

Study on the Structural, Electrical and Magnetic Properties of the $Ru(Sr_{2-x}Ba_x)GdCu_2O_{8\pm z}$ System

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Abstract—Samples of the $Ru(Sr_{2-x}Ba_x)GdCu_2O_{8\pm z}$ system, with $x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.25$ and 0.50 were prepared through solid-state reaction at ambient pressure at $980\text{--}1025^\circ\text{C}$. From the X-ray diffraction (XRD) patterns, it was observed that the substitution of Sr by Ba takes place iso-structurally into a tetragonal structure (space group $P4/mmm$). Rietveld refinement analysis indicates that both $Cu\text{-O}(1)$ and $Ru\text{-O}(1)$ bond lengths strongly depend on Ba content. The temperature dependence of the electrical resistance for the samples with $0.0 \leq x \leq 0.25$ annealed in flowing oxygen at 960°C for 2 hrs. show a semiconducting behavior, whereas samples annealed during 30 hrs. present a semiconducting-to-metal transition. Results of the DC magnetic susceptibility measurements on samples annealed for 2 hrs. indicate that all samples exhibit ferromagnetic ordering, with magnetic transition temperature T^{Curie} that depend on Ba content with a dependence that seems to be similar to one found for the bond lengths.

Index Terms—Magnetic materials, superconducting materials, X-ray diffraction.

I. INTRODUCTION

THE hybrid ruthenocuprate $RuSr_2GdCu_2O_8$ ($Ru\text{-}1212$) compound has attracted a strong attraction due to the extraordinary coexistence of high- T_c superconductivity and magnetism [1], [2]. This compound is structurally similar to the high- T_c superconductor $YBa_2Cu_3O_7$ [1]. It is believed that in these ruthenocuprates, the RuO_6 octahedra in the charge reservoirs are the main responsible for both magnetism and doping holes into the superconductive CuO_2 plane. In order to elucidate the interplay between SC and FM in ruthenocuprates, several substitutions in the Ru , Sr , Gd , and Cu sites have been carried out in the past few years. It is observed that magnetism and superconductivity depend on the type of cation and the substitution. These results are indicative of a strong correlation between superconductivity and magnetism. The substitution at Sr

site by another alkaline earth metals such as Ba , is very interesting, because allows us to study the effects of the cell-parameter variations on the physical properties of the ruthenocuprate compounds. It is expected that structural, electric and magnetic properties of $RuSr_{2-x}Ba_xGdCu_2O_8$ system should be affected due to the following main behaviors: 1) the Sr ions are located between the RuO_2 and the CuO_2 planes and 2) the Ba ion is larger than the Sr .

Yang *et al.* [3] have studied the superconducting properties of $RuSr_{2-x}Ba_xGdCu_2O_8$ ($0 \leq x \leq 0.1$) and have found that the superconducting transition temperature is enhanced by Ba substitution on the Sr sites.

In this paper, we investigate the effects of Ba substitution on the electrical, structural and magnetic properties of $Ru\text{-}1212$. The aim of our study is to find the limit of solubility of $RuSr_{2-x}Ba_xGdCu_2O_8$ system synthesized by solid-state reaction method at ambient pressure and study the effects of the substitution of Sr^{2+} by Ba^{2+} ions on the structural, electrical and magnetic properties, as well as to investigate the relationship among them for the samples annealed in flowing oxygen for 2 hrs. and 30 hrs.

II. EXPERIMENTAL PROCEDURE

The $RuSr_{2-x}Ba_xGdCu_2O_8$ system with $x = 0.00, 0.05, 0.10, 0.15, 0.20, 0.25,$ and 0.50 were synthesized through a solid-state reaction technique at ambient pressure from stoichiometric amounts of RuO_2 (99.9% STREM), Gd_2O_3 (99.99%, STREM), CuO (99.99%, ALDRICH), $BaCO_3$ (99.5%, ALDRICH) and $SrCO_3$ (99.5%, CERAC) reagents. Prior to weighing, $SrCO_3$ and $BaCO_3$ compounds were preheated for 10–20 min at 120°C for dehydration. A stoichiometric mixture for each desired composition was ground in an agate mortar in air. The reactions were carried out in air, in high alumina crucibles inside an electrical furnace ($\pm 4^\circ\text{C}$) operating at temperatures between 980°C and 1025°C for 24–72 hrs., with intermediate grindings of the samples. It is important to mention that for each composition, different temperature ranges were used (see below), in such a way that for $x = 0.00$, $T = 980\text{--}1000^\circ\text{C}$; for $0.05 \leq x \leq 0.15$, $T = 1000\text{--}1015^\circ\text{C}$, and for $0.20 \leq x \leq 0.50$, $T = 1000\text{--}1025^\circ\text{C}$. Following the treatment in air, X-ray data revealed that samples with $0.00 \leq x \leq 0.25$ presented a small $RuSrO_3$ impurity. Such an impurity, once formed, seems to be very stable and difficult to remove during the reaction at higher temperatures [1]. The materials, therefore, were ground again and annealed in flowing argon at 960°C after

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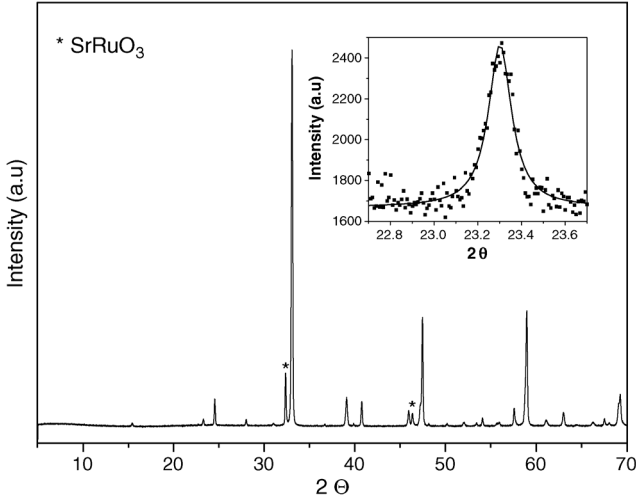


Fig. 1. XRD patterns of the $RuSr_{1.75}Ba_{0.25}GdCu_2O_8$ sample. The inset shows an amplification of the data for the interval $22.7-23.7^\circ$.

decomposition in air. With this particular procedure, the formation of such $RuSrO_3$ impurity was reduced only on the samples with $0.05 \leq x \leq 0.25$, in the range that we observe the solubility. The resulting powders were then pressed into pellets and annealed at $960^\circ C$ for 2 hrs. and 30 hrs. in flowing oxygen and then slowly cooled down to room temperature. XRD patterns were obtained on a Bruker D8 diffractometer with $Cu K\alpha_1$ radiation. Diffraction patterns were collected at room temperature over the 2θ range of $5-70^\circ$ with a step size of 0.02° and a time-per-step constant of 10 secs. Refinement of the crystal structures was carried out by using the Rietveld method with the *FullProf* program [4]. Electrical resistance measurements were performed in a closed cycle refrigerator instrumented with low-level measurement equipment. The four-probe technique, in combination with a commutation method in a constant-current mode, was utilized [5]. Copper wires were connected on the surface of the samples and were attached using commercial silver paint. Applied current used in all samples was 1.0 mA. DC-magnetization measurements were performed in a superconducting quantum interference devise (SQUID) based magnetometer, in the temperature range 4–250 K.

III. RESULTS AND DISCUSSIONS

A. Structural Properties

The results of the XRD patterns for the $RuSr_{2-x}Ba_xGdCu_2O_8$ system indicate that for $x = 0.00$, the sample is single phase, whereas for samples with $x = 0.05, 0.10, 0.15, 0.20$ and 0.25 , small additional intensities are observed. These additional reflections are attributed to the formation of the $SrRuO_3$ phase. The $SrRuO_3$ compound reveal magnetic order around 165 K; however, we have found no anomalies in the magnetic measurements around this temperature, indicating, therefore, that the amount of spurious phases is only marginal. All XRD performed at room temperature on the samples investigated revealed the same primitive tetragonal structure of the undoped $RuSr_2GdCu_2O_8$ compound. In Fig. 1, we present the XRD pattern for the $x = 0.25$ sample. Similar results were obtained

TABLE I
RESULTS STRUCTURAL PARAMETERS OF THE $RuSr_{2-x}Ba_xGdCu_2O_8$ SYSTEM

x	0	0.05	0.10	0.15	0.20	0.25
a (Å)	3.8305	3.8309	3.8320	3.8325	3.8329	3.8328
c (Å)	11.508	11.519	11.521	11.524	11.527	11.533
Bond lengths (Å)						
Ru-O(1)	2.157	2.116	2.089	2.073	2.139	2.163
Ru-O(3)	1.971	1.972	1.972	1.972	1.973	1.973
Cu-O(1)	1.845	1.931	1.964	1.981	1.938	1.934
Cu-O(2)	2.064	2.062	2.042	2.052	2.051	2.058
N(Ba)	0	0.003	0.006	0.009	0.012	0.016

for all samples. The Ba^{2+} substitution for the Sr^{2+} sites into a single $Ru-1212$ phase is successful only up to a 25% of Ba . For the sample with $x = 0.5$, a mixture of $SrRuO_3$, Sr_2GdRuO_6 , and $Ru-1212$ phases was detected.

The XRD patterns of all samples were Rietveld-fitted, taken into account the possibility that the Ba ion can also occupy the Sr ion sites. The presence of $SrRuO_3$ secondary phase was included using a space group (S.G.) $P4/mmm$ ($n^\circ 123$). The Ru ions occupy the crystallographic $1b$ sites (0, 0, 0.5); Gd ions, the $1c$ sites (0.5, 0.5, 0); Sr and Ba ions occupy the Wyckoff position $2h$ (0.5, 0.5, z); Cu , the $2g$ position (0, 0, z); and the oxygen ions are distributed among the $8s$ (x , 0, z), the $4o$ (x , 0.5, 0.5), and the $4i$ (0, 0.5, z) positions. The oxygen sites in the SrO , CuO_2 , and RuO_2 planes are denoted by $O(1)$, $O(2)$ and $O(3)$, respectively.

For the Rietveld refinement, a tetragonal base structure was chosen, with a $P4/mmm$ space group and lattice parameters $a = 3.83032$ Å, $c = 11.5494$ Å, as proposed by McLaughlin *et al.* [6]. The orthorhombic cell proposed by Martinelly *et al.* [7] was not taken into account. On one hand, Martinelly *et al.* point out that differences between tetragonal and orthorhombic structures are very subtle and that the Rietveld study using only the tetragonal cell is very successful even if the orthorhombic structure is present [7]. On the other hand, in our study, none of the analysed spectra showed a clear peak splitting for the ($h0l$) planes. The inset of Fig. 1 presents an amplification of the peak ($h0l$) = (100), showing that the peak doesn't present splitting.

The results of the refinement of the XRD patterns are summarized in Table I. From this data, we can confirm that the Ba ions indeed occupy the Sr ion sites, and, on the other hand, the structural parameter values of the undoped sample are in agreement with other published results [5], [8].

The partial substitution of Ba^{2+} for Sr^{2+} is accompanied by an insignificant increase in the a -axis, whereas the c -axis shows a considerable increase with x . The net result is an increase in the volume when increasing x , which can be attributed to the

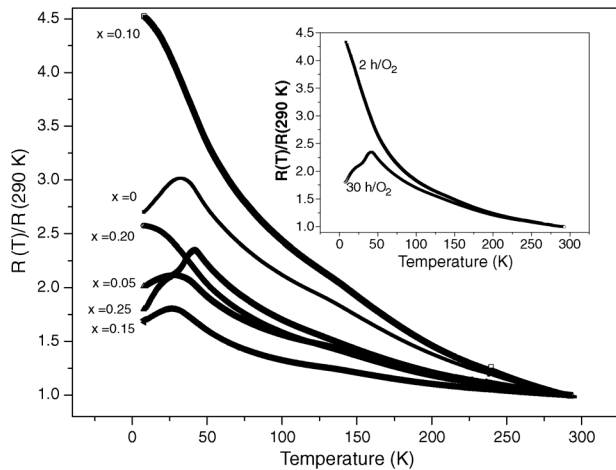


Fig. 2. Resistance as a function of temperature of the $RuSr_{2-x}Ba_xGdCu_2O_8$ system. The inset shows the resistance of the sample with $x = 0.25$ annealed in flowing oxygen for either 2 or 30 hrs.

fact that the Ba ion is larger than the Sr one ($IR^{XII}Ba^{2+} = 1.61 \text{ \AA}$ and $IR^{XII}Sr^{2+} = 1.44 \text{ \AA}$) [9], suggesting, therefore, that Ba ions successfully substitutes for Sr .

The bond lengths of the $RuSr_{2-x}Ba_xGdCu_2O_8$ system are also shown in Table I. The apical oxygen atoms $O(1)$ of the CuO_5 square pyramid are closer to the Sr ion site and are, therefore, the most affected by the Ba ion substitution. The Rietveld-refinement results presented in this table also show that the $Cu-O(1)$ bond length increases with increasing x , whereas the $Ru-O(1)$ bond length first decreases by increasing Ba substitution up to 15% and then increases. The former relationships could be attributed to the rise in the c -axis with x , as mentioned before. The later relationship, however, is related to the magnetic properties, as explained below, and represents one of the main contributions of this work. In contrast, it is observed that the $Cu-O(2)$ and $Ru-O(3)$ distances remain unchanged at the values of 2.06 and 1.97 \AA , respectively.

B. Electrical Properties

Fig. 2 shows the normalized electrical resistance as a function of temperature for the $RuSr_{2-x}Ba_xGdCu_2O_8$ samples with $x = 0.0, 0.05, 0.10, 0.15, 0.20,$ and 0.25 annealed in flowing oxygen for 30 hrs. We observe that the samples with $x = 0.0, 0.05, 0.15,$ and 0.25 show the same characteristic semiconducting behavior with a semiconductor-to-metal transition at temperatures $T = 32, 25, 25,$ and 41 K , respectively. In all samples tested, no superconductivity was found in the temperature interval measured. The inset of Fig. 2 shows the normalized resistance versus temperature of the sample with $x = 0.25$ annealed in flowing oxygen for two different times 2, and for 30 hrs., respectively. From this study, we note that long annealing time in flowing oxygen permits to obtain a semiconductor-to-metal transition with a drop of the resistance at $T = 41 \text{ K}$. Therefore, the annealing time in flowing oxygen plays an important role in improving the electrical properties. This behavior was observed for all samples.

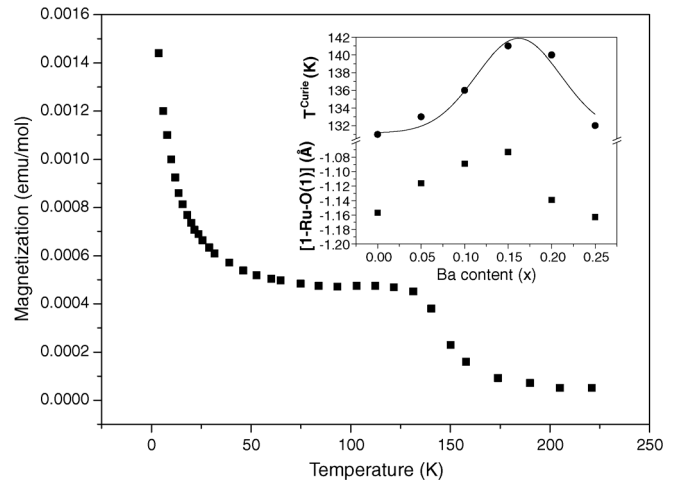


Fig. 3. Magnetization measurement as a function of temperature of the $RuSr_{1.75}Ba_{0.25}GdCu_2O_8$ sample. The inset shows T^{Curie} and $[1-Ru-O(1)]$ bond distances as a function of Ba content x in the $RuSr_{2-x}Ba_xGdCu_2O_8$ system.

C. Magnetic Properties

The results of the temperature dependence of the DC-magnetization measurements $M(T)$ performed in an applied magnetic field $H = 10 \text{ Oe}$ indicate that samples annealed at 2 hrs. show the characteristic ferromagnetic ordering transition at temperature between $T = 131 \text{ K}$ and 141 K . Fig. 3 presents the magnetization M as a function of the temperature T of the sample with $x = 0.25$. By taking the numerical derivative on this profile, that is, dM/dT , a value of $T^{Curie} = 132 \text{ K}$ was obtained for the ferromagnetic ordering transition temperature. Similar profiles (not shown) were obtained for the other samples, but the magnetic transitions obtained by the same numerical method were found to appear at different temperatures and to depend on Ba content x . T^{Curie} values obtained for $x = 0, 0.05, 0.1, 0.15, 0.20,$ and 0.25 were 131, 133, 136, 141, 140, and 132 K, respectively.

In Fig. 3, we also note that at temperatures below 40 K, the $M(T)$ curves show an increase in the magnetization due to the paramagnetic contribution of the Gd ions. The Gd sublattice remains in the paramagnetic state when the Ru sublattice is ordered ferromagnetically at $T = 132 \text{ K}$. The inset of Fig. 3 shows the Ba -content dependence of both the T^{Curie} and the relative distance that the $Ru-O(1)$ bond length makes with respect to 1 Angstrom, that is, the quantity $[1-Ru-O(1)]$. An interesting result that can be observed here is that the relative distance $[1-Ru-O(1)]$ increases with increasing Ba content with a maximum peak around $x = 0.15$, and then decreases for larger values of x , resulting into a broad peak. On the other hand, T^{Curie} values of the $RuSr_{2-x}Ba_xGdCu_2O_8$ system show a similar dependence on the substitution of the Ba in the Sr site with a broad peak centered around $x = 0.15$. This interesting similarity indicates that the Ru ions that appear in the $Ru-O(1)$ bond distances not only contribute to the layers of the charge reservoir, but also are responsible for the occurrence of the magnetic order in the $Ru-1212$ compound. It is expected, therefore, that a Ba -induced modification in the $Ru-O(1)$ distances be accompanied by a similar change in the

magnetic properties, in this case, in the magnetic transition temperature T^{Curie} . Note, however, that this dependence of the ferromagnetic transition temperature on the Ba content found for our non-superconducting $Ru-1212$ samples contrasts with that reported by Yang *et al.* [3] obtained on equivalent but superconducting samples. They have found that the substitution of Ba^{2+} for Sr^{2+} ions in their superconducting samples do not change the ferromagnetic transition temperature ($T^{\text{Curie}} = 136$ K), a result that seems to be different to what we have found in our study. Our results, however, permit the observation of variations in the ferromagnetic temperature transition in the non-superconducting $RuSr_{2-x}Ba_xGdCu_2O_8$ system, and the corresponding correlation with the $\text{Ru}-\text{O}(1)$ bond-length changes. This brings the question whether the non-superconducting phase is responsible or not to enhance the observation of appreciable changes in the ferromagnetic transition temperature when the Ba ions are introduced into the cell. Therefore, the opposite results obtained from the Ba substitution on the two phases that the $Ru-1212$ system is able to manifests in its electrical transport properties (superconducting and non-superconducting) seem to be complementary rather than contradictory, and may bring clues to elucidate the coexistence of the superconductivity and magnetism in the undoped $RuSr_2GdCu_2O_8$ System.

IV. CONCLUSIONS

Solid solutions from $x = 0.0$ to $x = 0.25$ were obtained with the non-superconducting $RuSr_{2-x}Ba_xGdCu_2O_8$ system by solid-state-reaction at ambient pressure. Rietveld-refinement results show that all samples are iso-structural with the undoped $Ru-1212$ compound, although cell volume increases with barium content. Temperature-dependent resistance profiles of the samples annealed in flowing oxygen for 2 hrs. show a semiconducting behavior, with no transition to a metal nor superconducting phases. Samples annealed in flowing oxygen for 30 hrs. show also a semiconducting behavior, although they do present a semiconducting-to-metal transition at temperatures between $T = 25$ and 41 K. The T^{Curie} values

show a strong dependence with Ba content x , increasing with x until reaching a maximum value around $x = 0.15$, and then decreasing for larger x values. A quite similar dependence on Ba content was found in the $Cu-O(1)$ and $[1 - Ru-O(1)]$ bond lengths obtained at room temperature, although the maximum values seem to occurs at a slightly different value of x . This study proves that there exists a relationship between the variation of $Cu - O(1)$ $Ru-O(1)$ and bond lengths with the magnetic properties of the semiconducting $Ru-1212$ system.

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