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**Synthesis of a new hollandite-type manganese oxide with
framework and interstitial Cr(III)**

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Summary

Hollandite with Cr(III) in both tunnel and framework sites has been prepared hydrothermally from layered manganese oxide precursors.

Hollandite-type manganese oxides are one-dimensional tunneled materials that consist of 2 x 2 arrangements of edge-shared MnO_6 octahedra with cations occupying the interstitial voids. They have been widely studied for potential applications in catalysis, cation sorption, chemical sensing, and rechargeable battery technology.^{1,2} By far, the most common and easily prepared member of this class is cryptomelane, a specific hollandite with K^+ in the tunnels. The prevalence of cryptomelane can be attributed to the widespread use of potassium salts in manganese oxide syntheses and stabilization from an excellent fit of K^+ in the 2 x 2 tunnels.³ Hollandite-type manganese oxides have been prepared with other alkali and alkaline earth cations in the tunnels,^{4,5} but similar routes have not been developed for hollandites with interstitial transition metal cations. Here we report the hydrothermal synthesis of the transition-metal-containing Cr-hollandite from a layered manganese oxide precursor. The formation of the 2 x 2 hollandite material is unusual because previous studies have found this route to yield the related 3 x 3 tunneled manganese oxide, todorokite.⁶⁻⁸

The overall synthetic scheme for Cr-hollandite is shown in Figure 1. A 1.69-g (10.0 mmol) sample of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ was dissolved in 20 mL of water in a plastic bottle and treated with 30 mL of aqueous 6 M NaOH to produce tan-colored $\text{Mn}(\text{OH})_2$. A solid mixture of 1.89 g (7.0 mmol) $\text{K}_2\text{S}_2\text{O}_8$ and 0.38 g (1.4 mmol) pulverized $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was then added very slowly with stirring over a 45-minute period. The resulting grey-black slurry of Cr-doped Na-birnessite was aged for two days before being isolated by filtration and washed three times with water. The Na-birnessite was then immediately slurried

with 100 mL of 0.25 M $\text{Cr}(\text{NO}_3)_3$ and stirred overnight to yield Cr-buserite, which was isolated in a very slow filtration step. Hydrothermal treatment of Cr-buserite at 160 °C for 24 h ultimately led to the transformation into Cr-hollandite, of which about 0.8 g (about 70% based on Mn) could be isolated.

The structures of Na-birnessite and Cr-buserite were confirmed by powder X-ray diffraction data collected on a Scintag PDS 2000 diffractometer using $\text{Cu-K}\alpha$ radiation. The diffraction pattern for Na-birnessite displayed characteristic peaks at 7.14 and 3.57 Å, which correspond to the interlayer spacing. In the pattern of Cr-buserite, peaks were observed at 9.63, 4.81, and 3.21 Å due to interlayer expansion from a second layer of water molecules being established in the gallery region. Scanning electron microscopy images reveal plate-like morphologies for both Na-birnessite and Cr-buserite, which are typical of these layered materials.

The Cr^{3+} ion was introduced in the synthesis of Na-birnessite as an isomorphous dopant in the manganese oxide framework. Similar modifications with other transition metal cations have been applied to birnessite and buserite materials to promote the formation of 3 x 3 tunneled todorokite materials.⁶⁻⁸ Elemental analysis of the Cr-doped Na-birnessite revealed a Cr/Mn ratio of 0.13, which compared favorably to the 0.14 ratio used in the reactants and was taken to indicate that most of the Cr^{3+} became incorporated in the manganese oxide structure. After ion exchange, a Cr/Mn ratio of 0.32 was determined for Cr-buserite. No soluble Mn was detected from the reaction, which suggested that the ion exchange process occurred topotactically without contributions from redox reactions involving the manganese oxide framework.^{3,9} From the Cr:Mn

ratios in Cr-doped Na-birnessite and Cr-buserite, it was determined that 44% of the total Cr³⁺ was doped into the manganese oxide framework while 56% was contained between the layers.

Hydrothermal treatment of Cr-buserite resulted in the collapse of the layered framework and formation of tunneled Cr-hollandite. The hollandite-type manganese oxide structure was confirmed by X-ray diffraction, Figure 5. The peaks were indexed to a tetragonal structure, which is analogous to the observed patterns for cryptomelane (K-hollandite).⁴ Scanning electron microscopy revealed needle-like formations of Cr-hollandite that ranged in thickness from 100-400 nm. By comparison, cryptomelane also has a fibrous morphology, but with thinner particles that are much less than 100 nm.^{10,11} A thermogravimetric profile showed essentially no weight loss (<0.5%) up to 300 °C, indicating a lack of interstitial water. Weight loss of 7% from 400 °C to 620 °C was assigned to the formation of M₂O₃ while further weight loss of 4% from 620 °C to 800 °C was due to the appearance of Mn₃O₄.

The chemical formula of Cr_{0.30}MnO_{2.41} was determined for Cr-hollandite using data from elemental analysis (14.4% Cr, 50.3% Mn) and the thermogravimetric results which showed the absence of water. There was no detectable Na in the material. The 0.30 Cr/Mn ratio indicated some loss of interstitial chromium during the hydrothermal treatment of Cr-buserite (Cr/Mn = 0.32). This was verified by an observed light yellow color in the Cr-hollandite filtrate and detection of soluble Cr by atomic absorption spectroscopy. There was no detectable Mn in the filtrate, indicating that Cr³⁺ was expelled from the interstitial region rather than from the manganese oxide framework.

Thus, the Cr-hollandite formula can be expressed as $\text{Cr}_{0.16}(\text{Cr}_{0.14}\text{Mn})\text{O}_{2.41}$ to show the distribution of chromium between tunnel and framework sites. Difficulties in sample preparation prevented a standard analysis of the average Mn oxidation state, but a value of 3.9 could be obtained indirectly from the chemical formula determined for Cr-hollandite. Cryptomelane samples have similar oxidation states. Considering the presence of Cr(III) in the $\text{Cr}_{0.14}\text{Mn}$ composition of the tunneled framework, the average oxidation state on each metal center in the framework is 3.8.

The synthesis of Cr-doped Na-birnessite is the key step in the overall preparative scheme for Cr-hollandite. The degree of crystallinity in Na-birnessite, as determined by X-ray diffraction peak intensities, correlates well with the crystallinities of busserite and hollandite obtained in subsequent steps. Slow addition of the $\text{K}_2\text{S}_2\text{O}_8/\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ oxidant/dopant mixture is critical to achieving high quality Na-birnessite, as rapid addition produced amorphous manganese oxide. In related birnessite syntheses, rapid addition of $\text{K}_2\text{S}_2\text{O}_8$ and divalent cation dopants (Mg^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+}) resulted in the formation of feitknechtite, a layered MnOOH material.⁸ A number of other oxidants have been used to prepare Na-birnessite and these can presumably be substituted for $\text{K}_2\text{S}_2\text{O}_8$ in this synthesis.¹ $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ was chosen as the other solid reagent with $\text{K}_2\text{S}_2\text{O}_8$ because it was less hygroscopic than other water-soluble Cr(III) salts. The effect of aging on Cr-doped Na-birnessite was interesting, since aging has been typically used to promote greater crystallinity in birnessites.^{12,13} However, in this case the most crystalline birnessites were obtained when aging was carried out between zero and three days, with

the optimum time being about two days. Prolonged aging yielded birnessite with poorly crystallinity or amorphous manganese oxide.

Successful syntheses of Cr-hollandite were dependent on having Cr^{3+} both as an isomorphous framework dopant and a gallery cation in the birnessite and busierite precursors. Na-birnessite with Cr^{3+} as a framework dopant could be ion exchanged with divalent cations such as Mg^{2+} , Co^{2+} , Ni^{2+} , and Cu^{2+} . However, the resulting busierites were converted feitknechtite (layered MnOOH) upon hydrothermal treatment, as determined by the appearance of a prominent X-ray diffraction peak at 4.70 \AA .^{8,12,13} Similar results were obtained when divalent cations were doped in the manganese oxide framework and Cr^{3+} was exchanged into the interlayer gallery. Interestingly, there was no evidence of the 3×3 tunneled todorokite phase from the hydrothermal reaction, even though this phase is favored when the divalent cations occupy both framework and interlayer sites in busierite.⁸ Attempts were also made to prepare Cr-hollandite in the absence of framework dopants. In these cases, some conversion of undoped Cr-buserite to Cr-hollandite was observed, but the process was slow and incomplete.

In addition to presenting the first example of a Cr-containing hollandite, the hydrothermal synthesis also provides a route to 2×2 tunneled manganese oxides that contain a high level of framework dopant. The cryptomelane framework has been doped with a variety of foreign cations, but the amounts are typically low (0.01-0.5% substitution of total manganese) using redox precipitation methods.¹¹ Significant improvement of up to 16% have has been reported for Fe^{3+} in cryptomelane through

calcination of Fe-doped K-birnessite.¹⁴ The framework doping of Cr³⁺ in Cr-hollandite represents a 12% substitution of total manganese.

Overall, the hydrothermal synthesis of Cr-hollandite from Cr-buserite is very unusual, especially given all the precedents that show buserite acting as a precursor to todorokite. Hydrothermal routes to todorokite are known with a variety of tunnel cations, including alkali metals (Li⁺, Na⁺),¹⁵ alkaline earth metals (Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺),¹⁵ transition metals (Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺),^{6-8,15} and even lanthanides (Eu³⁺, Tb³⁺).¹⁵ It is not yet clear why Cr³⁺ is able to direct this reaction toward the hollandite structure, but such information would undoubtedly be valuable in designing syntheses of tunneled manganese oxides.

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Figures

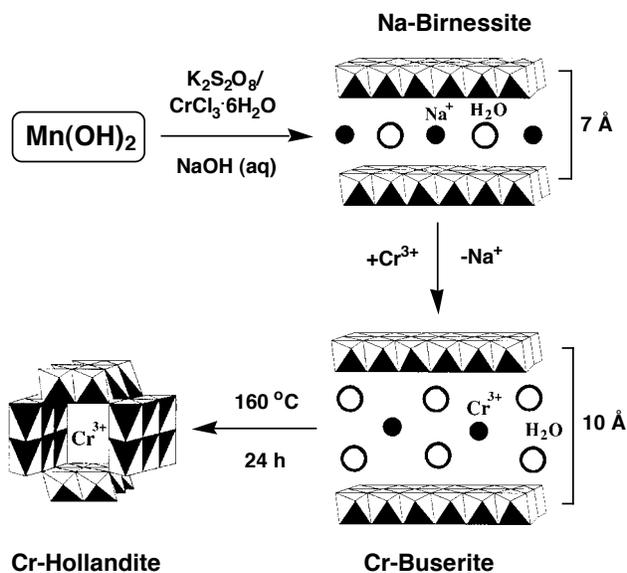


Figure 1. Synthetic scheme for Cr-hollandite.

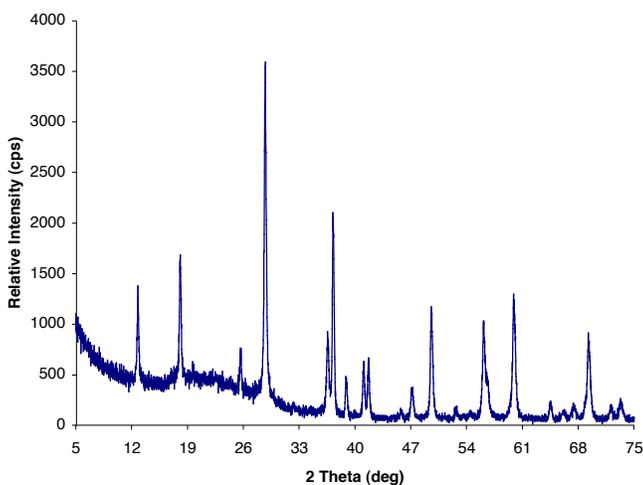


Figure 2. Powder X-ray diffraction pattern for Cr-hollandite. The d-spacings in \AA and indices (hkl) are provided: 6.95(110), 4.92(200), 3.48(220), 3.12(310), 2.46(400), 2.42(211), 2.32(330), 2.20(420), 2.17(301), 1.93(510), 1.84(411), 1.64(600), 1.63(431), 1.54(521), 1.44(002), 1.36(640).

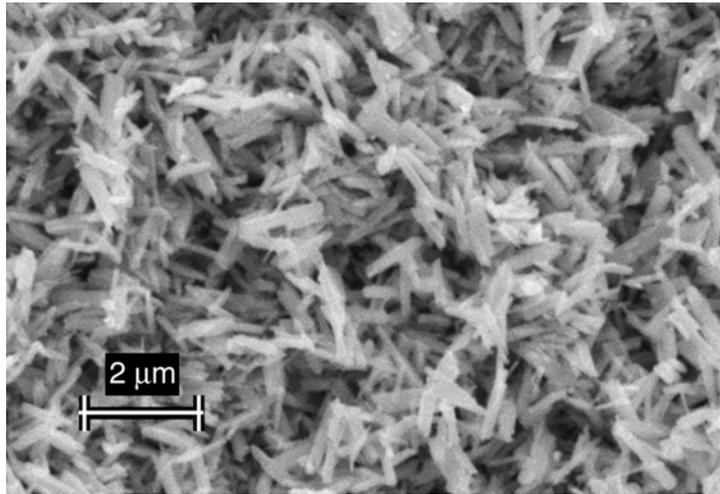


Figure 3. Scanning electron microscope image of Cr-hollandite.