Inorg. Chem. **2004**, *43*, 5–7

Inorganic Chemistry
Communication

Synthesis and Characterization of a Magnetic Semiconductor Na_2RuO_4 Containing One-Dimensional Chains of Ru^{6+}

Masahiro Shikano,[†,‡] Reinhard K. Kremer,[§] Martin Ahrens,[§] H.-J. Koo,[||] M.-H. Whangbo,[||] and Jacques Darriet*,[†]

Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB-CNRS), 87 Avenue du Docteur Schweitzer, 33608 Pessac Cedex, France, Special Division for Green Life Technology, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, 563-8577 Osaka, Japan, Max-Planck-Institut für Festkörperforschung (MPI-FPF), Heisenbergstrasse 1, D-70569 Stuttgart, Germany, and Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204

Received October 15, 2003

A new ternary ruthenium oxide Na_2RuO_4 was prepared and shown to crystallize with a new structure type. Single crystal X-ray diffraction measurements reveal that Na_2RuO_4 consists of RuO_4 chains made up of RuO_5 trigonal bipyramids by sharing axial corners. Na_2RuO_4 is a magnetic semiconductor with a variable range hopping behavior, and its molar magnetic susceptibility χ_{mol} has a broad maximum at ~74 K. The derivative $d(\chi_{mol}\cdot T)/dT$ exhibits a peak at 37.7 K which has been confirmed by heat capacity measurement to be due to long-range antiferromagnetic ordering.

Ternary Na−Ru−O phases that have been structurally characterized so far include Na_3RuO_4,[1,2] $Na_{3-x}Ru_4O_9$,[3] and $NaRu_2O_4$.[4] In all these compounds, the ruthenium oxidation state does not exceed +5. A reinvestigation of the Na−Ru−O system by solid state synthesis under oxygen led to the new oxide Na_2RuO_4 containing Ru^{6+} (d^2) ions, which is stable under oxygen up to 930 K. Several structure types of ternary transition metal oxides have the general formula A_2BO_4, e.g., the K_2NiF_4, olivine, and spinel type structures.[5] Our single crystal structure determination reveals that Na_2RuO_4 crystallizes with new structure type, which contains RuO_4 chains made up of RuO_5 trigonal bipyramids by sharing their apical oxygen atoms. Measurements of the electrical and magnetic properties show that Na_2RuO_4 is an antiferromagnetic semiconductor with T_N close to 37 K.

Na_2RuO_4 was prepared by solid state reactions from stoichiometric amounts of Na_2O_2 and RuO_2. Powders were ground in an agate mortar under argon. The mixture was heated at 720 K for 5 h, 800 K for 10 h, and 900 K for 20 h under oxygen atmosphere with gradual increasing temperature (less than 50 K/h) to avoid evaporation of sodium oxide. The reaction is highly exothermic. After grinding and further heating the mixture at 900 K for 50 h, we obtain a polycrystalline powder of Na_2RuO_4, which is air sensitive. Single crystals of Na_2RuO_4 were prepared by fast heating the starting stoichiometric mixture at 923 K followed by slowly decreasing the temperature in the range of 5 K/h. Single crystals are needle-shaped elongated along the *b* axis. The structure was solved and refined with the Jana 2000 program.[6] Magnetic susceptibility was measured on a powder sample with a SQUID magnetometer in the temperature range from 2 to 320 K, in a field of 1 T. The electrical resistivity was measured on a crystalline block between 12 and 300 K with a four-probe method. The heat capacity was measured with the quasiadiabatic step-heating method (Nernst's method) on a powder sample of 0.44 g, which was encapsulated in a glass ampule under ~1 bar He gas to ensure thermal coupling.[7] The heat capacity of the glass ampule was determined in a separate run and subtracted. The crystal structure of Na_2RuO_4 contains RuO_4 chains that are made up of slightly distorted RuO_5 trigonal bipyramids by sharing their axial oxygen atoms O_{ax} (Figure 1a). A unit cell has two nonequivalent RuO_4 chains, one based on $Ru1O_5$ and the other based on $Ru2O_5$ trigonal bipyramids (Figure 1b). In both types of trigonal bipyramids, the Ru−O bonds are long along the axial direction and short along the equatorial direction (i.e., $Ru-O_{ax} \approx 2.00$ Å and $Ru-O_{eq} \approx 1.76$ Å).[8] Such a trigonal bipyramidal coordination of Ru^{6+} (d^2) was found, e.g., for $Ba[RuO_3(OH)_2]$, which contains isolated

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* To whom correspondence should be addressed. E-mail: darriet@icmcb.u-bordeaux.fr.

[†] ICMCB-CNRS.

[‡] AIST.

[§] MPI-FPF.

[||] NCSU.

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10.1021/ic035191w CCC: $27.50

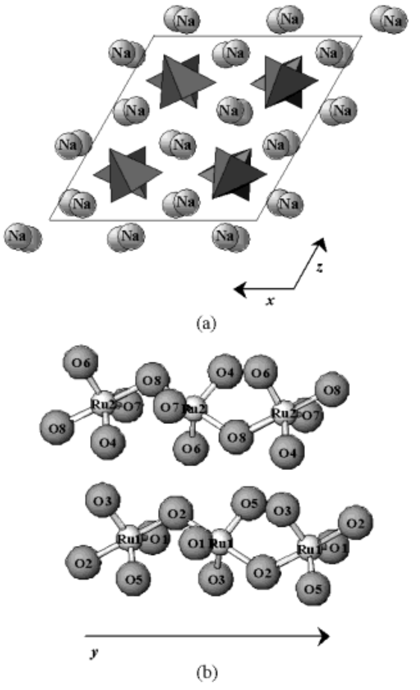

Figure 1. (a) Projection view of Na_2RuO_4 along the RuO_4 chain direction. (b) Perspective view of the corner sharing RuO_5 bipyramids along the *y*-axis.

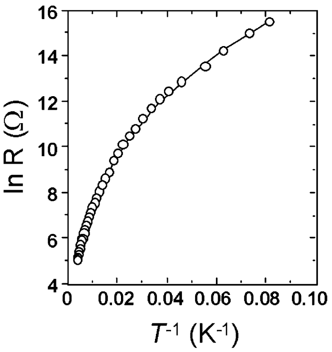

Figure 2. Resistance of Na_2RuO_4 as a function of reciprocal temperature.

$RuO_3(OH)_2^{2-}$ ions with OH^- ions occupying the axial positions.[9] The $-Ru-O_{ax}-Ru-O_{ax}-$ linkage of each RuO_4 chain is bent with a $Ru-O_{ax}-Ru$ angle ≈ 125° (O_{ax} = O2 or O8) (Figure 1b). The sodium atoms surround the chains forming hexagonal nets (Figure 1a) with the Na−O distances ranging between 2.327(7) and 2.912(12) Å. Bond valence sum calculations[10] yield an average oxidation state of +5.89 for Ru[11] and +1.10 for Na, in good agreement with the values expected for the formula Na_2RuO_4.

The volume per oxygen atom for Na_2RuO_4 is equal to 14.9 Å^3,[12] which is very close to the value found for a closed packed stacking (∼15−16 Å^3).[13] The unit cell parameters of Na_2RuO_4 can be approximated to a pseudohexagonal cell with $a_{hex} \approx 10.8$ Å and $c_{hex} = 7.04$ Å. If we assume an ideal structure in which the oxygen atoms of the equatorial plane of the bipyramids have the same height (*y* for the monoclinic cell or *z* for the pseudo hexagonal cell), as do the corresponding Ru atoms ($^1/_4$ or $^3/_4$), the structure can be viewed as a close stacking of closely packed layers of composition Na_8O_4 and O_{12} along the *z* direction of the pseudohexagonal cell. The Na_8O_4 layer results from the O_{12} layer by simply replacing 8 sodium atoms with 8 oxygen atoms. The sequence along the packing direction is *abaca*, where *a* represents the Na_8O_4 layer, and *b* and *c* the O_{12} layers. In the resulting lattice, the Ru atoms occupy all the trigonal bipyramidal sites made up of oxygen atoms, which are located in the O_{12} layers, hence leading to the composition Na_2RuO_4 ($Z = 8$). This structure corresponds to the simplest alternating sequence of Na_8O_4 and O_{12} layers with the small cations Ru^{6+} located at the trigonal bipyramidal sites in the O_{12} layers. One might imagine different phases based on the two types of layers with different sequences. Such phases should only be stabilized for transition metal cations with small ionic radius.

The temperature dependence of the electrical resistance *R* of Na_2RuO_4 (Figure 2) shows that Na_2RuO_4 is a semiconductor in all the temperature range studied. The temperature dependence of the resistance is well fitted by the expression expected for a variable range hopping model:[14] $R \propto \exp[(T_0/T)^{1/(n+1)}]$ with $T_0 \approx 9.5 \times 10^5$ K and $n \approx 2.8$. This model assumes the occurrence of several hopping

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(6) Crystal data: Na_2RuO_4, $M_r = 211.05$ g/mol, monoclinic, space group $P2_1/n$, cell parameters ($T = 293$ K) $a = 10.7098(1)$ Å, $b = 7.0356(1)$ Å, $c = 10.9253(2)$ Å, $\beta = 119.67(1)°$, $V = 715.30(5)$ Å^3, $Z = 8$, $\rho = 3.919$ g cm^{-3}, μ(Mo Kα) = 4.51 mm^{-1}, crystal size (cylindrical) 0.003 × 0.003 × 0.145 mm^3, wavelength = 0.71069 Å, $\theta_{max} = 35$ °, sin$(\theta/\lambda)_{max} = 0.807$, no. of reflections (obs/measd) 7711/22048 ($I > 3\sigma(I)$), no. of independent reflections 1200, no. of parameters refined 129, no constraint, weighting scheme $1/\sigma^2$, refinement on $|F^2|$, residual $\Delta\rho_{max} = 2.22$ e/Å^3, $\Delta\rho_{min} = -1.73$ e/Å^3, GOF = 1.56, reliability $R/R_w = 4.37\%/8.53\%$. The structure data were collected on a Nonius Kappa CCD diffractometer. The structure was solved and refined with the Jana 2000 program: Petřiček, V.; Dušek, M. Jana 2000 program. *Inst. Phys. Acad. Sci.* Czech Republik, Prague, 1998. The refined atomic positions are the following: Ru1, $x = 0.2522(1)$, $y = 0.26886(8)$, $z = 0.2516(1)$, $U_{iso} = 0.0069(4)$ Å^2; Ru2, $x = 0.2490(1)$, $y = 0.24411(6)$, $z = 0.7488(1)$, $U_{iso} = 0.0080(5)$ Å^2; Na1, $x = 0.0552(6)$, $y = 0.0060(5)$, $z = 0.0.9021(7)$, $U_{iso} = 0.019(2)$ Å^2; Na2, $x = 0.3950(5)$, $y = 0.0406(5)$, $z = 0.0894(6)$, $U_{iso} = 0.017(2)$ Å^2; Na3, $x = 0.0634(5)$, $y = 0.0636(5)$, $z = 0.4144(5)$, $U_{iso} = 0.021(2)$ Å^2; Na4, $x = 0.3961(5)$, $y = 0.0137(5)$, $z = 0.5878(6)$, $U_{iso} = 0.015(2)$ Å^2; O1, $x = 0.0847(8)$, $y = 0.2721(7)$, $z = 0.2502(9)$, $U_{iso} = 0.012(4)$ Å^2; O2, $x = 0.1968(9)$, $y = 0.0202(6)$, $z = 0.1498(9)$, $U_{iso} = 0.011(4)$ Å^2; O3, $x = 0.2251(7)$, $y = -0.1449(8)$, $z = 0.3879(7)$, $U_{iso} = 0.017(4)$ Å^2; O4, $x = 0.4084(7)$, $y = 0.1504(8)$, $z = 0.8887(7)$, $U_{iso} = 0.015(3)$ Å^2; O5, $x = 0.4052(6)$, $y = 0.1779(7)$, $z = 0.3982(7)$, $U_{iso} = 0.011(3)$ Å^2; O6, $x = 0.2576(7)$, $y = 0.3195(8)$, $z = 0.5985(7)$, $U_{iso} = 0.013(3)$ Å^2; O7, $x = 0.0882(9)$, $y = 0.2528(7)$, $z = 0.7588(11)$, $U_{iso} = 0.018(4)$ Å^2; O8, $x = 0.1878(9)$, $y = -0.0062(6)$, $z = 0.6532(10)$, $U_{iso} = 0.016(4)$ Å^2.

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(8) Selected bond distances: Ru1−O1 = 1.786(10) Å, Ru1−O2 = 2.000(6) and 2.000(6) Å, Ru1−O3 = 1.766(9) Å, Ru1−O5 = 1.749(5) Å, and Ru1−O2−Ru1 = 123.2(4)°; Ru2−O4 = 1.761(5) Å, Ru2−O6 = 1.771(8) Å, Ru2−O7 = 1.781(11) Å, Ru2−O8 = 1.987(6) and 1.994(6) Å, and Ru2−O8−Ru2 = 124.2(4)°.

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(11) The bond valence parameter for Ru6+ is unknown. This parameter has been deduced by considering the environment of the oxygen atoms in the structure and assuming that their charge is −2. An average parameter of 1.905 for Ru6+ has been calculated and used in the calculation of the BVS of this atom.

(12) The sodium is included in the calculation of the volume per anion site as it is usually done. Therefore, v/site = $V/6Z$ with $Z = 8$ and V = volume of the unit cell.

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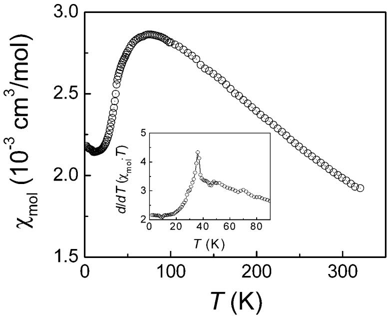

Figure 3. Molar magnetic susceptibility of Na_2RuO_4. The inset displays the quantity $d(\chi_{mol}\cdot T)/dT$ in the vicinity of the Néel temperature.

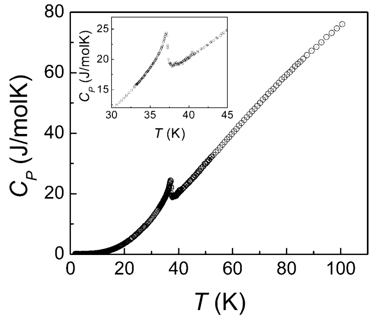

Figure 4. Heat capacity of Na_2RuO_4. The inset displays the long-range ordering anomaly at the Néel temperature. It contains about 5% of the entropy expected for an $S = 1$ system.

processes with slightly different activation energies. This is understandable because the $Ru1O_5$ and $Ru2O_5$ trigonal bipyramids are slightly different in structure and because each RuO_5 trigonal bipyramid does not possess a 3-fold rotational symmetry along the Ru−O_{ax} axis.[8] If each RuO_5 trigonal bipyramid has an ideal shape of C_{3h} point group symmetry, its d-block levels will be split into the 1e″ (*xz*, *yz*) < 1e′ ($x^2 - y^2$, *xy*) < 1a′ (z^2) pattern, so that the ground state electronic configuration of each Ru^{6+} (d^2) site will be given by $(d_{xz})^1(d_{yz})^1$ (with the *z*-axis taken along the Ru−O_{ax} bond). For the distorted RuO_5 trigonal bipyramids of Na_2RuO_4, the degeneracy of the 1e″ and 1e′ levels is lifted so that an electron hopping from one Ru^{6+} site to another will encounter several different activation energies.

The temperature dependence of the magnetic susceptibility χ_{mol} of Na_2RuO_4 is shown in Figure 3. The χ_{mol} versus *T* curve exhibits a broad maximum at $T_{max} \approx 74$ K, which is characteristic of short-range antiferromagnetic (AFM) ordering in low dimensional magnets. Above 200 K, the reciprocal susceptibility can be fitted by a Curie−Weiss law with a Weiss constant $\theta = -273(5)$ K and Curie constant $C = 1.14(2)$ cm^3 K/mol, which is close to 1 cm^3 K/mol expected for the spin only contribution from Ru^{6+} (d^2) (i.e., $g = 2$ and $S = 1$). However, attempts to fit the susceptibility to the theoretical result for an isolated $S = 1$ AFM Heisenberg chain with nearest-neighbor interaction along the chain failed.[15]

We ascribe this failure to the presence of considerable interchain interactions, which in fact lead to long-range magnetic ordering. As shown in Figure 4, the heat capacity exhibits a λ-type anomaly at 37 K characteristic of three-dimensional ordering. This ordering temperature is also confirmed by a prominent discontinuity at ≈37.7 K in the quantity $d(\chi_{mol}\cdot T)/dT$ (“Fishers heat capacity”, see the inset in Figure 3). We conclude that Na_2RuO_4 magnetically is not a well isolated one-dimensional chain system. Interchain interactions will also explain the sizable Weiss parameter. For an $S = 1$ Heisenberg chain, a short range ordering maximum in the susceptibility at 74 K corresponds to an exchange constant of about −28 K and a Weiss constant of about −75 K.[16]

Sizable interchain coupling will also prevent a Haldane gap scenario[15,17,18] (i.e., an energy gap between the ground state and the first excited magnetic states for an integer *S*) to open. Na_2RuO_4 is an example for which the analysis of structural features at room temperature alone is insufficient in predicting the dimensionality of the magnetic model.

Acknowledgment. This work was carried out during the stay of M.S. in ICMCB for one year, which was made possible by the financial support from a grant: bourse Egide 341477J of ministère français des affaires étrangères. The work at NCSU was supported by the Office of Basic Energy Sciences, Division of Materials Sciences, U.S. Department of Energy, under Grant DE-FG02-86ER45259.

Supporting Information Available: X-ray crystallographic information for Na_2RuO_4 in CIF format and a representation of ideal stacking of the layers in the structure of Na_2RuO_4. This material is available free of charge via the Internet at http://pubs.acs.org.

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