doping arises when the electronic configuration of the substituting ions induces a structural change, an oxygen disordering, and influences the structure of Cu(II) ions in the *a–b* plane. Au(III) substitution does not perturb the Cu(2) planes because its square planar geometry (consistent with its electronic configuration) does not induce an oxygen reordering sufficient to cause a structural change.

In conclusion, the *a* and *b* axes of the unit cell remain unchanged at 3.826 and 3.893 Å, respectively, and the *c* axis expands from 11.69 to 11.75 Å upon substitution of 10 mole% Au at Cu(1) on copper oxide chains. The *c* axis expansion correlates well with the doping level but the lack of *b* axis expansion could be the result of a slight oxygen reordering. The lack of a significant structural change upon substitution at the Cu(1) chains is reflected in the lack of a significant lowering of T_c. The observed structural chemistry of Au substituted into $Ba_2YCu_3O_{7-\delta}$ is consistent with known perovskite substitution chemistry and the well-known chemistry of Au(III). These results support earlier evidence of the importance of copper oxide planes for superconductivity in the perovskite superconductors (*6*) and point to Cu(1) chains as having more of a structural as opposed to an electronic influence on superconductivity in this class of ceramic superconductors. Finally, our results indicate that Au(III) substitution chemistry makes gold an excellent candidate for multiphased structures containing perovskite superconductors (*8*).

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