## BRIEF COMMUNICATIONS

# Novel Two-Dimensional Conductor Sr<sub>2</sub>RhO<sub>4</sub>

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A new complex oxide  $Sr_2RhO_4$  with  $K_2NiF_4$ -type structure has been synthesized. The crystal symmetry of  $Sr_2RhO_4$  is orthorhombic, and the temperature coefficient of resistivity is positive down to 10 K. Magnetic susceptibility measurement revealed a two-dimensional nature of the magnetic ordering. 1992 Academic Press, Inc.

#### Introduction

In the previous paper (1), we reported that a low spin state of  $Rh^{3+}$  (d<sup>6</sup>) and  $Rh^{4+}$  $(d^5)$  ions is stable in La<sub>1-x</sub> $M_x$ RhO<sub>3</sub> (M =Sr, Ba, and Ca). Rh<sup>4+</sup> with a low spin state at the center of oxygen octahedron has empty  $4d\gamma$  (e<sub>g</sub>) orbitals and mostly filled  $4d\varepsilon$  (t<sub>2g</sub>) orbitals containing one hole. This state is comparable to that of  $V^{4+}$  ion in  $Sr_{n+1}V_n$  $O_{3n+1}$ , where  $V^{4+}$  ion has empty  $3d\gamma$   $(e_g)$ orbitals and mostly empty  $3d\varepsilon$   $(t_{2\nu})$  orbitals having one electron. The temperature coefficient of resistivity is negative for Sr<sub>2</sub>VO<sub>4</sub> (n = 1), but it is positive for Sr<sub>3</sub>V<sub>2</sub>O<sub>7</sub> (n =2),  $Sr_4V_3O_{10}$  (n = 3), and  $SrVO_3$  ( $n = \infty$ ) (2).  $LaRhO_3$  (3) with a perovskite-type structure has been known for 35 years, but a  $K_2NiF_4$ -type  $Sr_2RhO_4$  is not yet known. In this note we report the synthesis of Sr<sub>2</sub>  $RhO_4$  (n = 1) and its positive temperature coefficient of resistivity and a magnetic ordering.

Experimental

 $Sr_2RhO_4$  was prepared by a conventional solid reaction method. Raw materials were  $SrCO_3$  and  $Rh_2O_3$  with the high-temperature form (4); their purities were 99.9%. Stoichiometric amounts of  $SrCO_3$  and  $Rh_2O_3$ were mixed in an agate mortar, and the powder was pressed into a pellet 12 mm in diameter. The pellet was calcinated at 1473 K for 12 hr in  $O_2$  gas flow and cooled to room temperature. The pellet was reground in an agate mortar and again pressed into a pellet. This pellet was sintered at 1523 K for 36 hr in  $O_2$  gas flow and cooled to room temperature.

Identification of the phase was carried out by powder X-ray diffraction analysis. Diffraction data were collected by step scanning between  $20^{\circ} \sim 120^{\circ}$  at intervals of  $0.02^{\circ}$ for 4 sec using a Rigaku  $\theta - \theta$  X-ray diffractometer equipped with the curved graphite monochromator. The lattice constant was



FIG. 1. Powder X-ray diffraction pattern of Sr<sub>2</sub>RhO<sub>4</sub>.

determined using the structural analysis program of Izumi *et al.* (5). Electrical resistivity was measured from 10 to 300 K by the dc four-probe method, and magnetic susceptibility was measured from 5 to 300 K by a SQUID magnetometer.

### **Results and Discussions**

Figure 1 shows the powder diffraction pattern of  $Sr_2RhO_4$ . The symmetry of crys-

tal is orthorhombic and the possible space groups are *Fmmm* (No. 69) or *Cmca* (No. 64). The crystallinity of the sample was not excellent so that the space group, which mainly depends on the tilting of the RhO<sub>6</sub> octahedra, could not be perfectly determined from the X-ray diffraction data. However, the analysis assuming the space group *Cmca* gave the smaller *R* factor. The lengths of the *a*, *b*, and *c* axis are 0.54518(1) nm,





FIG. 2. Temperature dependence of electrical resistivity of  $Sr_2RhO_4$ .

FIG. 3. Temperature dependence of magnetic susceptibility of  $Sr_2RhO_4$ .

TABLE I

LIST OF THE X-RAY DI	FFRACTION ANALYSIS	DATA
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h	k	ı	d <sub>obs.</sub> (nm)	( <i>I</i> / <i>I</i> <sub>0</sub> ) <sub>obs.</sub>	$(I/I_0)_{\text{calc.}}$
1	1	1	0.3692	0.3	0.2
0	4	0	0.3219	0.4	0.5
1	3	1	0.2867	100	100
0	0	2	0.2725	31.7	32.8
2	0	0	0.2724	31.9	32.0
0	2	2	0.2510	0.13	0.17
2	2	0	0.2509	0.13	0.16
0	6	0	0.2146	18.5	17.0
1	5	1	0.2141	14.7	13.6
0	4	2	0.2080	2.8	2.4
2	4	0	0.2079	2.8	2.4
2	0	2	0.1926	30.2	30.9
2	2	2	0.1846	2.3	2.2
1	1	3	0.1708	0.13	0.12
3	1	1	0.1707	0.14	0.13
0	6	2	0.16864	11.3	10.7
2	6	0	0.16860	11.4	10.8
1	7	1	0.16603	0.7	0.6
2	4	2	0.16535	0.5	0.4
0	8	0	0.16099	3.0	2.8
1	3	3	0.15997	18.9	17.7
3	3	1	0.15991	18.6	17.4
2	6	2	0.14339	16.5	15.8
1	5	3	0.14327	3.5	3.4
3	5	1	0.14322	3.6	3.4
0	8	2	0.13862	2.1	2.2
2	8	0	0.13860	2.1	2.2
0	0	4	0.13629	4.2	4.3
4	0	0	0.13622	4.3	4.4
1	9	1	0.13415	4.4	4.4
0	2	4	0.13334	0.4	0.3
4	2	0	0.13327	0.3	0.3
0	10	0	0.12879	0.2	0.2
1	7	3	0.12580	0.3	0.3
3	7	1	0.12577	0.3	0.3
4	4	0	0.12545	0.1	0.1
2	8	2	0.12354	4.0	4.2
3	3	3	0.12307	7.0	7.3
2	0	4	0.12189	4.6	4.8
4	0	2	0.12185	4.7	4.9

Note.  $CuK\alpha_1$  (0.15405 nm) data ( $I/I_0 < 0.1$ ) is not shown.

1.2879(1) nm, and 0.54487(1) nm, respectively. Table I shows the diffraction data for  $Sr_2RhO_4$ .

Figure 2 shows the temperature depen-

dence of resistivity of  $Sr_2RhO_4$ . The temperature coefficient of resistivity is positive below 150 K. The oxygen octahedra in the  $K_2NiF_4$  structure form a two-dimensional network perpendicular to the *b* axis; thus  $Sr_2RhO_4$  is considered to be a two-dimensional conductor. Qualitative measurement of the Seebeck coefficient suggests hole conduction; therefore the carriers are expected to be holes in  $4d\varepsilon$  orbitals of  $Rh^{4+}$ .

Figure 3 shows the temperature dependence of the magnetic susceptibility of  $Sr_2RhO_4$ . The shape of the susceptibility curve in Fig. 3 suggests an ordering of magnetic momenta. Since magnetic interactions among  $Rh^{4+}$  ions are possible only via  $O^{2-}$ ions in the two-dimensional  $RhO_2$  plane perpendicular to the *b* axis, the magnetic ordering may be strong in the two-dimensional plane.

A solid solution system between  $Sr_2RhO_4$ and  $SrLaRhO_4$  (6), that is,  $Sr_{2-x}La_xRhO_4$ , has been synthesized similar to the way  $Sr_2RhO_4$  was synthesized. A positive temperature coefficient of resistivity below 150 K and magnetic ordering have been observed in the region  $0.00 \le x \le 0.15$ . The details of the analysis of the properties of  $Sr_2RhO_4$  and  $Sr_{2-x}La_xRhO_4$  will be reported elsewhere.

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#### References

- 1. T. NAKANURA, T. SHIMURA, M. ITOH, AND Y. TAKEDA, submitted.
- M. Itoh, M. Shikano, H. Kawaji, and T. Naka-Mura, Solid State Commun. 80, 545 (1991).
- 3. A. WOLD, B. POST, AND E. BANKS, J. Am. Chem. Soc. 57, 6365 (1957).
- H. LEVIA, R. KERSHAW, AND K. DWIGHT, Mater. Res. Bull. 17, 1539 (1982).
- 5. F. IZUMI, H. ASANO, H. MURATA, AND N. WATA-NABE, J. Appl. Crystallogr. 20, 411 (1987).
- 6. G. BLASSE, J. Inorg. Nucl. Chem. 27, 2683 (1965).