Interrelation Between Structural and Electrical Properties in $RuSr_2GdCu_2O_{8\pm Z}$ Prepared Under Different Annealing Conditions

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***Abstract*—The effect of annealing in flowing oxygen on the structural and electrical properties of the rutheno-cuprate $RuSr_2GdCu_2O_{8\pm z}$ (Ru-1212) was investigated. The solid-state reaction method was used to synthesize the Ru-1212 compound at ambient pressure using temperatures between 960 and 1000 °C in air. Pure-phase samples were obtained and then annealed in flowing oxygen at 1060 °C for 0, 48, 72, or 168 hrs. The structural data of each sample were refined by the Rietveld method. Cell parameters, *a* and *c*, as well as the Cu-O(1) interatomic distances increase as the annealing time in flowing oxygen increases. The temperature-dependent electrical resistance of the sample that was not annealed in flowing oxygen shows semiconducting behavior. In contrast, samples annealed in flowing oxygen show superconducting transitions. All these results indicate that the structural and electrical properties of the Ru-1212 compound are related.**

***Index Terms*—Electrical resistance measurement, granular superconductors, magnetic materials, ruthenium, X-ray diffraction.**

I. Introduction

SUPERCONDUCTIVITY and magnetism are two ordered states into which materials can condense at low temperatures. These two states, in general, are detrimental to one another. Tremendous interest has been devoted to study compounds in which magnetism and superconductivity coexist. Examples of compounds that exhibit this exotic behavior are the copper-ruthenium oxides $RuSr_2LnCu_2O_8$ (Ru-1212) and $RuSr_2(Ln_{1+x}Ce_x)Cu_2O_{10}$ (Ru-1222) with Ln = Sm, Eu, and Gd, synthesized for the first time by Bauernfeind *et al*. [1]. The crystal structure of the Ru-1212 layered cuprate is derived from the $YBa_2Cu_3O_7$ system, where the Cu–O chains in the charge reservoir block are replaced by RuO_2 planes [2], [3]. The influence of cation substitution on the physical properties in the Ru-1212 system has been reported in the literature [4]–[10]. The superconducting transition Tc in Ru-1212 occurs at temperatures far below the ferromagnetic transition. Several values of Tc have been reported in the literature. The superconducting transition seems to depend on the sample synthesis and annealing conditions [11], [12]. Furthermore, several authors report the formation of a small amount of ferromagnetic SrRuO3 impurity. Some of them indicate the sintering method used to remove this impurity [13]–[17]. In the studies that use a sintering step with flowing oxygen, the annealing time may vary from 10 hours up to 7 days. So far, there is no report that presents precise time of oxygenation that is needed to obtain a pure-phase Ru-1212 superconductor.

We have obtained a pure phase of superconducting Ru-1212 compound without performing a reaction with N_2. The importance of this paper is to present a detailed study of the precise time of oxygenation for obtaining the superconducting phase. In the present contribution, we report the relationship between structural and electrical properties of the rutheno-cuprate $Ru_2Sr_2GdCu_2O_{8\pm z}$ annealed at different times in flowing oxygen.

II. Experiment

$RuSr_2GdCu_2O_{8\pm z}$ samples were sintered by the solid state reaction method from high purity (≥99.9%) starting powders of RuO_2, $SrCO_3$, Gd_2O_3, and CuO. The stoichiometric mixture of powders was ground in an agate mortar, homogenized, and heat treated at temperatures ranging from 960 to 1000 °C for 3 days in air. The process was repeated five times. The powders were then pelletized and annealed in oxygen flowing at 1060 °C for 0, 48, 72, or 168 hrs., followed by a slow cooling down to room temperature at 50 °C/hr.

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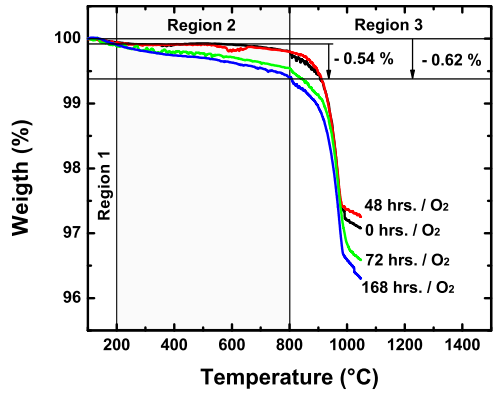

Fig. 1. Thermogravimetric analysis of $RuSr_2GdCu_2O_{8\pm z}$ samples annealed in flowing oxygen at 1060 °C for 0, 48, 72, or 168 hrs.

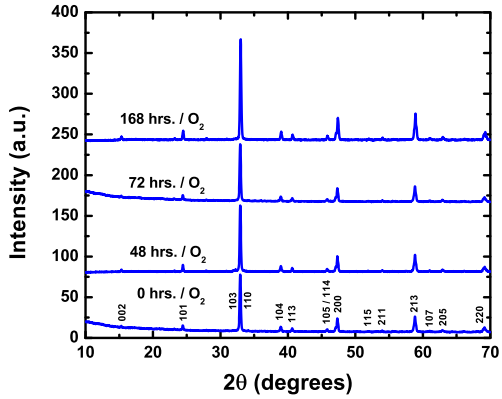

Fig. 2. XRD patterns of Ru-1212 samples annealed in flowing oxygen during different periods of time. All lines observed are indexed in space group P4/mmm.

Samples were characterized by X-ray powder diffraction (XRD) using an APD 2000 diffractometer with CuK_α radiation ($\lambda = 1.5406$) Å and a graphite monocromator. Diffraction patterns were collected at room temperature over the range $10° \leq 2\theta \leq 70°$ with a step size of 0.025° and a time per step of 15 sec. Refinement of the crystal structures was carried out by using the Rietveld method with the Fullprof program. The change in the morphology and grain size of the samples obtained under different heat treatments were observed by scanning electron microscopy (SEM) using a HITACHI S-3400N-II system. The micrographs at 5.00 K X were taken with a voltage of 20 kV, a current intensity of 1000 pA, and WD = 10 mm. Energy Dispersive X-Ray (EDX) was performed on the same system equipped with an EDAX 9900 device. Low temperature dc resistance measurements were performed using the standard four-probe method from room temperature down to 8 K.

III. Results and Discussion

Thermogravimetric analysis (TGA) of samples treated in flowing oxygen at high temperature is shown in Fig. 1. The data show that the amount of oxygen incorporated into the cell of the material is correlated with the duration of the heat treatment. Three characteristic weight loss regions were observed in all samples. In the first region, from room temperature to 200 °C, there is a weight loss of 0.1% that is associated with humidity and possible water formed on the surface of the materials. In the second stage of weight loss from 200 to 800 °C, a constant decrease of weight is observed and is attributed to the elimination of the oxygen that was adsorbed during the different oxygenation processes carried out at high temperature. The largest weight loss is observed in the sample that was annealed for the largest amount of time, 168 hrs. The final continuous weight loss occurring between 800 and 1025 °C is associated with the formation of strontium carbonate on the surface of the material, which is associated to the high reactivity of strontium with environmental CO_2.

XRD patterns of the annealed samples are shown in Fig. 2. They display a tetragonal structure with space group P4/mmm. No impurities were detected in the XRD patterns. In particular, the $SrRuO_3$ impurity commonly observed in the XRD patterns is not present in any of the samples represented in Fig. 2. The calculated structural parameters are presented in Table I, which are in good agreement with other reports [18], [19]. The lattice parameters *a* and *c* as well as the Cu-O(1) interatomic distances slightly increase with the duration of the annealing treatment.

TABLE I
Structural Parameters of Samples Annealed at Different Durations in Flowing Oxygen

	0 hrs.	48 hrs.	72 hrs.	168 hrs.
a	3.8364	3.83696	3.83930	3.83903
c	11.5601	11.56476	11.56446	11.56534
Ru-O(1)	1.93011	1.93088	1.93084	1.93098
Ru-O(3)	1.96761	1.96788	1.96908	1.96895
Cu-O(1)	2.18178	2.18265	2.18260	2.18277
Cu-O(2)	1.92567	1.92594	1.92710	1.92697
Ru-O(3)-Ru	154.269	154.269	154.269	154.269
Cu-O(2)-Cu	169.916	169.913	169.920	169.918
Cu-O(1)-Ru	171.536	171.538	171.533	171.534

Distances are in angstroms and angles in degrees.

The morphology of the annealed samples was characterized by SEM. We found that there is not a notable difference among the samples, showing similar characteristics in their morphology. Fig. 3 shows the SEM micrograph of one of them, revealing that the samples are porous with different size grains, from 1.1 up to 2.2 μm. The chemical composition of each sample was confirmed by EDX, showing that all of them are stoichiometric.

A remarkable difference was found in the electrical properties. The temperature dependence of the electrical resistance of each annealed sample is shown in Fig. 4. The sample that was not annealed in flowing oxygen shows semiconducting behavior, that is, its resistance rapidly increases as temperature decreases. At 10 K, resistance values are 125 times larger than the value obtained at room temperature; at 50 K, 36 times larger. No metallic transition was found in this sample. In contrast, the onset of superconductivity appears to show at 38, 42 and 37.5 K for the samples annealed in flowing oxygen during 48, 72, and 168 hrs., respectively. At 50 K, the resistance values in these three samples are, respectively, only 1.1, 1.4, and 1.6 times larger than the value obtained at room temperature.

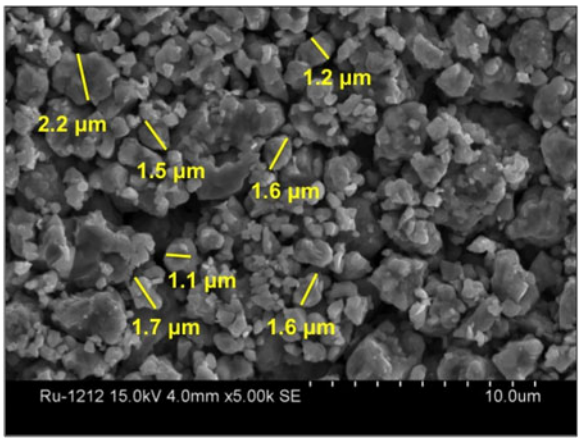

Fig. 3. Scanning electron microscopy of $RuSr_2GdCu_2O_{8\pm z}$ annealed in flowing oxygen at 1060 °C for 168 hrs. The sizes of different grains are indicated.

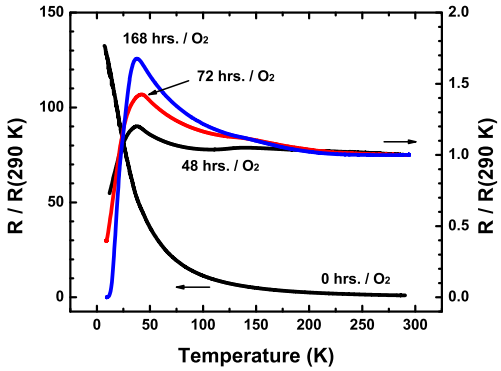

Fig. 4. Normalized resistance versus temperature of Ru-1212 samples annealed in flowing oxygen during different periods of time.

The 168 hrs. annealed sample is the only one to have zero resistance, which is observed at temperatures below 10 K. Such behavior is commonly seen in inhomogeneous or granular superconductors [20].

IV. Conclusion

In summary, we have succeeded in obtaining a pure phase of the $RuSr_2GdCu_2O_{8\pm z}$ system. The $SrRuO_3$ impurity commonly observed in XRD was eliminated without the need of reacting the samples with flowing nitrogen. TGA analysis confirms that samples annealed in flowing oxygen for longer time intervals present higher oxygen content. Rietveld refinement of the crystal structures shows that the duration of the annealing in flowing oxygen affects the structural parameters, whereas resistance measurements demonstrates that superconductivity can be induced in the samples. The required annealing time to produce the superconducting phase is 168 hrs., which is shorter than that reported by other groups.

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