

# Synthetic Loncreekite (NH<sub>4</sub>)




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## Summary

The crystal structure of the synthetic mineral loncreekite, (NH<sub>4</sub>)Al<sub>0.59</sub>Fe<sub>0.41</sub>(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O (I) has been determined from single-crystal X-ray diffraction. The crystal structure contains Centro symmetrical octahedral [M(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> (M = Al<sup>3+</sup> and Fe<sup>3+</sup>) and [(NH<sub>4</sub>)<sup>+</sup>(H<sub>2</sub>O)<sub>6</sub>] cations as well as (SO<sub>4</sub>)<sub>2</sub><sup>-</sup> anions. The M<sup>3+</sup>-OH<sub>2</sub> distance is between the analogical distances for Al<sup>3+</sup> and Fe<sup>3+</sup> cations. The M cation and N atom are placed on inversion 3-fold axis (4(a) and 4(b) special positions). The sulfate anion is distributed in two mutually pseudo reversed positions with the relative occupancies 0.91 and 0.09. The S and two mutually opposite positioned O atoms of the disordered sulfate anion are placed on a 3-fold axis (8(c) special position). The H atoms of the (NH<sub>4</sub>)<sup>+</sup> group are not located, but the geometry of the eight short contacts of the N atom corresponds to the H-bonds and shows that cation is oriented in two positions related to each other by an inversion center.

**Keywords:** Alum; X-ray diffraction; The crystal structure; Solid solution; Orientational disorder

## Introduction

Double sulfates described by simplest common formula AB(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O, where A = Na, K, Rb, Ce, or Tl, NH<sub>4</sub><sup>+</sup>, CH<sub>3</sub>NH<sub>3</sub><sup>+</sup> etc. and B = Al, Cr, Ti, Mn, V, Fe(3+), Co(3+), Ga(3+) etc., are known as alums [1]. There are three types of alums called as α-, β- and γ-alums [2]. Although alums have enough simple chemical composition, owing to disorder in the arrangement of the structural units in the crystal structures, they reveal some anomalous optical properties. Birefringence, or double refraction, is one of them. Kinetic ordering of cations in solid solutions of alums showing anomalous birefringence was studied by means of single-crystal X-ray diffraction way for KAl<sub>0.6</sub>Cr<sub>0.4</sub>(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O, K<sub>0.45</sub>(NH<sub>4</sub>)<sub>0.55</sub>Al(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O [3] and KAl<sub>0.95</sub>Cr<sub>0.05</sub>(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O [4]. Paramagnetic-resonance spectroscopy study of the Ti<sup>3+</sup>-substituted alums shows, that the distortion of the position of the (SO<sub>4</sub>)<sub>2</sub><sup>-</sup> group and the perceptible difference between ionic radius of the Ti<sup>3+</sup> and Al<sup>3+</sup> ions may be main cause of the reducing of the local crystal field symmetry [5]. According to the X-ray and neutron diffraction study, there are several types of distortions in the alum crystals. The orientational disorder of the sulfate oxygen atoms are often observed type of disorder. That was especially studied for several alums [6]. Disorder of the ammonium cation and as well as sulfate group has been observed in the crystal structure of ammonium aluminium alum [7]. In crystal structures of the sodium aluminium alum [8], rubidium chromium alum [9] and ammonium chromium alum [10] the disorder is absent.

The substitutional disorder of the trivalent cation in alum crystals is not widely known. The crystal structure of KAl<sub>0.6</sub>Cr<sub>0.4</sub>(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O [3] and KAl<sub>0.95</sub>Cr<sub>0.05</sub>(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O [4] are rare samples of solid solution of alum. Natural mineral loncreekite, (NH<sub>4</sub>)Fe<sub>0.75</sub>Al<sub>0.25</sub>(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O [11], is first the solid solution of alum containing two different M<sup>3+</sup> cations with perceptible difference in an ionic radius. The presence of two different M<sup>3+</sup> metal cations generates the additional distortions in the three-dimensional crystal structure of the alum and may lead to different interesting physical properties. For this reason, the new synthetic mineral loncreekite (NH<sub>4</sub>)Al<sub>0.59</sub>Fe<sub>0.41</sub>(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O (I) was obtained and studied by a single-crystal X-ray diffraction. The purpose of the present paper is to define the influence of the mutual

substitution of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  ions on the geometrical parameters of the  $[\text{M}(\text{H}_2\text{O})_6]^{3+}$  octahedron and also to discuss the problems arising by the refinement of the solid solution crystal structure.

### Methodology of the Experiment

Crystals of Fe, Al-alum,  $(\text{NH}_4)\text{Fe}_{0.40}\text{Al}_{0.60}(\text{SO}_4)\cdot 12\text{H}_2\text{O}$  (I) was obtained by addition of aluminium alum to sulfuric acid solution ( $\text{pH} < 4$ ) containing ammonium and iron atoms. The solution was slowly heated to 350K and then it was left for evaporation at room temperature. After one days, small size colorless octahedral crystals appears on the bottom of the glass. The crystals were isolated from solution, dried and chosen by sizes for single X-ray diffraction experiments. At the further evaporation of the solution, the octahedral crystals take up the hexagonal antiprism form. Thus, an inversion axis of symmetry appears in the habitus of the alum crystals. The crystal density was determined using the flotation method in the inert organic liquid.

### Refinement

All H atoms, except H atoms of ammonium group, were located in difference Fourier maps and refined isotopically. The O-H distance are in the range 0.67-0.89 (3) and H-O-H bond angles equal to 102 (3) and 111 (4)°. In all stages of the refinement one weak peak permanently appeared on the difference Fourier map near N atom. However, it was not identified as atom of hydrogen. The relatively occupancies of Al and Fe atoms also O1 and O2 atoms were refined using free variables. The relative occupancies for atoms Al and Fe respectively equal to 0.59 (5) and 0.41 (5). Obtained X-ray diffraction results agree with results of mass-spectrometry measurement within experimental error. The  $\text{SO}_4$  group is distributed in two mutually pseudo reversed orientations with relatively occupancies 0.907 (6) (0.91) and 0.093 (6) (0.09) respectively for "normal" orientation (for O1 and O2 atoms) and "pseudo reversed" orientation (for O1A and O2A atoms). The O1A and O2A atoms of the sulfate group have been located in the difference Fourier maps and both were sited in a general position. Because of this, for O1A atom the coordinates of analogical atom

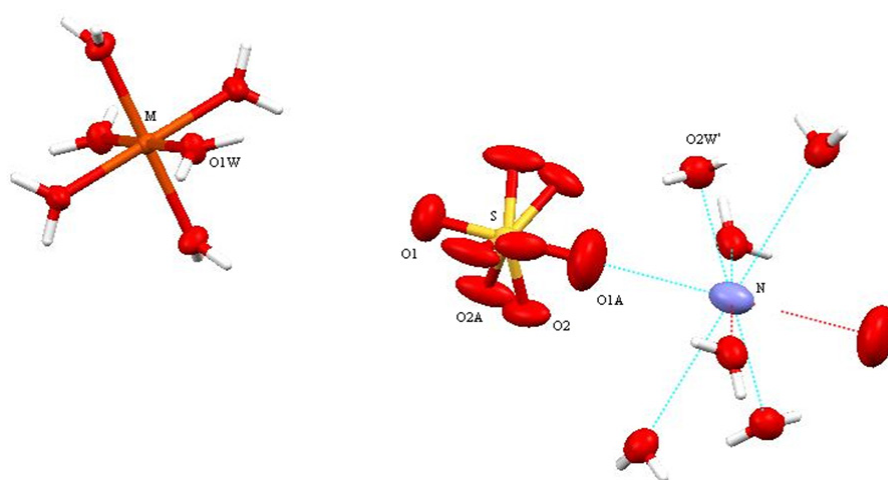
in the crystal structure of the ammonium-alum were used. The anisotropic displacement parameters of the O1A O2A atoms were very large and the sulfate group in "pseudo reversed" orientation had very distorted geometry. The anisotropic displacement parameters of the O1A and O2A atoms and also geometry of the  $\text{SO}_4$  tetrahedron were corrected using SIMU and SADI restriction instructions. Disorders in the loncreekite effect on the collected diffraction data and convergence of the calculated and experimental scattering factors. The 14 reflections forbidden in the space group  $P\bar{6}3$  were observed.

### Computing details

Data collection: CrysAlisPro [12]; cell refinement: CrysAlisPro; data reduction: CrysAlisPro; program(s) used to solve structure: SHELXS97 [13]; program(s) used to refine structure: SHELXL97 [13]; molecular graphics: SHELXTL [13] and Mercury [14]; software used to prepare material for publication: SHELXTL.

### Results and Discussion

The parameters of the unit cell of I (12.2722(14) Å) is appreciable more than that for  $(\text{NH}_4)\text{Al}(\text{SO}_4)_2\cdot 12\text{H}_2\text{O}$  (12.242 (1)Å) [7] and less than that for  $(\text{NH}_4)\text{Fe}_{0.75}\text{Al}_{0.25}(\text{SO}_4)_2\cdot 12\text{H}_2\text{O}$  (12.302 Å) [11] (all single-crystal X-ray diffraction experiments are performed at room temperature). Crystal ionic radius equal to 0.50Å and 0.64Å [15] respectively for  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  cations. Increasing of the share of the  $\text{Fe}^{3+}$  ion in aluminum alum tend to increasing of the crystal parameter *a* and the cell volume *V*. The crystal structure of I is isomorphous to the crystal structures of the others alums: the trivalent metal ion M ( $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$ ) is placed on inversion 3-fold axis (4(a) special position) and are coordinated in a regular octahedral geometry by six water molecules (Table 1 & Figure 1). In the  $[\text{M}(\text{H}_2\text{O})_6]^{3+}$  octahedron, the  $\text{M}^{3+}\text{-OH}_2$  distance equal to 1.9235 (14) Å, which is appreciably longer than the Al-OH<sub>2</sub> bond distance in the structures of ammonium alum 1.883 (1) Å [7], sodium alum 1.881 (1) [8] and potassium alum 1.908 (8) Å [16]. At the same time, the M-O distance is shorter than the sum of the ionic radii of the  $\text{Fe}^{3+}$  cation and oxygen atom (2.00Å) [15].



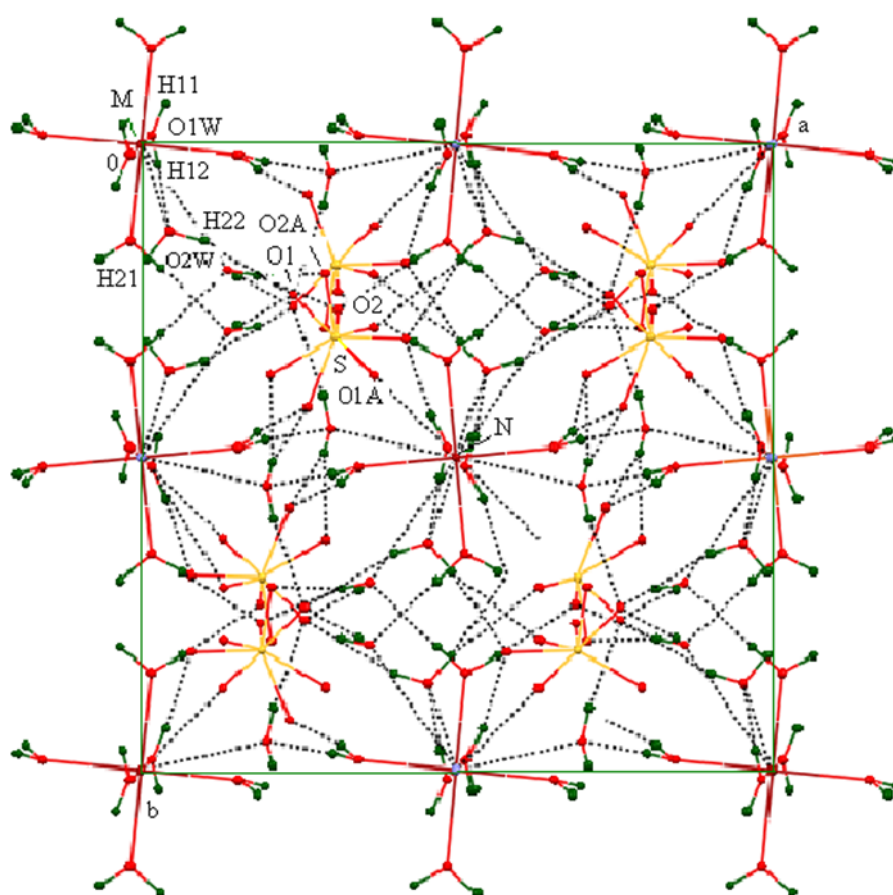
**Figure 1:** The  $[\text{M}(\text{H}_2\text{O})_6]^{3+}$  and  $[(\text{NH}_4)(\text{H}_2\text{O})_6]^{3+}$  cations (H atoms of the  $(\text{NH}_4)^+$  group were not positioned) also  $(\text{SO}_4)^{2-}$  anion with orientational disordered O atoms. Ellipsoids are shown with 50% probability.

**Table 1:** Crystallographic data and structure refinement summary for crystal I.

$\text{Al}_{0.59}\text{Fe}_{0.41}\text{H}_{28}\text{NO}_{20}\text{S}_2$	$\gamma = 90^\circ$
$M_r = 464.88$	$V = 1848.3 (4) \text{ \AA}^3$
Cubic, Pa	$Z = 4$
$a = 12.2722 (14) \text{ \AA}$	Cu K $\alpha$
$b = 12.2722 (14) \text{ \AA}$	$\mu = 6.28\text{mm}^{-1}$
$c = 12.2722 (14) \text{ \AA}$	$T = 293 (2)\text{K}$
$\alpha = 90^\circ$	$0.30 \times 0.20 \times 0.20\text{mm}$
$\beta = 90^\circ$	

The difference in the geometrical parameters of the coordination polyhedra  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$  and  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  causes the local distortions in the crystal lattice. Other type of the disorder is caused by the

stochastic distribution of the iron(3+) and aluminium cations in the crystal. In I, the sulfate group is disordered in two orientations with the relative occupancies 0.91 and 0.09. The S and mutually opposite placed O1 and O1A atoms are on a threefold axis (8(c) special position). The O2 and O2A atoms occupy a general position. The O atoms in the more occupied orientation form almost regular tetrahedron around S atom, but the O atoms from poorly populated positions form distorted tetrahedron. The H-bonds in I is similar in design to that in alum crystals with disordered sulfate group (Figure 2 & Table 2). The complex cation  $[\text{M}(\text{H}_2\text{O})_6]^{3+}$  is linked with two different  $(\text{SO}_4)^{2-}$  anions through intermolecular O1W-H11...O2 ( $-z+1/2, x-1/2$ ) and O1W-H11...O2A ( $-y+1/2, z-1/2$ ) H-bonds. The second water molecule is linked with that complex cation through O1W-H12...O2W H-bond (Table 3 & 4).

**Figure 2:** Packing diagram of I along the c axis (the broken lines show hydrogen bonds). Hydrogen atoms of the ammonium group are not located.**Table 2:**

Data Collection	
Xcalibur, Ruby diffractometer	647 independent reflections
Absorption correction: multi-scan CrysAlisPro (Oxford Diffraction Ltd., 2009)	544 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.262, T_{\max} = 1.000$	$R_{\text{int}} = 0.025$
2162 measured reflections	

Refinement	
$R[F^2 > 2\sigma(F^2)] = 0.034$	18 restraints
$wR(F^2) = 0.088$	All H-atom parameters refined
$S = 1.04$	$\Delta\rho_{\max} = 0.46 \text{ e } \text{\AA}^{-3}$
647 reflections	$\Delta\rho_{\min} = -0.39 \text{ e } \text{\AA}^{-3}$
69 parameters	

**Table 3:** Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Fe—O1W	1.9234(14)	S—O2A	1.458 (12)
S—O1	1.441(4)	S—O2	1.4690(18)
S—O1A	1.441(16)		
O1Wi—Fe—O1W	90.48(6)	O1A—S—O2A	107.6(9)
O1W—Fe—O1W <sup>ii</sup>	89.52(6)	O2A—S—O2A <sup>i</sup>	111.3(8)
O1—S—O1A	180.0(3)	O1—S—O2	109.93(12)
Symmetry codes: (i) z, x, y; (ii) -y, -z, -x.			

**Table 4:** Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

D—H...A	D—H	H...A	D...A	D—H...A
O1W—H11...O2 <sup>iii</sup>	0.73(2)	1.9(2)	2.622(3)	172(3)
O1W—H11...O2A <sup>iv</sup>	0.73(4)	2.15(3)	2.849(17)	160(4)
O1W—H12...O2W	0.89(4)	1.73(4)	2.621(2)	177(3)
O2W—H21...O1	0.75(4)	2.07(4)	2.803(3)	164(4)
O2W—H22...O2 <sup>v</sup>	0.67(4)	2.15(3)	2.751(3)	158(4)
O2W—H22...O2A <sup>vi</sup>	0.67(4)	2.24(4)	2.888(18)	164(4)
Symmetry codes: (iii) -z+1/2, x-1/2, y; (iv) -y+1/2, z-1/2, x; (v) z-1/2, x, -y+1/2; (vi) y-1/2, z, -x+1/2.				

The N atom of the  $(\text{NH}_4)^+$  group lays on inversion 3-fold axis (4(b) special position) at  $1/2 \ 1/2 \ 1/2$ . Analogical distribution of the monovalent cation was observed also in the crystal structures of the sodium alum [8] and ammonium chromium alum [10]. In the crystal structure of ammonium aluminum alum, the N atom is distributed on general position 24(d) around an inversion centre at two positions with equal probability [7]. The nitrogen atom N has eight Centro symmetrically related short contacts correspond to the H-bonds: two  $\text{N}\cdots\text{O1A}$  (2.629 (10)  $\text{\AA}$ ) and six  $\text{N}\cdots\text{O2W}$  (3.034 (2)  $\text{\AA}$ ). They reveal that the  $\text{NH}_4^+$  cation is oriented in two Centro symmetrically related positions. Symmetrically positioned around the N atom two O1A atoms and six O2W atoms form two Centro symmetrically related tetrahedron (Figure 1). The angles  $\text{O1A}\cdots\text{N}\cdots\text{O2W}$  104.4 (3) and  $\text{O2W}\cdots\text{N}\cdots\text{O2W}$  114.0 $^\circ$  close to tetrahedral. The ammonium cation in the crystal structure of the ammonium alum [7] also forms analogical H-bonds.

## Conclusion

Thus, performed X-ray diffraction study of the synthetic loncreekite reveals, that in the crystal structure of the solid solution of alum containing comparable amounts of Al and Fe, the main structural behaviours of the crystal structure of the alum are remain, but the unit cell and the cation octahedra  $[\text{M}(\text{H}_2\text{O})_6]^{3+}$  parameters are distinguished. Some infringement of the standard intermolecular distances is observed. Among the X-ray diffraction data several forbidden in the space group Pa [3] reflections are present.

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