Syntheses and crystal structures of the manganese hydroxide halides Mn$_5$(OH)$_6$Cl$_4$, Mn$_5$(OH)$_7$I$_3$, and Mn$_7$(OH)$_{10}$I$_4$

Abstract: Single-crystals of the new manganese hydroxide halides Mn$_{(4)}$(OH)$_6$Cl$_4$, Mn$_{(3)}$(OH)$_7$I$_3$, and Mn$_{(10)}$(OH)$_{10}$I$_4$ were obtained by means of high-pressure/high-temperature synthesis in a Walker-type multianvil apparatus. The chloride crystallizes in the monoclinic space group $P2_1/c$ (no. 14) with the lattice parameters (single-crystal data) $a = 592.55(8)$, $b = 1699.72(7)$, $c = 597.33(8)$ pm, and $\beta = 112.58(1)^\circ$. The iodides crystallize in the triclinic space group $P\bar{1}$ (no. 2) with $a = 653.16(2)$, $b = 905.98(3)$, $c = 1242.98(4)$ pm, $\alpha = 114.21(1)^\circ$, $\beta = 99.91(1)^\circ$, and $\gamma = 94.37(1)^\circ$ for Mn$_5$(OH)$_7$I$_3$ and $a = 656.90(3)$, $b = 906.59(4)$, $c = 909.32(4)$ pm, $\alpha = 119.29(1)^\circ$, $\beta = 97.99(1)^\circ$, and $\gamma = 909.32(4)$ for Mn$_7$(OH)$_{10}$I$_4$. The crystal structures consist of edge-sharing Mn(OH)$_6$ octahedra arranged in stacked sheets. Adjacent layers are connected by hydrogen bonds of type O–H···X confirmed by further characterization of single-crystals by IR-spectroscopy. The crystal chemical relationship with the aristotype Mg(OH)$_2$ (brucite) is discussed on the basis of Bärnighausen trees (group–subgroup relations).

Keywords: layered compound; manganese hydroxide halide; multianvil; single-crystal.

1 Introduction

The most common hydroxide halides of divalent metals have compositions $M$(OH)$_2$X and $M_2$(OH)$_3$X ($M$ = divalent metal, $X$ = Cl, Br, I). Many of them occur as minerals, such as Pb(OH)Cl (laurionite) and Cu(OH)Cl (belloite). Some possess polymorphs as in the case of Cu$_2$(OH)$_3$Cl (atacamite, botallackite, clinoatacamite, and paratacamite) [1–4]. These compounds are formally double-salts $m$(M(OH))$_r$X$_n$, but with respect to their structures they are better described as halide-substituted forms of the metal hydroxides $M$(OH)$_2$, indicated by the general formula $M_n$(OH)$_{2m}$·$rX_n$. Concerning synthesis and structural characterization, Oswald, Feitknecht, and coworkers were the main contributors, also summarizing their results in several review articles [4–8]. In addition, vibrational and magnetic properties as well as light absorption behavior of this compound class were topics of intense scrutiny [9–18]. Lutz et al. investigated laurionite-type hydroxide halides with IR and Raman spectroscopy and defined new distance limits for O–H···X hydrogen bonds [9, 15]. In recent years, the hydroxide halide phases with magnetic 3d transition-metal ions, like Cu$_2$(OH)$_3$X, $\beta$-Co$_2$(OH)$_3$Cl, Ni$_2$(OH)$_3$Cl, and $\beta$-Fe$_2$(OH)$_3$Cl, gained attention due to their behavior as geometrically frustrated magnetic materials [17, 19–24]. Their triangular, kagomé, and tetrahedral lattices of magnetically active sites can exhibit various exotic ground states and unconventional magnetic transitions. The compound Co$_2$(OH)$_3$Cl is also considered as auspicious electrode material for application in batteries and supercapacitors because of its outstanding electrochemical performance [25–27].

As hydroxide halides of the magnetically active 3d transition-metals show intriguing properties, our recent works focused on the less investigated manganese phases of this material class. Here, only Mn$_4$(OH)$_3$Cl, naturally occurring as the mineral kemprite, and its bromine counterpart were thoroughly characterized [4, 18, 28]. In the case of the other previously reported phases, i.e., the $\alpha$- and $\beta$-modification of Mn(OH)Cl as well as Mn$_3$(OH)$_3$I, the characterization is limited to their cell parameters and the isotopicity of Mn$_4$(OH)$_3$I to botallackite [4, 7].

Poor crystallinity and a tendency for polymorphism, polytypism, and stacking faults make detailed structural
characterizations of the manganese hydroxide halides a challenging task. Taking advantage of the provided opportunities for synthesis and improved crystallization behavior offered by the high-pressure/high-temperature method, we investigated this system under such conditions. In our preliminary work, we could already present a new modification of Mn(OH)Cl and the new compounds Mn(OH)Br and Mn(OH)I, successfully synthesized by this method [29, 30]. In the course of our inquiries, it was possible to identify further representatives of this material class. In this contribution, the syntheses, structural characterizations through single-crystal X-ray diffraction, IR spectroscopy, and the structural relationships of the new phases Mn₅(OH)₆Cl₄, Mn₅(OH)₇I₃, and Mn₇(OH)₁₀I₄ to Mg(OH)₂ are presented.

2 Experimental section

2.1 Synthesis

The compounds Mn₅(OH)₆Cl₄, Mn₅(OH)₇I₃, and Mn₇(OH)₁₀I₄ were obtained via high-pressure/high-temperature syntheses in a hydraulic 1000 t press (mavo press LPR 1000-400/50, Max Voggenreiter GmbH, Mainleus, Germany) with a modified Walker-type module (also Max Voggenreiter GmbH). The chloride phase could be obtained according to Eq. (1) at 1173 K and 3 GPa from a 3:2 molar mixture of MnO (99%, Sigma Aldrich, Steinheim, Germany) and MnCl₂·4H₂O (purum, p.a., Fluka, Buchs, Switzerland).

\[ \text{3MnO} + 2\text{MnCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow 10\text{GPa}1173K \text{Mn}_5\text{(OH)}_6\text{Cl}_4 + \text{H}_2\text{O} \quad (1) \]

Crystals of the iodide phases Mn₅(OH)₇I₃ and Mn₇(OH)₁₀I₄ occurred as side-phases from several reactions (all at 2.5 GPa/1273 K) of Mn (99%, Sigma Aldrich, Steinheim, Germany) and BiOI with different molar ratios, hydrolyzed by wetting with water vapor. Therefore, BiOI was synthesized by adding BiI₃ (99.95%, Alfa Aesar, Karlsruhe, Germany) in distilled water and precipitated with a 4BiOI (ICDD card No. 00-73-2062 [31]). Further attempts to synthesize phase pure samples of the iodide phases failed so far.

\[ \text{10Mn} + 6\text{BiOI} + 8\text{H}_2\text{O} \rightarrow 2.5\text{GPa1273K} \text{2Mn}_5\text{(OH)}_7\text{I}_3 + 6\text{Bi} + \text{H}_2 \quad (2) \]

\[ \text{7Mn} + 4\text{BiOI} + 6\text{H}_2\text{O} \rightarrow 2.5\text{GPa1273K} \text{3Mn}_7\text{(OH)}_{10}\text{I}_4 + 4\text{Bi} + \text{H}_2 \quad (3) \]
Reactions were carried out in molybdenum capsules (0.025 mm foil, 99.95%, Alfa Aesar, Karlsruhe, Germany) and transferred into crucibles made from 6-BN (HeBoSint® P100, Henze BNP GmbH, Kempten, Germany). The crucibles were built into 18/11 assemblies, which were compressed by eight tungsten carbide cubes (HA-7%Co, Hawedia, Marlkofen, Germany). Details on the construction of such assemblies can be found in the corresponding work [32].

Unlike the previously reported compounds Mn(OH)Br and Mn(OH)I [30], these phases, although slightly hygroscopic, showed reasonable air stability and did not require handling (but storage) in an inert atmosphere. The chloride phase shows the characteristic pale rose color of manganese(II) compounds, whereas the Mn₅(OH)₇I₃ and Mn₆(OH)₁₀I₄ platelets are initially clear, turning slightly yellow after several days of light exposure. The elemental bismuth formed during the reaction was present as small beads and could be separated from the hydroxide halides by hand.

### 2.2 Single-crystal X-ray diffraction (SCXRD)

For the single-crystal X-ray structure analysis, platelets of Mn₅(OH)₇Cl₄ and Mn₆(OH)₁₀I₄ were mounted on a Bruker D8 Quest diffractometer equipped with a Photon 100 detector and an Incoatec Microfocus source generator (Mo-Kα radiation with λ = 0.71073 pm, multi-layered optics monochromatized) and intensity data was collected at 173 and 190 K, respectively. Single-crystals of Mn₅(OH)₁₀I₄ were sealed in a glass capillary (0.5 mm, Hilgenberg, Malsfeld, Germany) and SCXRD data were collected with a Bruker CCD Kappa APEXII diffractometer, also using Mo-Kα radiation. Multi-scan absorption corrections based on equivalent and redundant intensities were applied with the program SADABS-2014/S [33, 34]. The crystal structures of the hydroxide halides
Table 5: Atomic coordinates, bond valence sums \((\sum v; \text{for oxygen atoms: } \text{O}^\text{v} / \text{OH})\) and equivalent isotropic displacement parameters \((U_{eq}/10^{-4} \text{ pm}^2)\) of Mn_5(OH)_7I_3 and Mn_7(OH)_{10}I_4. \(U_{eq}\) is defined as one third of the trace of the orthogonalized \(U_{ij}\) tensor (standard deviations in parentheses).

| Atom     | Wyck. | \(\sum v\) | \(x\)   | \(y\)   | \(z\)   | \(U_{eq}\) |
|----------|-------|------------|---------|---------|---------|------------|
| Mn_5(OH)_7I_3 |    |            |         |         |         |            |
| I1       | 2i    | -0.73      | 0.65765(4) | 0.70492(3) | 0.88703(2) | 0.01243(6) |
| I2       | 2i    | -0.67      | 0.62692(4) | 0.25245(3) | 0.45040(3) | 0.01412(6) |
| I3       | 2i    | -0.63      | 0.62111(4) | 0.80392(3) | 0.22178(2) | 0.01395(6) |
| Mn1      | 1a    | 2.00       | 0        | 0       | 0       | 0.0103(2)  |
| Mn2      | 2i    | 1.95       | 0.0426(2) | 0.58595(7) | 0.78827(5) | 0.0108(2)  |
| Mn3      | 2i    | 1.96       | 0.0082(2) | 0.19349(7) | 0.59568(5) | 0.0102(2)  |
| Mn4      | 2i    | 2.15       | 0.9695(2) | 0.67822(7) | 0.08979(4) | 0.0102(2)  |
| Mn5      | 2i    | 2.00       | 0.0579(2) | 0.90881(7) | 0.72416(5) | 0.0101(2)  |
| Mn6      | 1g    | 1.90       | 0        | 1/2     | 1/2     | 0.0109(2)  |
| O1       | 2i    | -1.14/-2.02| 0.8897(5) | 0.3365(3) | 0.7481(2) | 0.0104(6)  |
| O2       | 2i    | -1.18/-2.05| 0.9053(4) | 0.9493(6) | 0.5738(2) | 0.0090(5)  |
| O3       | 2i    | -1.12/-1.99| 0.8363(5) | 0.5679(3) | 0.3661(2) | 0.0094(6)  |
| O4       | 2i    | -1.12/-1.99| 0.8292(4) | 0.1505(3) | 0.1281(2) | 0.0093(6)  |
| O5       | 2i    | -1.07/-1.94| 0.8466(4) | 0.4280(3) | 0.0415(2) | 0.0082(5)  |
| O6       | 2i    | -1.12/-1.99| 0.9050(4) | 0.0710(3) | 0.8557(2) | 0.0092(6)  |
| O7       | 2i    | -1.13/-2.00| 0.9006(5) | 0.6646(3) | 0.6511(2) | 0.0090(5)  |
| H1       | 2i    | –          | 0.7613(3) | 0.319(7)  | 0.738(5)  | 0.052       |
| H2       | 2i    | –          | 0.784(4)  | 0.917(6)  | 0.569(4)  | 0.022       |
| H3       | 2i    | –          | 0.70(3)   | 0.556(8)  | 0.357(6)  | 0.072       |
| H4       | 2i    | –          | 0.701(3)  | 0.141(5)  | 0.100(4)  | 0.011       |
| H5       | 2i    | –          | 0.730(4)  | 0.380(6)  | 0.006(4)  | 0.032       |
| H6       | 2i    | –          | 0.780(4)  | 0.070(6)  | 0.831(4)  | 0.032       |
| H7       | 2i    | –          | 0.775(3)  | 0.650(8)  | 0.629(6)  | 0.06(2)     |
| Mn_7(OH)_{10}I_4 |    |            |         |         |         |            |
| I1       | 2i    | -0.60      | 0.36814(4) | 0.26630(3) | 0.08153(4) | 0.02300(7) |
| I2       | 2i    | -0.67      | 0.35498(4) | 0.74656(3) | 0.42638(4) | 0.02069(7) |
| Mn1      | 1g    | 1.95       | 0        | 0       | 0       | 0.0188(2)  |
| Mn2      | 2i    | 1.89       | 0.0282(2) | 0.43393(7) | 0.30934(8) | 0.0192(2)  |
| Mn3      | 2i    | 2.00       | 0.9843(2) | 0.87783(7) | 0.59164(7) | 0.0186(2)  |
| Mn4      | 2i    | 2.00       | 0.9946(2) | 0.29266(7) | 0.85544(8) | 0.0191(2)  |
| O1       | 2i    | -1.11/-1.98| 0.15195(5) | 0.9522(3)  | 0.1939(4)  | 0.0175(6)  |
| O2       | 2i    | -1.10/-1.97| 0.14715(5) | 0.3973(3)  | 0.5169(4)  | 0.0166(6)  |
| O3       | 2i    | -1.15/-2.02| 0.12145(5) | 0.8242(3)  | 0.7906(4)  | 0.0167(6)  |
| O4       | 2i    | -1.10/-1.97| 0.13275(5) | 0.1352(3)  | 0.6470(4)  | 0.0165(6)  |
| O5       | 2i    | -1.13/-2.00| 0.1059(5)  | 0.5470(3)  | 0.9057(3)  | 0.0149(5)  |
| H1       | 2i    | –          | 0.279(3)  | 0.980(7)  | 0.234(7)  | 0.052       |
| H2       | 2i    | –          | 0.273(3)  | 0.425(6)  | 0.557(6)  | 0.022       |
| H3       | 2i    | –          | 0.250(3)  | 0.841(7)  | 0.822(7)  | 0.052       |
| H4       | 2i    | –          | 0.262(3)  | 0.155(6)  | 0.664(6)  | 0.032       |
| H5       | 2i    | –          | 0.235(3)  | 0.569(8)  | 0.922(8)  | 0.06(2)     |

were standardized with the program STRUCTURE Tidy [35–37]. The chloride phase shows a substitutional disorder of the ligands Cl1/O1 and Cl3/O4, whereby the occupancy factors were refined close to 0.75 (Cl1 and O4) and 0.25 (O1 and Cl3) and fixed at these values. The protons binding to O1 and O4 could not be detected as they are situated close to the positions of Cl1 and Cl3. For all phases, the O–H distance was restrained to a value of 83 ± 2 pm. All non-hydrogen atoms were refined with anisotropic displacement parameters. Table 1 summarizes the experimental details of the data collection and evaluations. Tables 2–4 contain the positional parameters, anisotropic displacement parameters, and selected interatomic distances and angles of the chloride phase and Tables 5–7 those of the iodide compounds.

Additional information on the crystal structure investigations can be obtained from the joint CCDC/FIZ Karlsruhe deposition service on quoting the deposition number 1940191 (Mn_5(OH)_6Cl_3), 1940192 (Mn_6(OH)_7I_3), and 1940193 (Mn_7(OH)_10I_4).
Table 6: Anisotropic displacement parameters (Uᵢ/10⁻⁶ pm²) of Mn₅(OH)₃I₃ and Mn₇(OH)₁₀I₄ (standard deviations in parentheses).

| Atom     | U₁₁    | U₂₂    | U₃₃    | U₂₃    | U₁₃    | U₁₂    |
|----------|--------|--------|--------|--------|--------|--------|
| Mn₅(OH)₃I₃ |        |        |        |        |        |        |
| I1       | 0.0114(2) | 0.0143(2) | 0.0125(2) | 0.0064(2) | 0.0032(2) | 0.0024(2) |
| I2       | 0.0114(2) | 0.0134(2) | 0.0174(2) | 0.0078(2) | 0.0005(2) | 0.0006(2) |
| I3       | 0.0137(2) | 0.0143(2) | 0.0141(2) | 0.0065(2) | 0.0029(2) | 0.0016(2) |
| Mn1      | 0.0180(5) | 0.0081(4) | 0.0075(4) | 0.0048(3) | 0.0047(3) | 0.0046(3) |
| Mn2      | 0.0225(3) | 0.0054(3) | 0.0061(3) | 0.0034(2) | 0.0044(3) | 0.0029(2) |
| Mn3      | 0.0192(3) | 0.0051(3) | 0.0067(3) | 0.0025(2) | 0.0041(2) | 0.0024(2) |
| Mn4      | 0.0192(3) | 0.0056(3) | 0.0078(3) | 0.0039(2) | 0.0051(2) | 0.0034(2) |
| Mn5      | 0.0185(3) | 0.0065(3) | 0.0067(3) | 0.0038(2) | 0.0034(2) | 0.0023(2) |
| Mn6      | 0.0209(5) | 0.0075(4) | 0.0052(4) | 0.0029(3) | 0.0039(3) | 0.0044(3) |
| O1       | 0.013(2)  | 0.010(2)  | 0.009(2)  | 0.004(2)  | 0.002(2)  | 0.001(2)  |
| O2       | 0.010(2)  | 0.010(2)  | 0.007(2)  | 0.002(2)  | 0.003(2)  | 0.002(2)  |
| O3       | 0.013(2)  | 0.010(2)  | 0.005(2)  | 0.003(2)  | 0.002(2)  | 0.003(2)  |
| O4       | 0.009(2)  | 0.009(2)  | 0.005(2)  | 0.003(2)  | 0.002(2)  | 0.003(2)  |
| O5       | 0.011(2)  | 0.008(2)  | 0.006(2)  | 0.004(2)  | 0.001(2)  | 0.000(2)  |
| O6       | 0.012(2)  | 0.008(2)  | 0.005(2)  | 0.002(2)  | 0.003(2)  | 0.002(2)  |
| O7       | 0.011(2)  | 0.009(2)  | 0.009(2)  | 0.005(2)  | 0.002(2)  | 0.001(2)  |

| Atom     | U₁₁    | U₂₂    | U₃₃    | U₂₃    | U₁₃    | U₁₂    |
|----------|--------|--------|--------|--------|--------|--------|
| Mn₇(OH)₁₀I₄ |        |        |        |        |        |        |
| I1       | 0.0195(2) | 0.0216(2) | 0.0273(2) | 0.0131(2) | 0.0020(2) | 0.0016(2) |
| I2       | 0.0180(2) | 0.0202(2) | 0.0256(2) | 0.0125(2) | 0.0056(2) | 0.0040(2) |
| Mn1      | 0.0334(5) | 0.0138(4) | 0.0124(4) | 0.0081(3) | 0.0067(4) | 0.0068(4) |
| Mn2      | 0.0330(4) | 0.0138(3) | 0.0141(3) | 0.0092(2) | 0.0057(3) | 0.0054(3) |
| Mn3      | 0.0357(4) | 0.0116(3) | 0.0122(3) | 0.0080(2) | 0.0076(3) | 0.0064(3) |
| Mn4      | 0.0348(4) | 0.0100(3) | 0.0147(3) | 0.0066(2) | 0.0095(3) | 0.0051(3) |
| O1       | 0.021(2)  | 0.017(2)  | 0.018(2)  | 0.012(2)  | 0.010(2)  | 0.003(2)  |
| O2       | 0.018(2)  | 0.015(2)  | 0.019(2)  | 0.004(2)  | 0.004(2)  | 0.003(2)  |
| O3       | 0.021(2)  | 0.015(2)  | 0.016(2)  | 0.004(2)  | 0.004(2)  | 0.005(2)  |
| O4       | 0.018(2)  | 0.017(2)  | 0.015(2)  | 0.009(2)  | 0.004(2)  | 0.003(2)  |
| O5       | 0.017(2)  | 0.016(2)  | 0.015(2)  | 0.010(2)  | 0.004(2)  | 0.003(2)  |

2.3 Powder X-ray diffraction (PXRD)

A powdered sample containing the hydroxide halide Mn₅(OH)₃Cl₄ was additionally characterized using powder X-ray diffraction (PXRD) technique. Therefore, data were collected with a Bruker Vertex 70 FTIR spectrometer in transmission geometry with Mo-Kα (λ = 70.930 pm; Ge(III) primary beam monochromator) radiation and a Mythen2 1K detector (Dectris, Baden, Switzerland).

2.4 Vibrational spectroscopy

To confirm the hydroxide groups, single-crystal transmission FTIR spectra were measured with a Bruker Vertex 70 FTIR spectrometer (resolution 4 cm⁻¹), equipped with a KBr beam splitter, an LN-MCT (Mercury Cadmium Telluride) detector and a Hyperion 3000 microscope (Bruker, Vienna, Austria). The measurements were performed in absorption mode in the range of 600–6000 cm⁻¹ using a silicon carbide rod (Global) as mid-infrared source, and a 15x IR objective as focus was used. Mn₅(OH)₃Cl₄ was measured under a protective film of oil (Nujol for IR-spectroscopy, Alfa Aesar, Karlsruhe, Germany). About 260 scans of each single-crystal were acquired and a correction of atmospheric influences was performed with the software OPUS 7.2 [38].

2.5 Bond-length bond-strength (BL/BS) concept

By applying the bond-length bond-strength concept [39, 40], the bond valence sums (Σv) for all non-hydrogen atoms were calculated. The resulting values were compared to the formal ionic charges. The values for all oxygen atoms were calculated with and without the implication of a proton (O⁺/OH⁻) to affirm the presence of the hydroxide groups at each oxygen position.

3 Results and discussion

3.1 Crystal structures

Table 1 summarizes the results of the SCXRD analysis of the phases Mn₅(OH)₅Cl₄, Mn₇(OH)₁₀I₃, and Mn₇(OH)₁₀I₄.
In contrast to γ-Mn(OH)Cl [29], which can be derived from the CdCl₂ (C19) structure type, Mn₅(OH)₈Cl₄ can be seen as a C6 structure with (AyB)(AyB) stacking sequence. The layers consist of edge-sharing distorted Mn(OH)₆₋ₓCl₄ (x = 1, 2, 3, 4) octahedra forming corrugated, uncharged layers parallel to the (100) plane (Figure 1). This undulation prevents the formation of polytypes. The octahedral coordination around the manganese(II) atoms show substitutional disorder of the ligands ClI/O1 (occupancy: 0.75/0.25) and ClI3/O4 (occupancy: 0.25/0.75).

The Mn–Cl distances (Table 4) range from 255.6(3) to 265.4(1) pm with average values of 262.0 (Mn1–Cl), 260.7 (Mn2–Cl), and 262.4 pm (Mn3–Cl). These bonds are longer than in MnCl₂ (254.8(2) pm [41]) and similar to the ones in γ-Mn(OH)Cl (average 260.9 pm [29]). The oxygen atoms of the hydroxide groups are situated at Mn–O distances ranging from 214.6(2) to 221.1(8) pm and in average (Mn1–O: 218.8, Mn2–O: 217.2, Mn3–O: 215.8 pm) shorter than the mean Mn–O distance in Mn(OH)₂ (219.62 pm [42]). This behavior indicates that the hydroxide groups in Mn₅(OH)₈Cl₄ are stronger ligands to manganese(II) than the chloride ions and can be attributed to hydrogen bonding. The Cl–Mn and O–H bonds are weakened as part of the valence is used for Cl binding to H. Correspondingly, the O–Mn bond strength increases with weaker O–H bonds.

The bond valence sums (ΣV) for all non-hydrogen atoms were calculated (Table 2), whereby oxygen atoms were treated without and with the implication of a proton (O⁺/OH⁻). The calculated values for the oxygen atoms are −1.08/−1.95 (O1), −1.12/−1.99 (O2), −1.13/−2.01 (O3), and −1.39/−2.27 (O4), confirming the presence of hydroxide groups. For the non-oxygen atoms the values of 1.93 (Mn1), 1.95 (Mn2, Mn3), −1.08 (ClI), −0.76 (ClI2), and −1.12 (ClI3) correspond well to the formal ionic charges of the atoms.

The manganese hydroxide iodides Mn₅(OH)₈I₄ and Mn₄(OH)₁₀I₄ both crystallize in the triclinic space group

### Table 7: Selected interatomic distances (/pm) in Mn₅(OH)₁₂ and Mn₄(OH)₁₀I₄, calculated with the single-crystal lattice parameters (standard deviations in parentheses).

| Mn₅(OH)₁₂ |       |       |       |
|-----------|-------|-------|-------|
| Mn1–O6 (2×) | 215.4(3) | Mn3–O1 | 212.5(3) | Mn5–O7 | 211.2(3) |
| Mn1–O4 (2×) | 216.8(3) | Mn3–O3 | 214.2(3) | Mn5–O2 | 214.7(3) |
| Mn1–I1 (2×) | 300.83(3) | Mn3–O2 | 215.0(3) | Mn5–O4 | 214.7(3) |
| d (Mn1–O) | 216.10 | Mn3–O2 | 217.23 | Mn5–O6 | 215.5(3) |
| d (Mn1–I) | 300.83 | Mn3–I3 | 301.13(7) | Mn5–I3 | 297.85(7) |
|           |       | Mn3–I2 | 303.22(7) | Mn5–I2 | 323.67(6) |
| Mn2–O5 | 217.4(3) | d (Mn3–O) | 214.73 | d (Mn5–O) | 214.03 |
| Mn2–O3 | 217.9(3) | d (Mn3–I) | 302.18 | d (Mn5–I) | 310.76 |
| Mn2–O7 | 219.8(3) |       |       |       |       |
| Mn2–O4 | 220.1(3) | Mn4–O1 | 212.7(3) | Mn6–O7 (2×) | 210.8(3) |
| Mn2–O1 | 221.7(3) | Mn4–O6 | 213.4(3) | Mn6–O3 (2×) | 214.9(3) |
| Mn2–I1 | 306.28(7) | Mn4–I5 | 214.13(3) | Mn6–I2 (2×) | 297.7(5) |
| d (Mn2–O) | 219.38 | Mn4–O5 | 214.3(3) | d (Mn6–O) | 212.85 |
| d (Mn2–I) | 306.28 | Mn4–I3 | 305.20(7) | d (Mn6–I) | 297.75 |
|           |       | Mn4–I1 | 306.07(7) |       |       |
| d (Mn4–O) |       | 213.63 | d (Mn4–O) | 215.12 |
| d (Mn4–I) |       | 305.64 | d (Mn4–I) | 303.91 |

| Mn₄(OH)₁₀I₄ |       |       |       |
|-------------|-------|-------|-------|
| Mn1–O3 (2×) | 211.6(3) | d (Mn2–O) | 213.25 | Mn4–O4 | 212.4(3) |
| Mn1–O1 (2×) | 215.1(3) | d (Mn2–I) | 312.17 | Mn4–O1 | 214.1(3) |
| Mn1–I1 (2×) | 299.20(3) |       |       | Mn4–O5 | 215.4(3) |
| d (Mn1–O) | 213.35 | Mn3–O4 | 214.2(3) | Mn4–O5 | 217.8(3) |
| d (Mn1–I) | 299.20 | Mn3–O1 | 218.3(3) | Mn4–I2 | 304.89(7) |
|           |       | Mn3–O3 | 219.2(3) | Mn4–I1 | 308.00(7) |
| Mn2–O5 | 212.3(3) | Mn3–O2 | 221.7(3) | d (Mn4–O) | 214.93 |
| Mn2–O2 | 212.9(3) | Mn3–O4 | 222.7(3) | d (Mn4–I) | 306.45 |
| Mn2–O3 | 213.0(3) | Mn3–I2 | 306.23(7) |       |       |
| Mn2–O2 | 214.8(3) | d (Mn3–O) | 219.22 | d (Mn–O) | 215.19 |
| Mn2–I2 | 302.00(7) | d (Mn3–I) | 306.23 | d (Mn–I) | 306.01 |
| Mn2–I1 | 322.34(7) |       |       |       |       |
Also for the iodides, bond valence sums ($\sum v$) for all non-hydrogen atoms were determined (Table 5). The non-oxygen atoms have values close to their formal ionic charges. The values for the oxygen atoms calculated as $O^{2-}$ and OH are $-1.14/−2.02$ (O1), $-1.18/−2.05$ (O2), $-1.12/−1.99$ (O3, O4, O6), $-1.07/−1.94$ (O5), and $-1.13/−2.00$ (O7) for Mn$_5$(OH)$_6$I$_3$ and $-1.11/−1.98$ (O1), $-1.10/−1.97$ (O2, O4), $-1.15/−2.02$ (O3), and $-1.13/−2.00$ (O5) for Mn$_7$(OH)$_{10}$I$_4$. These values confirm the presence of hydroxide groups. The rather small bond-valence sums of the iodine atoms are presumably a result of the influence of the O–H... X hydrogen bonds, which were not considered in the BLBS calculations. The IR spectra (vide infra) show the presence of stronger hydrogen bonding in Mn$_5$(OH)$_6$I$_3$ and Mn$_7$(OH)$_{10}$I$_4$ than in Mn$_5$(OH)$_6$Cl$_4$, thus having more influence on the I–Mn bond valence and leading to the underestimation of the valence sum.

### 3.2 Powder X-ray diffraction of Mn$_5$(OH)$_6$Cl$_4$

A sample containing the chloride phase was additionally analyzed by PXRD. The measured diffraction pattern was compared to the theoretical pattern derived from SCXRD data (Figure 4). Besides Mn$_5$(OH)$_6$I$_3$, which represented the main phase, the sample contained an unidentified side phase.

### 3.3 Group–subgroup relationships

The manganese hydroxide halides Mn$_5$(OH)$_6$I$_3$, Mn$_5$(OH)$_6$I$_4$, and Mn$_7$(OH)$_{10}$I$_4$ reported herein are crystal chemically closely related to the well-known layer structure of cadmium iodide or brucite (Mg(OH)$_2$). CdI$_2$ crystallizes with space group $P\overline{3}2/m1$, which is a maximal subgroup of $P6_3/mmc$, the space group type of the hexagonal closest packing. In CdI$_2$, every other layer of octahedral voids of the hcp iodine packing remains empty. In the present case, we have distorted hexagonal packings of the hydroxide and halide ions and the octahedral voids are filled by Mn$^{2+}$.

These close relationships readily call for group–subgroup schemes, relating the three new structures with the aristotype CdI$_2$. The first Bärnighausen tree (Figure 5) [45–48] of the CdI$_2$ family was worked out by Meyer during his PhD work [49] in the Bärnighausen group. General considerations on subgroups for hcp packings with partial ordered occupancies of octahedral voids were published by Müller [48, 50, 51].

The Bärnighausen tree worked out by Meyer [49] has three different branches: (i) the structure of Na$_2$Sn(OH)$_6$, (ii) the structures of Li$_3$Pt(OH)$_6$, Bi$_3$Pt (h2), Na$_3$Pt(OD)$_6$ and
Figure 2: Octahedral coordination spheres of the manganese(II) atoms in Mn₅(OH)₇I₃ (displacement ellipsoids represent 90% probability at 190 K) and polyhedral representation of the crystal structure viewed along the a- and b-axis.

Tl₂S, and (iii) the structure of CrBr₂ and its lower symmetric derivatives NbTe₂, AgAuCl₄, AgAuTe₄, and Cu₃Cl(OH)₃, nicely underpinning the broad crystal chemical diversity of the CdI₂ family. The third part of the Bärnighausen tree from Meyer is included in Figure 5, since the superstructures of the manganese hydroxide halides Mn₅(OH)₆Cl₄, Mn₅(OH)₇I₃, and Mn₇(OH)₁₀I₄ also derive from CrBr₂ [52]. The structure of chromium dibromide is monoclinic. The space group symmetry is reduced by a \( \text{translationengleiche} \) symmetry reduction of index 3 (t3) from \( \text{P} \overline{3} \text{2} / \text{m} \) to \( \text{C} \overline{12} / \text{m} \).

Each, Mn₅(OH)₆Cl₄, Mn₅(OH)₇I₃, and Mn₇(OH)₁₀I₄, deserve two subsequent steps starting from CrBr₂. This is paralleled with unit cell enlargements. In Figure 6, we present a projection of the Mn₁₂ structure along the trigonal axis. The unit cells of the three hydroxide halide are incorporated into this drawing for better comparison with the aristotype. The individual Bärnighausen trees along with the evolution of the atomic parameters are shown in Figures 7–9.

We start with the structure of Mn₅(OH)₆Cl₄ (Figure 7). The subsequent i₅ and k₂ transitions lead to five crystallographically independent anion sites, which allow the hydroxide-halide ordering. Nevertheless, the structure shows some residual disorder. Especially these sites show the largest differences between the positional parameters calculated from the subcell and those refined from the X-ray data. The manganese
Figure 3: Octahedral coordination of the manganese(II) atoms in Mn₇(OH)₁₀I₄ (displacement ellipsoids represent 90% probability at 296 K) and polyhedral representation of the crystal structure viewed along the a- and b-axis.

Figure 4: The measured diffraction pattern of a sample containing Mn₅(OH)₆Cl₄ (top) compared to the simulated pattern from SCXRD data (bottom). Reflections marked with an asterisk originate from an unidentified side phase.
Figure 5: Group–subgroup scheme for CdI$_2$ superstructures. The indices for the translationengleiche ($t$), klassengleiche ($k$), and isomorphic ($i$) symmetry reductions are given. The highlighted part of the scheme was reproduced from [49].

Figure 6: Structure of MnI$_2$ [43] with view along the $c$-axis. The manganese and iodine atoms are drawn as gray and purple circles, respectively. The cell of MnI$_2$ is highlighted (gray) as well as the cells of the CdI$_2$ superstructures Mn$_5$(OH)$_6$Cl$_4$ (blue), Mn$_7$(OH)$_{10}$I$_4$ (green), and Mn$_5$(OH)$_7$I$_3$ (red).
cations also show small displacements from the ideal positions in order to account for the anion substructure (OH/Cl ordering).

For Mn$_7$(OH)$_3$I$_4$, the second step in symmetry reduction (Figure 8) is an isomorphic one from $P\bar{1}$ to $P\bar{1}$; with the rare index seven ($i_7$). Consequently, we obtain seven anion sites for the OH/I ordering. The latter was well resolved from the single-crystal X-ray diffraction data. Again, the anions show the largest displacements from the ideal subcell sites. This is expressed in the undulated layers of condensed octahedra, drastically deviating from planarity as in the aristotype.

Mn$_3$(OH)$_6$Cl$_4$ shows the most complicated of the three superstructures with 10 crystallographically independent anion sites, similar to Mn$_3$(OH)$_6$I$_4$ with complete OH/I ordering. The displacements of the different anions from the ideal subcell positions are similar to the two

![Figure 7](image)

**Figure 7:** Group–subgroup scheme in the Bärnighausen formalism [45–48] for the structures of Mn(OH)$_2$ [42], HP-CrBr$_2$ [52], and Mn$_3$(OH)$_6$Cl$_4$. The indices for the translationengleiche (t), klassengleiche (k), and isomorphic (i) symmetry reductions and the evolution of the atomic parameters are given.
compounds described above and also results in undulated layers of condensed octahedra.

The strong undulations of the Mn(OH/X)_2 layers for all three compounds show the limits of group–subgroup relations. The strong shifts in the atomic parameters underpin the differences in the radii OH/Cl versus OH/I but also changes in chemical bonding, i.e., ionicity toward covalence. In that view, it is interesting to mention the intermetallic phase Bi₂Pt [53]. The latter also derives from the CdI₂ type and is included in the Bärnighausen tree in Figure 5. The evolution of the atomic parameters presented in [53] shows substantial displacements for both the platinum and bismuth atoms, leading to distorted PtBi₆/₃ octahedra. Also, this example is a limit of a group–subgroup scheme. Besides the purely geometrical relationship, the chemical bonding pattern should match as close as possible, in order to have a close crystal chemical similarity.

### 3.4 FTIR-spectroscopy

Figures 10–12 show the experimental IR spectra of single-crystals of Mn₅(OH)₆Cl₄, Mn₅(OH)₇I₃, and Mn₇(OH)₁₀I₄ in the range from 600 to 4000 cm⁻¹ in absorbance mode. In the fingerprint region, the strong bands from 600 to 800 cm⁻¹ correspond to ν(Mn–O) stretching modes. In the range from 800 to 1200 cm⁻¹, O–H bending modes of the hydroxide groups can be found (very weak in Mn₅(OH)₆Cl₄, strong in the iodide phases). Marked peaks in Figure 10 are due to the protective Nujol film on the Mn₅(OH)₆Cl₄ crystal and the bands in the region from 1500 to 3000 cm⁻¹ in the spectra of the iodide compounds (Figures 11 and 12) originate from residual grease of the sample preparation procedure. In the spectrum of Mn₅(OH)₇I₃ (Figure 11), the band from 3000 to 3300 cm⁻¹ can be attributed to absorbed water and the
small shoulder at around 1600 cm$^{-1}$ to the corresponding bending vibration of O–H groups in the absorbed water molecules.

All spectra show sharp $\nu$(O–H) stretching vibrations at around 3500 cm$^{-1}$ (Mn$_5$(OH)$_6$Cl$_4$: 3560 cm$^{-1}$; Mn$_5$(OH)$_7$I$_3$: 3491, 3533, and 3573 cm$^{-1}$; Mn$_7$(OH)$_{10}$I$_4$: 3503, 3552, and 3595 cm$^{-1}$) and confirm the presence of the hydroxide groups. The red-shift of the values for these modes compared to the value for a free hydroxide group (3620 cm$^{-1}$ [54]) is an indication for the occurrence of hydrogen bonding of the type O–H···X (X = Cl, I) between the layers. The occurring peak splitting in the IR spectra of the iodide phases (Figures 11 and 12) can be interpreted as a result of existing hydrogen bonds of different strengths arising from different O–H···I distances.

### 4 Conclusions

Three new manganese(II) hydroxide halides were obtained by means of high-pressure/high-temperature synthesis using a multianvil apparatus. Single-crystals of the compounds Mn$_5$(OH)$_6$Cl$_4$, Mn$_5$(OH)$_7$I$_3$, and Mn$_7$(OH)$_{10}$I$_4$ were characterized via X-ray diffraction, showing layered crystal structures derived from the CdI$_2$/Mg(OH)$_2$ crystal structure. The chloride phase crystallizes in the space group $P2_1/n$ and exhibits a substitutional disorder concerning half of the ligand positions, whereas the iodide phases both crystallize in $P1$ and do not exhibit any disorder. In contrast to the aristotype, these hydroxide halide phases show a distortion of the coordination polyhedra and strong
undulation of the layers that prevents the formation of polytypes. Additional FTIR spectroscopy affirm the hydroxide groups of the compounds and indicate the occurrence of hydrogen bonding of type O–H···X.

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