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Preparative Conditions for the Transition from Superconductivity to Nonsuperconductivity in Oxygenated Orthorhombic $YBa_2(Cu_{1-x}Ni_x)_3O_y$

Donggeun Ko & Hans Oesterreicher

Materials Science Program and Department of Chemistry, University of California, San Diego, La Jolla, CA 92093-0317, USA

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Abstract: When materials $YBa_2(Cu_{1-x})_3O_y$ with $x = 0{\cdot}05$ are quenched from $T_A \sim 1000$ K in air (designated Kp compounds in this state) and subsequently reoxygenated near $T_a = 670$ K (Ko compounds), they are orthorhombic but can have lost superconductivity and gained paramagnetism. This contrasts with the behavior of conventionally slow cooled oxygenating preparations (OP) which produce $T_c \sim 75$ K. Presented here are structural, magnetic and superconducting behaviors for materials given various thermal treatments. It is demonstrated that materials quenched from air annealing temperatures in the range of 950–1100 K (designated Kp) show volume expansion anomalies and slow reoxygenation kinetics, probably connected with charge localization. On reoxygenation a complex sequence of states is indicated, including the loss of diamagnetism and the gain of semiconductive type behavior. After long equilibrating annealing at 673 K in air, a reversal to conventional superconducting behavior can be achieved.

1 INTRODUCTION

The authors have recently observed[1] transitions from superconductivity to semiconductivity in oxygenated $YBa_2(Cu_{1-x}M_x)_3O_y$ with M = Ni and $x = 0{\cdot}05$. In particular it was found that an anneal of specimens with $x = 0{\cdot}05$ near 1020 K in air with subsequent quenching (materials are orthorhombic and designated Kp or K parent compounds in this state) and reoxidation near 670 K (Ko compound) results in orthorhombic materials with $y \sim 6{\cdot}9$ and $T_c < 4$K, which are semiconducting and paramagnetic. Kp compounds can have small amounts of superconducting phase and are diamagnetic in the temperature range of measurement. By contrast, the conventional oxygenation preparations,[2–6] (designated OP) yield $T_c \sim 75$ K. Both Ko and Kp are not noticeably different in their structures from the conventional materials, indicating that subtle differences may be responsible for the dramatic electronic effects. However, here it is shown that anomalous volume expansions are characteristic for Kp in some interval of T_A. This appears to indicate that charge localization is characteristic for these Kp materials, which in turn appears to be retained in their Ko counterparts. Some of the unusual electronic behavior of these materials is presented.

In order to facilitate discussion earlier[1,6,7] nomenclature is followed. Distinctions are made between annealings at temperatures higher than the kinetic limit of M diffusion (designated $T_A > 1000$ K) and lower (designated T_a). The incremental enthalpy of oxide desorption ΔH^* (asterisk denotes quantity per mol O_2) is used as a parameter to organize the relative strength of the redox treatment according to the vant Hoff representation $\log p = -\Delta H^*/19{\cdot}1T + \Delta S^*/19{\cdot}1$. We designate Ni in Cu(1) site with 4-fold O coordination as Ni(1)4. For a local thermodynamic model of inhomogeneous M distributions, the reader is referred to Ref. 7. The gist of this work is that distribution

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d = *M*(1) /*M*(2), as well as type of clustering, are strong functions of ΔH^* and form unavoidable responses of an *M* substituted O intercalation environment to changing redox conditions. Several states are accordingly predicted depending on the predominant local environment. We have designated a relatively ordered cluster state with one dimensional, spatially unlimited extent as U state, which is bordered by more disordered L and S states at higher and lower ΔH^*, respectively. These states can be subsequently reoxidized at T_a = 670 K. At these lower temperatures a further consideration is the attainment of different O chain lengths on Cu(1) sites depending on the magnitude of T_a. In addition, near $\Delta H^* \sim 230$ kJ a gradual transition from Ni^{2+} to Ni^{3+} oxidation state is expected. For Cu this transition occurs near ΔH^* = 200 kJ.

Generally for *M* = Ni the behavior described for *M* = Fe should be characteristically shifted[7] with respect to the relevant ΔH^*. The strong reduction in d = *M*(1)/*M*(2) near ΔH^* = 260 kJ and massive clustering observed near ΔH^* = 240 kJ for *M* = Fe should occur at lower ΔH^*. The massive clustering should just barely be observable under conventional preparation conditions due to the kinetic limit of *M* diffusion near 1000 K.

2 METHODS

Materials were initially prepared from the component oxides in the conventional way[1] with several intermittent regrindings and annealings in air near T_A = 1200 K and subsequent slow cooling in air (OP). In one series of experiments, parts of these samples were subsequently annealed in air at various temperatures and times and quenched into liquid N_2. Parts of these samples were characterized in this state, while other parts were subsequently reoxygenated at T_a = 673 K for varying times in air. The symbol for a reoxygenated material with the initial annealing at T_A = 1173 K is [1173 AQ; 673 AC] where A stands for air, Q for quenching, C for cooling, and the parentheses for separate independent thermal treatments. X-ray diffraction data were obtained with CuKα, and magnetization was measured on a vibrating sample magnetometer and a SQUID. Resistivities were determined by a 4 point probe method.

3 RESULTS

In Table 1 we show structural parameters obtained after quenching of $YBa_2(Cu_{1-x}M_x)_3O_y$ with x = 0·05 from various temperatures T_A. One notes that orthorhombic splitting occurs for T_A < 1050 K, which is considerably higher than that for the unsubstituted (x = 0) material ($T_A \sim 960$ K). This is opposite to common behavior for *M* = Co, Fe, etc. One also notes that two peaks in volume vs T_A are observed near T_A = 970 and 1083 K, mainly stemming from anomalous *c* axis expansion. When the material quenched from T_A = 1023 K is reoxygenated at 673 K for various times a continuous volume shrinkage over a period of more than 12 h was observed. This is also different from *M* = Fe, where volumes become stable after about 10 min reoxygenation.

It is interesting to note that the volume expansion corresponding to T_A = 1083 K can also be observed as a temporal phenomenon when a material, annealed at 1200 K and quenched, is subsequently reannealed at 673 K. After several hours,

Table 1. Lattice parameters of $YBa_2(Cu_{1-x}Ni_x)_3O_y$ with x = 0·05 as quenched into liquid N_2 from various air annealing temperatures T_A

T_A(K)	*a*(Å)	*b*(Å)	*c*/3(Å)	*V*(Å^3)
923	3·847	3·895	3·895	175·1
973	3·847	3·885	3·912	175·4
1063	3·867	—	3·927	176·1
1023	3·848	3·871	3·915	174·9
1050	3·864	—	3·914	175·3
1083	3·864	—	3·920	175·6
1123	3·857	—	3·919	174·8

Table 2. Structural and electronic properties of $YBa_2(Cu_{1-x}Ni_x)_3O_y$ with x = 0·05 given selected thermal treatments

Treatment[a]	*a*(Å)	*b*(Å)	*c*/3(Å)	T_c	Remarks[b]
OP	3.821	3.888	3.893	75	
Kp OP; 1023 AQ	—	—	—	—	Dia.
Ko OP; 1023 AQ; 673 AC	3.814	3.893	3.895	<5	0·36 μ_B
Ko OP; 1023 AQ; 673 AC	3.834	3.879	3.894	<5	Semi

[a] Typical preparation of Ko involves annealing of conventional material (OP) in air at 1023 K, quenching (Q), reoxygenation at 673 K (673), and air cooling (C).

[b] Dia. indicates diamagnetism to ~200 K, μ_B are effective magnetic moments per transition metal estimated from paramagnetism. Semi means semiconducting behavior in the resistivities.

volume increases and subsequently again diminishes. This indicates that the volume anomaly is connected with the degree and nature of oxidation rather than with temperature per se or insufficient oxygen uptake y. We shall generally refer to materials in the region of volume anomalies as Kp materials. It is these materials which, when reoxygenated for various times at $T_a = 673$ K, can show the complex phenomenology of Ko compounds, including semiconductivity (absence of superconductivity) and paramagnetism. Aspects of this phenomenology are presented in Table 2 for selected materials. The semiconducting and paramagnetic nature of Ko compounds have been described elsewhere.[1] After annealing for more than several days at 673 K in air, conventional superconductivity can be recovered.

4 DISCUSSION

In comparison with conventional OP materials which are only slightly depressed in their T_c on partial Ni substitution, materials given an extended heat treatment in the range from 950–1100 K (Kp materials) do not readily reoxidize to a superconducting state. It is therefore important to better understand the properties of Kp compounds. In this paper we demonstrate novel aspects of Kp compounds, namely anomalous volume expansions in the range of $T_A \sim 950$–1100 K or $\Delta H^* = 200$–230 kJ. We tentatively ascribe these anomalies to unusual localizations of positive charge. We also show that the orthorhombic region for M = Ni is expanded in temperature over the one for unsubstituted ($x = 0$) materials. Longtime annealing in an orthorhombic structure could also have special effects on the state of the materials.

The transition from Kp to Ko compounds appears to be a complex one involving an unfolding in time of various states in a manner yet to be explored in more detail. In the initial stages a transition from diamagnetic to paramagnetic can occur. When enough time is given on reoxygenation, the conventional superconductivity can be re-established. The key to understanding this transition lies in an understanding of special properties of Kp. In principle, transitions to Ko are most readily obtained from Kp materials with $T_A < 1000$K. In this region Kp are orthorhombic and have rather slow reoxygenation kinetics. We ascribe the orthohombic nature of the material to extensive Ni clustering along <100> which forces preferential O filling in micro-domains dominated by the Ni. A similar situation can also be assumed to extend into the tetragonal regime, although the micro-domains are now too small to be noticeable by X-ray diffraction. In addition, there are two regions of relative volume expansion near 970 and 1080 K, respectively. The first may be connected with localization of Cu^{3+} states and the second with localization of Ni^{3+} states, given the general expectations for the trends in oxidation of the two metals as described above. These charge localizations probably reduce the reoxydation kinetics and contribute to some disorder in the O chains. At lower temperatures more of the oxidized Cu or Ni species are obtained but they are more successful in delocalizing their charge with neighboring atoms, resulting in a volume shrinkage. The unusual microstructure, together with the volume expansion and anticipated valence transitions, appears to influence the extent and nature of subsequent reoxygenation to Ko.

Neutron diffraction[1] has shown rather normal structural behavior for a Ko compound with roughly equal occupation of Ni on Cu(1) and Cu(2) sites and $y \sim 6{\cdot}9$. However, this material is not superconducting to 5 K and shows semiconducting type behavior in the resistivities. We tentatively ascribe this behavior to the O chain disorder brought about by the Cu^{3+} charge localization originating in Kp. We want now to generalize the implications of this behavior and suggest that the region near $\Delta H^* = 200$ kJ plays a more general role in producing somewhat disordered O chain growth in partly substituted materials (also for M = Co, Fe, etc.) We assume that this has to do with an initial localized Cu^{3+} as given by a special local O configuration. The disordered chain growth established near $\Delta H^* \sim 200$ kJ does not allow a high degree of O order at lower temperatures. This results in relatively low T_c and trends to tetragonal for OP that is conventionally slow cooled oxygenating preparations. When materials are first reduced at elevated temperatures, quenched, and reoxygenated at lower T_a (referred to as RP in Refs 1, 6 and 7), dramatically different properties are obtained as a rule. In this case the range of incipient charge localization on Cu with concomitant O chain disorder is avoided.

The most intriguing points of this study pertain to the fundamental complex interplay of redox treatment with local environment. This can have pronounced consequences on electronic properties such as magnetism and superconductivity. From an applied point of view, this study shows how to create unusual electronic properties in materials which are structurally very similar to the conventional materials and can therefore form non-superconducting substrates for conventional superconductors.

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