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$NaRuO_2$ and $Na_xRuO_2{\cdot}yH_2O$: New Oxide and Oxyhydrate with Two Dimensional RuO_2 Layers

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The new oxide and oxyhydrate $NaRuO_2$ and $Na_xRuO_2{\cdot}yH_2O$ ($x = 0.22$, $y = 0.45$) have been characterized. $NaRuO_2$ is isostructural with α-$NaFeO_2$. The symmetry is rhombohedral ($R\bar{3}m$ space group) with lattice parameters of $a = 3.018(2)$ Å and $c = 16.493(3)$ Å. The structure has been refined by the Rietveld method. The oxyhydrate $Na_xRuO_2{\cdot}yH_2O$ has been prepared by stirring a sample of $NaRuO_2$ in water at ambient temperature. $Na_xRuO_2{\cdot}yH_2O$ crystallizes in the space group $R\bar{3}m$ with lattice parameters of $a = 2.930(2)$ Å and $c = 21.913(5)$ Å. The structure is related to the $CuFeO_2$ 3R polytype structure with the AABBCC sequence of the oxygen close packed layers along the *c*-axis. Analogies with the related cobalt phases are discussed. The susceptibilities of $NaRuO_2$ and $Na_xRuO_2{\cdot}yH_2O$ are small and constant in a large temperature range.

The understanding of the physical and chemical properties of materials with low dimensional structure has become more attractive since the discovery of high-T_c superconductors in layered copper oxides.[1] In 1994, it has also been discovered that Sr_2RuO_4 which is isostructural with the K_2NiF_4 type structure is a superconductor at $T \leq 0.93$ K.[2] Recently, Takada et al.[3] reported that $Na_{0.35}CoO_2{\cdot}1.3H_2O$ shows superconductivity near 5 K. Its crystal structure consists of the stacking of two-dimensional CoO_2 layers isolated by one layer of Na ions and two layers of H_2O molecules. Therefore, the CoO_2 layers are well separated (≈9.81 Å), which could be the origin of the superconductivity. Foo et al.[4] pointed out that the variations of Na and H_2O concentrations within the layers affect their crystal structure and superconductivity. $Na_{0.5}CoO_2$ is known as one candidate material for thermoelectric devices because it has metallic conductivity and a high Seebeck coefficient.[5] All these properties have been related to the roles of CoO_2 layers. In line with this observation, it appears interesting to replace Co by another d transition metal especially 4d or 5d. Generally, for a given structural type, an enhancement of the metallic behavior is observed when 3d transition metals are replaced by 4d or 5d transition elements. Our choice turned to substitute ruthenium for cobalt in such systems. Until now, few Na−Ru−O oxides have been isolated.[6] The different phases are characterized by various ruthenium valence states from +6 to a mixture of +3 and +4. It is surprising to notice that $Na_{0.5}RuO_2$ ($NaRu_2O_4$) is not a two-dimensional system like $Na_{0.5}CoO_2$ but is isostructural with $CaFe_2O_4$[7] where Na or Ca occupies the channels of the three-dimensional network. However, it will be shown in this paper that the two new phases $NaRuO_2$ and $Na_xRuO_2{\cdot}yH_2O$ exhibit two-dimensional structures.

$NaRuO_2$ was prepared by solid state reactions from stoichiometric amounts of Na_2RuO_4[6e] and Ru. As Na_2RuO_4 is air sensitive, the mixture was weighed and ground under Ar in a drybox. The mixture was introduced into a gold tube and then dried under a primary vacuum at 420−470 K for 12 h, and finally, the tube was sealed under Ar. The sample was heated at 1173 K for 12 h and then at 1273 K for 120 h. XRD shows that the reaction is complete giving rise to the new oxide $NaRuO_2$ as shown in Figure 1a.

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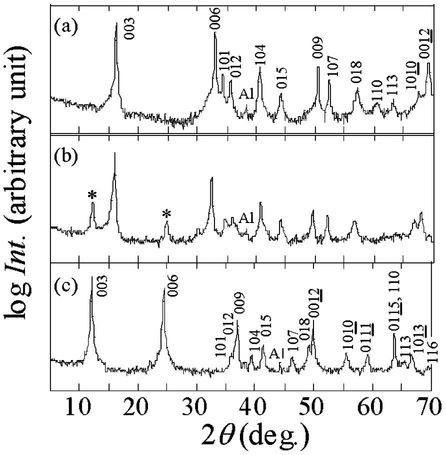

Figure 1. XRD profiles of (a) $NaRuO_2$ (as sintered), (b) $NaRuO_2$ (after 1 night in air), and (c) $Na_xRuO_2 \cdot yH_2O$. The scale of the intensity is logarithmic to enhance the weak peaks.

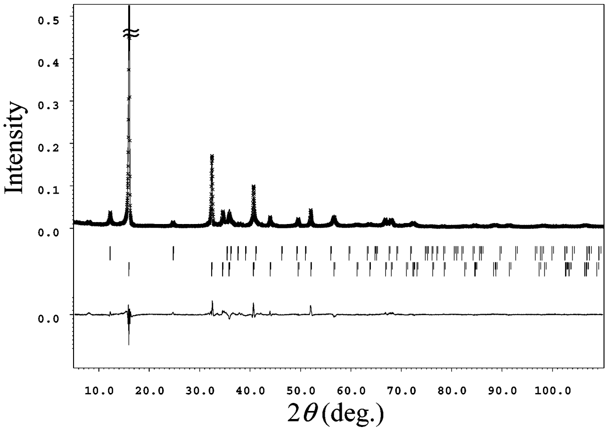

Figure 2. Rietveld refinement for $NaRuO_2$. The upper ticks correspond to the hydrate.

It is well crystallized, and very small plate shaped crystals can be observed under microscope. However, $NaRuO_2$ is also air sensitive, and after one night in air, some peaks appear in the XRD pattern as shown in Figure 1b. Indeed, they correspond to the main peaks of the new oxyhydrate $Na_xRuO_2 \cdot yH_2O$ (Figure 1c). Monophasic samples of $Na_xRuO_2 \cdot yH_2O$ have been prepared by stirring 0.4 g of $NaRuO_2$ in 1000 cm^3 of H_2O for 1−3 days. After filtering, the XRD pattern shows a single phase (Figure 1c). A very small plate shaped crystal has been mechanically isolated from the batch for structural determination.

The structure of $NaRuO_2$ has been refined by the Rietveld method (Figure 2).[8]

$NaRuO_2$ is isostructural with the well-known structure of α-$NaFeO_2$[9] (Figure 3a). The structure consists of a stacking of close packed oxygen layers with the ABC sequence along the *c*-axis (O3 structural type). It derives from a NaCl type structure with an ordering of the Na^+ and Ru^{3+} ions in the (111) planes. All cations are in octahedral sites.

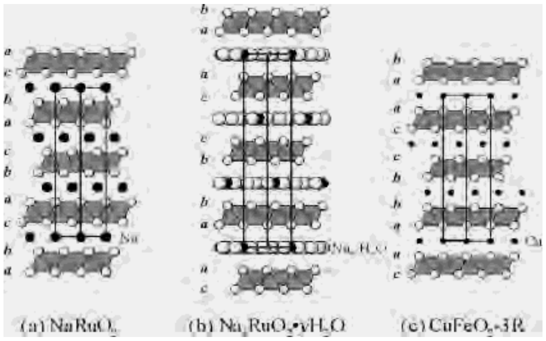

Figure 3. Schematic representations of crystal structure for (a) $NaRuO_2$, (b) $Na_xRuO_2 \cdot yH_2O$, and (c) $CuFeO_2$-3R.

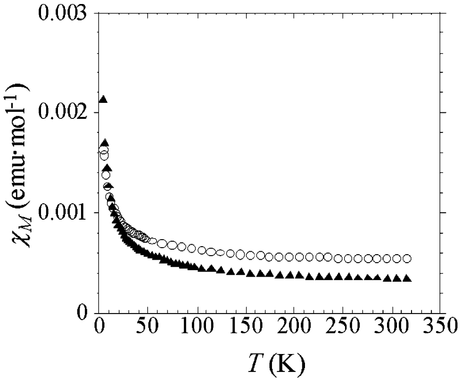

Figure 4. Temperature dependences of molar magnetic susceptibility for $NaRuO_2$ (○) and $Na_xRuO_2 \cdot yH_2O$ (▲).

The metal−oxygen bond distances within the two types of octahedra are Ru−O 2.073(19) Å and Na−O 2.38(2) Å, respectively. This is in good agreement with the corresponding ionic radii: 0.68 Å for Ru^{3+}, 1.02 Å for Na^+, and 1.40 Å for O^{2-}.[10] The distance between two adjacent RuO_2 layers, 5.5 Å, is longer than that in α-$NaFeO_2$ (5.36 Å). The difference in the interlayer distance can be related to the increase of the ionic radius of Ru^{3+} compared to Fe^{3+} (0.645 Å).[10] Magnetic measurements under low field show that $NaRuO_2$ is nonsuperconducting down to $T = 2$ K. The molar magnetic susceptibility of $NaRuO_2$ is small ($\approx 500 \times 10^{-6}$ emu·mol^{-1}) in a wide temperature range and characteristic of a Pauli paramagnetism (Figure 4).[11]

The Na content *x* in the $Na_xRuO_2 \cdot yH_2O$ oxyhydrate has been deduced as 0.22.[12] A TGA of $Na_xRuO_2 \cdot yH_2O$ under Ar shows a plateau weight loss of 5.5% at $T \approx 200$ K which corresponds to 0.45 H_2O per formula unit. These values are in agreement with the lower oxyhydrate $Na_{0.3}CoO_2 \cdot 0.6H_2O$ observed in the Co system.[4a] It was assumed that the structure of $Na_{0.3}CoO_2 \cdot 0.6H_2O$ is a P2 phase with a *c* parameter of

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(8) Rietveld refinement $NaRuO_2$: MM = 156.7 g/mol, trigonal space group $R\bar{3}m$, $a = 3.0184(2)$ Å, $c = 16.4929(3)$ Å, $V = 130.13(5)$ Å^3, $Z = 3$. Program software: Petricek, V.; Dusek, M. *Jana2000: the crystallographic computing system*; Institute of Physics: Praha, Czech Republic, 2000. Final $R_B = 6.89\%$, $R_p = 10.14\%$, $R_{wp} = 13.60\%$. Atomic coordinates (*x*, *y*, *z*) and isotropic displacement parameters: Ru (0, 0, 0.5) 0.41(17) Å^2; Na (0, 0, 0) 4.9(1.1) Å^2; O (0, 0, 0.235(2)) 5.1(1.3) Å^2.

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(11) Magnetic susceptibility was measured on a powder sample by a SQUID magnetometer (Quantum Design MPMSXL) in a temperature range from 2 to 320 K under an applied field of 1.0 T for $NaRuO_2$ and 0.5 T for $Na_xRuO_2 \cdot yH_2O$. No difference has been observed in the zero-field-cooled mode and field-cooled mode.

(12) By assuming that the starting material was $NaRuO_2$, the filtrate was used for the analysis of Na concentration by emission spectrometry.

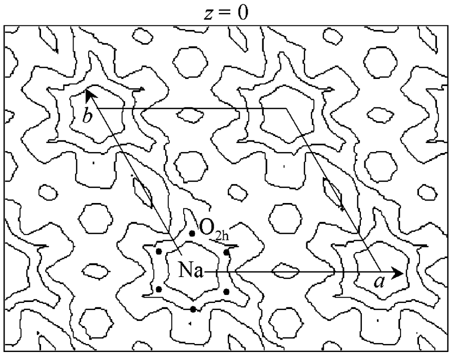

Figure 5. Observed Fourier map of $Na_xRuO_2{\cdot}yH_2O$ at $z = 0$ (contour $1e^-/Å^3$). Closed circles show atomic positions of O_{2h}.

13.8 Å (hexagonal symmetry with ABBA... sequence) which corresponds to an intercalant layer thickness of 6.9 Å.[4a] The crystal structure of $Na_xRuO_2{\cdot}yH_2O$ oxyhydrate ($x = 0.22$, $y = 0.45$) has been determined on a single crystal.[13] The symmetry is rhombohedral ($R\bar{3}m$ space group) with a c_{hex} of 21.913(5) Å. The structure corresponds to the ABBCCA sequence of the oxygen close packed layers (Figure 3b). This sequence is identical to that encountered in the $CuFeO_2$-3R polytype structure (Figure 3c).[14] A Fourier map shows clearly that Na and H_2O are located almost at the same z coordinate in two different positions (Figure 5).

This result indicates that the sum of occupancy ($x + y$) in the $Na_xRuO_2{\cdot}yH_2O$ formula cannot exceed 1 as it is observed by the analysis. The Na atoms and the water molecules occupy the two positions: 3a (0, 0, 0) and 18h (x, $2x$, z) with $x = 0.155(6)$ and $z = -0.0002(16)$, respectively. The 3a position is the same as Cu in the $CuFeO_2$-3R polytype structure. The Ru−O1 bond distance in $Na_xRuO_2{\cdot}yH_2O$ (2.009(4) Å) is shorter than that observed in $NaRuO_2$ (2.073(19) Å) which is in good agreement with the oxidation of Ru in the oxyhydrate. Though it is difficult to figure out the environment of Na due to the nonstoichiometry of the layer, one can notice that the axial bond distance Na−O1 along the c-axis is 2.568(7) Å. Whatever the stoichiometry in Na within the layer and as the O1 position is fully occupied, this distance must be compatible for this cation as it is observed. The expansion of the c-axis of the unit cell of $NaRuO_2$ from 16.493 to 21.913 Å in $Na_xRuO_2{\cdot}yH_2O$ implies an expansion of 1.8 Å per intercalant layer. This is less than the diameter of an oxygen ion (about 2.8 Å). This means that Na and H_2O are located in the same nonstoichiometric plane as has also been assumed in $Na_{0.3}CoO_2{\cdot}0.6H_2O$.[4a] The stacking of the oxygen close packed layers is different for the Ru and Co oxyhydrates. In $Na_xRuO_2{\cdot}yH_2O$, the sequence is ABBCCA while it is ABBA in the Co corresponding compound. This difference results from the nature of the precursor: a P2 type phase in the cobalt system and an O3 one for $NaRuO_2$. Magnetic susceptibility shows that $Na_xRuO_2{\cdot}yH_2O$ ($x = 0.22$, $y = 0.45$) is nonsuperconducting down 2 K[11] as has also been observed for the Co related phase.[4] The susceptibility is small ($\approx 400 \times 10^{-6}$ emu·mol^{-1}) in a large temperature range (Figure 4) and comparable to that of $NaRuO_2$. In summary, it seems to us that one of the criteria to observe superconductivity in such systems implies MO_2 layer spacing greater than one intercalant layer. Furthermore, it is interesting to notice the extreme flexibility of the stacking sequences that can be changed even at ambient temperature. In comparison to γ-type nickel oxyhydroxide with general formula $H_xK_yNiO_2{\cdot}zH_2O$[15] which exhibits the same slab stacking, we cannot exclude the existence of protons in the interslab of this phase.

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Supporting Information Available: X-ray crystallographic information for $Na_xRuO_2{\cdot}yH_2O$ ($x = 0.22$, $y = 0.45$) in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Crystal data for $Na_xRuO_2{\cdot}yH_2O$ ($x = 0.22$, $y = 0.45$): MM = 146.3 g/mol, trigonal space group $R\bar{3}m$, $a = 2.930(2)$ Å, $c = 21.913(5)$ Å, $V = 162.89(6)$ Å^3, $Z = 3$, $T = 293$ K, $\lambda = 0.71073$ Å, $D_c = 4.47$ g/cm^3, crystal size $0.04 \times 0.03 \times 0.005$ mm^3, $\mu = 6.9$ mm^{-1}, $\theta_{max} = 40°$, indep reflns 88 ($I > 3\sigma(I)$), data/restraints/params 88/0/10, least-squares refinement on F^2, final $R = 0.0417$, $R_w(F^2) = 0.0774$, goodness = 1.58. Atomic coordinates (x, y, z) and isotropic or equivalent isotropic displacement parameters (U_{iso} or U_{eq}): Ru (0, 0, 0.5) 0.043(1) Å^2; O1 (0, 0, 0.1172(3)) 0.031(2) Å^2; Na (0, 0, 0) $U_{iso} = 0.045(8)$ Å^2; O_{2h} (0.155(6), $2x$, −0.0002(16)) $U_{iso} = 0.033(7)$ Å^2. The Na and O_{2h} site occupancies have been fixed to 22% and 7.5%, respectively.

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