



Ferromagnetic behavior of the $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_{8\pm z}$ system with $0.0 < x < 1.0$, synthesized at ambient pressure

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ABSTRACT

The $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_{8\pm z}$ system with $x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.9$ and 1.0 was studied by differential thermal analysis (DTA) in air in order to determine the temperature interval at which the formation of the $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ (Ru-1212) compound should be formed. For DTA data, samples were prepared by the solid-state reaction method at ambient pressure between 940°C and 1050°C . From the X-ray powder diffraction (XRD) patterns it was observed that this system is isostructural to the Ru-1212 compound. In addition, a pure phase up to $x = 0.4$ was obtained. Studies by the Scanning Electron Microscopy (SEM) technique produced a particle size around $1\text{--}5\ \mu\text{m}$. The results of Transmission Electronic Microscopy (TEM) studies confirm the tetragonal unit cell in the $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_{8\pm z}$ system. The temperature dependence of the electrical resistivity of the samples with $x = 0.1, 0.2$ and 0.4 annealed in oxygen flux for 6, 12 and 41 h, at $T = 960^\circ\text{C}$, shows a semiconducting behavior. The AC magnetic susceptibility measurement indicates ferromagnetic behavior with T^{Curie} between 130 and 138 K.

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1. Introduction

Copper–ruthenium oxides $\text{RuSr}_2\text{LnCu}_2\text{O}_8$ with $\text{Ln} = \text{Sm}, \text{Eu}$ and Gd were synthesized for the first time by Bauernfeind et al. [1,2]. The crystal structure of these compounds can be described as a triple perovskite represented by successive layers of $\text{RuO}_2/\text{SrO}/\text{CuO}_2/\text{Gd}/\text{CuO}_2/\text{SrO}$. After the discovery of the coexistence of ferromagnetism and superconductivity in this system by Bernhard et al. [3] intensive experimental and theoretical investigations have been focused on studying these phenomena, which are generally believed to be of two mutually antagonistic orders. The effect of substitution on the physical properties of this system has been reported in the literature [3–6]. Sn doping [5] decreases the magnetic temperature T_M from 138 K for $x = 0.0$ to 78 K for $x = 0.4$ in the $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ system and T_c increases from 36 K at $x = 0.0$ to 48 K at $x = 0.2$. On the other hand, a small fraction of Zn on the Cu site rapidly reduces T_c and superconductivity is completely suppressed for the 3% substituted sample [3,4]. The

$\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_8$ system allows the study of superconductivity and magnetism phenomena modifying the Cu–O and Ru–O planes responsible for each phenomenon. Klamut et al. [7] have reported the synthesis at high-pressure oxygen atmosphere of the $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_8$ system, ($0 \leq x \leq 0.75$) finding that the substitution of Cu ions on the RuO_2 planes increases the temperature of the superconducting transition from 45 K at $x = 0.0$ to 72 K for the $x = 0.3$ and 0.4 compositions. This paper, deals with the synthesis of $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_8$ system with $0.0 < x < 1.0$ by solid-state reaction with temperature readings less than 1085°C [6,7] without applying high oxygen pressure. The results of XRD, SEM, TEM analysis, electric and magnetic measurements are also reported.

2. Experimental procedure

2.1. Synthesis

By solid-state reaction technique, at ambient pressure, the samples with $x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.9$ and 1.0 of the $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_z$ system were prepared. The starting materials were

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polycrystals of RuO₂ anhydrous (99.9% STREM), Gd₂O₃ (99.99%, STREM), CuO (99.99%, ALDRICH) and SrCO₃ (99.5%, CERAC). Prior to weighing, SrCO₃ was preheated for 10–20 min at 120 °C to dehydration. RuO₂ was weighed in argon flowing glove bag to avoid the decomposition of this reagent. A stoichiometric mixture of these compounds was ground in an agate mortar in air. The DTA results exhibit an idea about the temperature interval in which the formation of the Ru-1212 compound should be formed for each composition. The reactions were carried out in platinum crucibles inside an electric furnace (± 4 °C). The interval of reaction temperature was 940–1050 °C; in air for 6–72 h, although it is important to mention that we have used different temperature range for each composition, so that for $x = 0.1$ and 0.2 , $T = 960$ – 1000 °C, for $x = 0.4$, $T = 980$ – 1050 °C, and for $x = 0.9$, $T = 940$ – 1005 °C. Planning obtained single phase. After of air treatment, we noted that only the compositions with $x = 0.4$ and $x = 0.9$ present the SrRuO₃ impurity which therefore were annealing in argon flux, at 980 °C for 4–13 h. Following of this treatment we observed that for $x = 0.4$ composition, the SrRuO₃ phase was eliminated and for $x = 0.9$ sample, the SrRuO₃ impurity was only reduced. In both atmospheres, intermediate grindings were carried out. The resulting polycrystals were pressed into pellets and annealed in an oxygen flux for 6, 12 and 41 h at 960 °C and then slowly cooled to room temperature at a rate of 30 °C min⁻¹.

2.2. Characterization

DTA experiments were performed using a Modulated DSC 9210, TA instruments, with the purpose of determining the temperature interval at which the reaction should be accomplished. The samples were placed in platinum crucibles and heated from ambient temperature to 1200 °C at heating rates of 10 °C min⁻¹ in air. XRD patterns were obtained on a SIEMENS D5000 diffractometer using CuK α_1 radiation, a graphite monochromator on the counter site and an auto-divergence slit system. Diffraction patterns were collected at room temperature over the 2θ range 10–80° with a step size of 0.02° and time per step of 10 s. SEM and electron dispersive X-ray (EDX) microanalysis probes were performed on a Leica-Cambridge Stereoscan 400, equipped with an Oxford/Link System electron probe microanalyser (EPMA). The micrographs were a magnified 5.00 K.X, current intensity of 500 pay, voltage of 20 KV and a work distance of 25 mm. The TEM studies of the crystal structure were carried out on a JEM-1200EXII microscope. The diffraction patterns were taken with a beam intensity of 120 KV. A standard experimental system to perform four-probe DC resistance measurements as a function of temperature was used. The system consists of a close-cycle refrigerator instrumented with conventional equipment for low-level electrical measurements. Continuous monitoring of all electrical parameters during a measurement cycle allowed systematic errors in the resistance values to be detected in real-time, thus permitting clean resistance-versus-temperature profiles to be obtained with no need of additional mathematical treatment to the experimental data. Details of this system are given elsewhere [8]. AC susceptibility measurements were performed using a susceptometer with the temperature range 4–250 K in a zero magnetic field. The pressed sample was wrapped with a very small piece of Teflon tape and then suspended into the stem.

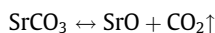
3. Results and discussions

We present the most representative DTA data. For the composition with $x = 0.4$ when we observe the limited of solubility of Ru ion in Cu ion sites for $x = 0.4$ (Fig. 1) and for $x = 0.9$ when the solid solution do not exist (Fig. 2).

DTA results show several endothermic and exothermic transitions in the temperature ranges: $T = 20$ – 1200 °C. Table 1 shows the temperature ranges where occurred different phase transitions for $x = 0.4$ and $x = 0.9$ compositions.

The temperature intervals 1 and 2 which correspond to endothermic transition can be associated to the energy necessary to remove the water molecules within the stoichiometric mixture.

The endothermic transition observed in the temperature intervals 3 and 4 can be related to the oxials decomposition and beginning of some reactions. The corresponding reaction can be represented by the reversible stoichiometric equation.



To expel the CO₂ molecules that remain into the crystalline cell, much energy is needed.

The phase transition observed from $T = 900$ °C (for $x = 0.4$) and 920 °C (for $x = 0.9$) that correspond to endothermic reaction can be attributed to the formation of Ru-1212 phase and different impurities such as SrRuO₃.

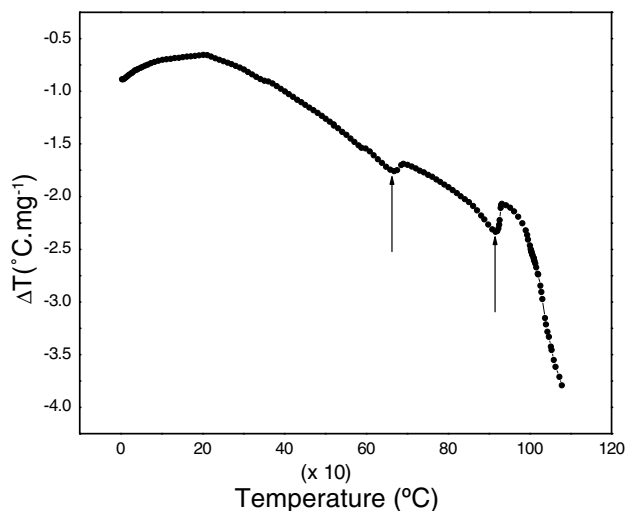


Fig. 1. DTA of Ru_{0.6}Sr₂GdCu_{2.4}O₈ composition.

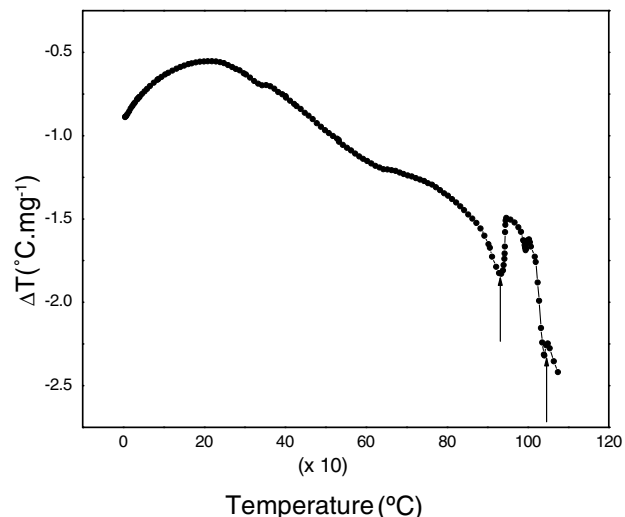


Fig. 2. DTA of Ru_{0.1}Sr₂GdCu_{2.9}O₈ composition.

Table 1
Temperature intervals of phase transitions for $x = 0.4$ and $x = 0.9$ compositions

x	Temperature intervals (°C)			
0.4	1: 70–200	3: 640–900	5: $T > 900$	
0.9	2: 70–350	4: 620–920	6: $T > 920$	

The XRD patterns of the $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_8$ system with $0.0 \leq x \leq 0.9$ are shown in Fig. 3. A solid solution (ss) of the system up to $x = 0.4$ was obtained. The reported tetragonal unit cell with space group $P4/mmm$ to index the spectra was used [5,6]. The sample with $x = 0.9$ shows a reflection of a small secondary phase (identified as SrRuO_3). For $x = 1.0$, the mixture of $\text{Sr}_2\text{CuO}_{3+x}$, CuSrO_2 and Ru-1212 was detected.

The variation of lattice parameters with x of the $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_8$ system is given in Fig. 4. It can be seen that both a and c decrease with the substitution of Cu by Ru in the composition range $0.0 < x < 0.4$ except for $x = 0.2$, whose c parameter increases slightly. Possibly a disorder of the Ru, Cu ions exists in the structure.

To obtain information about the grain size and homogeneity of the compounds, SEM micrographs were taken. Fig. 5 presents the

micrograph of the $\text{Ru}_{0.6}\text{Sr}_2\text{GdCu}_{2.4}\text{O}_8$ compound, where we observed three different kinds of grains: in the first, the diameter is between 4 and 5 μm , in the second, the diameter is about 3 μm and in the third, the diameter is lower than 2 μm .

The chemical compositions of the $\text{Ru}_{0.6}\text{Sr}_2\text{GdCu}_{2.4}\text{O}_8$ sample were determined using EDX. Table 2 presents the corresponding chemical compositions of the general and dot analysis of the spots A and B, marked in Fig. 5. The results of the quantitative EDX analysis indicate that all elements were detectable with different atomic percentages. Considering that the error range of the analysis is between ± 1 and 6 wt.% [9], the experimental and theoretical results of the atomic percentages of the elements are similar.

The sample with $x = 0.4$ was characterized using TEM technique. By electron diffraction, the tetragonal unit cell was checked (Fig. 6). The lattice parameters were calculated by the formula $\lambda L/R = d_{hkl}$ [9], where L is the variable distance between the specimen and the analyzing crystal = 100 cm, λ is the wavelength of the incident ray beam = 0.4 Å, R is the distance between the center and the different spots and d_{hkl} is the space between the planes in the atomic lattice. The cell parameters were $a = 3.56$ Å and $c = 11.43$ Å. These values are slightly different from those obtained by XRD method, this is normal since the TEM pattern was carried

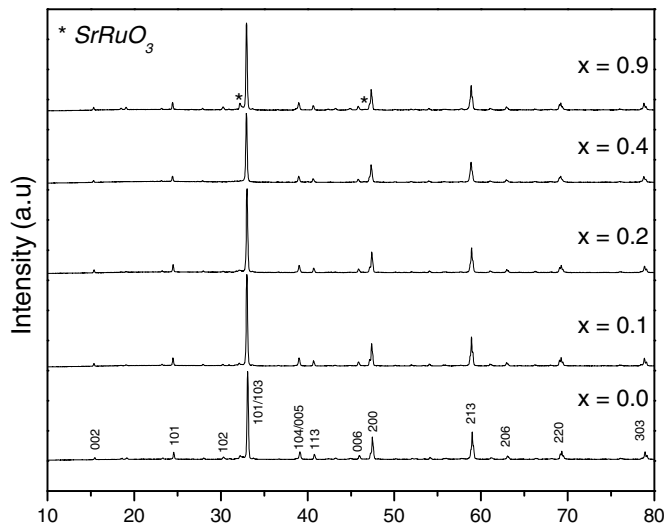


Fig. 3. XRD patterns of $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_8$ system.

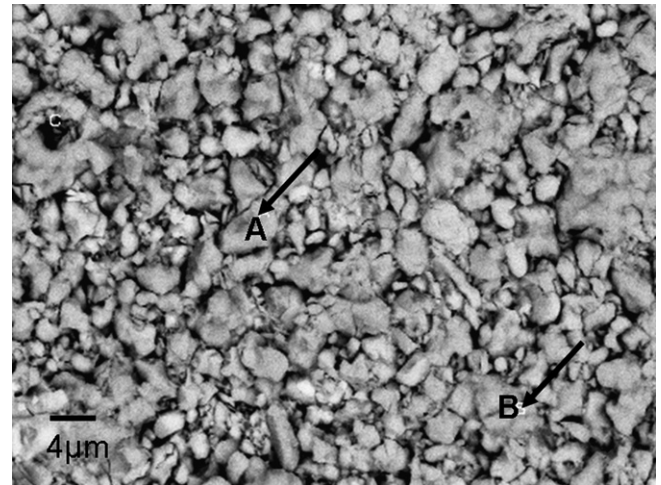


Fig. 5. SEM of $\text{Ru}_{0.6}\text{Sr}_2\text{GdCu}_{2.4}\text{O}_8$ composition. The arrows indicate spots for further EDX analysis.

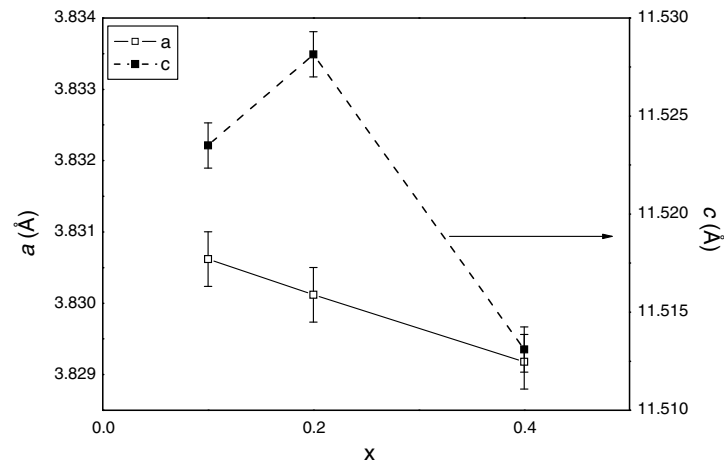


Fig. 4. The lattice parameters variation in $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_8$ system.

Table 2
EDX analysis results (wt.%) of the $\text{Ru}_{0.6}\text{Sr}_2\text{GdCu}_{2.4}\text{O}_8$ compound

Elements	Ru	Cu	Gd	Sr	O
Theoretical percentage	4.58	18.32	7.63	15.27	54.20
General analysis	3.95	19.97	8.95	9.52	57.62
Spot A	4.69	17.82	8.41	9.64	59.44
Spot B	5.64	23.92	11.34	10.38	48.72



Fig. 6. TEM of the $\text{Ru}_{0.6}\text{Sr}_2\text{GdCu}_{2.4}\text{O}_8$ composition.

out from a monocrystal, while the XRD pattern is obtained from an average of all crystals.

Fig. 7 shows the temperature dependence of resistance for $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_8$ system, with $x = 0.1, 0.2$ and 0.4 annealing in oxygen flux for 41 h at 960°C . We observed that all samples show a semi-conducting behavior with a drop of the resistance at 37, 35 and 39 K for $x = 0.1, 0.2$ and 0.4 successively and then without observing a superconductor behavior that was reported by Klamut [6,7]. This change in the transport properties could be due to the difference

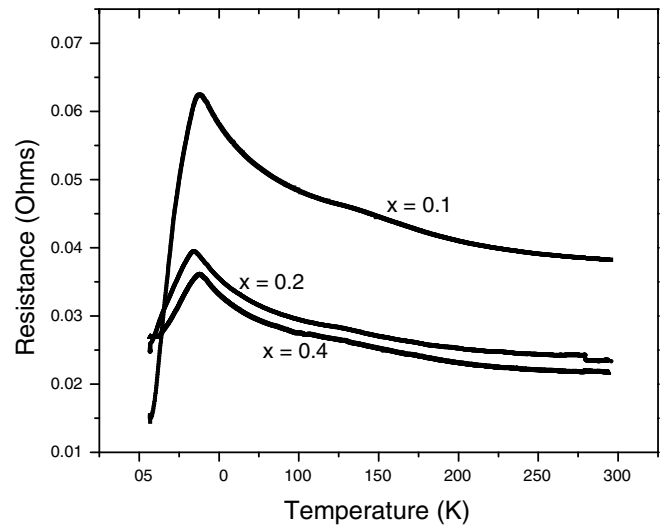


Fig. 7. R versus T for $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_8$ system.

of the synthesis method and preparation procedure including the annealing time in oxygen flux [10–24]. Also we noted that increasing Cu ion concentration reduced the resistance values except for $x = 0.2$ composition, this non-linear behavior in the resistance values is very similar that the variation of c parameter with the compositions. We can say that exist a relation of lattice parameters and electric properties. Nevertheless needs supplementary work to do to elucidate this behavior.

Fig. 8 shows the R versus T measurements for the sample with $x = 0.4$ annealing in air and in oxygen flux for 6 and 41 h. From this study we concluded that annealing time in oxygen flux affect the electric properties in the $\text{Ru}_{0.6}\text{Sr}_2\text{GdCu}_{2.4}\text{O}_8$ sample.

The AC susceptibility versus temperature plots in a zero magnetic field for $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_8$ system with $0.0 < x < 0.4$ are shown in Fig. 9. In this graph the magnetic transitions of the samples are observed. The signals of the transitions indicate that the materials present ferromagnetic behavior with $T_M = 130\text{--}138$ K. The variation of T_M with x is shown in the inset. Similar behavior has been observed by Klamut et al. [6] and a partial substitution of Ru by Cu also has the effect of decreasing the magnetic ordering temperature.

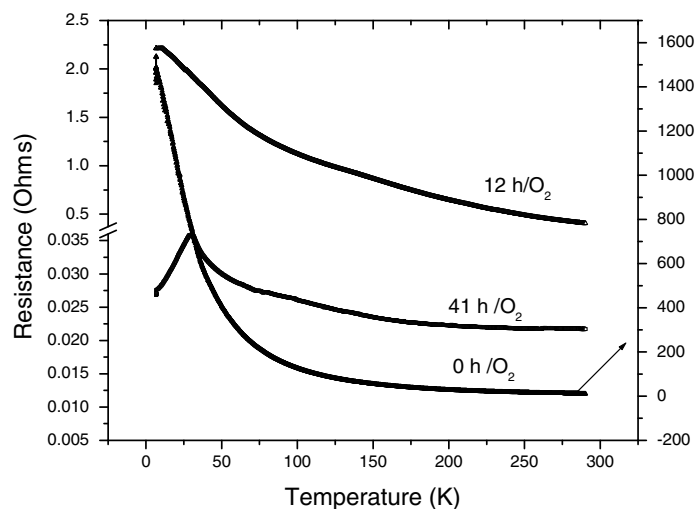


Fig. 8. R versus T for $\text{Ru}_{0.6}\text{Sr}_2\text{GdCu}_{2.4}\text{O}_8$ sample.

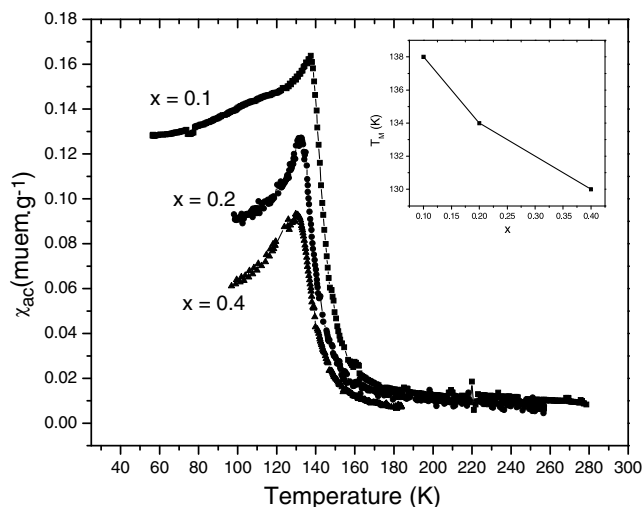


Fig. 9. χ_{ac} versus T for $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_8$ system.

4. Conclusions

By solid-state reaction method at ambient pressure a complete solubility up to $x = 0.4$ was obtained in the $\text{Ru}_{1-x}\text{Sr}_2\text{GdCu}_{2+x}\text{O}_8$ system. The compounds with $0.0 < x < 0.4$ exhibit semiconductor behavior and ferromagnetic transition with Curie temperature varied between 130 and 138 K.

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