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NaRuO₂ and Na_xRuO₂·yH₂O: New Oxide and Oxyhydrate with Two Dimensional RuO₂ Layers

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The new oxide and oxyhydrate NaRuO₂ and Na_xRuO₂·yH₂O ($x = 0.22$, $y = 0.45$) have been characterized. NaRuO₂ is isostructural with α -NaFeO₂. 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_xRuO₂·yH₂O has been prepared by stirring a sample of NaRuO₂ in water at ambient temperature. Na_xRuO₂·yH₂O 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 CuFeO₂ 3R polytype structure with the AABCC sequence of the oxygen close packed layers along the c -axis. Analogies with the related cobalt phases are discussed. The susceptibilities of NaRuO₂ and Na_xRuO₂·yH₂O 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 Sr₂RuO₄ which is isostructural with the K₂NiF₄ type structure is a superconductor at $T \leq 0.93$ K.² Recently, Takada et al.³ reported that Na_{0.35}CoO₂·1.3H₂O shows superconductivity near 5 K. Its crystal structure consists of the stacking of two-dimensional CoO₂ layers isolated by one layer of Na ions and two layers of H₂O molecules. Therefore, the CoO₂ 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 H₂O concentrations within the layers affect their crystal structure and superconductivity.

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Na_{0.5}CoO₂ 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 CoO₂ 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}RuO₂ (NaRu₂O₄) is not a two-dimensional system like Na_{0.5}CoO₂ but is isostructural with CaFe₂O₄⁷ 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 NaRuO₂ and Na_xRuO₂·yH₂O exhibit two-dimensional structures.

NaRuO₂ was prepared by solid state reactions from stoichiometric amounts of Na₂RuO₄^{6e} and Ru. As Na₂RuO₄ 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 NaRuO₂ as shown in Figure 1a.

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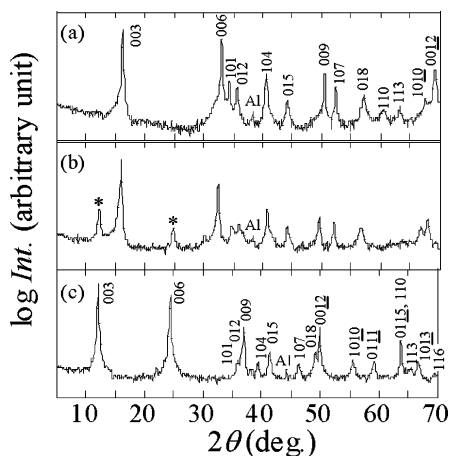


Figure 1. XRD profiles of (a) NaRuO₂ (as sintered), (b) NaRuO₂ (after 1 night in air), and (c) Na_xRuO₂·yH₂O. The scale of the intensity is logarithmic to enhance the weak peaks.

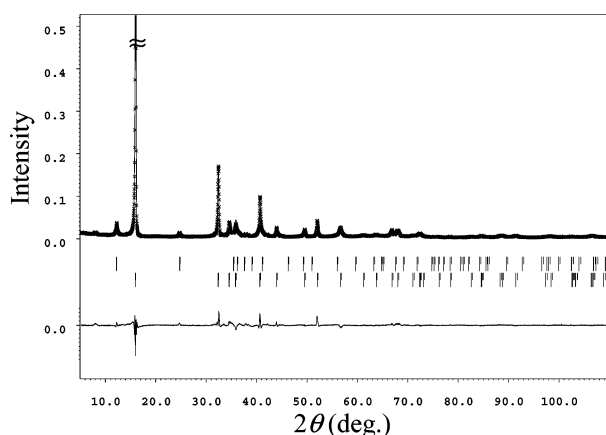


Figure 2. Rietveld refinement for NaRuO₂. The upper ticks correspond to the hydrate.

It is well crystallized, and very small plate shaped crystals can be observed under microscope. However, NaRuO₂ 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_xRuO₂·yH₂O (Figure 1c). Monophasic samples of Na_xRuO₂·yH₂O have been prepared by stirring 0.4 g of NaRuO₂ in 1000 cm³ of H₂O 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 NaRuO₂ has been refined by the Rietveld method (Figure 2).⁸

NaRuO₂ is isostructural with the well-known structure of α-NaFeO₂⁹ (Figure 3a). The structure consists of a stacking of close packed oxygen layers with the ABC sequence along

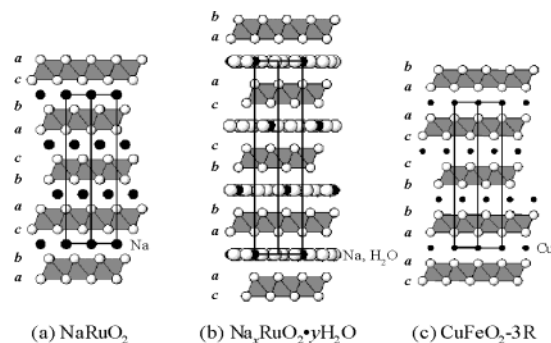


Figure 3. Schematic representations of crystal structure for (a) NaRuO₂, (b) Na_xRuO₂·yH₂O, and (c) CuFeO₂·3R.

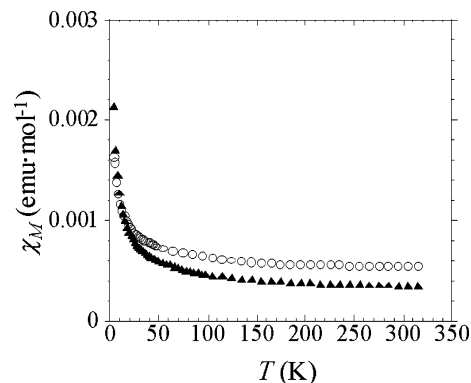


Figure 4. Temperature dependences of molar magnetic susceptibility for NaRuO₂ (O) and Na_xRuO₂·yH₂O (▲).

the *c*-axis (O3 structural type). It derives from a NaCl type structure with an ordering of the Na⁺ and Ru³⁺ ions in the (111) planes. All cations are in octahedral sites.

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 Ru³⁺, 1.02 Å for Na⁺, and 1.40 Å for O²⁻.¹⁰ The distance between two adjacent RuO₂ layers, 5.5 Å, is longer than that in α-NaFeO₂ (5.36 Å). The difference in the interlayer distance can be related to the increase of the ionic radius of Ru³⁺ compared to Fe³⁺ (0.645 Å).¹⁰ Magnetic measurements under low field show that NaRuO₂ is nonsuperconducting down to *T* = 2 K. The molar magnetic susceptibility of NaRuO₂ is small (≈500 × 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_xRuO₂·yH₂O oxyhydrate has been deduced as 0.22.¹² A TGA of Na_xRuO₂·yH₂O under Ar shows a plateau weight loss of 5.5% at *T* ≈ 200 K which corresponds to 0.45 H₂O per formula unit. These values are in agreement with the lower oxyhydrate Na_{0.3}CoO₂·0.6H₂O observed in the Co system.^{4a} It was assumed that the structure of Na_{0.3}CoO₂·0.6H₂O is a P2 phase with a *c* parameter of

(8) Rietveld refinement NaRuO₂: MM = 156.7 g/mol, trigonal space group *R*3̄m, *a* = 3.0184(2) Å, *c* = 16.4929(3) Å, *V* = 130.13(5) Å³, *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) Å²; Na (0, 0, 0) 4.9(1.1) Å²; O (0, 0, 0.235(2)) 5.1(1.3) Å².

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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 NaRuO₂ and 0.5 T for Na_xRuO₂·yH₂O. No difference has been observed in the zero-field-cooled mode and field-cooled mode.

(12) By assuming that the starting material was NaRuO₂, the filtrate was used for the analysis of Na concentration by emission spectrometry.

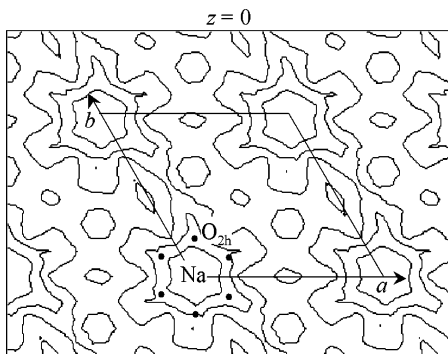


Figure 5. Observed Fourier map of $\text{Na}_x\text{RuO}_2 \cdot y\text{H}_2\text{O}$ at $z = 0$ (contour $1\text{e}^{-\text{\AA}^3}$). Closed circles show atomic positions of O_{2h} .

13.8 Å (hexagonal symmetry with ABBA... sequence) which corresponds to an intercalant layer thickness of 6.9 Å.^{4a} The crystal structure of $\text{Na}_x\text{RuO}_2 \cdot y\text{H}_2\text{O}$ 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 $\text{CuFeO}_2\text{-3R}$ 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 $\text{Na}_x\text{RuO}_2 \cdot y\text{H}_2\text{O}$ 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 $\text{CuFeO}_2\text{-3R}$ polytype structure. The Ru–O1 bond distance in $\text{Na}_x\text{RuO}_2 \cdot y\text{H}_2\text{O}$ (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

(13) Crystal data for $\text{Na}_x\text{RuO}_2 \cdot y\text{H}_2\text{O}$ ($x = 0.22$, $y = 0.45$): MM = 146.3 g/mol, trigonal space group $R\bar{3}m$, $a = 2.930(2)$ Å, $c = 21.913(5)$ Å, $V = 162.89(6)$ Å³, $Z = 3$, $T = 293$ K, $\lambda = 0.71073$ Å, $D_c = 4.47$ g/cm³, crystal size $0.04 \times 0.03 \times 0.005$ mm³, $\mu = 6.9$ mm⁻¹, $\theta_{\text{max}} = 40^\circ$, 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) Å²; O1 (0, 0, 0.1172(3)) 0.031(2) Å²; Na (0, 0, 0) $U_{\text{iso}} = 0.045(8)$ Å²; O_{2h} (0.155(6), $2x$, $-0.0002(16)$) $U_{\text{iso}} = 0.033(7)$ Å². The Na and O_{2h} site occupancies have been fixed to 22% and 7.5%, respectively.

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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 $\text{Na}_x\text{RuO}_2 \cdot y\text{H}_2\text{O}$ 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 $\text{Na}_{0.3}\text{CoO}_2 \cdot 0.6\text{H}_2\text{O}$.^{4a} The stacking of the oxygen close packed layers is different for the Ru and Co oxyhydrates. In $\text{Na}_x\text{RuO}_2 \cdot y\text{H}_2\text{O}$, 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 $\text{Na}_x\text{RuO}_2 \cdot y\text{H}_2\text{O}$ ($x = 0.22$, $y = 0.45$) is nonsuperconducting down 2 K¹¹ 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 $\text{H}_x\text{K}_y\text{NiO}_2 \cdot z\text{H}_2\text{O}$ 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 $\text{Na}_x\text{RuO}_2 \cdot y\text{H}_2\text{O}$ ($x = 0.22$, $y = 0.45$) in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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