

Sr₂RuO₄ · 0.25 CO₂ and the Synthesis and Elementary Properties of Sr₃Ru₂O₇

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We report the synthesis of a new strontium ruthenium oxycarbonate, Sr₂RuO₄ · 0.25 CO₂, and its use to synthesize Sr₃Ru₂O₇, the $n = 2$ member of the (SrO) _{$n+1$} (RuO₂) _{n} Ruddlesden-Popper series. Like layered K₂NiF₄-type Sr₂RuO₄, and three-dimensional perovskite-type SrRuO₃, Sr₃Ru₂O₇ is a metallic conductor. In Sr₃Ru₂O₇, the magnetic moments (d^4 , low spin) interact weakly with each other and develop strong antiferromagnetic correlations below 15 K. Small substitutions of Ir for Ru in Sr₃Ru₂O₇ result in a metal-insulator transition. © 1995 Academic Press, Inc.

INTRODUCTION

The strontium ruthenates SrRuO₃ and Sr₂RuO₄, while well known materials for some time (1-4), have recently been the subject of renewed interest due to their low, metallic resistivities and chemical compatibility with YBa₂Cu₃O₇, suggesting that they might be useful as normal metal electrodes in superconducting thin film devices (5-7). The magnetic properties of these two ruthenates are quite different. The three-dimensional perovskite structure SrRuO₃ is a high T_c ferromagnet ($T_c = 160$ K) with a full Ru⁴⁺ $s = 1$ moment for $T > T_c$ and an ordered moment of $1 \mu_B$ (2). Layered K₂NiF₄-type Sr₂RuO₄, on the other hand, has been recently shown to display no local moment ordering, or even the presence of the moment expected for $s = 1$ Ru⁴⁺ (8). This existence of local moments in a three-dimensional structure and itinerant moments in a two-dimensional structure is contrary to what is expected; lower dimensionality should, in fact, encourage localization. To explore the effect of dimensionality on the localized-itinerant transition and the magnetic properties in this system, we set out to study the elementary physical properties of Sr₃Ru₂O₇, which has been reported (9-11) to form in the $n = 2$ Ruddlesden-Popper structure type, (SrO) _{$n+1$} (RuO₂) _{n} , made by stacking double layers of RuO₂ planes. Here we describe its synthesis in flowing O₂ in a narrow temperature inter-

val in very short times from a new strontium ruthenium oxycarbonate, Sr₂RuO₄ · 0.25 CO₂, found during the course of this study. The synthesis of Sr₂RuO₄ · 0.25 CO₂ is also described. The electrical and magnetic properties of Sr₃Ru₂O₇ are briefly described, as are the results of Ir doping experiments.

Sr₂RuO₄ · 0.25 CO₂

This phase was first observed in a mixture of 2 SrCO₃ + RuO₂ heated overnight at 850°C in air. Decomposition of the new phase to yield Sr₂RuO₄ was found to begin only at temperatures of 1000°C and higher. To test the Sr to Ru ratio of the phase, mixtures of $(2 \pm x)$ SrCO₃ · $(1 \mp x)$ RuO₂, for $0 \leq x \leq 0.3$, $\Delta x = 0.1$, were made and heated for 3 days at 850°C in air with daily grinding. For Sr:Ru mixtures Sr rich of 2:1, SrCO₃ was present as an impurity phase; for Sr:Ru mixtures Ru rich of 2:1, SrRuO₃ was present as an impurity phase. In the absence of CO₂ in the starting materials and the firing ambient (e.g., at 850°C in O₂ from 2 Sr(NO₃)₂ + RuO₂ (after slow heating)), the phase did not form in any detectable amount.

To determine the CO₂ content, material free of significant quantities of impurity phases, synthesized 3 days at 850°C in air from a mixture of 2 SrCO₃ + RuO₂, was heated in a commercial TGA in a 5% H₂-95% N₂ mixture to 800°C at 5°/min. The result of this experiment is shown in Fig. 1. The stoichiometry of the starting material was determined from the reaction: Sr₂RuO₄ · x CO₂ → 2 SrO + Ru + x CO₂ (gas) + O₂ (gas). The CO₂ content was found to be 0.25 per formula unit.

Crushed polycrystalline samples of Sr₂RuO₄ · 0.25 CO₂ were examined by electron microscopy. Electron diffraction patterns were taken on a Phillips CM30ST electron microscope equipped with a field emission gun operating at 300 kV and equipped with a side-entry 25°/25° tilt specimen holder. Electron diffraction patterns (Fig. 2) indicated that the unit cell of Sr₂RuO₄ · 0.25 CO₂ had primitive, hexagonal symmetry, with $a = 9.7$ and $c = 8.2$ Å.

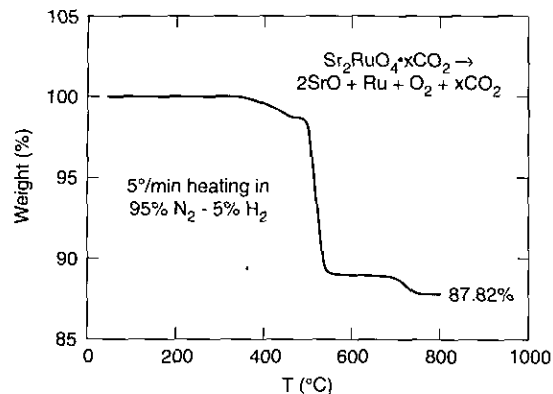


FIG. 1. Weight loss for a powder of $\text{Sr}_2\text{RuO}_4 \cdot 0.25 \text{CO}_2$ heated in a 5% H_2 -95% N_2 atmosphere in a commercial TGA to 800°C at 5°/min.

The strength of $hk0$ reflections with $h + k \neq 3n$ was variable from crystallite to crystallite (Figs. 2a and 2b) suggesting variation in perfection of atomic ordering. Further, there was considerable streaking of the diffraction spots, especially along the c -axis. This streaking may be due to variability in the CO_2 content of the phase or the perfection of CO_2 ordering. To refine the synthetic conditions, $\text{Sr}_2\text{RuO}_4 \cdot x\text{CO}_2$ was synthesized from starting materials mixed in the ratio $2[(\text{SrCO}_3)_{1-x}(\text{Sr}(\text{NO}_3)_2)_x] : 1 \text{RuO}_2$ heated in air or oxygen at temperatures of 850, 875, or 900°C for periods of 3–5 days for $0 \leq x \leq 0.9$. Samples free of significant amounts SrRuO_3 impurity were obtained only for $x \leq 0.5$, indicating that a minimal CO_2 content of 1 per formula unit is required in the starting materials to compensate for CO_2 loss during reaction. The sharpness of the powder X-ray diffraction peaks and the apparent c -axis spacing varied with the CO_2 content of the starting materials and the temperature of synthesis. The most uniform product, at average stoi-

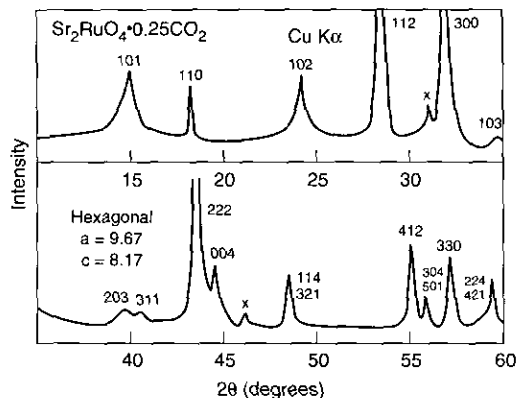


FIG. 3. X-ray powder diffraction pattern for $\text{Sr}_2\text{RuO}_4 \cdot 0.25 \text{CO}_2$, $\text{CuK}\alpha$ radiation, expanded scale. The (112), (300), and (222) peaks are 7.3, 9.2 and 4.3 times the intensity of the (110) peak, respectively. Peaks marked with an "X" do not belong to $\text{Sr}_2\text{RuO}_4 \cdot 0.25 \text{CO}_2$.

chiometry $\text{Sr}_2\text{RuO}_4 \cdot 0.25 \text{CO}_2$, was obtained for $x = 0$ at 875°C on firing in air for 3–5 days; however, the X-ray diffraction pattern showed the presence of broad lines, suggesting inhomogeneity in CO_2 content or ordering. A representative powder diffraction pattern is presented in Fig. 3. Further chemical and structural characterization of this phase are beyond the scope of this study. A polycrystalline pellet of $\text{Sr}_2\text{RuO}_4 \cdot 0.25 \text{CO}_2$ fired at 875°C in air was found to be highly insulating.

$\text{Sr}_3\text{Ru}_2\text{O}_7$

Polycrystalline $\text{Sr}_3\text{Ru}_2\text{O}_7$, with 2% or less SrRuO_3 impurity, was made from the reaction of presynthesized $\text{Sr}_2\text{RuO}_4 \cdot 0.25 \text{CO}_2$ with RuO_2 , mixed in the appropriate ratio to yield $\text{Sr} : \text{Ru} = 3 : 2$. This mixture was ground and pressed into a 1-g, 0.5-in.-diameter pellet and inserted

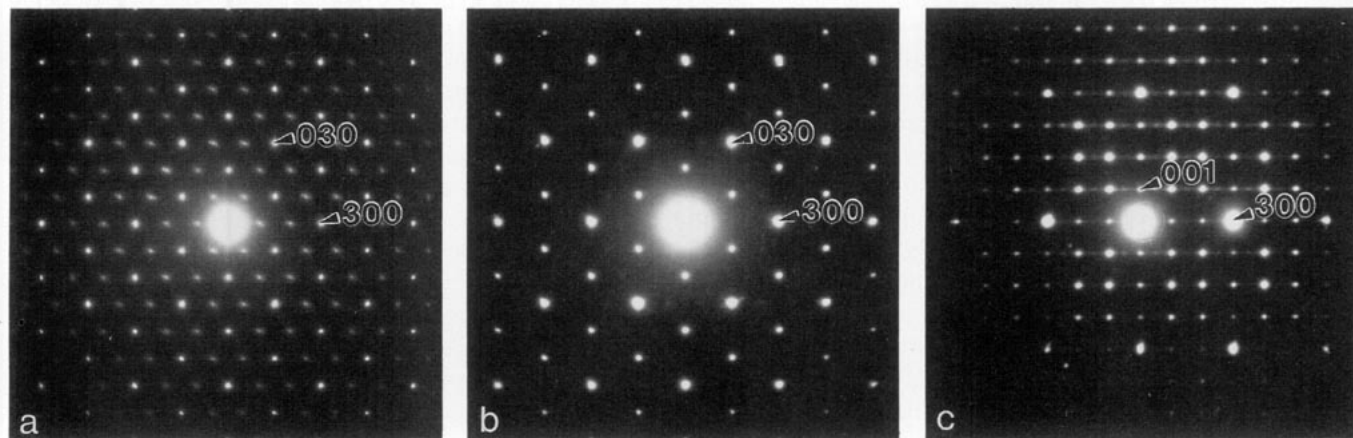


FIG. 2. Electron diffraction patterns of $\text{Sr}_2\text{RuO}_4 \cdot 0.25 \text{CO}_2$: $hk0$ planes for crystallites showing (a) strong and (b) weak $h + k \neq 3n$ reflections; (c) hhl plane.

directly into a hot furnace in flowing O_2 . Heating temperatures between 1175 and 1325°C were explored, in 25°C intervals. Samples were pulled out of the furnace hot and quenched on an Al plate. Heating periods of 2 and 5 hr were employed, with only the latter yielding satisfactory results. $\text{Sr}_3\text{Ru}_2\text{O}_7$ formed as single-phase material in 5 hr for temperatures between 1250 and 1325°C. At lower temperatures, $\text{Sr}_3\text{Ru}_2\text{O}_7$ was present, but was mixed with SrRuO_3 and Sr_2RuO_4 . Excellent crystallinity was obtained for the 1275 and 1300°C treatments. We also found that "single-phase" $\text{Sr}_3\text{Ru}_2\text{O}_7$ could be synthesized by heating from room temperature in a rapid-heating furnace to 1300°C in air (heating time 1 hr), holding for 5 hr, and then allowing the furnace to cool at its natural (rapid) rate. The X-ray diffraction peaks for the $\text{Sr}_3\text{Ru}_2\text{O}_7$ in this case, however, were relatively broad, suggesting the occurrence of a significant amount of structural disorder, probably from the presence of Sr_2RuO_4 and SrRuO_3 intergrowths, indicating the importance of quenching to obtain high quality materials. Attempts to synthesize $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ by this method were not successful.

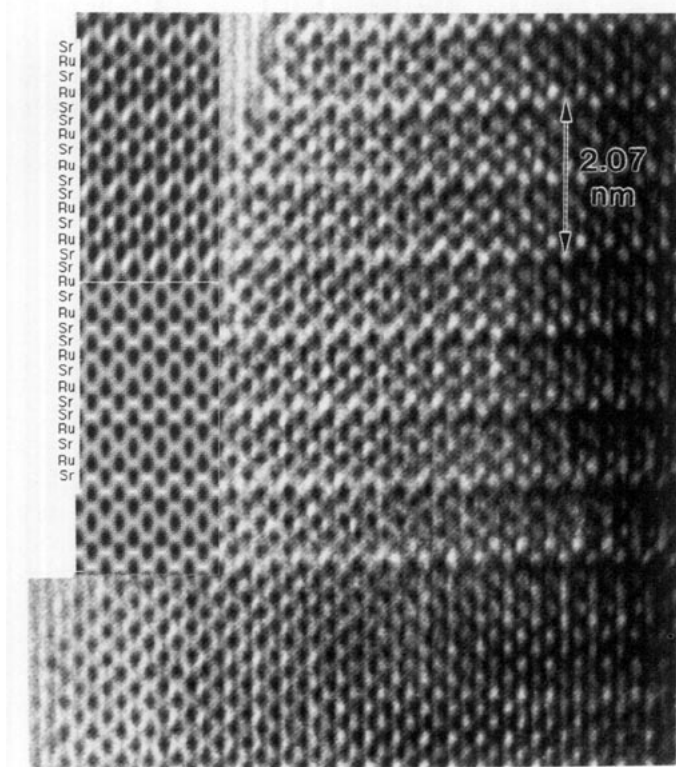


FIG. 4. High-resolution transmission electron micrograph of $\text{Sr}_3\text{Ru}_2\text{O}_7$ in the $[101]$ plane. Inset: (top) part of the experimental image after averaging over eight unit cells; (bottom) calculated structure image (thickness = 2 nm and defocus = -100 nm) showing agreement with the $n = 2$ Ruddlesden-Popper structure type, $(\text{SrO})_{n+1}(\text{RuO}_2)_n$. The SrO and RuO_2 planes are as marked. The Sr and Ru atom columns are imaged as black dots.

The crystal structure of $\text{Sr}_3\text{Ir}_2\text{O}_7$ has recently been reported as that of an $n = 2$ Ruddlesden-Popper phase (12). In order to study the effect of Ir doping on the electrical properties of $\text{Sr}_3\text{Ru}_2\text{O}_7$, we attempted to synthesize $\text{Sr}_3\text{Ru}_{2-x}\text{Ir}_x\text{O}_7$. Single-phase $\text{Sr}_3\text{Ru}_{2-x}\text{Ir}_x\text{O}_7$ for $x = 0.25$ and 0.50 could be synthesized from mixtures of single-phase Sr_2IrO_4 and $\text{Sr}_2\text{RuO}_4 \cdot 0.25 \text{CO}_2$ precursors and RuO_2 ground together and pressed into pellets. Pellets were heated for 5 hr at 1275°C in flowing O_2 , inserted into the furnace at temperature, and quenched on an Al plate upon removal. Samples with higher Ir content could not be made single phase by this method.

The powder X-ray diffraction pattern of $\text{Sr}_3\text{Ru}_2\text{O}_7$ was consistent with a body-centered tetragonal cell and in agreement with previous reports (9–11). The crystallographic cell dimensions were refined from fits of the positions of 20 diffracted lines between 4° and $80^\circ 2\theta$ ($\text{CuK}\alpha$ radiation) and found to be $a = 3.8923(2)$ and $c = 20.716(1)$ Å. Electron diffraction measurements confirmed the ideal $n = 2$ Ruddlesden-Popper unit cell, with no supercell ordering such as might be present if the RuO_6 octahedra were rotated such that Ru–O–Ru bonds were not 180° . High-resolution transmission electron microscopy showed the structure to be of the $n = 2$ Ruddlesden-Popper type and to be free of stacking defects for samples quenched from 1300°C. Observed and calculated structure images, the latter employing the published coordinates (10), are shown in Fig. 4.

PHYSICAL PROPERTIES OF $\text{Sr}_3\text{Ru}_2\text{O}_7$

The magnetic susceptibility of $\text{Sr}_3\text{Ru}_2\text{O}_7$ was measured between 2 and 400 K on a SQUID magnetometer in a field of 15 kOe. Representative data, taken on cooling in the field, are shown in Fig. 5. In most preparations there is a

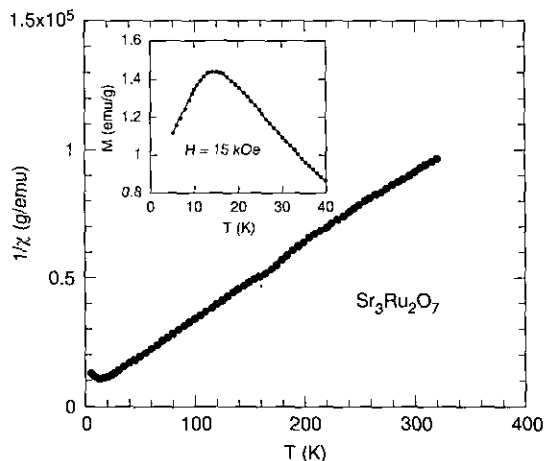


FIG. 5. Temperature-dependent magnetic susceptibility ($=M/H$) measured at 15 kOe, for $\text{Sr}_3\text{Ru}_2\text{O}_7$.

small increase and plateau in the susceptibility which begins at 160 K due to the presence of 1–2% of ferromagnetic SrRuO_3 impurity. The ferromagnetic component of $M(T)$ below 160 K is relatively lower in proportion for larger measuring fields, and so the data in Fig. 5 represent the essentially intrinsic behavior of $\text{Sr}_3\text{Ru}_2\text{O}_7$ obtained from measurements of $M(T)$ in various magnetic fields. Analysis of the data yields a moment of approximately $2.8 \mu_B/\text{Ru}$, and a small antiferromagnetic interaction temperature, $\theta = -15 \text{ K}$. Thus the Ru^{4+} display their full $s = 1$ moment, typical for the low-spin configuration d^4 . The moments are only weakly interacting, a very different case from SrRuO_3 which orders ferromagnetically at 160 K. At 15 K there is a peak in $\chi(T)$, which we believe is due to the development of antiferromagnetic correlations in this 2D arrangement. The shape of $\chi(T)$ is typical for a rapidly increasing correlation length, and not of a 3D Néel transition. Evidence for the antiferromagnetic nature of the 15 K transition is presented in Fig. 6, which shows Magnetization vs applied field (on cooling) for $\text{Sr}_3\text{Ru}_2\text{O}_7$ for temperatures of 15, 10, and 5 K. At 5 K the slope of $M(H)$ is seen to increase with increasing H , characteristic of aligning antiferromagnetically interacting spins by the applied field. Thus the magnetic data do indeed show the behavior of $\text{Sr}_3\text{Ru}_2\text{O}_7$ to be intermediate to that of SrRuO_3 , which is ferromagnetic, and Sr_2RuO_4 , which displays only a weak moment and no magnetic ordering above 4 K.

The Ir doping experiments were performed in order to drive $\text{Sr}_3\text{Ru}_2\text{O}_7$ through a metal-semiconductor transition. The resistivities of polycrystalline pellets of $\text{Sr}_3\text{Ru}_{2-x}\text{Ir}_x\text{O}_7$ for $x = 0.0$ and 0.5 were measured between 4.2 and 300 K, as shown in Fig. 7. As is found also for

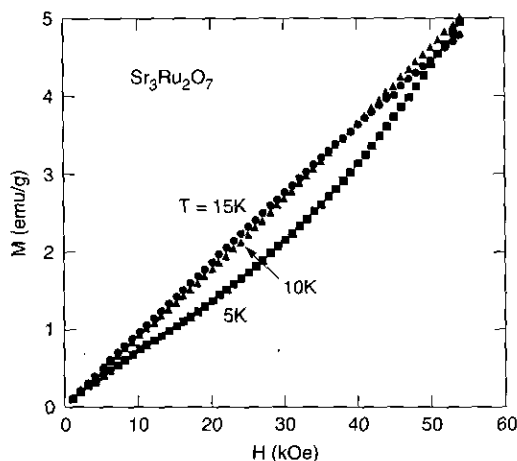


FIG. 6. Magnetization (M) vs applied magnetic field (H) for polycrystalline $\text{Sr}_3\text{Ru}_2\text{O}_7$ measured in the vicinity of the magnetic transition temperature.

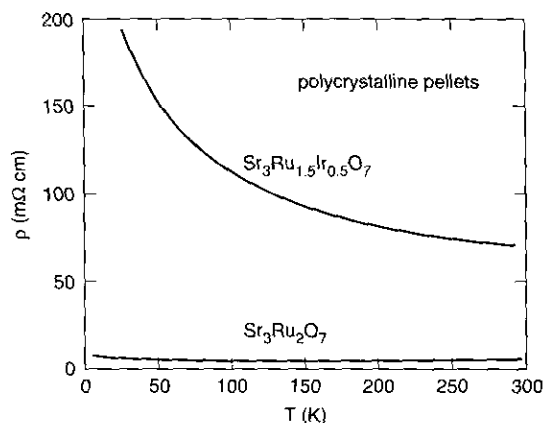


FIG. 7. Temperature-dependent resistivities of polycrystalline pellets of $\text{Sr}_3\text{Ru}_{2-x}\text{Ir}_x\text{O}_7$, $x = 0$ and 0.5 .

SrRuO_3 and Sr_2RuO_4 , the very low pellet densities obtained by conventional sintering result in the measured resistivities showing a significant contribution from grain boundaries. As for metallic SrRuO_3 and Sr_2RuO_4 , the resistivity of $\text{Sr}_3\text{Ru}_2\text{O}_7$ measured on polycrystalline pellets is approximately $10 \text{ m}\Omega\text{-cm}$, and is essentially independent of temperature between 4 and 300 K. $\text{Sr}_3\text{Ru}_2\text{O}_7$ therefore is likely to have a very low intrinsic resistivity and an intrinsically metallic $\rho(T)$, such as has been measured on single crystals of SrRuO_3 and Sr_2RuO_4 (4, 5). On doping with Ir, a clear metal-semiconductor transition occurs, without, however, the appearance of superconductivity above 4 K.

CONCLUSIONS

Through the synthesis of the new strontium ruthenium oxycarbonate $\text{Sr}_2\text{RuO}_4 \cdot 0.25 \text{ CO}_2$, we have been able to synthesize $\text{Sr}_3\text{Ru}_2\text{O}_7$ in bulk by a straightforward route, a compound of intermediary dimensionality to fully layered Sr_2RuO_4 and three-dimensional SrRuO_3 . Taken as a whole, this series of compounds appears to be magnetically anomalous, with the most layered materials showing the least tendency toward localization, contrary to what is expected. It will be of interest to further characterize the physical properties of the $(\text{SrO})_{n+1}(\text{RuO}_2)_n$ series; in that context, the study of the physical properties of single crystals of $\text{Sr}_3\text{Ru}_2\text{O}_7$ would be very helpful.

Note added in proof. Sr_2RuO_4 , the $n = 1$ member of the $(\text{SrO})_{n+1}(\text{RuO}_2)_n$ series, has recently been shown to be superconducting (Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz, and F. Lichtenberg, *Nature* **372**, 532 (1994)) at temperatures below 1 K.

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