

Article

# Crystal Chemistry and High-Temperature Behaviour of Ammonium Phases NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>Fe<sup>3+</sup>Cl<sub>5</sub>·H<sub>2</sub>O from the Burned Dumps of the Chelyabinsk Coal Basin

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Received: 30 July 2019; Accepted: 12 August 2019; Published: 14 August 2019



**Abstract:** The technogenic mineral phases NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>Fe<sup>3+</sup>Cl<sub>5</sub>·H<sub>2</sub>O from the burned dumps of the Chelyabinsk coal basin have been investigated by single-crystal X-ray diffraction, scanning electron microscopy and high-temperature powder X-ray diffraction. The NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O phase is monoclinic, space group C2/*c*, unit cell parameters *a* = 9.3091(9), *b* = 9.5353(7), *c* = 13.2941(12) Å,  $\beta$  = 90.089(8)° and *V* = 1180.05(18) Å<sup>3</sup>. The crystal structure of NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O was refined to *R*<sub>1</sub> = 0.078 (*wR*<sub>2</sub> = 0.185) on the basis of 1678 unique reflections. The (NH<sub>4</sub>)<sub>2</sub>Fe<sup>3+</sup>Cl<sub>5</sub>·H<sub>2</sub>O phase is orthorhombic, space group *Pnma*, unit cell parameters *a* = 13.725(2), *b* = 9.9365(16), *c* = 7.0370(11) Å and *V* = 959.7(3) Å<sup>3</sup>. The crystal structure of (NH<sub>4</sub>)<sub>2</sub>Fe<sup>3+</sup>Cl<sub>5</sub>·H<sub>2</sub>O was refined to *R*<sub>1</sub> = 0.023 (*wR*<sub>2</sub> = 0.066) on the basis of 2256 unique reflections. NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O is stable up to 90 °C and then transforms to the less hydrated phase isotypic to β-Rb(MnCl<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub> (i.e., NH<sub>4</sub>MgCl<sub>3</sub>·2H<sub>2</sub>O), the latter phase being stable up to 150 °C. (NH<sub>4</sub>)<sub>2</sub>Fe<sup>3+</sup>Cl<sub>5</sub>·H<sub>2</sub>O is stable up to 120 °C and then transforms to an X-ray amorphous phase. Hydrogen bonds provide an important linkage between the main structural units and play the key role in determining structural stability and physical properties of the studied phases. The mineral phases NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>Fe<sup>3+</sup>Cl<sub>5</sub>·H<sub>2</sub>O are isostructural with natural minerals novograblenovite and kremersite, respectively.

**Keywords:** ammonium phases; novograblenovite; kremersite; Chelyabinsk coal basin; burned dumps; technogenic (anthropogenic) mineralogy; hydrogen bonds

# 1. Introduction

The present publication is devoted to the detailed crystal chemical study of  $NH_4MgCl_3 \cdot 6H_2O$  and  $(NH_4)_2Fe^{3+}Cl_5 \cdot H_2O$ , two ammonium phases from the burned dumps of the Chelyabinsk coal basin (Chelyabinsk Oblast, Russia). Nowadays the phases from that mine are considered as anthropogenic, despite the fact that eight phases from the same locality have previously been accepted as mineral species: bazhenovite [1], godovikovite [2], dmisteinbergite [3], svyatoslavite [4], rorisite [5], effremovite [6], srebrodolskite [7] and fluorellestadite [8]. It is worthy to note that many phases first described from the burned dumps of the Chelyabinsk coal basin by Chesnokov and co-authors [9] were later found in



natural environments (e.g., novograblenovite [10], pyracmonite [11], kumtyubeite [12], harmunite [13], ghiaraite [14], steklite [15], khesinite [16], rusinovite [17], etc.).

The mineral phase with the chemical composition NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O was first described from the Chelyabinsk coal basin as an ammonium analogue of carnallite, KMgCl<sub>3</sub>·6H<sub>2</sub>O [18], and named as "redikortsevite" [19], but this naming as well as the mineral species have not been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (CNMNC IMA). Later, this phase was found in Germany [20] and Poland [21]. Very recently, the same phase was found in a natural environment forming on the surface of basalts of the 2012–2013 Tolbachik effusive eruption (Plosky Tolbachik volcano, Kamchatka area, Far-Eastern Region, Russia) and approved by the CNMNC IMA as a mineral species named novograblenovite (NH<sub>4</sub>,K)MgCl<sub>3</sub>·6H<sub>2</sub>O [10]. Another phase studied here is the technogenic analogue of the rare mineral kremersite, (NH<sub>4</sub>,K)<sub>2</sub>[Fe<sup>3+</sup>Cl<sub>5</sub>(H<sub>2</sub>O)], that was originally described from Mt. Vesuvius (Somma-Vesuvius Complex, Naples, Campania, Italy) [22]. The pure ammonium phase, (NH<sub>4</sub>)<sub>2</sub>Fe<sup>3+</sup>Cl<sub>5</sub>·H<sub>2</sub>O, from the burned dumps of Kopeisk (Chelyabinsk coal basin) was proposed by Chesnokov [9] as a separate mineral species, the ammonium analogue of erythrosiderite, K<sub>2</sub>Fe<sup>3+</sup>Cl<sub>5</sub>·H<sub>2</sub>O [23], and named "kopeiskite". However, this proposal was not approved by the CNMNC MMA as a species identical to kremersite. The synthetic analogue of kremersite has been suggested recently as a new multiferroic material with a strong magnetoelectric coupling [24,25].

In general, about 80 NH<sub>4</sub>-bearing minerals are known to date, with many of them being discovered recently (Table 1).

Mineral	Locality, Scenarios of Formation	Reference
Acmonidesite (NH4,K,Pb <sup>2+</sup> ,Na)9Fe4 <sup>2+</sup> (SO4)5Cl <sub>8</sub>	La Fossa Crater, Vulcano, Aeolian Islands, Sicily, Italy. Fumarolic phase, (T ~ 250 °C).	[26]
Ammoniolasalite [(NH <sub>4</sub> ) <sub>2</sub> Mg <sub>2</sub> (H <sub>2</sub> O) <sub>20</sub> ]·[V <sub>10</sub> O <sub>28</sub> ]		[27]
Ammoniomathesiusite (NH4)5(UO2)4(SO4)4(VO5)·4H2O	Burro Mine, San Miguel County, Utah, USA. Secondary phases.	[28]
Burroite $Ca_2(NH_4)_2(V_{10}O_{28})\cdot15H_2O$		[29]
$\begin{array}{c} Ammoniovoltaite \\ (NH_4)_2 Fe^{2+}{}_5 Fe^{3+}{}_3 Al(SO_4)_{12}(H_2O)_{18} \end{array}$	Severo-Kambalny geothermal field, southern Kamchatka, Russia. Efflorescence around gas-steam hydrothermal vents.	[30]
Ammoniozippeite (NH4)2[(UO2)2(SO4)O2]·H2O	Blue Lizard Mine, San Juan County, Utah, and the Burro Mine,	[31]
Redcanyonite (NH4)2Mn[(UO2)4O4(SO4)2](H2O)4	San Miguel County, Colorado, USA. Low-temperature, secondary phase within organic-rich beds.	[32]
Cuatrocapaite-(NH <sub>4</sub> ) (NH <sub>4</sub> ) <sub>3</sub> (NaM□)(As <sub>2</sub> O <sub>3</sub> ) <sub>6</sub> Cl <sub>6</sub> ·16H <sub>2</sub> O	Torrecillas Mine, Salar Grande, Iquique Province, Tarapacá Region, Chile.	[33]
Davidbrownite-(NH <sub>4</sub> ) (NH <sub>4</sub> ) <sub>5</sub> (V <sup>4+</sup> O) <sub>2</sub> (C <sub>2</sub> O <sub>4</sub> )[PO <sub>2.75</sub> (OH) <sub>1.25</sub> ] <sub>4</sub> ·3H <sub>2</sub> O	Rowley Mine, Painted Rock Mts, Arizona, USA.	[34]
Phoxite $(NH_4)_2Mg_2(C_2O_4)(PO_3OH)_2(H_2O)_4$	Low-temperature, apparently post-mining suite of phases that include various vanadates, phosphates, oxalates and chlorides.	[35]
Rowleyite [Na(NH <sub>4</sub> ,K) <sub>9</sub> Cl <sub>4</sub> ][V <sup>5+,4+</sup> <sub>2</sub> (P,As)O <sub>8</sub> ] <sub>6</sub> · <i>n</i> [H <sub>2</sub> O,Na, NH <sub>4</sub> ,K,Cl]	some containing $NH_4^+$ .	[36]
Ferrierite-NH4 (NH4,Mg <sub>0.5</sub> ) <sub>5</sub> (Al <sub>5</sub> Si <sub>31</sub> O <sub>72</sub> )·22H <sub>2</sub> O	Northern Bohemia, Czech Republic.	[37]
Greenlizardite (NH4)Na(UO2)2(SO4)2(OH)2·4H2O	Green Lizard Mine. Red Canvon. San Juan County. Utah. USA.	[38]
Meitnerite (NH <sub>4</sub> )(UO <sub>2</sub> )(SO <sub>4</sub> )(OH)·2H <sub>2</sub> O	Secondary alteration phase.	[39]
Katerinopoulosite (NH <sub>4</sub> ) <sub>2</sub> Zn(SO <sub>4</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	Esperanza Mine, Lavrion District, Attikí Prefecture, Greece. Oxidation zone of a sphalerite-rich orebody.	[40]
Novograblenovite (NH <sub>4</sub> ,K)MgCl <sub>3</sub> ·6H <sub>2</sub> O	2012–2013 Tolbachik effusive eruption basalts, Plosky Tolbachik volcano, Kamchatka Oblast, Far-Eastern Region, Russia. Exhalation due to volcanic gas exposure.	[10]
Russoite (NH <sub>4</sub> )ClAs <sub>2</sub> O <sub>3</sub> (H <sub>2</sub> O) <sub>0.5</sub>	Solfatara di Pozzuoli, Pozzuoli, Napoli, Italy. Fumarolic phase.	[41]

Table 1. Recently discovered ammonium minerals.

These minerals originate either as fumarolic or mofettic (i.e., "volcanic" minerals) [10,26,30,41] or as secondary phases formed due to the contact with organic matter including burning of coal seams and dumps as well as in guano deposits (Table 1). The burned dumps of the Chelyabinsk coal basin appeared to be an important locality of ammonium compounds: at least 16 minerals and technogenic mineral-like phases were described there (Table 2). The genesis of mineral-like phases at burning coal dumps is closely related to the fumarolic formation, because both processes occur at elevated temperatures and require the principal role of gases as mineral-forming media. In principle, ammonium compounds are typical for burned coal dumps and they can form mostly during the "pseudofumarolic" stage and as a result of supergene processes [42]. The appearance of ammonium phases on burned coal dumps can be a useful indicator of the presence of underground fires [42]. At the same time, it should be noted that the origin of ferrierite-NH<sub>4</sub> [37], which is wide spread over a large area, is not connected with underground fires.

Ideal Chemical Formula	Mineral Analogue If Known	Chesnakov's Name
NH <sub>4</sub> Cl	salammoniac	
NH <sub>4</sub> MgCl <sub>3</sub> ·6H <sub>2</sub> O	novograblenovite	redikortsevite
(NH <sub>4</sub> ) <sub>2</sub> Fe <sup>3+</sup> Cl <sub>5</sub> ·H <sub>2</sub> O	kremersite	kopeiskite
$(NH_4)_2Mg_2(SO_4)_3$	efremovite <sup>1</sup>	efremovite
$(NH_4)Al(SO_4)_2$	godovikovite <sup>1</sup>	godovikovite
$NH_4Fe^{3+}_{3}(SO_4)_2(OH)_6$	ammoniojarosite	
$(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$	boussingaultite	
$(NH_4)_2Ca(SO_4)_2 \cdot H_2O$	koktaite	
$(NH_4)Fe^{3+}(SO_4)_2$	sabieite	terriconite
$(NH_4)_2SO_4$	mascagnite	
$(NH_4)_3 Fe^{3+} (SO_4)_3$	pyracmonite	$(NH_4)_3Fe^{3+}(SO_4)_3$
$(NH_4)_2Fe^{2+}(SO_4)_2\cdot 6H_2O$	mohrite	
$NH_4Al(SO_4)_2 \cdot 12H_2O$	tschermigite	
$NH_4Fe^{3+}(SO_4)_2 \cdot 12H_2O$	lonecreekite	
$NH_4Al(SO_4)_2 \cdot 4H_2O$	-	$NH_4Al(SO_4)_2 \cdot 4H_2O$
$(NH_4)_2Mg(SO_4)_2\cdot 4H_2O$	-	ammonioleonite

Table 2.	Ammonium	phases	described	in the	burned	dumps	of the	Chelyabinsk	coal	basin	by
Chesnoke	ov et al. [9].										

<sup>1</sup> Chelyabinsk coal basin is the type of locality of the mineral.

The high-temperature study of such exhalative minerals is of interest for establishing relations between species formed at the same geochemical environment, but under different temperature regimes. Such studies have been recently performed for fumarolic minerals: saranchinaite,  $Na_2Cu(SO_4)_2$ , and euchlorine,  $KNaCu_3O(SO_4)_3$ , from the Tolbachik volcano (Kamchatka, Russia) [43,44] and the efflorescence mineral tschermigite,  $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ , from geothermal fields of Southern Kamchatka (Russia) [45]. The aim of the present study is to provide the first crystal chemical description of  $NH_4MgCl_3 \cdot 6H_2O$  and  $(NH_4)_2Fe^{3+}Cl_5 \cdot H_2O$  phases from the Chelyabinsk coal basin, including their first structure refinements and determinations of their stability at increasing temperatures coupled with the calculation of thermal expansion coefficients and their crystal chemical analysis.

#### 2. Materials and Methods

#### 2.1. Occurrence

The samples of  $NH_4MgCl_3 \cdot 6H_2O$  and  $(NH_4)_2Fe^{3+}Cl_5 \cdot H_2O$  phases investigated in this study were taken from the personal collection of B.V. Chesnokov currently deposited in the Natural Science Museum of the Ilmen State Reserve (Miass, Russia). Initially these samples were discovered from the coal dumps of mine No. 50 near Kopeisk city, Chelyabinsk area, Southern Urals, Russia [9]. Both phases were found in the chloride-rich crusts formed in the upper parts of the heaps of mines.

"Redikortsevite",  $NH_4MgCl_3.6H_2O$ , crystallizes as colourless or light-yellow crystals with a flat prismatic shape. The crystals of "redikortsevite" are associated with "kopeiskite",  $(NH_4)_2Fe^{3+}Cl_5\cdot H_2O$ , that forms prismatic and pseudo-octahedral crystals with a bright orange colour [9]. Both phases are very hygroscopic, easily dissolve in water and should be stored under favourable environmental conditions only, which hinders their investigation under usual atmospheric conditions.

## 2.2. Chemical Composition

Four crystals of "redikortsevite", NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O, and "kopeiskite", (NH<sub>4</sub>)<sub>2</sub>Fe<sup>3+</sup>Cl<sub>5</sub>·H<sub>2</sub>O, were mounted in epoxy blocks and polished. The polishing process was started on dry sandpaper and was completed on paper medium with 1  $\mu$ m diamond suspension oil. The samples avoided water at all stages of polishing. The samples were coated with a 10 nm conductive carbon layer for the scanning electron microscopy (SEM) studies. Quantitative elemental analyses were carried out using a scanning electron microscope Hitachi S3400N equipped with the Oxford X-Max 20 energy-dispersive spectrometer at the Resource Centre "Geomodel" of St. Petersburg State University. The working conditions were 20 kV accelerating voltage and 1.5 nA beam current. The spectra were obtained at the spot mode for 30 s each and revealed that NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O contains abundant Mg, Cl, O and N, whereas (NH<sub>4</sub>)<sub>2</sub>Fe<sup>3+</sup>Cl<sub>5</sub>·H<sub>2</sub>O contains abundant Fe, Cl, O and N (Table 3). No significant zoning of crystals was observed.

Table 3.	Chemical	composition	of NH <sub>4</sub> Mg	Cl <sub>3</sub> ·6H <sub>2</sub> O	and (NH <sub>4</sub> ) <sub>2</sub> F	e <sup>3+</sup> Cl <sub>5</sub> ·H <sub>2</sub> O
				,	( 1/2	<u> </u>

Ν	NH <sub>4</sub> MgCl <sub>3</sub>	·6H <sub>2</sub> O	(N)	$H_4)_2 Fe^{3+}Cl$	l₅·(H <sub>2</sub> O)	Standard
Constituent	Wt. %	Atoms Per Formula Unit <sup>3</sup>	Constituent	Wt. %	Atoms Per Formula Unit <sup>4</sup>	
(NH <sub>4</sub> ) <sub>2</sub> O <sup>1</sup>	9.68	0.96	(NH <sub>4</sub> ) <sub>2</sub> O <sup>1</sup>	15.96	1.70	BN (N)
MgO	15.61	1.00	Fe <sub>2</sub> O <sub>3</sub>	27.19	0.94	MgO (Mg) FeS <sub>2</sub> (Fe)
Cl	42.34	3.08	Cl	64.64	5.06	NaCl (Cl)
H <sub>2</sub> O <sup>2</sup>	41.93	6.00	H <sub>2</sub> O <sup>(2)</sup>	6.50	1.00	
$Cl_2=O$	-9.55		Cl <sub>2</sub> =O	-14.29		
Total	100.00		Total	100.00		

<sup>1</sup> Nitrogen (ammonium) content can be taken as approximate due to problems with measuring elements with Z < 8 using energy-dispersive spectroscopy; <sup>2</sup> calculated from the crystal-structure data; <sup>3</sup> calculated on the basis of Mg = 1; <sup>4</sup> calculated on the basis of Fe + Cl = 6.

# 2.3. Single-Crystal XRD

Single-crystal X-ray diffraction studies of NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>Fe<sup>3+</sup>Cl<sub>5</sub>·H<sub>2</sub>O were performed at the Resource Centre "X-ray Diffraction Methods" of St. Petersburg State University using a Bruker Kappa APEX DUO diffractometer operated at 45 kV and 0.6 mA and equipped with a CCD area detector. The study was done by means of a monochromatic MoK $\alpha$  X-radiation  $(\lambda = 0.71073 \text{ Å})$ , frame widths of  $0.5^{\circ}$  in  $\omega$  and 10 s counting time for each frame. The intensity data were reduced and corrected for Lorentz, polarization and background effects using the Bruker software APEX2 [46]. A semiempirical absorption-correction based upon the intensities of equivalent reflections was applied [47]. The unit-cell parameters were refined by least square techniques. The structures were solved and refined using ShelX program package [48] within the Olex2 shell [49]. Crystal data, data collection information and structure refinement details are given in Table 4; atom coordinates and displacement parameters are in Tables 5 and 6, and selected interatomic distances and angles are in Table 7. All H atoms were derived from the analysis of Fourier difference electron-density maps and refined in an isotropic approximation. The H atoms forming ammonium groups have been fixed using DFIX instruction in order to maintain a reasonable geometry of the NH<sub>4</sub> groups with Uiso(H) set to 1.5 Ueq(N) and N–H 0.86 Å. The crystals of  $NH_4MgCl_3 \cdot 6H_2O$  were found to display a non-merohedral twinning. De-twinning treatment was achieved by the application of the CrysAlisPro software [50].

Compound	NH4MgCl3·6H2O	(NH <sub>4</sub> ) <sub>2</sub> FeCl <sub>5</sub> ·H <sub>2</sub> O
Crystal system	monoclinic	orthorhombic
Space group	C2/c	Pnma
a, Å	9.3091(9)	13.725(2)
b, Å	9.5353(7)	9.9365(16)
<i>c</i> , Å	13.2941(12)	7.0370(11)
β,°	90.089(8)	-
V, Å <sup>3</sup>	1180.05(18)	959.7(3)
Z	4	4
$\rho_{calc}$ , g/cm <sup>3</sup>	1.445	1.988
$\mu$ , mm <sup>-1</sup>	0.822	2.900
F(000)	536.0	572.0
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )	MoKα ( $\lambda = 0.71073$ )
2θ range, deg.	8.55–59.99	5.936-71.776
Index ranges	$-13 \le h \le 12, -13 \le k \le 13,$ $-18 \le l \le 18$	$-18 \le h \le 21, -13 \le k \le 16, \\ -11 \le l \le 11$
Reflections collected	5504	11813
Independent reflections	$1678 (R_{int} = 0.066, R_{sigma} = 0.037)$	2256 ( $R_{int} = 0.0230, R_{sigma} = 0.0173$ )
Data/restraints/parameters	1678/4/84	2256/7/65
Goodness of Fit	1.243	1.091
Final <i>R</i> indexes $(I \ge 2\sigma(I))$	$R_1 = 0.0783, wR_2 = 0.1847$	$R_1 = 0.0229, wR_2 = 0.0660$
Final <i>R</i> indexes (all data)	$R_1 = 0.0883, wR_2 = 0.1907$	$R_1 = 0.0292, wR_2 = 0.0690$
Largest diff. peak/hole / $e$ Å $^{-3}$	0.53/-0.32	0.34/-0.80

 $\textbf{Table 4. Crystal data and structure refinement for NH_4MgCl_3 \cdot 6H_2O and (NH_4)_2Fe^{3+}Cl_5 \cdot (H_2O).}$ 

**Table 5.** Atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>).  $U_{eq}$  is defined as 1/3 of the trace of the orthogonalised  $U_{IJ}$  tensor.

Atom	x	x y z		U <sub>eq</sub>						
NH4MgCl3·6H2O										
Cl1	0.5	0.5	0.5	0.0414(3)						
Cl2	0.7542(1)	0.73838(9)	0.74664(6)	0.0401(3)						
Mg	0	0.5	0.5	0.0225(3)						
N	0.5	0.5012(6)	0.75	0.061(1)						
HA	0.496(4)	0.454(2)	0.8028(7)	0.053						
HB	0.429(4)	0.560(3)	0.749(3)	0.053						
O1	0.1795(3)	0.6010(3)	0.4481(2)	0.0420(6)						
O2	0.4099(3)	0.1877(3)	0.5379(2)	0.0398(6)						
O3	0.9089(3)	0.5131(3)	0.3603(2)	0.0403(6)						
H1A	0.198(5)	0.652(5)	0.404(4)	0.06(1)						
H1B	0.250(5)	0.58105(4)	0.463(3)	0.04(1)						
H2A	0.440(6)	0.248(5)	0.515(4)	0.05(1)						
H2B	0.360(5)	0.193(5)	0.586(4)	0.05(1)						
H3A	0.890(6)	0.447(6)	0.329(4)	0.06(2)						
H3B	0.885(5)	0.579(5)	0.332(3)	0.04(1)						
		(NH <sub>4</sub> ) <sub>2</sub> FeCl <sub>5</sub> ·H	20							
N	0.14167(9)	0.0006(1)	0.6594(2)	0.0360(2)						
HA	0.191(1)	0.050(2)	0.671(2)	0.054						
HB	0.114(1)	0.05(2)	0.771(2)	0.054						
HC	0.119(1)	0.053(2)	0.585(2)	0.054						
HD	0.148(1)	-0.075(2)	0.614(2)	0.054						
Fe	0.11623(2)	0.25	0.18959(2)	0.02252(6)						
Cl1	0.10486(2)	0.01065(3)	0.17604(4)	0.03113(8)						
Cl2	0.00609(3)	0.25	0.45303(6)	0.03264(9)						
Cl3	0.24790(3)	0.25	0.39805(5)	0.02664(8)						
Cl4	0.22324(3)	0.25	-0.07176(6)	0.0340(1)						
O1	-0.0033(1)	0.25	0.0011(2)	0.0388(3)						
H1	-0.028(2)	0.184(2)	-0.033(3)	0.072(7)						

Atom	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>23</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>12</sub>				
NH4MgCl3·6H2O										
Cl1	0.0346(6)	0.0335(6)	0.0561(8)	0.0098(4)	-0.0010(5)	-0.0015(4)				
Cl2	0.0503(5)	0.0378(5)	0.0323(5)	0.0002(3)	-0.0001(3)	0.0102(3)				
Mg	0.0214(7)	0.0227(6)	0.0234(7)	0.0006(4)	-0.0011(5)	-0.0007(4)				
Ň	0.058(3)	0.063(4)	0.062(4)	0	-0.003(3)	0				
O1	0.023(1)	0.056(2)	0.048(2)	0.020(1)	-0.002(1)	-0.008(1)				
O2	0.049(2)	0.025(1)	0.046(2)	0.002(1)	0.018(1)	0.006(1)				
O3	0.057(2)	0.033(1)	0.031(1)	0.002(1)	-0.020(1)	0.002(1)				
			(NH <sub>4</sub> ) <sub>2</sub> FeCl <sub>5</sub> .	H <sub>2</sub> O						
N	0.0369(5)	0.0319(6)	0.0392(6)	0.0037(4)	-0.0035(3)	-0.0013(4)				
Fe	0.0229(1)	0.0197(1)	0.0250(1)	0	-0.00326(7)	0				
Cl1	0.0353(1)	0.0186(1)	0.0395(2)	-0.00229(9)	-0.0073(1)	-0.00072(9)				
Cl2	0.0282(2)	0.0307(2)	0.0390(2)	0	0.0085(1)	0				
Cl3	0.0244(1)	0.0293(2)	0.0263(2)	0	-0.0054(1)	0				
Cl4	0.0398(2)	0.0372(2)	0.0250(2)	0	0.0054(1)	0				
01	0.0370(6)	0.0240(6)	0.0553(9)	0	-0.0237(6)	0				

**Table 6.** Anisotropic displacement atom parameters ( $Å^2$ ).

**Table 7.** Selected bond lengths (Å) and angles (°) in the crystal structure of  $NH_4MgCl_3 \cdot 6H_2O$  and  $(NH_4)_2Fe^{3+}Cl_5 \cdot H_2O$ .

NH4MgCl3·6H2O										
Mg	g–O	Cl	-N	$\angle$ H–N–H in NH <sub>4</sub>						
Mg–O1	2.052(2) ×2	Cl1–N	3.3235(4) ×2	HA-N-HB	110(2)					
Mg-O2	$2.040(2) \times 2$	Cl2–N	3.273(5) ×2	HA–N–HA <sup>1</sup>	115(3)					
Mg-O3	$2.044(2) \times 2$	Cl2 <sup>2</sup> –N	3.394(5) ×2	HB–N–HB <sup>1</sup>	100(6)					
<mg–o></mg–o>	2.045	<cl-n></cl-n>	3.330	HA–N–HB <sup>1</sup>	111(2)					
$Di^4$	0.00153	$Di^4$	0.01269							
				∠ H–O–H in	H <sub>2</sub> O					
				H1A-O1-H1B	106(4)					
				H2A-O2-H2B	120(5)					
				НЗА-ОЗ-НЗВ	110(5)					
		(NH <sub>4</sub> ) <sub>2</sub> Fe	Cl₅·H₂O							
Fe-	Cl,O	∠ H–O–l	H in H <sub>2</sub> O	∠ H–N–H in	NH <sub>4</sub>					
Fe-Cl1	2.3853(5) ×2	H1–O1–H1 <sup>3</sup>	115(3)	HA-N-HB	104(1)					
Fe-Cl2	2.3920(5)			HA-N-HC	90(2)					
Fe-Cl3	2.3276(5)			HA-N-HD	118(2)					
Fe-Cl4	2.3537(5)			HB-N-HC	113(2)					
Fe-O1	2.109(1)			HB-N-HD	116(2)					
<fecl,o></fecl,o>	2.325			HC-N-HD	112(2)					
Di <sup>4</sup>	0.03097									

<sup>1</sup> 1 - x, y, 1.5 - z; <sup>2</sup> x + 0.5, y + 0.5; <sup>3</sup> x, 0.5 - y, z; <sup>4</sup> Di is distortion index,  $Di = \frac{1}{n} \sum_{i=1}^{n} \frac{|i-lav|}{lav}$  [51].

## 2.4. High-Temperature Powder X-Ray Diffraction

In situ high-temperature powder X-ray diffraction (HTXRD) experiments of NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O and  $(NH_4)_2Fe^{3+}Cl_5 \cdot H_2O$  phases up to 540 and 260 °C (Figure 1) were done in air using a Rigaku Ultima IV powder X-ray diffractometer (Co $K\alpha_{1+2}$  radiation, 40 kV/30 mA, Bragg-Brentano geometry, PSD D-Tex Ultra) with Rigaku HT 1500 high-temperature attachment. Thin powder samples were deposited on Pt sample holders (20 × 12 × 2 mm<sup>3</sup>) from heptane suspensions. The temperature steps and the average heating rates were 10 °C and 2/3°/min, respectively; the collecting time at each temperature step was about 20 min. Silicon was used as an external standard.



Figure 1. Powder X-ray diffraction pattern recorded for NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O up to 540 °C.

It was found that NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O transforms to another phase at  $T \sim 90$  °C, which is stable up to 140 °C. No reflections were observed in the powder patterns in the temperature range 160–370 °C. Above 370 °C, broad reflections of periclase, MgO, appeared. The unit-cell parameters of NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O and its high-temperature phase (HT phase) (Tables S1 and S2) were refined by the Rietveld method. The refinements were based on the reflections in the 20 region 10–75°. The refinement of the unit-cell parameters was done in the temperature ranges 23–80 °C and 100–140 °C for NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O and HT phase, respectively (powder pattern recorded at 90 °C was excluded from the refinement due to the appearance of reflections of the HT phase).

 $(NH_4)_2Fe^{3+}Cl_5 \cdot H_2O$  is stable up to 120 °C and then transforms to an X-ray amorphous phase. It is interesting that the shape of reflections and their intensity is slightly different at each of the patterns recorded at different temperatures, most likely, due to some changes in the structure of the phase. Therefore, the unit-cell parameters refined by the Rietveld method in the 20 region 10–75° and in temperature range 24–80 °C (Table S3) should be taken as approximate only.

In all cases, the Rietveld refinements were carried out using Topas 4.2 [52]; the crystallographic data of starting models used for refinement are given in Table 8. Rietveld refinements were done with the fixed atom coordinates, site scattering and isotropic-displacement parameters. The background was modelled using a Chebyshev polynomial approximation of the 18th order. The peak profile was described using the fundamental parameters approach. The main coefficients of the thermal-expansion tensor were determined using the TTT program package [53,54] and the TEV program [55].

**Table 8.** Crystallographic data used as starting models for the refinement of  $NH_4MgCl_3 \cdot 6H_2O$ , its HT phase and of the  $(NH_4)_2FeCl_5 \cdot H_2O$  phase by the Rietveld method.

	NH4MgCl3·6H2O	β-Rb(MnCl <sub>3</sub> )·2H <sub>2</sub> O <sup>1</sup> (Isotypic to HT Modification of NH <sub>4</sub> MgCl <sub>3</sub> ·6H <sub>2</sub> O)	(NH <sub>4</sub> ) <sub>2</sub> FeCl <sub>5</sub> ·H <sub>2</sub> O
Symmetry	Monoclinic	Triclinic	Orthorhombic
Space group	C2/c	P-1	Pnma
a (Å)	9.3091(9)	6.65	13.725(2)
b (Å)	9.5353(7)	7.01	9.9365(16)
c (Å)	13.2941(12)	9.03	7.0370(11)
α (°)	90	92.3	90
β (°)	90.089(8)	109.4	90
γ (°)	90	112.9	90
$V(Å^3)$	1180.05(18)	358.74	959.7(3)
Reference	this work	[56]	this work

<sup>1</sup> In the process of refinement Rb was replaced by N, and Mn was replaced by Mg, leading to the chemical formula  $NH_4MgCl_3 \cdot 2H_2O$ .

#### 3. Results

#### 3.1. Chemical Composition

The chemical compositions were averaged based on 15/10 analyses for  $NH_4MgCl_3 \cdot 6H_2O$  and  $(NH_4)_2Fe^{3+}Cl_5 \cdot H_2O$ , respectively. Due to the low quality of crystal surfaces and the high rate of their dehydration in vacuum, the data were normalized to 100 wt. %. The ratios between the specie-defining cations and anions were determined as  $NH_4/Mg/Cl = 0.96/1/3.08$  and  $NH_4/Fe/Cl = 1.70/0.94/5.06$  (Table 3), which is close to those in the ideal chemical formulas of the studied phases.

#### 3.2. Crystal Structures

The crystal structure of synthetic  $NH_4MgCl_3 \cdot 6H_2O$  was described by Solans et al. [57] and Marsh [58] without localization of hydrogen atoms. Recently, the crystal structure of novograblenovite,  $(NH_4,K)MgCl_3 \cdot 6H_2O$ , was described in detail, including localization of hydrogen atoms, description of structural peculiarities and structural relationships with carnallite,  $KMgCl_3 \cdot 6H_2O$  [10].

The crystal structure of NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O is based upon regular Mg(H<sub>2</sub>O)<sub>6</sub> octahedra that are connected to Cl<sup>-</sup> anions, and indirectly to NH<sub>4</sub><sup>+</sup> cations, through hydrogen bonds into a three-dimensional framework (Figure 2, Tables 7 and 9). The Mg site is octahedrally coordinated by six H<sub>2</sub>O molecules with the mean <Mg–O> bond length of 2.045 Å (Table 7). Each NH<sub>4</sub><sup>+</sup> ion is surrounded by six Cl<sup>-</sup> ions in an octahedral arrangement with the average <Cl–N> distance of 3.330 Å (Table 7). In general, the crystal structure of NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O can be represented as a perovskite-like network of (NH<sub>4</sub>)Cl<sub>6</sub> octahedra with Mg(H<sub>2</sub>O)<sub>6</sub> octahedra localized in framework cavities. Table 10 provides the results of bond-valence analysis for NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O phase with bond-valence parameters taken from [59–62].



Figure 2. The crystal structure and hydrogen bonding of NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O phase.

D-H	d(D–H) (Å)	d(HA) (Å)	<dha (°)<="" th=""><th>d(DA) (Å)</th><th>Α</th></dha>	d(DA) (Å)	Α					
NH4MgCl3·6H2O										
O1-H1A	0.783	2.395	166.88	3.164	Cl2 <sup>1</sup>					
O1–H1B	0.701	2.514	171.80	3.209	Cl1					
O2–H2A	0.710	2.472	156.34	3.135	Cl1					
O2–H2B	0.794	2.390	167.42	3.169	Cl2 <sup>2</sup>					
O3–H3A	0.773	2.435	161.92	3.178	Cl2 <sup>3</sup>					
O3–H3B	0.762	2.411	164.46	3.152	Cl2 <sup>4</sup>					
N-HA	0.834	2.659	137.70	3.224	Cl1 <sup>5</sup>					
N–HB	0.863	2.414	174.62	3.274	Cl2 <sup>5</sup>					
		(NH <sub>4</sub> ) <sub>2</sub> FeC	l₅·H₂O							
O1-H1	0.775	2.424	173.29	3.195	Cl1 <sup>6</sup>					
N-HA	0.842	2.862	132.12	3.483	Cl1 <sup>7</sup>					
N-HA	0.842	2.873	123.80	3.414	Cl3					
N–HA	0.842	2.726	128.12	3.313	Cl4 <sup>8</sup>					
N–HB	0.872	2.855	156.62	3.672	Cl1 <sup>8</sup>					
N-HC	0.806	2.907	125.71	3.440	Cl1					
N-HC	0.806	2.662	158.11	3.423	Cl2					
N-HC	0.806	2.947	119.25	3.414	Cl3					
N-HD	0.818	2.784	123.53	3.307	Cl2 <sup>9</sup>					
N-HD	0.818	2.802	145.15	3.505	Cl4 <sup>7</sup>					

**Table 9.** Hydrogen bonds of NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>FeCl<sub>5</sub>·H<sub>2</sub>O.

 ${}^{1}x - {1/2}, - \overline{y + {3/2}, z - {1/2}; {}^{2}x - {1/2}, y - {1/2}, z; {}^{3}x, - y + 1, z - {1/2}; {}^{4}-x + {3/2}, - y + {3/2}, - z + 1; {}^{5}-x + 1, y, - z + {3/2}; {}^{6}-x, - y, - z; {}^{7}-x + {1/2}, - y, z + {1/2}; {}^{8}x, y, z + 1; {}^{9}-x, - y, - z + 1. }$ 

**Table 10.** Bond-valence analysis (v.u. = valence units) for  $NH_4MgCl_3 \cdot 6H_2O$  phase.

Atom	$NH_4$	Mg	H1A	H1B	H2A	H2B	H3A	H3B	Total
01		0.38↓×2	0.80	0.87					2.05
O2		0.39↓×2			0.86	0.79			2.04
O3		0.39↓×2					0.81	0.82	2.02
Cl1	$0.16 \downarrow \rightarrow \times 2$			$0.11 \rightarrow \times 2$	$0.12 \rightarrow \times 2$				0.78
Cl2	0.18↓ ×2 0.13↓ ×2		0.13			0.14	0.13	0.13	0.84
Total	0.96	2.32	0.93	0.98	0.98	0.93	0.94	0.95	

The crystal structure of kremersite,  $(NH_4,K)_2[Fe^{3+}Cl_5(H_2O)]$ , was described earlier based on the data obtained from its pure synthetic analogue,  $(NH_4)_2Fe^{3+}Cl_5 \cdot H_2O$  [63]. It is based upon isolated FeCl<sub>5</sub>(H<sub>2</sub>O) octahedra that are connected to  $NH_4^+$  cations through hydrogen bonds into a three-dimensional framework (Figure 3, Table 9). The Fe site is octahedrally coordinated by five Cl atoms and one H<sub>2</sub>O molecule with the average <Fe–Cl,O> distance of 2.325 Å (Table 7). A bond-valence calculation for  $(NH_4)_2Fe^{3+}Cl_5 \cdot H_2O$  phase with bond-valence parameters taken from [59–62] is given in Table S4.



**Figure 3.** The crystal structure and hydrogen bonding of  $(NH_4)_2$ FeCl<sub>5</sub>·H<sub>2</sub>O phase.

# 3.3. HTXRD

The NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O phase dehydrates to NH<sub>4</sub>MgCl<sub>3</sub>·2H<sub>2</sub>O (further denoted as HT phase), which is isotypic to  $\beta$ -Rb(MnCl<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub> [56]. The unit-cell parameters at different temperatures are provided in Tables S1–S3 for NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O, NH<sub>4</sub>MgCl<sub>3</sub>·2H<sub>2</sub>O, and (NH<sub>4</sub>)<sub>2</sub>Fe<sup>3+</sup>Cl<sub>5</sub>·H<sub>2</sub>O, respectively, and are visualized in Figure 4, Figure 5 and Figure S1. The main thermal expansion coefficients for NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>Fe<sup>3+</sup>Cl<sub>5</sub>·H<sub>2</sub>O were determined using linear approximations (Tables S5 and S6) of temperature dependencies of the unit-cell parameters (Table 11).



Figure 4. The dependencies of the unit-cell parameters versus temperature for NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O phase.



Figure 5. The dependencies of the unit-cell parameters versus temperature for  $(NH_4)_2 Fe^{3+}Cl_5 \cdot H_2O$  phase.

**Table 11.** The main characteristics of thermal expansion of  $NH_4MgCl_3 \cdot 6H_2O$ , its HT phase and  $(NH_4)_2Fe^{3+}Cl_5 \cdot H_2O$  phase (°C<sup>-1</sup>, ×10<sup>-6</sup>).

	NH4MgCl3·6H2O	HT Phase <sup>1</sup>	(NH <sub>4</sub> ) <sub>2</sub> Fe <sup>3+</sup> Cl <sub>5</sub> ·H <sub>2</sub> O
α <sub>11</sub>	36.3	-30.7	40.8
$\alpha_{22}$	11.5	161.1	45.9
$\alpha_{33}$	25.2	275.2	47.0
$< \alpha_{11}a$	12.8	70.7	-
$< \alpha_{22}b$	-	24.3	-
< \alpha_{33} c	12.7	35.8	-
$\alpha_a$	36(1)	182(9)	41(6)
$\alpha_b$	11.5(6)	159(22)	46(6)
$\alpha_c$	26(1)	172(7)	47(4)
αα	-	73(9)	-
αβ	-3(1)	97(12)	-
αγ	-	-10(8)	-
$\alpha_V$	73(2)	406(25)	134(9)

<sup>1</sup> At *T* = 120 °C;  $\alpha$ —coefficient of thermal expansion ( $\alpha_{11}$ ,  $\alpha_{22}$ ,  $\alpha_{33}$ —eigenvalues (main values);  $\alpha_a$ ,  $\alpha_b$ ,  $\alpha_c$ —values along crystallographic axes);  $<\alpha_{11}a$ —angle between  $\alpha_{11}$  and *a*.

The NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O phase is characterized by rather strong anisotropy of thermal expansion with the  $\alpha_a/\alpha_b/\alpha_c$  ratio equal to 3.2/1/2.2 (Table 11). The strongest anisotropy is observed within the *xy* plane (Figure 6). In contrast, thermal expansion of (NH<sub>4</sub>)<sub>2</sub>Fe<sup>3+</sup>Cl<sub>5</sub>·H<sub>2</sub>O is rather uniform with the  $\alpha_a/\alpha_b/\alpha_c$  ratio equal to 1/1.1/1.2 (Table 11). The data obtained for the HT phase are less accurate with larger ESDs and only five points available for approximation (Table S5). In general, the behaviour of the HT phase at elevated temperatures can be described as a strong expansion with the thermal expansion coefficients changing abruptly, due to the rather abrupt and nonlinear changes of the unit-cell parameters (Figure S1).



**Figure 6.** The crystal structure of  $NH_4MgCl_3 \cdot 6H_2O$  and a section of the figure of thermal expansion coefficients oriented relative to the crystallographic axes (ammonium is excluded for simplicity).

#### 4. Discussion

The crystal-structure study of the technogenic phase "kopeiskite" confirmed that  $(NH_4)_2Fe^{3+}Cl_5 \cdot H_2O$  is a complete analogue of kremersite. The technogenic phase "redikortsevite",  $NH_4MgCl_3 \cdot 6H_2O$ , is not a dimorph, but an direct analogue of novograblenovite,  $(NH_4,K)MgCl_3 \cdot 6H_2O$ . The only difference is the presence of K in the mineral, while the technogenic phase contains ammonium only. It is interesting that the pure potassium analogue of novograblenovite, carnallite,  $KMgCl_3 \cdot 6H_2O$ , belongs to a different structure type [10]. The previous studies of  $XMgCl_3 \cdot 6H_2O$  compounds (X = Li, K,  $NH_4$ , Rb, Cs) [10,25,64] demonstrated that the crystal structures of the Li and K phases differ from those of the  $NH_4$ , Rb and Cs phases. In contrast, for (X)<sub>2</sub>Fe<sup>3+</sup>Cl<sub>5</sub>·H<sub>2</sub>O compounds (X = K,  $NH_4$ , Rb, Cs), the crystal structure of the Cs phase differs from those of the  $NH_4$ , K and Rb phases. Therefore, the ionic radii have a significant impact upon the structure type in the compounds under consideration (Table 12).

Formula	Symmetry	Cation X <sup>+</sup>	Ionic Radii <sup>1</sup> of X+, Å	Reference		
XMgCl <sub>3</sub> ·6H <sub>2</sub> O						
CsMgCl <sub>3</sub> ·6H <sub>2</sub> O	Monoclinic C2/c	Cs	1.81	[64]		
RbMgCl <sub>3</sub> .6H <sub>2</sub> O	Monoclinic C2/c	Rb	1.52	[58]		
NH4MgCl3·6H2O	Monoclinic C2/c	$NH_4$	1.48	[57], this work		
KMgCl <sub>3</sub> .6H <sub>2</sub> O	Orthorhombic Pnna	K	1.38	[65]		
LiMgCl <sub>3</sub> ·7H <sub>2</sub> O	Trigonal R3	Li	0.76	[66]		
		$(X)_2$ FeCl <sub>5</sub> ·H <sub>2</sub> O				
Cs <sub>2</sub> FeCl <sub>5</sub> ·H <sub>2</sub> O	Orthorhombic Cmcm	Cs	1.81	[67]		
Rb <sub>2</sub> FeCl <sub>5</sub> ·H <sub>2</sub> O	Orthorhombic Pnma	Rb	1.52	[67]		
$(NH_4)_2$ FeCl <sub>5</sub> ·H <sub>2</sub> O	Orthorhombic Pnma	NH <sub>4</sub>	1.48	[63], this work		
K <sub>2</sub> FeCl <sub>5</sub> ·H <sub>2</sub> O	Orthorhombic Pnma	K	1.38	[68]		

**Table 12.** Compounds with formulas  $XMgCl_3 \cdot 6H_2O$  and  $(X)_2FeCl_5 \cdot H_2O$ .

<sup>1</sup> Effective ionic radii for CN = 6 by Shannon [69] and for  $NH_4$  by Sidey [70].

The structural nature of thermal expansion anisotropy observed for NH<sub>4</sub>MgCl<sub>3</sub>·6H<sub>2</sub>O phase deserves special attention. The three-dimensional integrity of its structure is controlled by the hydrogen bonding network. Assuming that weaker bonds are more prone to stretching, one should analyse the hydrogen bonding system responsible for the linkage of  $Mg(H_2O)_6$  octahedra via Cl atoms (Figure 6). The analysis of interatomic distances indicates that the Cl1–H bonds are located either along a (Cl1–H1B bond) or b (Cl1–H2A bond) axes. The Cl1–H1B distance is longer (2.50 (5) Å with the distance between two donor oxygen atoms O1 ··· O1 equal to 6.418 Å) than the Cl1–H2A distance (2.45 (5) Å with the O2 ··· O2 distance of 6.270 Å) (Figure 6). Therefore, the anisotropy of thermal expansion within the xy plane reflects the anisotropy of the strength of the hydrogen bonding network involving Cl atoms. Along the c axis, the  $Mg(H_2O)_6$  octahedra are linked via hydrogen bonds through Cl2 atoms (Figure 6) with the Cl2–H distances ranging from 2.39 to 2.45 Å. However, the Cl2–H bonds are oriented differently (i.e., the network is not unidirectional) and thus cannot be directly compared with the Cl1–H distances. It is worthy to note that the dehydration-induced  $NH_4MgCl_3 \cdot 6H_2O \rightarrow$ NH<sub>4</sub>MgCl<sub>3</sub>·2H<sub>2</sub>O transformation is associated with restructuring of the coordination sphere of the  $NH_4^+$  cations. The latter are coordinated mainly by  $H_2O$  molecules in the high hydrated phase, whereas, in the dihydrate, the coordination is mostly by the Cl<sup>-</sup> anions. For  $NH_4MgCl_3 \cdot 6H_2O$ , the hydrogen bonding network plays a crucial role in the structural stability and the character of the physical properties such as thermal expansion. For  $(NH_4)_2Fe^{3+}Cl_5 \cdot H_2O$ , no preferred orientation of the Cl-H bonds is observed, resulting in the absence of thermal expansion anisotropy.

#### 5. Conclusions

The study of the technogenic  $NH_4MgCl_3 \cdot 6H_2O$  and  $(NH_4)_2Fe^{3+}Cl_5 \cdot H_2O$  phases from the burned dumps of the Chelyabinsk coal basin shows that they are complete analogues of novograblenovite and kremersite, respectively. In contrast to the two minerals, the technogenic phases do not contain K and are almost pure ammonium compounds. As was shown earlier [10], and confirmed in the present study, structural integrity of the studied phases is determined by the hydrogen bonding networks that serve as the most important intermediates providing linkage between main structural units. The distribution of the hydrogen bonds also explains the high-temperature behaviour of the crystal structures of the compounds under consideration and therefore determines their physical properties.

The analogy between the two studied phases and their natural counterparts, novograblenovite and kremersite, points to the geochemical analogy between technogenic (burned coal dumps) and natural (volcanic fumaroles) environments. Thus, one may expect the discoveries of more NH<sub>4</sub>-bearing mineral species analogous to the technogenic phases previously described by Chesnokov et al. [9] (Table 2).

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2075-163X/9/8/486/s1, Figure S1: The dependencies of unit-cell parameters of HT modification of  $NH_4MgCl_3 \cdot 2H_2O$ , Table S1: The refined unit-cell parameters for  $NH_4MgCl_3 \cdot 6H_2O$  phase at different temperatures, Table S2: The refined unit-cell parameters for HT phase of  $NH_4MgCl_3 \cdot 2H_2O$ , at different temperatures, Table S3: The refined unit-cell parameters for  $(NH_4)_2Fe^{3+}Cl_5 \cdot H_2O$  phase at different temperatures, Table S4: Bond-valence analysis (v.u. = valence units) for  $(NH_4)_2Fe^{3+}Cl_5 \cdot H_2O$  phase, Table S5: Approximation equations for  $NH_4MgCl_3 \cdot 6H_2O$  phase and its HT modification, Table S6: Approximation equations for  $(NH_4)_2Fe^{3+}Cl_5 \cdot H_2O$  phase,  $NH_4MgCl_3 \cdot 6H_2O$ .CIF: crystallographic Information file (CIF) for the crystal structure of  $NH_4MgCl_3 \cdot 6H_2O$ ,  $(NH_4)_2FeCl_5 \cdot H_2O$ .CIF: crystallographic Information file (CIF) for the crystal structure of  $(NH_4)_2FeCl_5 \cdot H_2O$ .

Author Contributions: Conceptualization, A.A.Z., E.S.Z. and S.V.K.; methodology, A.A.Z. and E.S.Z.; investigation, A.A.Z., E.S.Z., M.G.K., M.A.R. and V.V.S.; writing–original draft preparation, A.A.Z. and E.S.Z.; writing–review and editing, S.V.K.; visualization, A.A.Z. and E.S.Z.

**Funding:** This research was funded by the Russian Foundation for Basic Research (grant No. 19-05-00628). E.S.Z. is grateful to the President Federation Grant for Young Candidates of Sciences (MK- 3246.2019.5).

**Acknowledgments:** The X-ray diffraction studies were performed in the X-ray Diffraction Resource Centre of St. Petersburg State University. The chemical analytical studies were done in the "Geomodel" Resource Centre of St. Petersburg State University.

Conflicts of Interest: The authors declare no conflicts of interest.

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