



ISSN: 2350-0328

International Journal of Advanced Research in Science,
Engineering and Technology

Vol. 7, Issue 5, May 2020

Substitutional And Orientational Disorders in the Crystal Structure of the Solid solution $(\text{NH}_4)\text{Al}_{0,43}\text{Fe}_{0,57}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

SABIROV VAKHOBJon HUSANOVICH, IRKABAEV DJUMANALI USMANOVICH,
TURDIBAYEVZHAXONGIR ERALIYEVICH, JUMAEV MANNON NAFASOVICH.

Professor of the department "Mathematics and natural science disciplines" of the Almalyk branch of the Tashkent State Technical University named after Islam Karimov, Almalyk, Uzbekistan;

Head of the department "Mathematics and natural science disciplines" of the Almalyk branch of the Tashkent State Technical University named after Islam Karimov, Almalyk, Uzbekistan;

Senior lecturer of the department "Mathematics and natural science disciplines" of the Almalyk branch of the Tashkent State Technical University named after Islam Karimov, Almalyk, Uzbekistan;

Assistant of the department "Mathematics and natural science disciplines" of the Almalyk branch of the Tashkent State Technical University named after Islam Karimov, Almalyk, Uzbekistan;

ABSTRACT. The crystal structure of a weakly anisotropic aluminum, iron(III) alum solid solution, $(\text{NH}_4)\text{Al}_{0,43}\text{Fe}_{0,57}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, has been studied from single-crystal X-ray diffraction. X-ray reflection pattern contains forbidden reflections of space group $\text{Pa}\bar{3}$ of $hk0$ with h odd, $0kl$ with k odd, and $h0l$ with l odd. Forbidden reflections for space group $\text{P}2_1\bar{3}$ of $h00$ with h odd, $0k0$ with k odd, and $00l$ with l odd also present. Full set of X-ray reflections displays a reducing of the cubic space group until triclinic. Because of that, crystal structure was solved and refined in the higher symmetry space group $\text{Pa}\bar{3}$ and its maximal subgroups $\text{P}\bar{1}$ and $\text{P}1$. It is built from octahedral cation $[\text{M}(\text{H}_2\text{O})_6]^{3+}$ ($\text{M} = \text{Fe}^{3+}$ and Al^{3+}), hydrated ammonium group $[(\text{NH}_4)^+(\text{H}_2\text{O})_6]$ and two $(\text{SO}_4)^{2-}$ anions which are linked to three-dimensional network through intermolecular H-bonds. In the cubic space group $\text{Pa}\bar{3}$, the M^{3+} and $(\text{NH}_4)^{2+}$ cations are placed on the 3-fold rotation-inversion axis and distributed on 4a and 4b positions respectively. The sulfate group is statistically oriented in two orientations: the S atom and O atom from main as well as additional orientations lie on the threefold axis, i.e. on 8c position. Small fluctuations in values of the site occupancy factors for M^{3+} cations in both triclinic space groups are observed. The M^{3+} and $(\text{NH}_4)^{2+}$ cations in the space group $\text{P}\bar{1}$ ($Z=4$) are placed on an inversion centre of symmetry. All sulfate groups are disordered in two pseudo-reversed orientations. In non-centro symmetrically space group $\text{P}1$, four of the eight sulfate groups oriented only in one orientation.

KEY WORDS: alum, solid solutions, forbidden X-ray reflections, maximal subgroups, orientational disorder.

I. INTRODUCTION

Recently, a symmetry reduction or growth dissymmetrization in some crystalline alum solid solutions has been discussed [1-3]. A symmetry reduction led to new nonlinear physical properties of the crystals, for example, birefringence or double refraction of the monochromatic light. Alum is unique because of its ability to form continuous sets of solid solutions.

Alum solid solutions may be prepared by partial replacement of either monovalent or trivalent metal cations, as well as both cations.

Structural studies have shown that alum crystallizes in the cubic space group $\text{Pa}\bar{3}$ and many alum crystal structures have been studied by the single crystal X-ray ways [4-9]. These works reveal the orientational disorder of the sulfate group in the crystals.

In present paper, we describe the results of the detailed X-ray diffraction study of the two types disorders: 1) replacement disorder of Al^{3+} and Fe^{3+} cations, and 2) the orientational disorder of the $(\text{SO}_4)^{2-}$ anion in the crystal structure of the solid solution $(\text{NH}_4)\text{Al}_{0,43}\text{Fe}_{0,57}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (I).

Few forbidden reflections in cubic space group $\text{Pa}\bar{3}$ occurrence in the diffraction pattern. The reflections of $hk0$ with h odd, $0kl$ with k odd, and $h0l$ with l odd are contrary to the glide plan symmetry. Reflections of $h00$ with h odd, $0k0$



with k odd, and $00l$ with l odd not agree with the screw axes 2_1 . The forbidden reflections of hkl with $h+k$, $h+l$ and $k+l$ odd indicate to the loss of the symmetry $\bar{3}$ of the Wyckoff positions $4a$ and $4b$. By taking into account these extra reflections, the cubic symmetry is reduced until triclinic. For determination of the influences the lowering of the symmetry to the crystal structure, it has solved and refined crystal structure of the solid solution I in the higher symmetric space group $Pa\bar{3}$, and its maximal triclinic subgroups $P\bar{1}$ and $P1$.

The occurrence of the forbidden in the cubic space group reflections may be related to replacement by cations Al^{3+} and Fe^{3+} with different atomic scattering factors of the special equivalent positions in the cell. The forbidden reflections has been previously observed in X-ray analysis of a solid solution of alum $K_{0.9}(NH_4)_{0.1}Al(SO_4)_2 \cdot 12H_2O$ containing a small proportion of monovalent cation NH_4^+ , but they not was discussed in detail [2]. The lattice parameter of I ($a=12.263(3)$ Å) is distinctly more than that of a $(NH_4)Al(SO_4)_2 \cdot 12H_2O$ ($12.242(1)$ Å) [5] and while is less than that for natural mineral "loncreekite" $(NH_4)Fe_{0.75}Al_{0.25}(SO_4)_2 \cdot 12H_2O$ (12.302 Å) [10] (all single-crystal X-ray diffraction experiments are performed at room temperature). The information about ammonium iron alum's lattice parameters is absent, and to compare with the lattice parameters of ammonium iron alum is not available.

II. MATERIALS AND METHODS

The single crystals of $(NH_4)Al_{0.43}Fe_{0.57}(SO_4)_2 \cdot 12H_2O$ (I) were obtained by addition of ammonium alum to the sulfuric acid solution ($pH < 4$) of the iron (III) sulfate. The solution was slowly heated to 350 K and after that, was left for evaporation at room temperature. After one days, small size colorless octahedral crystals appears on the bottom of the glass. The single crystals for X-Ray diffraction experiment were isolated from solution, dried at the air. By further evaporation of the solution, the colorless octahedral crystals take up the hexagonal antiprism form. Thus, an inversion axis of symmetry $\bar{3}$ appears in the *HABITUS* of the alum crystals. The colorless, octahedral-shaped crystals of I have the following parameters: $a = b = c = 12.263(1)$ Å, $V = 1844.3(4)$ Å³, $Z = 4$, $d_{calc.} = 1.69$ g/cm³.

The X-ray experiment with a $0.3 \times 0.2 \times 0.2$ mm single crystal was performed on an Xcalibur, Ruby diffractometer ($\lambda CuK\alpha$ radiation, room temperature, $6.25 < \theta < 75.89^\circ$, $-15 \leq h \leq 15$, $-15 \leq k \leq 15$, $-15 \leq l \leq 15$, 37 700 reflections with $I \geq 2\sigma(I)$, graphite monochromator, ω -scanning). In the space group $Pa\bar{3}$, 255 of the observed reflections are forbidden. The empirical absorption corrections, Lorentz factor, and polarization were applied using the CrysAlisPro software [11]. The calculations were performed using the SHELX-97 software in the full-matrix anisotropic approximation for all non-hydrogen atoms [12-14]. Molecular graphics was performed by programs *SHELX* [14] and *Mercury* [15].

In the space group $Pa\bar{3}$ H atoms of both water molecules were located from the Fourier difference maps and refined in the isotropic approximation, in the group $P\bar{1}$ they refined using the riding model, and in the $P1$ group they were not refined. Only in the space group $Pa\bar{3}$ H atoms of the NH_4^+ cation were located from the Fourier difference maps. Further they were refined in the riding model. For the space group $P1$ the coordinates of H atoms were calculated by the data for the group $Pa\bar{3}$. The Fe^{3+} and Al^{3+} cations in the space group $Pa\bar{3}$ share the same position with populations 0.521 (5) and 0.479 (5) respectively. In the space groups $P\bar{1}$, and $P1$, the populations of Fe and Al atomic positions were determined with the restriction $\sin\theta/\lambda \leq 0.4$. The obtained occupancies of 0.57 (Fe) and 0.43 (Al) correspond to the results of the chemical analysis. The final refinements of the structure in all space groups were carried out with these values of the populations. In the structure refinement, the standard values of geometric parameters of a SO_4 tetrahedron were used. The anisotropic displacement parameters of crystal-chemically equivalent atoms were established to be same in all space groups. The main experimental dates and refinement parameters for the crystal structure of I in different space groups are given in Table 1; the atomic coordinates and isotropic atomic displacement parameters may be received from author by *E-mail*. The most important interatomic distances and bond angles are given in Table 2. The very difficult problem in the refinement of the crystal structure of I was to determinate the positions of the O atoms of the disordered sulfate group. Coordinates of the O atoms in the "normal" orientation being on the 3-fold rotation axis in the space group $Pa\bar{3}$ is determinated easy but the O atoms in "reversed" positions with respect to the latter exhibit abnormally large anisotropic displacement parameters. By anisotropic refinement, some O atoms become "non-positive defined" or its anisotropic displacement parameters became abnormal. The attribute "non-positive defined" atom disappears by independent refinement of the coordinates of each O atom, but at the same time, the site occupation factors for each «pseudo-reversed» O atom show a small s.o.f. than O atoms this group in general position. For correction abovementioned problems in the space groups $Pa\bar{3}$ and $P\bar{1}$, the O atoms of the sulfate groups in "reversed" positions and in the space group $P1$ both disordered O atoms were refined in isotropic approach by application of the restraints SIMU and SADI. The ISOR instruction was applied to the crystallization hydrate molecules in both space groups. The hydrogen atoms in all space groups, except the H atoms of ammonium group in both triclinic space groups,

were localized by difference Fourier maps. It is noteworthy, that in space group $P1$, the H atoms of the water molecules were defined from the further residual peaks of the difference Fourier maps.

In cubic space group $Pa\bar{3}$ all H atoms, except H atoms of the ammonium group, were refined isotropically. The H atoms of the ammonium group were refined using a 'riding' model. The H atoms in space group $P1$ were refined also using a "riding" model, but in space group $P1$, no ways applied to refine of the positions of the H atoms were successful. The geometry of the water molecules in all space groups is slightly distorted from ideal.

In cubic group $Pa\bar{3}$ among the 37700 total observed reflections, there are 255 forbidden reflections, *i.e.* a number of forbidden reflections consist of ~0.672% from total observed reflections.

For non-centrosymmetrical space group $P1$, TWIN and BASF instructions were applied, a Flack parameter equal to 0.3369 (3).

Table 1– Refinement parameters for the structure of I the space groups $Pa\bar{3}$, $P\bar{1}$, and $P1$

Parameter	Space group		
	$Pa\bar{3}$	$P\bar{1}$	$P1$
Independent reflections, $F_o > 4\sigma(F_o)$	648	7582	7582
Refined	65	624	865
Number restriction	25	512	848
$GOOF$ on F^2	1.162	1.198	1.107
$R(\Sigma)$	0.0113	0.0353	0.0355
R_{int}	0.0811	0.0724	0.0728
$R_1 (I > 2\sigma(I))$	0.0322	0.043	0.0432
$wR_2 (I > 2\sigma(I))$	0.077	0.1268	0.1264
R_1 (по всем отражениям)	0.0299	0.0513	0.0515
$\Delta\rho_{max}/\Delta\rho_{min}, e^2/\text{\AA}^3$	0.507 /	0.673 /	0.999 /
μ, mm^{-1}	-0.386	-0.825	-0.868
Flack	6.961	7.185	7.073
			0.51(6)

III. RESULTS AND DISCUSSION

The crystal structure of the solid solution I in the space group $Pa\bar{3}$ is isostructural to ammonium alum, $\text{NH}_4\text{Al}(\text{SO}_4)\cdot 12\text{H}_2\text{O}$, [5]. It consists of the octahedral $[M(\text{H}_2\text{O})_6]^{3+}$ cation ($M = \text{Fe}^{3+}$ and Al^{3+}), $[(\text{NH}_4)^+(\text{H}_2\text{O})_6]$ hydrated ammonium group and $(\text{SO}_4)^{2-}$ anion. These structural units alternate along the crystallographic 3-fold rotation-inversion axis and are linked through intermolecular H-bonds in the three-dimensional network (Fig. 1). The M^{3+} and $(\text{NH}_4)^+$ cations are distributed on Wyckoff positions $4a$ and $4b$, respectively. The disordered $(\text{SO}_4)^{2-}$ tetrahedra are distorted and in a reversed orientation along the threefold axis ($8c$ position). In the $[M(\text{H}_2\text{O})_6]^{3+}$ octahedron, the $M^{3+}-\text{OH}_2$ distance (1.9399(14) Å) (Tabl. 2) is appreciably longer than the $\text{Al}-\text{OH}_2$ bond distance in the ammonium alum (1.883(1) Å) [5], the sodium alum (1.881(1) Å) [6] and the potassium alum (1.908 (8) Å) [7]. At the same time, the $M-\text{O}$ distance is shorter than the sum of the ionic radii of the Fe^{3+} cation and oxygen atom (2.00 Å) [16] or than the $\text{Fe}-\text{OH}_2$ distance 1.997(3) Å [17].

The $(\text{SO}_4)^{2-}$ group is distributed in two mutually pseudo reversed orientations with respect to the threefold axis with the site occupancy factors 0.866(8) and 0.134(8) respectively for the "normal" and the "pseudo-reversed" orientations. The O atoms in the "normal" orientations form an almost regular tetrahedron around the S atom in contrary to the O atoms of the "reversed" orientation. Both O atoms on the threefold axis have large isotropic displacement parameters, those points to a large uncertainty in the positions those atoms. The N atom of the $(\text{NH}_4)^+$ group is placed on the 3-fold rotation-inversion symmetry axis between two sulfate anions and disordered with equal probability in two orientations related to each other by a centre of symmetry (Fig. 1).

The ammonium group in each orientation is surrounded by a highly disordered tetrahedron, which is formed by three water molecules $\text{O}_w(2)$, which involved in the hydrogen bond $\text{N}-\text{HO}_w(2)$ and related to each other by the 3-fold axis and one $\text{O}(1A)$ atom participating in the hydrogen bond $\text{N}-\text{HO}(1A)$. The significantly difference in the distance $\text{N} \cdots \text{OH}_2$ 3.034(2) Å and $\text{N} \cdots \text{O}(\text{sulfate})$ 2.721(4) Å is typical properties of all α -alum crystal structures (Abdeen *et al.*, 1981; Nyburget *et al.*, 2000). The various hydrogen bond distances and angles are given in Tabl. 2.

Table2–Most important distances $d(\text{\AA})$, angles $\omega(\text{deg})$, and site populationsp in structure of I

Parameter	Space group		
	$Pa\bar{3}$	$P\bar{1}$	$P1$
$d(M^{3+}-O)$	1.9399(14)	1.934(2)-1.940(3) 1.938(av.)	1.920(7)-1.957(7) 1.938(av.)
$\omega(O_w-M-O'_w)$	89.31(6)	89.16(12)-89.35(12)	88.7(3)-89.9(3)
Geometry of sulfate groups			
$d(S-O(1))$	1.439(4)	1.436(4)-1.442(4)	1.446; 1.440(av.)**
$d(S-O(2))^*$	1.4686(19)	1.464(3)-1.471(3)	1.473; 1.461(av.)**
$d(S-O(1A))$	1.34(3)	1.454(11)-1.461(11)	1.455(av.)
$d(S-O(2A))$	1.455(11)	1.448(11)-1.469(11)	1.456(av.)
$\omega(O(1)-S-O(1A))$	180	163.3(10); 164.1(11) 171.9(11); 176.1(10)	156.9(9); 169.4(10) 175.7(9); 176.8(10)
$d(N...O(1A))$	2.721(4)	2.608-2.708	2.626-2.769
$d(N...O_w)$	3.034(4)	3.028-3.035	2.962-3.134
p	0.866(8)	0.873(4); 0.876(4) 0.869(4); 0.874(4)	0.791(6); 0.796(6) 0.796(6); 0.829(6)

* In the space groups $P\bar{1}$, and $P1$, the symbol O(2) denotes O atoms of the SO_4 group, which are in a general position in the space group $Pa\bar{3}$.

** O atoms belong to the ordered sulfate groups.

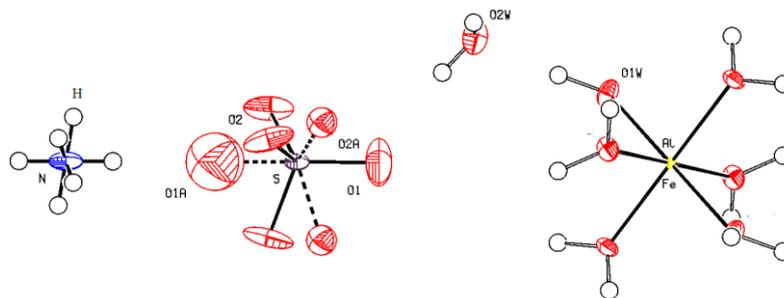


Fig 1 -The row formed by alternated along the crystallographic 3-fold rotation-inversion axis $[M(H_2O)_6]^+$ and NH_4^+ cations and disordered $(SO_4)^{2-}$ anion in the space group $Pa\bar{3}$. The O atoms of the disordered sulfate group are shown specially as ellipsoids with 50% probability.

In the space group $P\bar{1}$ ($Z=4$), the M^{3+} cations are on the crystallographic centers of symmetry: at the vertices and on the face of a cube (Fig. 2). The $M^{3+}-O$ distances in the centrosymmetrical coordination octahedron of the M^{3+} cation are various in the range of 1.934 (2)-1.940(2) \AA . That distances in the range 3σ are comparable to analogical distance observed in the space group $Pa\bar{3}$ (1.9399(14) \AA).

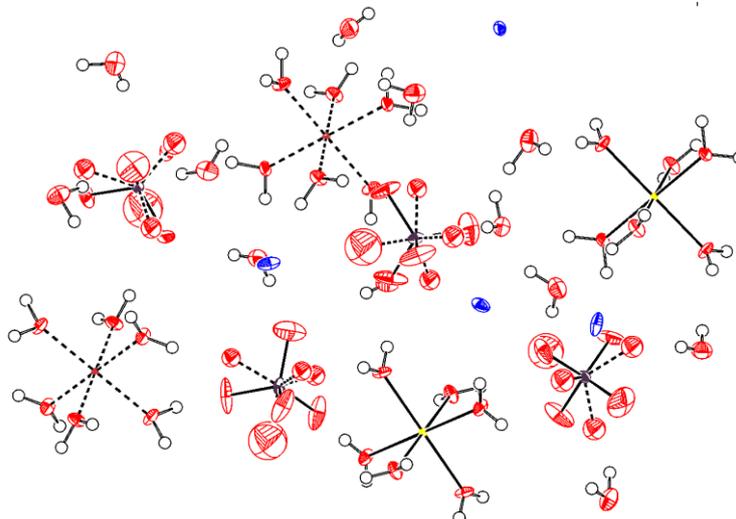


Fig 2 - Crystal packing of I in space group $P\bar{1}$. Atom's labels do not show for simplicity.

All four NH_4^+ groups are placed in the body center and at a half of the lattice period, forming thus, an own a face-centered sublattice shifted on a half of a lattice period relatively to a face-centered sublattice of M^{3+} cations. The distances $\text{N}\dots\text{OH}_2$ are in the range of 3.028–3.035 Å and the distances $\text{N}\dots\text{O}(\text{sulfate})$ are in the range of 2.608 - 2.708 Å. All four sulfate groups are distributed in two mutually pseudo-reversed orientations. The angles O—S—O formed between two inverted O atoms owing to applied restrictions to the geometry of the sulfate group are closely to 180°. The site occupancy factor for "normal" orientations equal to 0.873(4), 0.876(4), 0.869(4) and 0.874(4). The coordinates of the M^{3+} ions in non-symmetric triclinic space group $P1$ ($Z=8$) do not differ in a range of 3σ from that in cubic space groups $Pa\bar{3}$ and $P\bar{1}$. The $M\text{—OH}_2$ distances vary in a range of 1.920(7)–1.957(7) Å. The coordination angles O—M—O are almost regular. It should be noted that the sum of any two *trans* located M—O distances have almost the equal value, i.e. two *trans*—M—O distances have either closely values or a one shorter distance is located opposite to a longer. In that space group, only four from eight sulfate groups are disordered in two mutually pseudo reversed orientations; other four has a fully ordered orientation having an unit population. There is a visible dispersion in the relative populations of the "normal" orientations of the sulfate groups: 0.791(6), 0.796(6), 0.796(6), 0.829(6) and. The O-S-O angles formed by two opposite located O atoms exhibit a visible deviations from linearity: 156.9(9), 169.4(10), 175.7(9) and 176.8(10). That angles indicate on the fact that O atoms of the "reversed" sulfate groups do not located on the 3-fold rotation axis in space group $Pa\bar{3}$. Because of this the O atoms of the "reversed" sulfate groups have large anisotropic displacement parameters and coordinates with have large standard uncertainties. In space group $P1$, the N atoms of all four ammonium groups do not reveal distinct shifts from their positions as in both $Pa\bar{3}$ and $P\bar{1}$ space groups. However, large standard uncertainties of the coordinates have pointed to the possibility of aslightly disturbance in the positions of these atoms.

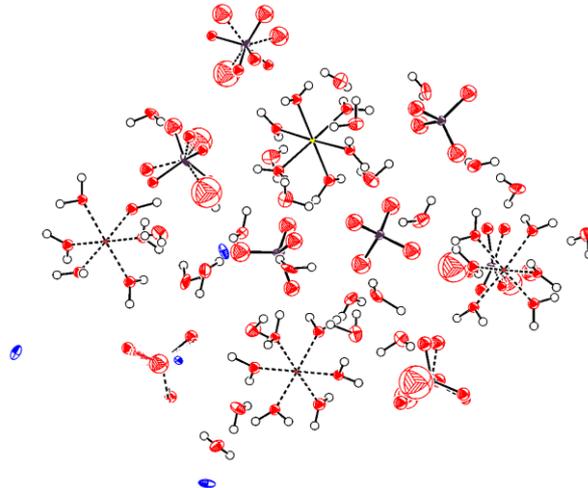


Fig 3 - Crystal packing of I in the space group $P1$. Atom's symbols do not show.

The ammonium groups being between full ordered and disordered sulfate groups may to form either one or no H-bonds with the sulfate groups. One H-bonds may be to form with the O atom of the sulfate group in the "reversed" orientation. If the sulfate group is in "normal" orientation, the ammonium group form no H-bond with the sulfate groups.

Thus, a centrosymmetric surrounding around the ammonium groups may be realized depends on the relative orientations of the sulfate groups around ammonium group.

Six short contacts $N...OH_2$ corresponding to the intermolecular H-bonds indicate on the orientational disorder of the ammonium group. The $N \cdots O$ distances are in the range of 2.962–3.134 Å. The short contacts $N...O(\text{sulfate})$ lie in the range of 2.626–2.769 Å. Because of complexity of the presentation a bulk table of the intermolecular distances and analogy in the motif of the H-bonds architecture in all three space groups, the H-bonding pattern and a short intermolecular contacts are presented only for space group $Pa\bar{3}$ (Fig.2). It is necessary to notice that in all space groups intermolecular short contacts $H...H$ (≈ 2.0 Å) are observed. These short contacts are formed by water molecules coordinated with M^{3+} cation, *i.e.* by the Fe^{3+} and Al^{3+} cations having a different ionic radii. Averaged coordination surrounds of the M^{3+} cation have been deformed and differ from that for each metal cations.

IV. CONCLUSION

Results of the solution and refinement of the crystal structure of $(NH_4)Fe_{0.55}Al_{0.45}(SO_4)_2 \cdot 12H_2O$ in the space groups $Pa\bar{3}, P\bar{1}$ and $P1$ have showed, that:

- the substitution for one other two metal ions in the crystal lattice of the alum solid solution with close ratios led to reduction of the crystal space group symmetry, that appears in the lack of the reflections systematic absence, *i.e.* collected X-ray reflections are characteristic for the triclinic crystal system,
- the $M^{3+}-O$ distance in the coordination polyhedron shown some averaged values, which is more than the usual $Al^{3+}-O$ distance and less than the usual distance $Fe^{3+}-O$, caused by local deformation of the metal environment in the crystal structure,
- the site occupancy factor of the Fe^{3+}/Al^{3+} ions in the space groups $Pa\bar{3}, P\bar{1}$ and $P1$ have a different values,
- some of the sulfate groups in both the triclinic space groups show a different orientations with respect to the noncrystallographic 3-fold axis, for example, part of the sulfate groups in the space group $P1$ are found only in the ordered orientation.

REFERENCES

- [1] Shtukenberg A. G., Euler H., Kirfel A. Symmetry reduction and cation ordering in alum solid solutions. *Zeitschrift für Kristallographie*, 2007, vol.222, no.1, pp.73–82.
- [2] Rozhdestvenskaya I. V., Frank-Kamenetskaya O. V., Shtukenberg A. G., Bannova I. I. Triclinic crystal structure of the birefringence crystal of alum $K(Al_{0.95}Cr_{0.05})(SO_4)_2 \cdot 12H_2O$. *J. Struct. Chem.*, 2001, vol. 42, no. 4, pp.628-638.
- [3] Shtukenberg A. G., Punin Yu. O., Frank-Kamenetskaya O. V. Kinetic ordering and growth dissymmetrization of the crystalline solid solutions. *Russ. Chem. Rev.*, 2006, vol.75, pp.1083-1106.



ISSN: 2350-0328

International Journal of Advanced Research in Science, Engineering and Technology

Vol. 7, Issue 5 , May 2020

[4]Lipson H. The relation between the alum structures.*Proc. R. Soc.*, 1935, vol. A151, pp. 347-356.

[5]Abdeen A. M., Will G., Schafer W., Kirfel A., Bargouth M. O., Recker K., Weiss A.X-ray and neutron diffraction study of alums: II. The crystal structure of methylammoniumaluminium alum III.The crystal structure of ammonium aluminium alum.*Z. Kristallogr.*, 1981, vol.157, no. 1,pp.147-166.

[6]Cromer D. T., Kay M. I., Larson A. C.Refinement of the alum structures. II. X-ray and neutron diffraction of $\text{NaAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, gamma alum.*Acta Crystallogr.*,1967, vol.B22, no. 2, pp.182-187.

AUTHOR'S BIOGRAPHY

<p>Sabirov Vakhobjon Husanovich, Professor of the department "Mathematics and natural science disciplines" of the Almalyk branch of the Tashkent State Technical University named after Islam Karimov, Almalyk, Uzbekistan;</p>	
<p>Irkabaev Djumanali Usmanovich, Head of the department "Mathematics and natural science disciplines" of the Almalyk branch of the Tashkent State Technical University named after Islam ov, Almalyk, Uzbekistan;</p>	
<p>Turdibayev Zhaxongir Eraliyevich, Senior lecturer of the department "Mathematics and natural science disciplines" of the Almalyk branch of the Tashkent State Technical University named after Islam Karimov, Almalyk, Uzbekistan;</p>	
<p>Jumaev Mannon Nafasovich, Assistant of the department "Mathematics and natural science disciplines" of the Almalyk branch of the Tashkent State Technical University named after Islam Karimov, Almalyk, Uzbekistan;</p>	