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

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Abstract: Single-crystals of the new manganese hydroxide halides $\text{Mn}_5(\text{OH})_6\text{Cl}_4$, $\text{Mn}_5(\text{OH})_7\text{I}_3$, and $\text{Mn}_7(\text{OH})_{10}\text{I}_4$ 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) $a = 592.55(8)$, $b = 1699.7(2)$, $c = 597.33(8)$ 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 $\text{Mn}_5(\text{OH})_7\text{I}_3$ 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 $\gamma = 95.03(1)^\circ$ for $\text{Mn}_7(\text{OH})_{10}\text{I}_4$. The crystal structures consist of edge-sharing $\text{Mn}(\text{OH})_{6-n}\text{X}_n$ ($X = \text{Cl}, \text{I}$; $n = 1, 2, 3$) octahedra arranged in stacked sheets. Adjacent layers are connected by hydrogen bonds of type $\text{O}-\text{H}\cdots\text{X}$, confirmed by further characterization of single-crystals by IR-spectroscopy. The crystal chemical relationship with the aristotype $\text{Mg}(\text{OH})_2$ (brucite) is discussed on the basis of Bärnighausen trees (group–subgroup relations).

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

Dedicated to Professor Dr. Ulrich Müller on the occasion of his 80th birthday.

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1 Introduction

The most common hydroxide halides of divalent metals have compositions $M(\text{OH})X$ and $M_2(\text{OH})_3X$ (M = divalent metal, $X = \text{Cl}, \text{Br}, \text{I}$). Many of them occur as minerals, such as $\text{Pb}(\text{OH})\text{Cl}$ (laurionite) and $\text{Cu}(\text{OH})\text{Cl}$ (belloite). Some possess polymorphs as in the case of $\text{Cu}_2(\text{OH})_3\text{Cl}$ (atacamite, botallackite, clinoatacamite, and paratacamite) [1–4]. These compounds are formally double-salts $mM(\text{OH})_2 \cdot nMX_2$, but with respect to their structures they are better described as halide-substituted forms of the metal hydroxides $M(\text{OH})_2$, indicated by the general formula $M_m(\text{OH})_{2m-n}X_n$. Concerning synthesis and structural characterization, Oswald, Feitknecht, and co-workers 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 $\text{O}-\text{H}\cdots\text{X}$ hydrogen bonds [9, 15]. In recent years, the hydroxide halide phases with magnetic 3d transition-metal ions, like $\text{Cu}_2(\text{OH})_3\text{X}$, $\beta\text{-Co}_2(\text{OH})_3\text{Cl}$, $\text{Ni}_2(\text{OH})_3\text{Cl}$, and $\beta\text{-Fe}_2(\text{OH})_3\text{Cl}$, 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 $\text{Co}_2(\text{OH})_3\text{Cl}$ 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 $\text{Mn}_2(\text{OH})_3\text{Cl}$, naturally occurring as the mineral kempite, and its bromine counterpart were thoroughly characterized [4, 18, 28]. In the case of the other previously reported phases, i.e., the α - and β -modification of $\text{Mn}(\text{OH})\text{Cl}$ as well as $\text{Mn}_2(\text{OH})_3\text{I}$, the characterization is limited to their cell parameters and the isotypicity of $\text{Mn}_2(\text{OH})_3\text{I}$ to botallackite [4, 7].

Poor crystallinity and a tendency for polymorphism, polytypism, and stacking faults make detailed structural

Table 1: Crystal data and structure refinement of $\text{Mn}_5(\text{OH})_6\text{Cl}_4$, $\text{Mn}_5(\text{OH})_7\text{I}_3$, and $\text{Mn}_7(\text{OH})_{10}\text{I}_4$ (standard deviations in parentheses).

Formula	$\text{Mn}_5(\text{OH})_6\text{Cl}_4$	$\text{Mn}_5(\text{OH})_7\text{I}_3$	$\text{Mn}_7(\text{OH})_{10}\text{I}_4$
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
Single-crystal data			
Single-crystal diffractometer	Bruker D8 Quest		Bruker APEXII Kappa CCD
Radiation		Mo- K_α ($\lambda = 71.073$ pm)	
Temperature/K	173(2)	190(2)	296(2)
a/pm	592.55(8)	653.16(2)	656.90(3)
b/pm	1699.7(2)	905.98(3)	906.59(4)
c/pm	597.33(8)	1242.98(3)	909.32(4)
$\alpha/^\circ$	90	114.21(1)	119.29(1)
$\beta/^\circ$	112.58(1)	99.91(1)	97.99(1)
$\gamma/^\circ$	90	94.37(1)	95.03(1)
$V/10^6 \text{ pm}^3$	555.50	652.00	460.04
Formula units per cell	$Z = 2$	$Z = 2$	$Z = 1$
Calculated density/($\text{g}\cdot\text{cm}^{-3}$)	3.10	3.95	3.83
Absorption coefficient/ mm^{-1}	6.5	11.8	11.4
Crystal size/ mm^3	$0.030 \times 0.050 \times 0.070$	$0.010 \times 0.020 \times 0.030$	$0.010 \times 0.030 \times 0.030$
θ range/ $^\circ$	2.4–32.5	2.4–30.0	2.6–32.6
Range in hkl	$-8 \leq h \leq 8$ $-25 \leq k \leq 25$ $-9 \leq l \leq 9$	$-9 \leq h \leq 9$ $-12 \leq k \leq 12$ $-17 \leq l \leq 17$	$-9 \leq h \leq 9$ $-13 \leq k \leq 13$ $-13 \leq l \leq 13$
Total no. of reflections	13,354	23,118	9659
Independent reflections	1998 ($R_{\text{int}} = 0.050$)	3802 ($R_{\text{int}} = 0.051$)	3306 ($R_{\text{int}} = 0.032$)
Reflections with $I \geq 2\sigma(I)$	1253 ($R_\sigma = 0.031$)	3149 ($R_\sigma = 0.037$)	2415 ($R_\sigma = 0.050$)
Data/restraints/parameters	1998/2/94	3802/7/167	3306/5/117
Goodness-of-fit on F^2	1.040	1.035	0.945
R indices [$I \geq 2\sigma(I)$]	$R1 = 0.030$, $wR2 = 0.054$	$R1 = 0.027$, $wR2 = 0.043$	$R1 = 0.032$, $wR2 = 0.051$
R indices (all data)	$R1 = 0.066$, $wR2 = 0.062$	$R1 = 0.041$, $wR2 = 0.045$	$R1 = 0.058$, $wR2 = 0.056$
Largest diff. peak and hole/($\text{e}\cdot\text{\AA}^{-3}$)	0.73/−0.62	1.25/−1.27	1.46/−1.19

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 $\text{Mn}(\text{OH})\text{Cl}$ and the new compounds $\text{Mn}(\text{OH})\text{Br}$ and $\text{Mn}(\text{OH})\text{I}$, 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 $\text{Mn}_5(\text{OH})_6\text{Cl}_4$, $\text{Mn}_5(\text{OH})_7\text{I}_3$, and $\text{Mn}_7(\text{OH})_{10}\text{I}_4$ to $\text{Mg}(\text{OH})_2$ are presented.

2 Experimental section

2.1 Synthesis

The compounds $\text{Mn}_5(\text{OH})_6\text{Cl}_4$, $\text{Mn}_5(\text{OH})_7\text{I}_3$, and $\text{Mn}_7(\text{OH})_{10}\text{I}_4$ 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 $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (*purum, p.a.*, Fluka, Buchs, Switzerland).

Crystals of the iodide phases $\text{Mn}_5(\text{OH})_7\text{I}_3$ and $\text{Mn}_7(\text{OH})_{10}\text{I}_4$ 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 diluted KOH solution. The precipitate was filtered and washed with EtOH and H₂O until the resulting BiOI (ICDD card No. 00-73-2062 [31]) was found to be phase pure by PXRD. Possible reactions for the formation of the iodide phase are presented in Eqs. (2) and (3). Further attempts to synthesize phase pure samples of the iodide phases failed so far.

Table 2: Atomic coordinates, occupancy, bond valence sums $\sum v$ (for oxygen atoms as O^{2-}/OH) and equivalent isotropic displacement parameters ($U_{eq}/10^{-4} \text{ pm}^2$) of $Mn_5(OH)_6Cl_4$. All atoms except Mn3 (2b) have the Wyckoff position 4e. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor (standard deviations in parentheses).

Atom	Occ.	$\sum v$	x	y	z	U_{eq}
Mn1	1	1.93	0	0	0	0.0131(2)
Mn2	1	1.95	0.03843(8)	0.90259(3)	0.53171(8)	0.0136(2)
Mn3	1	1.95	0.06984(7)	0.80102(3)	0.05025(6)	0.0119(2)
Cl1	0.75	−1.08	0.3443(2)	0.91429(6)	0.31052(18)	0.0125(2)
Cl2	1	−0.76	0.3728(2)	0.80546(6)	0.8240(2)	0.0153(2)
Cl3	0.25	−1.12	0.3048(5)	0.0175(2)	0.7795(5)	0.0133(5)
O1	0.25	−1.08/−1.95	0.207(2)	0.9084(4)	0.261(2)	0.013(2)
O2	1	−1.12/−1.99	0.1220(4)	0.3915(2)	0.7017(4)	0.0162(4)
O3	1	−1.13/−2.01	0.0894(3)	0.2977(2)	0.1811(3)	0.0122(3)
O4	0.75	−1.39/−2.27	0.1698(6)	0.0116(2)	0.7354(5)	0.0129(6)
H2	1	–	0.271(3)	0.384(2)	0.744(6)	0.015
H3	1	–	0.230(3)	0.287(2)	0.231(5)	0.015

Table 3: Anisotropic displacement parameters ($U_{ij}/10^{-4} \text{ pm}^2$) of $Mn_5(OH)_6Cl_4$ (standard deviations in parentheses).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mn1	0.0195(3)	0.0108(3)	0.0112(3)	−0.0001(2)	0.0084(2)	0.0014(2)
Mn2	0.0217(2)	0.0101(2)	0.0100(2)	−0.0001(2)	0.0072(2)	−0.0005(2)
Mn3	0.0202(2)	0.0088(2)	0.0073(2)	−0.0006(2)	0.0060(2)	−0.0010(2)
Cl1	0.0162(4)	0.0116(4)	0.0093(4)	−0.0009(3)	0.0046(3)	−0.0032(4)
Cl2	0.0173(3)	0.0165(3)	0.0115(3)	0.0002(3)	0.0050(2)	−0.0023(3)
Cl3	0.013(2)	0.011(2)	0.016(2)	0.0010(9)	0.005(2)	−0.001(2)
O1	0.020(4)	0.014(4)	0.008(4)	0.001(3)	0.010(4)	0.004(3)
O2	0.027(2)	0.0113(9)	0.014(2)	−0.0009(8)	0.011(2)	−0.0018(8)
O3	0.0163(8)	0.0114(7)	0.0089(7)	0.0003(9)	0.0049(7)	−0.0009(9)
O4	0.024(2)	0.007(2)	0.011(2)	0.002(2)	0.009(2)	0.002(2)

Table 4: Interatomic distances (/pm) in $Mn_5(OH)_6Cl_4$, calculated with the single-crystal lattice parameters (standard deviations in parentheses).

Mn1–O2 (2×)	217.0(2)	Mn2–O3	215.2(2)	Mn3–O2	214.6(2)
Mn1–O4 (2×)	218.4(3)	Mn2–O2	215.3(2)	Mn3–O3	214.7(2)
Mn1–O1 (2×)	221.1(8)	Mn2–O4	216.4(3)	Mn3–O3	215.2(2)
Mn1–Cl1 (2×)	261.1(2)	Mn2–O4	218.9(3)	Mn3–O1	218.7(8)
Mn1–Cl3 (2×)	262.9(3)	Mn2–O1	220.4(8)	Mn3–Cl1	261.3(2)
$\bar{d}$ (Mn1–O)	218.8	Mn2–Cl3	255.6(3)	Mn3–Cl2 (2×)	263.0(1)
$\bar{d}$ (Mn1–Cl)	262.0	Mn2–Cl3	258.9(3)	$\bar{d}$ (Mn3–O)	215.8
		Mn2–Cl1	262.9(2)	$\bar{d}$ (Mn3–Cl)	262.4
		Mn2–Cl2	265.4(1)		
		$\bar{d}$ (Mn2–O)	217.2	$\bar{d}$ (Mn–O)	217.3
		$\bar{d}$ (Mn2–Cl)	260.7	$\bar{d}$ (Mn–Cl)	261.7

Reactions were carried out in molybdenum capsules (0.025 mm foil, 99.95%, Alfa Aesar, Karlsruhe, Germany) and transferred into crucibles made from *h*-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, Marklkofen, 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 $Mn_5(OH)_7I_3$ and $Mn_7(OH)_{10}I_4$ 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 $Mn_5(OH)_6Cl_4$ and $Mn_5(OH)_7I_3$ were mounted on a Bruker D8 Quest diffractometer equipped with a Photon 100 detector and an Incoatec Microfocus source generator (Mo- K_α radiation with $\lambda = 71.073 \text{ pm}$, multi-layered optics monochromatized) and intensity data was collected at 173 and 190 K, respectively. Single-crystals of $Mn_7(OH)_{10}I_4$ 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- K_α radiation. Multi-scan absorption corrections based on equivalent and redundant intensities were applied with the program SADABS-2014/5 [33, 34]. The crystal structures of the hydroxide halides

Table 5: Atomic coordinates, bond valence sums ($\sum v$; for oxygen atoms: O^{2-}/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(5)	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)	0.9496(3)	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	$2i$	—	0.761(3)	0.319(7)	0.738(5)	0.05(2)
H2	$2i$	—	0.784(4)	0.917(6)	0.569(4)	0.02(2)
H3	$2i$	—	0.708(3)	0.556(8)	0.357(6)	0.07(2)
H4	$2i$	—	0.701(3)	0.141(5)	0.100(4)	0.01(2)
H5	$2i$	—	0.730(4)	0.380(6)	0.006(4)	0.03(2)
H6	$2i$	—	0.780(4)	0.070(6)	0.831(4)	0.03(2)
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	$1a$	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	0.1519(5)	0.9522(3)	0.1939(4)	0.0175(6)
O2	$2i$	−1.10/−1.97	0.1471(5)	0.3973(3)	0.5169(4)	0.0166(6)
O3	$2i$	−1.15/−2.02	0.1214(5)	0.8242(3)	0.7906(4)	0.0167(6)
O4	$2i$	−1.10/−1.97	0.1327(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)	0.05(2)
H2	$2i$	—	0.273(3)	0.425(6)	0.557(6)	0.02(2)
H3	$2i$	—	0.250(3)	0.841(7)	0.822(7)	0.05(2)
H4	$2i$	—	0.262(3)	0.155(6)	0.664(6)	0.03(2)
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 ($Mn_5(OH)_6Cl_4$), 1940192 ($Mn_5(OH)_7I_3$), and 1940193 ($Mn_7(OH)_{10}I_4$).

Table 6: Anisotropic displacement parameters ($U_{ij}/10^{-4} \text{ pm}^2$) of $\text{Mn}_5(\text{OH})_7\text{I}_3$ and $\text{Mn}_7(\text{OH})_{10}\text{I}_4$ (standard deviations in parentheses).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$\text{Mn}_5(\text{OH})_7\text{I}_3$						
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)	0.010(2)	0.007(2)	0.004(2)	0.003(2)
O3	0.013(2)	0.010(2)	0.007(2)	0.005(2)	0.003(2)	0.002(2)
O4	0.009(2)	0.009(2)	0.010(2)	0.005(2)	0.003(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)	0.008(2)	0.005(2)	0.001(2)	0.002(2)
O7	0.011(2)	0.009(2)	0.009(2)	0.005(2)	0.002(2)	0.001(2)
$\text{Mn}_7(\text{OH})_{10}\text{I}_4$						
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)	0.005(2)	0.003(2)
O2	0.018(2)	0.015(2)	0.019(2)	0.010(2)	0.004(2)	0.003(2)
O3	0.021(2)	0.015(2)	0.016(2)	0.008(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 $\text{Mn}_5(\text{OH})_6\text{Cl}_4$ was additionally characterized using powder X-ray diffraction (PXRD) technique. Therefore, data were collected with a Stoe Stadi P powder diffractometer in transmission geometry with Mo- $K_{\alpha 1}$ ($\lambda = 70.930 \text{ pm}$; Ge(111) 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 $600\text{--}4000 \text{ cm}^{-1}$ using a silicon carbide rod (Globar) as mid-infrared source, and a $15\times$ IR objective as focus was used. $\text{Mn}_5(\text{OH})_6\text{Cl}_4$ 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 ($\sum v$) 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 ($\text{O}^{2-}/\text{OH}^-$) 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 $\text{Mn}_5(\text{OH})_6\text{Cl}_4$, $\text{Mn}_5(\text{OH})_7\text{I}_3$, and $\text{Mn}_7(\text{OH})_{10}\text{I}_4$.

Table 7: Selected interatomic distances (/pm) in $\text{Mn}_5(\text{OH})_7\text{I}_3$ and $\text{Mn}_7(\text{OH})_{10}\text{I}_4$, calculated with the single-crystal lattice parameters (standard deviations in parentheses).

$\text{Mn}_5(\text{OH})_7\text{I}_3$					
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)
$\bar{d}$ (Mn1–O)	216.10	Mn3–O2	217.2(3)	Mn5–O6	215.5(3)
$\bar{d}$ (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)	$\bar{d}$ (Mn3–O)	214.73	$\bar{d}$ (Mn5–O)	214.03
Mn2–O3	217.9(3)	$\bar{d}$ (Mn3–I)	302.18	$\bar{d}$ (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–O5	214.1(3)	Mn6–I2 (2×)	297.75(3)
$\bar{d}$ (Mn2–O)	219.38	Mn4–O5	214.3(3)	$\bar{d}$ (Mn6–O)	212.85
$\bar{d}$ (Mn2–I)	306.28	Mn4–I3	305.20(7)	$\bar{d}$ (Mn6–I)	297.75
		Mn4–I1	306.07(7)		
		$\bar{d}$ (Mn4–O)	213.63	$\bar{d}(\text{Mn–O})$	215.12
		$\bar{d}$ (Mn4–I)	305.64	$\bar{d}(\text{Mn–I})$	303.91
$\text{Mn}_7(\text{OH})_{10}\text{I}_4$					
Mn1–O3 (2×)	211.6(3)	$\bar{d}$ (Mn2–O)	213.25	Mn4–O4	212.4(3)
Mn1–O1 (2×)	215.1(3)	$\bar{d}$ (Mn2–I)	312.17	Mn4–O1	214.1(3)
Mn1–I1 (2×)	299.20(3)			Mn4–O5	215.4(3)
$\bar{d}$ (Mn1–O)	213.35	Mn3–O4	214.2(3)	Mn4–O5	217.8(3)
$\bar{d}$ (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)	$\bar{d}$ (Mn4–O)	214.93
Mn2–O2	212.9(3)	Mn3–O4	222.7(3)	$\bar{d}$ (Mn4–I)	306.45
Mn2–O3	213.0(3)	Mn3–I2	306.23(7)		
Mn2–O2	214.8(3)	$\bar{d}$ (Mn3–O)	219.22	$\bar{d}(\text{Mn–O})$	215.19
Mn2–I2	302.00(7)	$\bar{d}$ (Mn3–I)	306.23	$\bar{d}(\text{Mn–I})$	306.01
Mn2–I1	322.34(7)				

In contrast to $\gamma\text{-Mn}(\text{OH})\text{Cl}$ [29], which can be derived from the CdCl_2 (C19) structure type, $\text{Mn}_5(\text{OH})_6\text{Cl}_4$ can be seen as a C6 structure with (A γ B)(A γ B) stacking sequence. The layers consist of edge-sharing distorted $\text{Mn}(\text{OH})_{6-x}\text{Cl}_x$ ($x = 1, 2, 3, 4$) 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 Cl1/O1 (occupancy: 0.75/0.25) and Cl3/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 MnCl_2 (254.8(2) pm [41]) and similar to the ones in $\gamma\text{-Mn}(\text{OH})\text{Cl}$ (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 $\text{Mn}(\text{OH})_2$ (219.62 pm [42]). This behavior indicates that the hydroxide groups in $\text{Mn}_5(\text{OH})_6\text{Cl}_4$ 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 ($\sum v$) for all non-hydrogen atoms were calculated (Table 2), whereby oxygen atoms were treated without and with the implication of a proton ($\text{O}^{2-}/\text{OH}^-$). 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 (Cl1), –0.76 (Cl2), and –1.12 (Cl3) correspond well to the formal ionic charges of the atoms.

The manganese hydroxide iodides $\text{Mn}_5(\text{OH})_7\text{I}_3$ and $\text{Mn}_7(\text{OH})_{10}\text{I}_4$ both crystallize in the triclinic space group

Figure 1: The crystal structure of $\text{Mn}_5(\text{OH})_6\text{Cl}_4$ viewed along the a - and c -axis and coordination of the manganese atoms (displacement ellipsoids represent 90% probability at 173 K). The occupancies of the disordered atom pairs O1/Cl1 and O4/Cl3 are 0.25/0.75 and 0.75/0.25, respectively.

$P\bar{1}$ (no. 2) and similar to $\text{Mn}(\text{OH})\text{I}$ [30] and $\text{Mn}_5(\text{OH})_6\text{Cl}_4$ described above, their crystal structure is related to the brucite ($\text{C}_6, \text{Mg}(\text{OH})_2/\text{CdI}_2$) structure. The single layers are formed by distorted $\text{Mn}(\text{OH})_{6-x}\text{I}_x$ ($x = 1, 2$) octahedra parallel to the (100)-plane (Figures 2 and 3). Within the octahedra having two iodine atoms, the halogen atoms occur both in *cis* and *trans* position. In contrast to $\text{Mn}_5(\text{OH})_6\text{Cl}_4$, the iodides show no substitutional disorder of the ligands.

The Mn–I distances (Table 7) range from 297.75(3) to 323.67(6) pm (average 303.91 pm) in $\text{Mn}_5(\text{OH})_7\text{I}_3$, and 299.20(3) to 322.34(7) pm (average 306.01 pm) in $\text{Mn}_7(\text{OH})_{10}\text{I}_4$. These bonds are considerably longer than in MnI_2 (292.02 pm [43]) and in $\text{MnI}_2 \cdot 4\text{H}_2\text{O}$ (292.16 pm [44]).

The values for the Mn–O bond-lengths are between 210.8(3) and 221.7(3) pm (average 215.2 pm) for $\text{Mn}_5(\text{OH})_7\text{I}_3$, and 211.6(3) and 222.7(3) pm (average 215.1 pm) in $\text{Mn}_7(\text{OH})_{10}\text{I}_4$ and are shorter than the average Mn–O distances in $\text{Mn}(\text{OH})_2$ (219.62 pm [42]). Like in $\text{Mn}_5(\text{OH})_6\text{Cl}_4$, this behavior can be seen as a result of the existing hydrogen bonds.

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 $\text{Mn}_5(\text{OH})_7\text{I}_3$ and $-1.11/-1.98$ (O1), $-1.10/-1.97$ (O2, O4), $-1.15/-2.02$ (O3), and $-1.13/-2.00$ (O5) for $\text{Mn}_7(\text{OH})_{10}\text{I}_4$. 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 $\text{O}-\text{H} \cdots \text{X}$ hydrogen bonds, which were not considered in the BLBS calculations. The IR spectra (*vide infra*) show the presence of stronger hydrogen bonding in $\text{Mn}_5(\text{OH})_7\text{I}_3$ and $\text{Mn}_7(\text{OH})_{10}\text{I}_4$ than in $\text{Mn}_5(\text{OH})_6\text{Cl}_4$, 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 $\text{Mn}_5(\text{OH})_6\text{Cl}_4$

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 $\text{Mn}_5(\text{OH})_6\text{Cl}_4$, which represented the main phase, the sample contained an unidentified side phase.

3.3 Group–subgroup relationships

The manganese hydroxide halides $\text{Mn}_5(\text{OH})_6\text{Cl}_4$, $\text{Mn}_5(\text{OH})_7\text{I}_3$, and $\text{Mn}_7(\text{OH})_{10}\text{I}_4$ reported herein are crystal chemically closely related to the well-known layer structure of cadmium iodide or brucite ($\text{Mg}(\text{OH})_2$). CdI_2 crystallizes with space group $P\bar{3}2/m1$, 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 $\text{Na}_2\text{Sn}(\text{OH})_6$, (ii) the structures of $\text{Li}_2\text{Pt}(\text{OH})_6$, $\text{Bi}_2\text{Pt}(\text{h}_2)$, $\text{Na}_2\text{Pt}(\text{OD})_6$ and

Figure 2: Octahedral coordination spheres of the manganese(II) atoms in $\text{Mn}_5(\text{OH})_7\text{I}_3$ (displacement ellipsoids represent 90% probability at 190 K) and polyhedral representation of the crystal structure viewed along the a - and b -axis.

Ti_2S , and (iii) the structure of CrBr_2 and its lower symmetric derivatives NbTe_2 , AgAuCl_4 , AgAuTe_4 , and $\text{Cu}_2\text{Cl}(\text{OH})_3$, nicely underpinning the broad crystal chemical diversity of the CdI_2 family. The third part of the Bärnighausen tree from Meyer is included in Figure 5, since the superstructures of the manganese hydroxide halides $\text{Mn}_5(\text{OH})_6\text{Cl}_4$, $\text{Mn}_5(\text{OH})_7\text{I}_3$, and $\text{Mn}_7(\text{OH})_{10}\text{I}_4$ also derive from CrBr_2 [52]. The structure of chromium dibromide is monoclinic. The space group symmetry is reduced by a *translationengleiche* symmetry reduction of index 3 (t_3) from $P\bar{3}2/m1$ to $C12/m1$.

Each, $\text{Mn}_5(\text{OH})_6\text{Cl}_4$, $\text{Mn}_5(\text{OH})_7\text{I}_3$, and $\text{Mn}_7(\text{OH})_{10}\text{I}_4$ deserve two subsequent steps starting from CrBr_2 . This is paralleled with unit cell enlargements. In Figure 6, we

present a projection of the MnI_2 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 $\text{Mn}_5(\text{OH})_6\text{Cl}_4$ (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 $\text{Mn}_7(\text{OH})_{10}\text{I}_4$ (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 $\text{Mn}_5(\text{OH})_6\text{Cl}_4$ (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 $\text{Mn}_5(\text{OH})_6\text{Cl}_4$ (blue), $\text{Mn}_7(\text{OH})_{10}\text{I}_4$ (green), and $\text{Mn}_5(\text{OH})_7\text{I}_3$ (red).

Figure 7: Group-subgroup scheme in the Bärnighausen formalism [45–48] for the structures of $\text{Mn}(\text{OH})_2$ [42], HP-CrBr_2 [52], and $\text{Mn}_5(\text{OH})_6\text{Cl}_4$. The indices for the translationengleiche (t), klassengleiche (k), and isomorphic (i) symmetry reductions and the evolution of the atomic parameters are given.

cations also show small displacements from the ideal positions in order to account for the anion substructure (OH/Cl ordering).

For $\text{Mn}_7(\text{OH})_{10}\text{I}_4$, 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 (i7). 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.

$\text{Mn}_5(\text{OH})_7\text{I}_3$ shows the most complicated of the three superstructures with 10 crystallographically independent anion sites, similar to $\text{Mn}_7(\text{OH})_{10}\text{I}_4$ with complete OH/I ordering. The displacements of the different anions from the ideal subcell positions are similar to the two

Figure 8: Group-subgroup scheme in the Bärnighausen formalism [45–48] for the structures of MnI_2 [43], HP-CrBr_2 [52] and $\text{Mn}_7(\text{OH})_{10}\text{I}_4$. 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 $\text{Mn}(\text{OH}/\text{X})_2$ 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 Bi_2Pt [53]. The latter also derives from the CdI_2 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 $\text{PtBi}_{6/3}$ 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 $\text{Mn}_5(\text{OH})_6\text{Cl}_4$, $\text{Mn}_5(\text{OH})_7\text{I}_3$, and $\text{Mn}_7(\text{OH})_{10}\text{I}_4$ 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 $\nu(\text{Mn}-\text{O})$ stretching modes. In the range from 800 to 1200 cm^{-1} , $\text{O}-\text{H}$ bending modes of the hydroxide groups can be found (very weak in $\text{Mn}_5(\text{OH})_6\text{Cl}_4$, strong in the iodide phases). Marked peaks in Figure 10 are due to the protective Nujol film on the $\text{Mn}_5(\text{OH})_6\text{Cl}_4$ 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 $\text{Mn}_5(\text{OH})_7\text{I}_3$ (Figure 11), the band from 3000 to 3300 cm^{-1} can be attributed to absorbed water and the

Figure 9: Group-subgroup scheme in the Bärnighausen formalism [45–48] for the structures of MnI_2 [43], HP-CrBr_2 [52] and $\text{Mn}_5(\text{OH})_{10}\text{I}_4$. The indices for the *translationengleiche* (t), *klassengleiche* (k), and isomorphic (i) symmetry reductions and the evolution of the atomic parameters are given.

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 $\nu(\text{O-H})$ stretching vibrations at around 3500 cm^{-1} ($\text{Mn}_5(\text{OH})_6\text{Cl}_4$: 3550 cm^{-1} ; $\text{Mn}_5(\text{OH})_7\text{I}_3$: 3491 , 3533 , and 3573 cm^{-1} ; $\text{Mn}_7(\text{OH})_{10}\text{I}_4$: 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 $\text{O-H}\cdots\text{X}$ ($\text{X} = \text{Cl}, \text{I}$) 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 $\cdots$ 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 $\text{Mn}_5(\text{OH})_6\text{Cl}_4$, $\text{Mn}_5(\text{OH})_7\text{I}_3$, and $\text{Mn}_7(\text{OH})_{10}\text{I}_4$ were characterized via X-ray diffraction, showing layered crystal structures derived from the $\text{CdI}_2/\text{Mg}(\text{OH})_2$ crystal structure. The chloride phase crystallizes in the space group $P2_1/c$ and exhibits a substitutional disorder concerning half of the ligand positions, whereas the iodide phases both crystallize in $P\bar{1}$ and do not exhibit any disorder. In contrast to the aristotype, these hydroxide halide phases show a distortion of the coordination polyhedra and strong

Figure 10: FTIR spectrum of a single-crystal of $\text{Mn}_5(\text{OH})_6\text{Cl}_4$ under a protective layer of Nujol (bands marked with an asterisk).

Figure 12: FTIR spectrum of a single-crystal of $\text{Mn}_7(\text{OH})_{10}\text{I}_4$.

Figure 11: FTIR spectrum of a single-crystal of $\text{Mn}_5(\text{OH})_7\text{I}_3$.

undulation of the layers that prevents the formation of polytypes. Additional FTIR spectroscopy affirms the hydroxide groups of the compounds and indicates the occurrence of hydrogen bonding of type $\text{O}-\text{H}\cdots\text{X}$.

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