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Preparation, Thermal Behaviour, and Crystal Structure of $MgAl_2F_8(H_2O)_2$

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Summary. Single crystals of $MgAl_2F_8(H_2O)_2$ have been obtained under hydrothermal conditions (250°C, 14 d) from a starting mixture of AlF_3 and $MgAlF_5(H_2O)_2$ in a 5% (w/w) HF solution. The crystal structure has been determined and refined from single crystal data (*Fmmm* (#69), $Z=4$, $a=7.2691(7)$, $b=7.0954(16)$, $c=12.452(2)$ Å, 281 structure factors, 27 parameters, $R(F^2>2\sigma(F^2))=0.0282$, $wR(F^2 \text{ all})=0.0885$). The obtained crystals were systematically twinned according to (010/100/001) as twinning matrix, reflecting the *pseudo*-tetragonal metric. The crystal structure is composed of perowskite-type $^2_\infty[AlF_{4/2}F_{2/1}]$ layers built of corner sharing AlF_6 octahedra with an overall composition of AlF_4^- which are connected *via* common fluorine atoms of $[MgF_{4/2}(H_2O)_{2/1}]$ octahedra. Group-subgroup relations of $MgAl_2F_8(H_2O)_2$ to $WO_3(H_2O)_{0.33}$ and to other $M(II)M(III)_2F_8(H_2O)_2$ structures are briefly discussed. Above 570°C, $MgAl_2F_8(H_2O)_2$ decomposes under elimination of water into α-AlF_3, β-AlF_3, and MgF_2.

Keywords. Hydrothermal synthesis; $MgAl_2F_8(H_2O)_2$; X-Ray structure determination; Group-subgroup relations; Thermal analysis.

Introduction

Complex solid fluorides are interesting compounds for optical hole burning or as host lattices for doping with luminescent rare earth ions [1, 2]. They are efficient materials that can be used in a number of optical applications ranging from phosphors to lasers. This motivated us to search for new compounds and structure types of this composition. Most of these materials have been synthesized by traditional solid state or ceramic reactions. Preparations by other methods remain rare; from these, hydrothermal synthesis seems to be the most promising technique to obtain a number of compounds (hydrated or not) which are inaccessible from high temperature reactions. In the course of these investigations we recently have been able to prepare and characterize $MgAlF_5(H_2O)_2$ [3]. During some of the experiments for single crystal growth of $MgAlF_5(H_2O)_2$, very few crystals with a chess-board pattern (viewed under polarized light) have been observed. X-ray powder diffraction (XRPD) of selected crystals revealed an unidentified pattern, and therefore it seemed desirable to determine the crystal structure of the unknown phase.

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In this article, preparation, single crystal structure analysis, and thermal behaviour of the new compound $MgAl_2F_8(H_2O)_2$ are reported. The relation of its crystal structure to that of other compounds of the type $M(II)M(III)_2F_8(H_2O)_2$ and to $WO_3(H_2O)_{0.33}$ is briefly discussed.

Results and Discussion

All obtained $MgAl_2F_8(H_2O)_2$ crystals showed interpenetration twinning as depicted in Fig. 1 according to (010/100/001) as twinning matrix. This might be caused by the *pseudo*-tetragonal metric with lattice parameters $a \approx b \approx 7.18$ Å.

Besides entry No. 39-0665 which describes a compound of composition '$MgAlF_5 \cdot 1.5H_2O$' (and which in fact turned out to be $MgAlF_5(H_2O)_2$ [3]), the Powder Diffraction File contains another entry (No. 44-0773) within the $MgF_2/AlF_3/H_2O$ system having the same composition as the title compound. This phase has been characterized as a by-product obtained during mineral fertilizer production [4]. Since the corresponding powder diffraction simulation and the measurement of microcrystalline $MgAl_2F_8(H_2O)_2$ showed no match with this entry and both entries exhibit nearly the same diffraction pattern in terms of reflection intensities and positions (except for reflections with *d*-spacings of 3.65, 3.10, 3.08, and 2.32 Å for No. 44-0773), it is most likely that the latter entry in fact describes the phase $MgAlF_5(H_2O)_2$ with some unidentified impurities.

The crystal structure of $MgAl_2F_8(H_2O)_2$ consists of nearly ideal AlF_6 and $MgF_4(H_2O)_2$ octahedra as building units (Fig. 2a). The presence of water molecules is confirmed by IR measurements. The vibration bands at 3570 and

Fig. 1. $MgAl_2F_8(H_2O)_2$; typical interpenetrating twin with a chess-board pattern viewed along [001] under a polarizing microscope; edge length of the crystal: *ca.* 0.1 mm

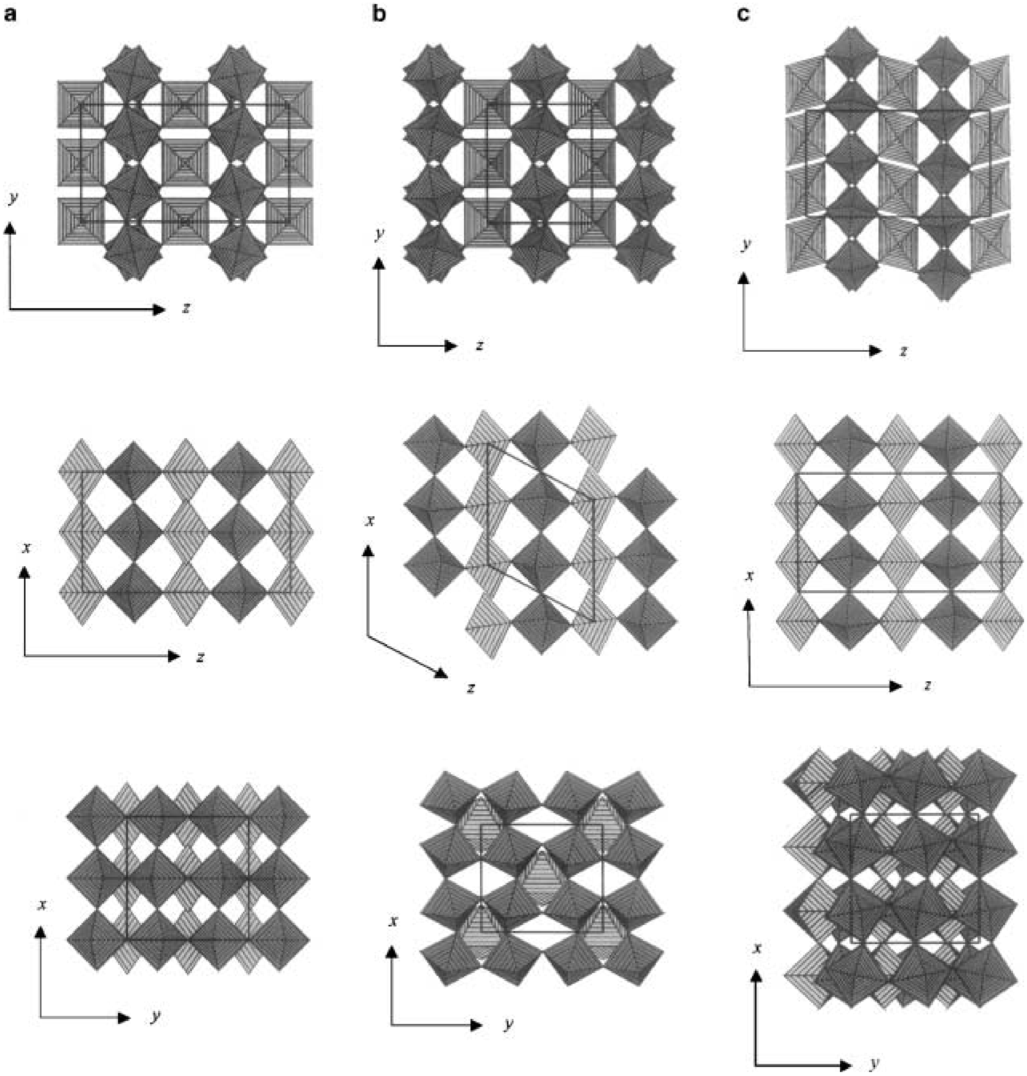

Fig. 2. Comparison of the crystal structures of a) $MgAl_2F_8(H_2O)_2$, b) $FeFe_2F_8(H_2O)_2$, and c) $CuFe_2F_8(H_2O)_2$ with projections along [100] (first row), [010] (second row), and [001] (third row); $M(II)F_4(H_2O)_2$ octahedra: light grey, $M(III)F_6$ octahedra: dark grey; the crystal structure of $WO_3(H_2O)_{0.33}$ is nearly identical to that of $MgAl_2F_8(H_2O)_2$

1620 cm^{-1} are assigned to stretching $\nu(OH)$ and bending $\delta(H_2O)$ vibrations, respectively, and are similar to those found in the closely related $FeFe_2F_8(H_2O)_2$ [6]. The bond valence sums using the bond valence parameters provided by *Brese* and *O'Keefe* [10] are equal to 2.25 (Mg), 2.96 (Al), 0.89 (F1), 0.96 (F2), 0.95 (F3) and 0.40 (O), thus clearly indicating that the oxygen atom is part of the water molecule.

Corner sharing AlF_6 octahedra form perowskite-type layers ${}^{2}_{\infty}[AlF_{4/2}F_{2/1}]$ parallel to the *ab* plane (at $z = 1/4$ and 3/4) with an overall composition of AlF_4^-.

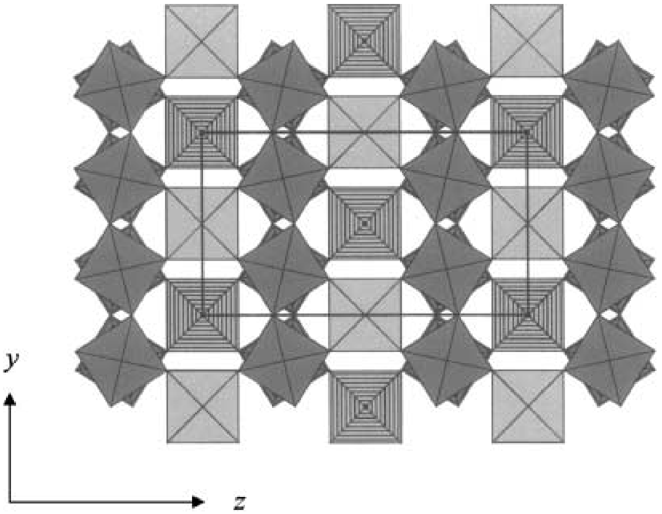

Fig. 3. $MgAl_2F_8(H_2O)_2$; HTB type layers viewed along [100]; for better distinction, the shifted layer on the back is plotted with hatched polyhedra; $MgF_4(H_2O)_2$ octahedra: light grey, AlF_6 octahedra: dark grey

Within these layers, the equatorial mean distance $\bar{d}(\text{Al–F})_e = 1.820$ Å (F2, F3) is slightly longer than the axial distance $d(\text{Al–F})_a = 1.783$ Å (F1). The perowskite-type layers are connected *via* common fluorine atoms (F1) of $MgF_{4/2}(H_2O)_{2/1}$ octahedra. The water molecules are placed at the non bridging vertices, and the distance $d(\text{Mg–F}) = 1.958$ Å is shorter than the distance $d(\text{Mg–O}) = 2.028$ Å. An alternative description of the structure can be given in terms of hexagonal tungsten bronze (HTB) type layers. Figure 3 demonstrates that the HTB type layers are stacked along the [100] direction with a shift of $b/2$ from one layer to the next with the axial (F1) atoms of AlF_6 octahedra as bridging atoms. The water molecules of the $MgF_4(H_2O)_2$ octahedra point to the center of hexagonal cavities of adjacent layers. These HTB type layers are also observed in $MgAlF_5(H_2O)_2$ [3], a structure which likewise comprises AlF_6 and $MgF_4(H_2O)_2$ octahedra. Both structures show comparable distances $\bar{d}(\text{Al–F}) = 1.808, 1.805$ Å ($MgAl_2F_8(H_2O)_2$, $MgAlF_5(H_2O)_2$), $d(\text{Mg–F}) = 1.958, 1.969$ Å, and $\bar{d}(\text{Mg–O}) = 2.028, 2.028$ Å, but owing to the minor amount of AlF_3 per formula unit the connection of the HTB type layers is different in both compounds; hence, $MgAlF_5(H_2O)_2$ crystallizes in the *anti*-weberite type in space group *Imma* (#74).

The structure of $MgAl_2F_8(H_2O)_2$ is the aristotype of other closely related structures of the type $M(\text{II})M(\text{III})_2F_8(H_2O)_2$ ($CuFe_2F_8(H_2O)_2$ [5], $FeFe_2F_8(H_2O)_2$ [6, 7], $MnFe_2F_8(H_2O)_2$ [6]) and of the hydrated tungsten oxide $WO_3(H_2O)_{0.33}$ [8, 9]. The structural data of these compounds are summarized in Table 1, and a comparison of the structures is given in Fig. 2. Group-subgroup relations according to the *Bärnighausen* notation [11, 12] are shown in a compact and concise way in Fig. 4. The *translationengleiche* (*t*2) [13] symmetry reduction from $MgAl_2F_8(H_2O)_2$ to $WO_3(H_2O)_{0.33}$ (with W atoms on the Mg and Al and O atoms on the F positions, respectively) is caused by the presence of $WO_4O(H_2O)$ octahedra with site symmetry *m*2*m* (instead of $MgF_4(H_2O)_2$ octahedra with site

Table 1. Structural data of compounds derived from $MgAl_2F_8(H_2O)_2$

Compound	Lattice parameters				Space group	Z	Reference
	a/Å	b/Å	c/Å	β/°			
$MgAl_2F_8(H_2O)_2$	7.2691(7)	7.0954(16)	12.542(2)		*Fmmm* (#69)	4	this work
$WO_3(H_2O)_{0.33}$	7.704(5)	7.359(3)	12.513(6)		*Fm*2*m* (#42)[a]	4	[8, 9]
$CuFe_2F_8(H_2O)_2$	7.541(3)	7.501(3)	13.027(7)	90.52(4)	*C*2/*c* (#15)	4	[5]
$FeFe_2F_8(H_2O)_2$	7.612(3)	7.500(1)	7.469(3)	118.38(2)	*C*2/*m* (#12)	2	[6, 7]

[a] For better comparison, the original standard cell setting in *Fmm*2 was transformed to the non-standard setting in *Fm*2*m*

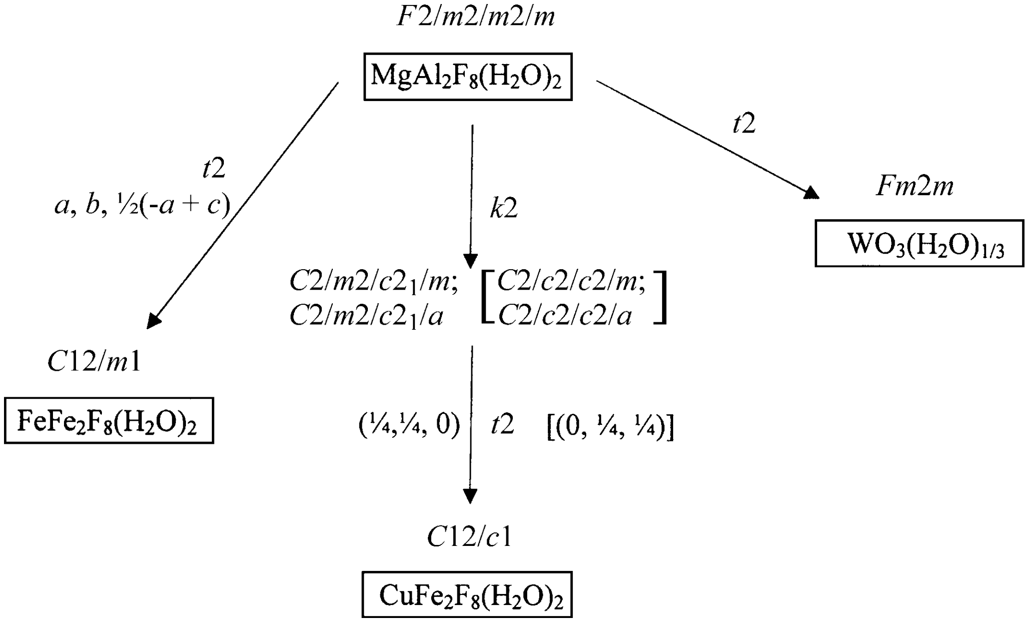

Fig. 4. Group-subgroup relations of structures derived from $MgAl_2F_8(H_2O)_2$ according to the *Bärnighausen* notation [11, 12]; the symbols *t* and *k* represent *translationengleiche* and *klassengleiche* [13] symmetry reductions

symmetry *mmm*) with one short distance *d*(W–O) and a long distance *d*(W–H_2O). The *t*2 symmetry reduction to the monoclinic $FeFe_2F_8(H_2O)_2$ is accompanied by a bisection of the corresponding unit cell and the subgroup chain to the *pseudo*-orthorhombic $CuFe_2F_8(H_2O)_2$ with a *Jahn-Teller* distorted $CuF_4(H_2O)_2$ octahedron (two short distances *d*(Cu–H_2O), two short distances *d*(Cu–F), and two long distances *d*(Cu–F)) involves a *klassengleiche* (*k*2) [13] symmetry reduction to four possible orthorhombic *C* centered space groups for which no structural representative is known up to now.

The thermal analysis curves of $MgAl_2F_8(H_2O)_2$ (Fig. 5) look similar to those of $MgAlF_5(H_2O)_2$ [3] and indicate a clearly visible two-step mechanism for the

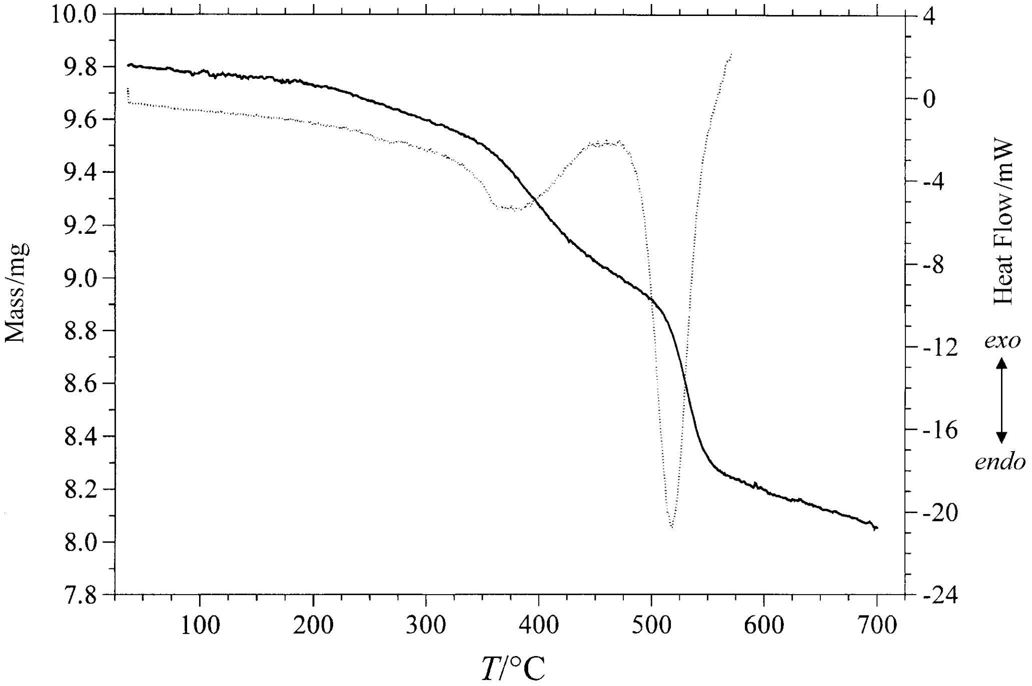

Fig. 5. Thermoanalysis of $MgAl_2F_8(H_2O)_2$ in the range of 35–570°C (DSC, dotted line) and 35–700°C (TG)

dehydration of the hydrous phase.[1] The decomposition starts at *ca.* 320°C and is associated with a weak endothermic effect (broad peak). At *ca.* 520°C a second step with an intense endothermic effect (strong narrow peak) can be observed. The dehydration is complete above 570°C. After heating the material in N_2 at that temperature, subsequent XRPD analyses revealed decomposition into α-AlF_3, β-AlF_3, and MgF_2; an intermediate phase of the material heated between 320 and 550°C could not be observed by this technique.

Experimental

The $MgAl_2F_8(H_2O)_2$ crystal used for structure analysis was obtained in a batch for the preparation of $MgAlF_5(H_2O)_2$ [3] where very few interpenetrating twin crystals with a typical chess-board pattern as viewed under a polarizing microscope (Fig. 1) were formed as a minor by-product. The selected crystal was mounted on a glass slide, and a single crystal domain was broken off by means of pressure applied with a thin needle perpendicular to the main crystal face {001}. The separated single crystal domain was then measured on a CAD4 (Nonius) four-circle goniometer with MoK_α

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[1] An accurate evaluation of the dehydration mechanism was not possible with our experimental equipment. For more detailed mechanistic investigations it has to be considered that during thermolysis of hydrous fluorides, formation of HF and partial hydrated phases accompanied by incorporation of OH^- into the structure is a frequently observed competetive reaction to the elimination of H_2O. However, the overall water content of 14.6% for $MgAl_2F_8(H_2O)_2$ determined by TGA is in good agreement with the theoretical value of 13.5%.

radiation. Data reduction was performed with the PLATON program [14], structure solution and refinement with the SHELX97 [15] package. Although there are no heavy atoms in the structure present, it was not possible to localize the H atom(s) of the water molecule by difference *Fourier* synthesis, which indicates a disorder of the hydrogen atoms. This assumption is supported by the fact that there are no strong hydrogen bonds established and that the water molecule points to the cavities of the structure; the shortest interpolyhedral distance between the donor oxygen atom and an possible acceptor atom is $d(\text{O–F1}) = 3.012(2)$ Å.

All structure representations were produced with ATOMS [16]. Further details of single crystal measurement and refinement of $MgAl_2F_8(H_2O)_2$ are summarized in Table 2, atomic parameters and anisotropic displacement parameters are given in Tables 3 and 4, respectively. Selected interatomic distances are listed in Table 5. Additional crystallographic information on $MgAl_2F_8(H_2O)_2$ can be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, e-mail: crysdata@fiz-karlsruhe.de, on quoting the names of the authors, the literature citation, and the depository number CSD-411819.

Experiments for single phase preparation of $MgAl_2F_8(H_2O)_2$ were carried out under hydrothermal conditions (steel autoclave equipped with a teflon inlay, filling degree: *ca.* 70%, 250°C, 14 d). Starting from stoichiometric amounts of soluble salts like Al and Mg sulfates or chlorides in

Table 2. $MgAl_2F_8(H_2O)_2$; crystallographic data and details of data collection, structure solution, and refinement

Diffractometer	Nonius CAD4
Radiation; wavelength λ (Å)	MoK_α; 0.71073
Temperature (°C)	20(2)
Crystal dimensions (mm^3)	$0.16 \times 0.12 \times 0.10$
Crystal description	colourless triangular plate
Space group (no.)	*Fmmm* (#69)
Formula units	$Z = 4$
Lattice parameters (Å)	$a = 7.2691(7)$ $b = 7.0954(16)$ $c = 12.452(2)$
Volume (Å^3)	$V = 642.24(19)$
Formula weight (g · mol^{-1})	266.30
μ (mm^{-1})	0.687
X-ray density (g · cm^{-3})	2.754
Range $\theta_{\min}$–$\theta_{\max}$ (°)	3.27–29.91
Range *hkl*	$-10 \rightarrow 10$; $-9 \rightarrow 9$; $-17 \rightarrow 17$
Structure solution and refinement	SHELX97 [15]
Measured reflections	1862
Independent reflections	281
Observed reflections ($I > 2\sigma(I)$)	266
R_i	0.054
Absorption correction	Empirical (ψ-scans) [18]
Transmissions coefficients $T_{\min}$; $T_{\max}$	0.6277; 0.7830
Number of parameters	27
Extinction coefficient (SHELXL97)	0.0029(16)
Difference electron density (e · Å^{-3}) with distance to atom (Å)	$\Delta\rho_{\max} = 0.88$; $\Delta\rho_{\min} = -0.46$ (1.61; O); (0.76; Al)
$R(F^2 > 2\sigma(F^2))$; $wR(F^2$ all)	0.0282; 0.0885
Goof	1.265

Table 3. $MgAl_2F_8(H_2O)_2$; atomic coordinates and equivalent isotropic displacement parameters (Å^2)

Atom	*Wyckoff* position	x	y	z	U_{eq} [a]
Mg	4*a*	0	0	0	0.0093(4)
Al	8*c*	0	1/4	1/4	0.0072(3)
F1	16*m*	0	0.1972(2)	0.11001(11)	0.0179(4)
F2	8*i*	0	0	0.28354(18)	0.0164(5)
F3	8*f*	1/4	1/4	1/4	0.0217(6)
O	8*g*	0.2790(4)	0	0	0.0247(6)

[a] $U_{eq} = (1/3)\Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$

Table 4. $MgAl_2F_8(H_2O)_2$; anisotropic displacement parameters (Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mg	0.0135(8)	0.0071(7)	0.0073(7)	0	0	0
Al	0.0074(5)	0.0062(5)	0.0078(4)	−0.0003(3)	0	0
F1	0.0294(8)	0.0131(8)	0.0114(7)	−0.0017(5)	0	0
F2	0.0240(11)	0.0071(9)	0.0182(10)	0	0	0
F3	0.0096(10)	0.0245(13)	0.0309(12)	0	0	0
O	0.0176(13)	0.0268(16)	0.0298(15)	0	0	0

Table 5. $MgAl_2F_8(H_2O)_2$; interatomic distances (Å) and angles (°) within the $MgF_4(H_2O)_2$ and AlF_6 octahedra

Mg	F1	F1^{i}	F1^{ii}	F1^{iii}	O^{i}	O
F1	1.9580(15)	3.916(3)	2.740(3)	2.798(3)	2.819(2)	2.819(2)
F1^{i}	180.00(6)	1.9580(15)	2.798(3)	2.740(3)	2.819(2)	2.819(2)
F1^{ii}	88.79(9)	91.21(9)	1.9580(15)	3.916(3)	2.819(2)	2.819(2)
F1^{iii}	91.21(9)	88.79(9)	180.00(6)	1.9580(15)	2.819(2)	2.819(2)
O^{i}	90.00	90.00	90.00	90.00	2.028(3)	4.056(6)
O	90.00	90.00	90.00	90.00	180.00	2.028(3)
Al	**F1**	**F1^{iv}**	**F3^{iv}**	**F3**	**F2**	**F2^{iv}**
F1	1.7830(14)	3.566(3)	2.5459(10)	2.5459(10)	2.574(2)	2.525(2)
F1^{iv}	180.00	1.7830(14)	2.5459(10)	2.5459(10)	2.525(2)	2.574(2)
F3^{iv}	90.00	90.00	1.8173(2)	3.6345(4)	2.5736(5)	2.5736(5)
F3	90.00	90.00	180.00	1.8173(2)	2.5736(5)	2.5736(5)
F2	91.11(9)	88.89(9)	90.00	90.00	1.8223(6)	3.6447(13)
F2^{iv}	88.89(9)	91.11(9)	90.00	90.00	180.00	1.8223(6)

Al–F2–Al^{iii} 153.50(14)

Symmetry codes: ^{i} $-x, -y, -z$; ^{ii} $x, y, -z$; ^{iii} $-x, -y, z$; ^{iv} $-x, -y+1/2, -z+1/2$

10% (w/w) HF solutions, in each case phase mixtures of $MgAl_2F_8(H_2O)_2$ and $MgAlF_5(H_2O)_2$ were obtained in ratios of about 3:1 to 1:1 as determined by *Rietveld* analyses [17]. If AlF_3 and $MgAlF_5(H_2O)_2$ were used as educts in a 5% (w/w) HF solution, the obtained crystalline product contained *ca.* 95% $MgAl_2F_8(H_2O)_2$, 5% unreacted $MgAlF_5(H_2O)_2$, and traces of AlF_3. These batches were used for further investigations (thermal analysis, IR measurements). It was not possible to obtain microcrystalline $MgAl_2F_8(H_2O)_2$ by direct precipitation of Mg and Al solutions in a stoichiometric ratio of 1:2 with diluted HF or NaF solutions. During these experiments, $MgAlF_5(H_2O)_2$ was the only phase observed.

For X-ray powder diffraction analysis (XRPD), a Philips X'Pert system in *Bragg-Brentano* geometry was used. For infrared studies, small amounts of the material were measured in a nujol matrix. The thermal analyses were performed on a Mettler-Toledo DSC-25 and TG-50 system under N_2 at a heating rate of $5°C \cdot min^{-1}$ (Fig. 5).

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