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Synthesis of the $RuSr_2GdCu_2O_{8\pm z}$ Compound at Ambient Pressure Through a Solid State Reaction, Melts and Sol-Gel by Acrylamide Polymerization Methods

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Abstract The $RuSr_2GdCu_2O_{8\pm z}$ (Ru-1:2:1:2) compound, was synthesized at ambient pressure by solid-state reaction, melts, and sol-gel by acrylamide polymerization methods with the following intervals of temperature reaction: $T = 960$–1015°C, $T = 1450$°C, 135–980°C respectively. Differential Thermal Analysis (DTA) result gave us an idea about the temperature interval where the Ru-1:2:1:2 compound was formed. Results of X-Ray powder Diffraction (XRD) data show the formation of the Ru-1:2:1:2 phase, which crystallizes in a tetragonal structure with a space group $P4/mmm$. The synthesis of the Ru-1:2:1:2 compound by the melts route was found to be faster than the other synthesis methods. Studies by the Scanning Electron Microscopy (SEM) technique gives a particle size around 1–6 μm. The chemical compositions of the samples were obtained by Energy Dispersive X-ray (EDX) spectroscopy. The resistance vs. temperature data of the samples annealed in oxygen flux for 6, 12, 41 and 64 h, at $T = 960$°C, shows a semiconductor behavior.

Keywords Synthesis · XRD · SEM · Electrical properties

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1 Introduction

Rutheno-cuprate compound $RuSr_2GdCu_2O_{8\pm z}$ (Ru-1:2:1:2) synthesized for the first time by Baurnfeind et al. [1], was found to display superconductivity (SC), yet coexisting with ferromagnetism (FM) and SC, as reported by Bernhard et al. [2]. Consequently, most recent experimental [2–11] and theoretical [12, 13] investigations have focused on studying the coexistence of FM and SC in this material. The Ru-1:2:1:2 layered cuprate exhibits a unit cell very similar to $YBa_2Cu_3O_7$ compound, with Y and Ba being completely replaced by Gd and Sr, respectively, with CuO chains replaced by RuO_2 planes [10]. The superconducting properties depend sensitively on subtle details of the preparation process [2–11]. The onset of SC for the Ru-1:2:1:2 compound is ∼45 K, while the value of the Curie temperature (T_c) is ∼132 K [3, 5]. In this paper, the optimal conditions at ambient pressure for the synthesis of the Ru-1:2:1:2 compound via solid state reaction, melts, and sol-gel by acrylamide polymerization methods are shown. The results of XRD, and SEM analysis, electric and magnetic measurements are reported and the influence of annealing time in oxygen flux on the electric properties of the samples is discussed.

2 Experimental Procedure

2.1 Sample Preparation

Solid-State Reaction The sample of $RuSr_2GdCu_2O_8$ was synthesized from stoichiometric amounts of RuO_2 anhydrous (99.9%, STREM), $SrCO_3$ (99.5%, CERAC), Gd_2O_3 (99.99%, STREM) and CuO (99.99%, ALDRICH). Prior to weighing, $SrCO_3$ was preheated for 10–20 min at 120°C to dehydratation. RuO_2 was weighed in argon flowing glove bag to avoid the decomposition of this reagent. A stoichiometric mixture of this compound was ground in an agate mortar in air. The reactions were carried out in an electric furnace (±4°C) between 960–1015°C in air, for 17–111 h in high-density alumina crucibles followed by annealing at 960°C for 12 h in argon flux with intermediate grindings. This step was necessary to minimize the formation of $SrRuO_3$ [11]. The resulting powders were pressed between 2–2.5 Ton·cm^{-2} into pellets with a diameter 10 mm and annealed at a rate of 50°C min^{-1} in oxygen flux at 960°C for 6, 12, 41 and 64 h, then slowly cooled to room temperature with a ramp of 30°C min^{-1}.

Melts The $RuSr_2GdCu_2O_8$ sample was synthesized from a mixture of CuO reagent and Sr_2GdRuO_6 compound, which was obtained by solid-state reaction method at ambient pressure. The mixture was covered in a platinum envelope and melted at 1450°C for 30 min in air, and then cooled rapidly under room temperature using liquid mercury submerged in ice. The sample was ground and heated at 950°C for 2 h in argon flux. Then the powders were pressed (2–2.5 Ton·cm^{-2}) into pellets (10 mm) and annealed in oxygen flux at 950°C for 2 h.

Sol-Gel Method by Acrylamide Polymerization Three steps were employed to prepare the $RuSr_2GdCu_2O_8$ compound.

1. Sol Formation

The policrystalline powders of $SrCO_3$ (99.5%, CERAC) were dissolved in acetic acid ($H_4C_2O_2$) (99.8%, J. Baker), CuO (99.99%, ALDRICH) and Gd_2O_3 (99.99%, STREM) were dissolved separately in nitric acid (HNO_3) (69–70%, J. Baker) at ∼100°C using an electric grill with a magnetic agitation in order to increase the velocity of the dissolution, all in an aqueous solution of 50 ml distilled H_2O.

$$SrCO_3 + H_2O + 2H_4C_2O_2 \rightarrow Sr(CH_3CO)_2 \text{ (transparent solution)} + 2H_2O + CO_2\uparrow$$

$$Gd_2O_3 + H_2O + 2HNO_3 \rightarrow Gd_2(NO_3)_2 \text{ (transparent solution)} + 2H_2O + O_2\uparrow$$

$$CuO + H_2O + 2HNO_3 \rightarrow Cu(NO_3)_2 \text{ (clear blue solution)} + 2H_2O$$

To the solution obtained, a stoichiometric amount of ethylenediaminetetraacetic (EDTA) acid $[CH_2N(CH_2CO_2H)_2]_2$ (≥ 99%, Fulka) was added so as to enclose the Gd and Cu metals.

$$4Gd(NO_3) + [CH_2N(CH_2CO_2H)_2]_2 \rightarrow [CH_2N(CH_2CO_2Gd)_2]_2 + 4HNO_3$$

$$4Cu(NO_3) + [CH_2N(CH_2CO_2H)_2]_2 \rightarrow [CH_2N(CH_2CO_2Cu)_2]_2 + 4HNO_3$$

The solution pH was adjusted to 6 with the addition of ammonia.

2. Gel Formation

The formation of Ru-1:2:1:2 gels takes place by mixing all solutions and successively adding a stoichiometric quantities of Acrylamide, $H_2C = CHCONH_2$ (∼99%, Fulka), N–N′ metilenbisacrilamida $C_7H_{10}N_2O_2$ (≥99.5%, Fulka) and α–α' azoisobutinitril $C_8H_{18}N_6$-2HCl (≥98%, Fulka).

The polymerization is performed by heating to 100°C for 10 min.

3. Xerogel Formation

In order to obtain xerogel, the gel was dehydrated in a microwave furnace between 80–135°C for 4 h in an argon atmosphere. Then the xerogel was mixed with a stoichiometric amount of RuO_2 powder using an agate electric mortar (Retsch). Lastly, the mixture was submitted to thermal treatments at 950°C for 3 d + 5 h in air, in argon flux at 950°C for 2 h and in oxygen atmosphere at 950°C for 4 h.

2.2 Characterization

DTA measurements were carried out using Modulated DSC 9210, TA instruments. The sample was placed in platinum crucibles and heated from ambient temperature up to 1200°C with heating rates of 10°C min^{-1} in air.

Powder XRD patterns were taken by means of SIEMENS D5000 diffractometer using $CuK_{\alpha 1}$ radiation. 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. The cell

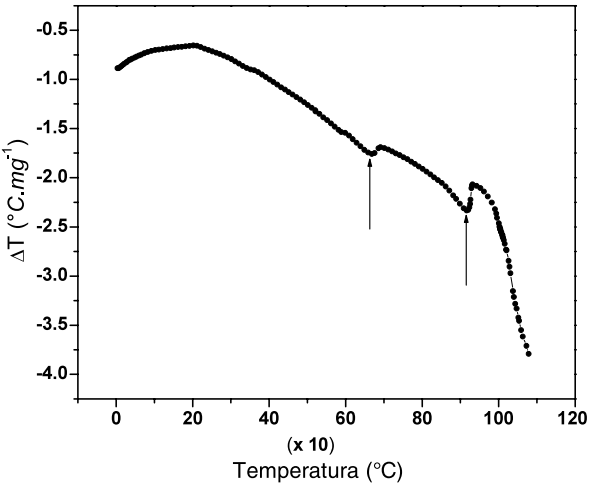

Fig. 1 DTA of $RuSr_2Gd/Cu_2O_8$ compound

parameters a and c were calculated considering the reflections (200) and (005) respectively.

The morphology of the samples was analyzed by SEM on a Leica-Cambridge Stereoscan 400. This microscope was equipped with an Oxford/Link System electron probe microanalyser (EPMA), by which the chemical composition of the selected areas of the sample was analyzed. The micrographs were taken with 5.00 K.X, voltage of 20 KV, current intensity of 1000 pA and WD = 25 mm.

Resistance measurements were carried out using a standard four-probe method. High purity silver paint (SPI supplies) was used for the contacts. The system is made up in a close-cycle refrigerator (CH-Series, Oxford instruments) tool 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, permitting clean R vs. T profiles to be obtained with no need of additional mathematical treatment on the experimental data [15].

The magnetic properties of the sample were determined by a superconducting quantum interference device (SQUID) Quantum Design MPMS.

3 Experimental Results

Figure 1 presents the result of DTA of the $RuSr_2GdCu_2O_8$ compound in the temperature range T = 20–1200°C. Table 1 show the temperature ranges where different phase transitions for $RuSr_2GdCu_2O_8$ compound occurred.

The temperature interval 1 can be associated to the energy necessary to remove the water molecules within the stoichiometric mixture.

The endothermic transition observed in the temperature interval 2 can be related to the oxisals decomposition and beginning of some reactions. The corresponding reaction can be represented by the reversible stoichiometric equation:

$$SrCO_3 \leftrightarrow SrO + CO_2\uparrow$$

Table 1 Temperature intervals of phase transitions for $RuSr_2GdCu_2O_8$ compound

Temperature intervals (°C)		
1: 70–200	2: 640–900	3: $T > 900$

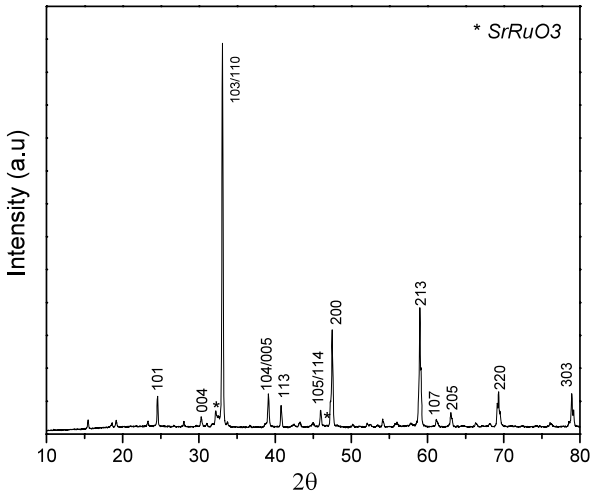

Fig. 2 XRD pattern of the $RuGd_2CuSr_2O_8$ compound synthesized by solid state reaction method

To expel the CO_2 molecules that remain into the crystalline cell, much energy is needed.

The phase transition observed from $T = 900$°C that correspond to endothermic reaction can be attributed to the formation of Ru:1:2:1:2 and different impurities such as $SrRuO_3$.

Figure 2 shows the XRD pattern of the Ru-1:2:1:2 sample synthesized by solid-state reaction method (1015°C, 60 h in air). Phase analysis by XRD indicates formation of the Ru-1:2:1:2 phase. Reflexions marked by stars are due to amounts of $SrRuO_3$ impurity. The XRD pattern was analyzed and indexed on the basis of the reported tetragonal unit cell [8, 9] with a space group $P4/mmm$. The lattice parameters are $a = b = 3.8370$ Å and $c = 11.5610$ Å. These values are in perfect agreement with data published in [14] ($a = 3.8375$ Å and $c = 11.5602$ Å).

The XRD pattern of the sample prepared by melts is shown in Fig. 3. As seen from this figure, this compound is crystallized in a single phase from an in-space group $P4/mmm$ with lattice parameters $a = b = 3.8381$ Å and $c = 11.549$ Å.

Figure 4 depicts the XRD pattern of the Ru-1:2:1:2 sample prepared via sol-gel method by acrylamide polymerization. Ru-1:2:1:2 crystallizes in space group $P4/mmm$ with lattice parameters $a = b = 3.834$ Å and $c = 11.558$ Å. Small reflections of a second phase (identified as $SrRuO_3$) are marked by crosses on the pattern.

Table 2 shows a summary of the three synthesis techniques used in this work.

From the results obtained, melts method was considered adequate for the synthesis of the Ru-1:2:1:2 compound due to its speed compared with solid-state reaction and sol gel methods.

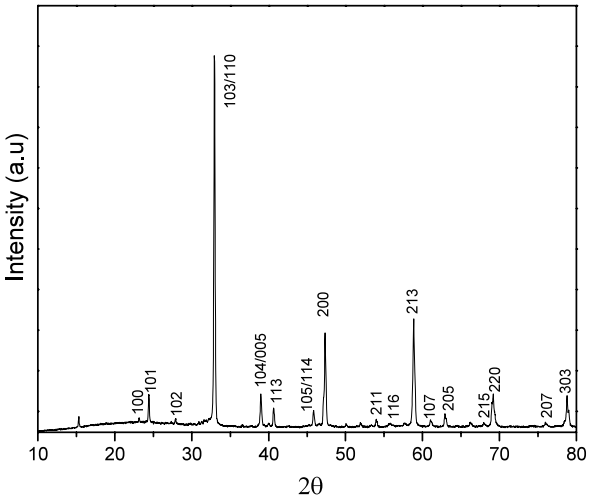

Fig. 3 XRD pattern of the $RuGd_2CuSr_2O_8$ compound synthesized by melts

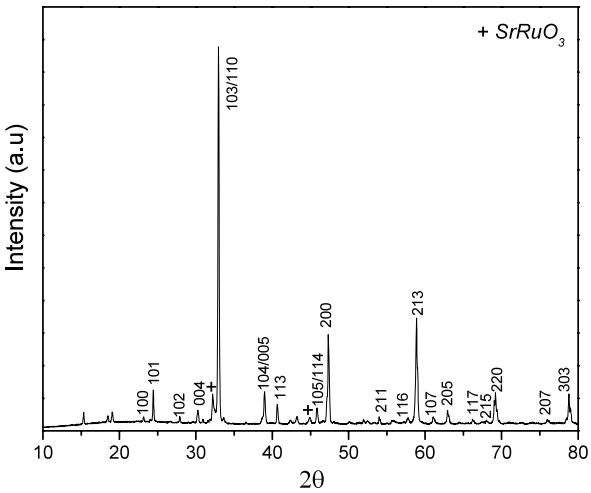

Fig. 4 XRD pattern of the $RuSr_2GdCu_2O_8$ compound synthesized by sol-gel polymerized with acrylamide

Table 2 Conditions of the synthesis of the Ru-1:2:1:2 compound by solid-state reaction, melts and sol-gel techniques

Reaction conditions	Synthesis methods		
	Solid-state reaction	Melts	Sol-gel
T (°C)	960–1015	1450	135–980
Time in air flux	28 d + 23 h	30 min	3 d + 5 h
Time in argon flux	12 h	2 h	2 h

Particle size and morphology of the sample prepared by solid state reaction were obtained by the SEM technique. Figure 5 shows the micrograph of Ru-1:2:1:2 compound. Different grain sizes that vary between 1 and 6 μm can be observed.

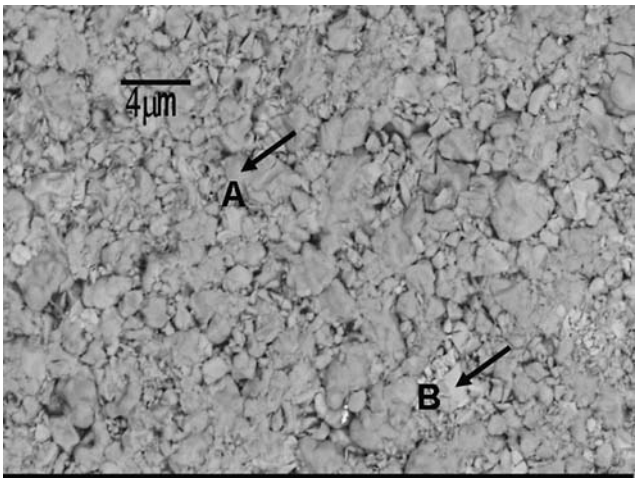

Fig. 5 SEM of the Ru-1:2:1:2 compound synthesized by solid-state reaction. The *arrows* indicate spots for EDX analysis

Table 3 EDX analysis results (wt%) of Ru-1:2:1:2 compound synthesized by solid-state reaction

Elements	Ru	Sr	Gd	Cu	O
Theoretical percentage	7.41	14.81	7.41	14.81	55.55
General analysis	6.90	15.02	6.42	13.09	58.58
Spot A	5.69	10.64	6.74	12.97	63.00
Spot B	4.78	9.50	10.79	17.13	57.80

By EDX, a general and dot analysis, in the Ru-1:2:1:2 sample, synthesized by solid-state reaction was carried out.

Table 3 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 are detectable with different atomic percentage. Considering that the error range of the analysis is between ± 1 and 6 wt% [16], the experimental and theoretical results of the atomic percentages of the elements are similar.

To investigate the effect of annealing time in oxygen flux on the crystalline structure of Ru-1:2:1:2 compound synthesized by solid state reaction method, the cell parameters a and c of the samples annealing in oxygen atmosphere for 41 and 64 h are calculated. Table 4 show the results obtained. It was found that a and c increase with the time in oxygen flux, which indicates that the oxygen entered into the crystalline structure.

Figure 6 shows the temperature dependence of resistance for the Ru-1:2:1:2 compound prepared by solid state reaction method at ambient pressure annealed in oxygen flux at 960°C for 6 and 41 h.

From this study we concluded that annealing time in oxygen flux affects the electric properties of the Ru-1:2:1:2 compound. We observed that all samples present a semiconducting behavior and we noted that with an additional annealing in oxygen

Table 4 Variation of the lattice parameters *a* and *c* with the annealing time in oxygen atmosphere of the Ru-1:2:1:2 compound synthesized by solid-state reaction

Lattice parameters	Annealing time in oxygen flux (h)		
	0	41	64
a (Å)	3,837	3,848	3,850
c (Å)	11,561	11,582	11,600

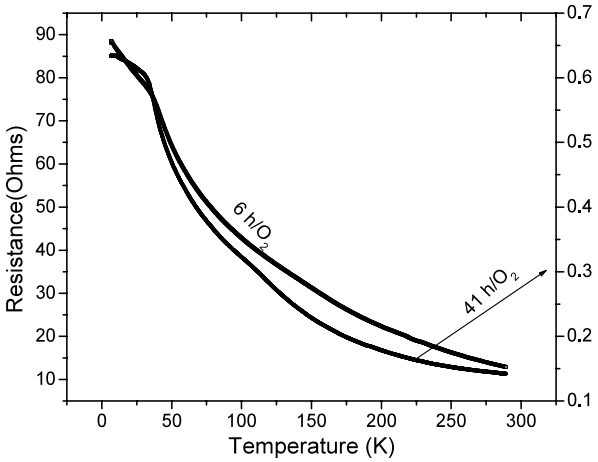

Fig. 6 *R* vs. *T* of the Ru-1:2:1:2 compound synthesized by solid state reaction method

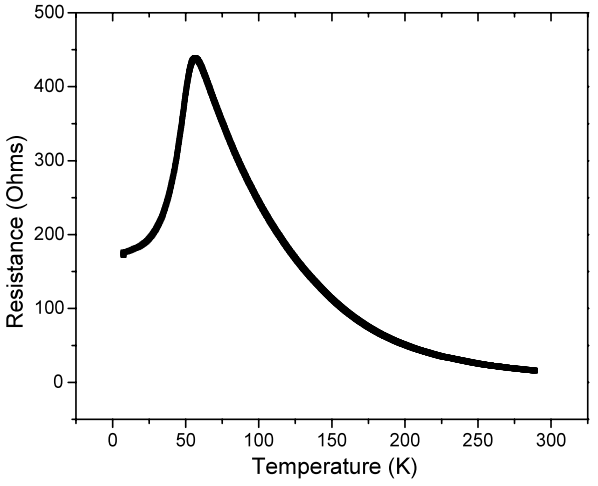

Fig. 7 *R* vs. *T* of the Ru-1:2:1:2 compound synthesized by solid state reaction method

flux (41 h), the resistance values are 50 to 130 times smaller compared to the sample annealed in oxygen flux for 6 h.

Figure 7 shows the *R* vs. *T* curve of Ru-1:2:1:2 compound synthesized via solid-state reaction technique at ambient pressure annealed in oxygen flux for 64 h. This plot indicates that the sample has semiconductor behavior with a drop in resistance around 52 K.

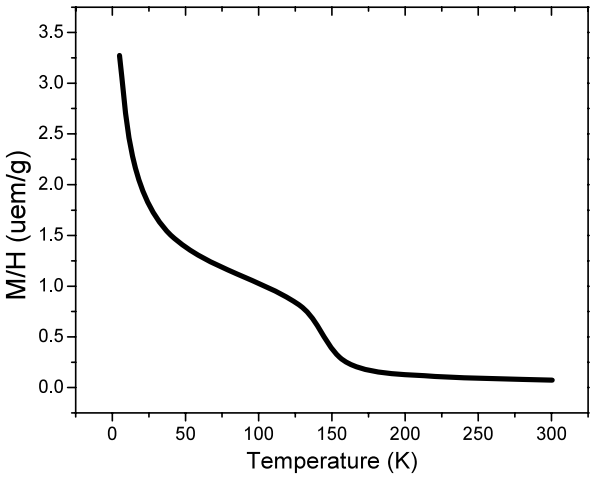

Fig. 8 M/H vs. T of Ru-1:2:1:2 compound synthesized by solid state reaction method

Different groups synthesized $RuSr_2GdCu_2O_8$ samples whose properties varied from superconducting [2, 7–10, 17–24] to semiconducting [3, 6] depending on the preparation procedure. In general, the superconducting Ru-1:2:1:2 samples were synthesized by the following conditions: in air, $T = 600$–1060°C for 10–96 h, and in oxygen flux with $T = 1015$–1085°C for 10 h–14 d. It was proposed that the annealing at high temperature with long-time (14 d) in oxygen flux is essential for achieving SC. The semiconducting Ru-1212 samples were obtained at $T = 950$–1000°C in air, for 1 d and at $T = 1060$°C in oxygen flux for 72 h [3, 6].

From all these studies [2, 3, 6–10, 17–24], we noted that the temperatures of annealing in oxygen flux are higher than 960°C. By TG measurements, we observed that the Ru-1:2:1:2 compound loses oxygen up to 960°C, to avoid it, all samples were oxygenated at 960°C. We consider that our route of synthesis did not give superconductive samples although they are a high-purity phases as shown in Figs. 2, 3 and 4.

The Ru-1:2:1:2 compound synthesized by solid-state reaction method was characterized by means of Quantum Design SQUID magnetometer. Sample was measured from 10 to 300 K in an applied field of 5 kOe. The temperature dependence of magnetization/field (M/H) is shown in Fig. 8. Ferromagnetic ordering at $T_c \sim 138$ K was obtained in this compound and no sign of superconductivity transition was observed, possibly that signifies a very poor grain-grain alignment.

4 Conclusions

The synthesis of the $RuSr_2GdCu_2O_8$ compound was obtained through the solid state reaction, melt and sol-gel methods. The conditions of the synthesis showed that the melts technique has been the fastest for the formation of the Ru-1:2:1:2 compound. The samples synthesized via solid state reaction method exhibit semiconductor behavior with a drop in resistance at 52 K and ferromagnetic transition around 138 K. The resistance of the samples decreases with the annealing time in oxygen flux, whereas the cell parameters crease without change in their crystalline structure.

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