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# Magnetic, electrical and structural properties of the Re-doped ruthenocuprate $Ru_{1-x}Re_xSr_2GdCu_2O_y$

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ABSTRACT

Despite the discovery of new superconductors classes, high-Tc oxides continue to be a current topic, because of their complex phase diagrams and doping-dependant effects (allowing one to investigate the interaction between orbitals), as well as structural properties such as lattice distortion and charge ordering, among many others. Ruthenocuprates are magnetic superconductors in which the magnetic transition temperature is much higher than the critical superconducting temperature, making them unique compounds. With the aim of investigating the dilution of the magnetic Ru sub-lattice, we proposed the synthesis of the $Ru_{1-x}Re_xSr_2GdCu_2O_y$ ruthenocuprate-type family, adapting the known two-step process (double perovskite + CuO) by directly doping the double perovskite, thus obtaining the perovskite compound $Sr_2GdRu_{1-x}Re_xO_y$, which represents a new synthesis process to the best of our knowledge. Our samples were structurally characterized through X-ray diffraction, and the patterns were analysed via Rietveld refinement. A complete magnetic characterization as a function of temperature and applied field, as well as transport measurements were carried out. We discuss our results in the light of the two-lattice model for ruthenocuprates, and a relation between $RuO_2$ (magnetic) and $CuO_2$ (superconductor) sub-lattices can clearly be observed.

## 1. Introduction

The discovery of superconductivity in the ruthenocuprates $RuSr_2GdCu_2O_8$ (Ru1212) and $RuSr_2(R_{1+x}Ce_{1-x})Cu_2O_{10}$ (R=Sm, Eu and Gd) by Bauernfeind et al. [1], and the report, two years later, by Felner et al. [2] of the coexistence of superconductivity and magnetism in these compounds renewed the interest of both theoreticians and experimentalists, in the study of the interplay between superconductivity and magnetism [3–8].

The distinguishing characteristic of these compounds in comparison with other magnetic superconductors such as Chevrel phases [9] or rare earth ternary borides [10] is the fact that the magnetic transition temperature is much higher than the critical superconducting temperature, making them unique materials. However, these compounds are extremely sensitive to the synthesis process, making their study difficult. In order to reduce the synthesis-dependent characteristics, a method for ruthenocuprate production involving the synthesis of double perovskites $Sr_2LnRuO_6$ (Ln = lanthanide) as precursor oxides, called the two-step process, was developed [11–13], opening at the same time a new research line dealing with these interesting lanthanide perovskites [14–17].

In accordance with these ideas, we proposed the synthesis of the Re-doped ruthenocuprate $Ru_{1-x}Re_xSr_2GdCu_2O_y$ in the interest of investigating the dilution of the magnetic Ru sub-lattice. After facing serious problems in obtaining this compound through the standard two-step process (adding the doping agent together with $Sr_2GdRuO_6$), we adapted it by directly doping the double perovskite with Rhenium to get $Sr_2GdRu_{1-x}Re_xO_y$. This represents a completely new ruthenocuprate preparation technique to the best of our knowledge.

Felner et al. [2] found via magnetic susceptibility and Mössbauer spectroscopy that superconductivity seems to be confined to the $CuO_2$ planes whereas the magnetism is due to

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the Ru sublattice. In the present paper, we discuss our results in light of the two-lattice model for ruthenocuprates, where an alternating sequence of weakly ferromagnetic ($RuO_2$), insulating (SrO), and superconducting ($CuO_2$) sheets along the *c*-axis is formed (SIFIS), exhibiting an intrinsic Josephson effect.

## 2. Experimental details

When $RuSr_2GdCu_2O_8$ was sintered for the first time, the sample did not have a single phase character, and the magnetic transition was observed at 138 K, which was attributed to the possible presence of $SrRuO_3$, known by its ferromagnetism. Impurities are caused by the volatility of $RuO_x$, which plays a fundamental role in the final Ru/Cu ratio, affecting the physical properties of the samples. The appearance of perovskite impurities was minimized through a two-step method that consisted in producing the double perovskite $Sr_2GdRuO_6$ (SGRO) and using it as a precursor powder together with CuO. This is currently the most accepted method for producing ruthenocuprate systems, and we applied it to our system, as explained above.

In our case, $Sr_2GdRu_{1-x}Re_xO_y$ (SGRRO) with $x = 0.00$, 0.03, 0.06, 0.09, and 0.12 was prepared using the solid state reaction method, as described elsewhere [17]. SGRRO perovskite powders were then mixed with CuO Aldrich powder (99,995 %) (previously dried at 200 °C for 24 h), ground in an agate mortar for two hours, and then pressed into pellets of approximately 5 mm diameter and 1 mm thickness. The samples were thermally treated at 1050 °C for 45 h, with three intermediate grindings.

Once obtained, an oxygen treatment was carried out with the aim of optimizing the superconductor properties of the sample, see Fig. 1. A quartz tube with two valves, $V_{in}$ and $V_{out}$, was used. Initially, $V_{in}$ remains closed and $V_{out}$ open, in order to avoid pressure increases. When the system reaches 1050 °C, $V_{out}$ is closed and the oxygen flows through $V_{in}$, until the pressure gauge attached to the tube indicates 1 atm, then $V_{in}$ is closed. During the process the pressure in the tube keeps constant, which guarantees optimal treatment conditions. Several lengths of times were tried but for times longer than 120 h in oxygen flux, the samples properties remained the same.

The crystal structure was studied through X-ray powder diffraction, using a PanAlytical Pro diffractometer with Cu-k$\alpha$ radiation (1.5406 Å) and PiXcel detection. The morphology and the qualitative chemical composition were studied with a FEI Quanta 200 ESEM, and its corresponding EDX accessory. The diffraction patterns were analyzed through Rietveld refinement using GSAS software. Magnetic measurements were carried out on a Quantum Design MPMS (Magnetic Properties Measurement System) SQUID magnetometer, and transport measurements were performed with a Quantum Design PPMS (Physical Properties Measurement System).

## 3. Results and discussion

### 3.1. Structural characterization

X-ray diffraction results are shown in Fig. 2. All the samples are tetragonal, with space group P4mmm (#123). Previous reports on similar samples have found $SrRuO_3$ magnetic impurity, which makes the interpretation of the characterization results difficult [18]. However, with the two-step process previously described, that impurity does not appear. This has been attributed to the presence of pentavalent $Sr_2GdRuO_6$, which inhibits the formation of $SrRuO_3$, with tetravalent Ru, under oxidant conditions [19].

Rietveld refinement of X-ray diffraction patterns revealed that the samples are nearly single phase (see Fig. 2(b) for results with $x = 0.03$ sample). The presence of $Sr_2GdRuO_6$ was detected in the samples, in percentages between 0.3 and 2.2%: however, no Re phases were detected. This was confirmed through SEM imaging, where a compact structure with grains sizes between 2 and 10 μm were analyzed through EDX. This showed that no Re oxides were segregated, indicating, together with the diffraction results, that Re successfully enters into the structure.

Lattice parameters *a* and *b* show a slight tendency to increase, while *c* diminishes to doping level $x = 0.09$. At this point, the structure seems to re-accommodate, diminishing *a* and *b* and increasing *c*, as can be seen in Table 1.

The difference in the ionic ratio between Ru and Re is $\Delta r = 0.055$ if both of them are considered pentavalent, $Ru^{5+}/Re^{5+}$, and $\Delta r = 0.050$ if considered tetravalent, $Ru^{4+}/Re^{4+}$. To have an idea of the possible valences of Ru/Re in the compounds, nominal distances of Ru/Re–O bonds were calculated with the ionic ratios listed by Shannon [20]: for pentavalent Ru and Re ions this distance is approximately 1.965 Åand 1.980 Å respectively, and for tetravalent ions, 2.02 Åand 2.03 Årespectively. For our samples, the distances calculated from Rietveld refinement data have values between 1.972 and 2.032 Å. This result suggests a mixed valence of Ru/Re ions in the compound, in the same way as reported for Ru-1212Gd type samples from NMR studies [21–23].

### 3.2. Magnetic properties

In order to obtain information about the influence of Re on the Ru magnetic lattice, susceptibility measurements were performed. Fig. 3(a) shows the temperature dependence of the normalized dc

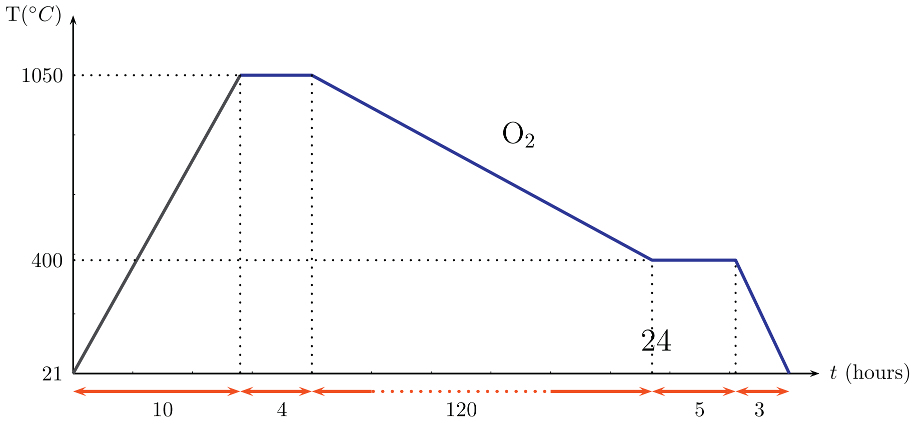

**Fig. 1.** Oxygenation treatment process, showing its different stages. The cooling rate in the segment 1050–400 °C was 0.5 °C/min.