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ab initio X-ray structure determination of NaAl(SO4)2

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Abstract

The sodium aluminium disulphate $NaAl(SO_4)_2$ has been obtained after calcinations at 300 °C of $NaAl(SO_4)_2.12H_2O$ alum. The structure of this compound has been refined from powder X-ray diffraction data using the Rietveld method. This compound crystallises in trigonal system P 3 2 1 with the following parameters: a = 4.749(12) Å, c = 8.314 (4) Å (Z = 1). The final refinement led to R_F = 6.3 %, R_B = 4.12 %. In the proposed model the sulfate ions is in disorder between two nonequivalent crystallographic sites with probabilities p_1/p_2= 0.30/70. The atomic arrangement of $NaAl(SO_4)_2$ is characterised by two different alternating layers parallel to (001): the first layer is composed of corner-linked AlO_6 octhahedra and SO_4 tetrahedra, the second layer is built from monovalent Na^+.

Key words: Alum; Rietveld method; X-ray powder diffraction; Anhydrous Alum ; disordered structure.

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I. Introduction

The extensive $AB(TO_4)_2$ family where A = monovalent Na, K, Rb, Cs, Ag,NH_4 or divalent Ca, Sr, Ba, B = trivalent Sc, V, Cr, Mn, Fe, Al, Ga, Rh, or tetravalent Mo, Ge, Ti, Zr, Hf, Sn, or pentavalent Ta, and T = hexavalent S, Se, Cr or pentavalent P, As[1-2], is intensively investigated. From a structural point of view, $RbFe(SeO_4)_2$ [3](P321 symmetry and $a_0 = b_0 = 5.005$ Å and $c_0 = 8.548$ Å) can be considered as a reference in this family of compounds. Several type of supergroup are reported in literature, examples: Yavapaiite $KFe(SO_4)_2$, and $NaFe(SeO_4)_2$ [4], and phosphates such as $BaMo(PO_4)_2$ [5], Ba(Hf, Zr)$(PO_4)_2$ [6], all crystallise in the system monoclinic, space group C2/m, the unit cell parameters $a \approx \sqrt{3}\, a_0$, $b \approx b_0$ and $c \approx c_0$. Compounds from other supergroup are selenates like $KMn(SeO_4)_2$ [4]. $CsTa(PO_4)_2$ [7] Crystallise in the system triclinic, space group P -1 the unit cell parameters $a \approx a_0$, $b \approx a_0$ and $c \approx c_0$

The existence of $NaAl(SO_4)_2$ was first reported by Bernard [8](1966), unit cell parameters and space group have been proposed, but this structure has not determined. In this paper we proposed the X-ray determination of the structure by X-ray powder diffraction.

II. Experimental

1- Preparation

Alum $NaAl(SO_4)_2.12H_2O$ crystals were prepared by a slow evaporation of aqueous solutions containing stoichiometric amounts of Na_2SO_4 and $Al_2(SO_4)_3.XH_2O$ salts. The sodium aluminium disulphate $NaAl(SO_4)_2$ has been obtained after calcinations at 300 °C of $NaAl(SO_4)_2.12H_2O$ alum.

X-ray diffraction: the powder X-ray pattern of this compound was collected by using a Siemens D 5001 diffractometer with a monochromated CoKα radiation. Diffraction intensity was measured between 10° and 140°, with a 2θ step of 0.017° for 17s per point. The data was collected at room temperature. Crystalline structure was refined with the Rietveld technique [9] using Fullprof 2009 code [10]. Peak profiles were modelled with pseudo-Voigt functions [11]. The observed intensities as extracted from the X-ray data by the program Fullprof [12].

Thermal analysis

The thermo gravimetric (TG) Netzsch and differential thermal analysis (DTA) were performed in air atmosphere with a thermal analyzer. Measurements were taken from 25 to 400° with a heating rate of 5°/min.

The experimental curve of the thermo gravimetric analysis (TG) and differential thermal analysis (DSC) measurement of $NaAl(SO_4)_2.12H_2O$ are reported in fig1. The $12H_2O$ per formula were confirmed, and several intermediates were revealed, $NaAl(SO_4)_2 8H_2O$, $NaAl(SO_4)_2 4H_2O$ and $NaAl(SO_4)_2$. The anhydrous compound $NaAl(SO_4)_2$ (that can be obtained at 250°C) is instable at room temperature in ambient air.

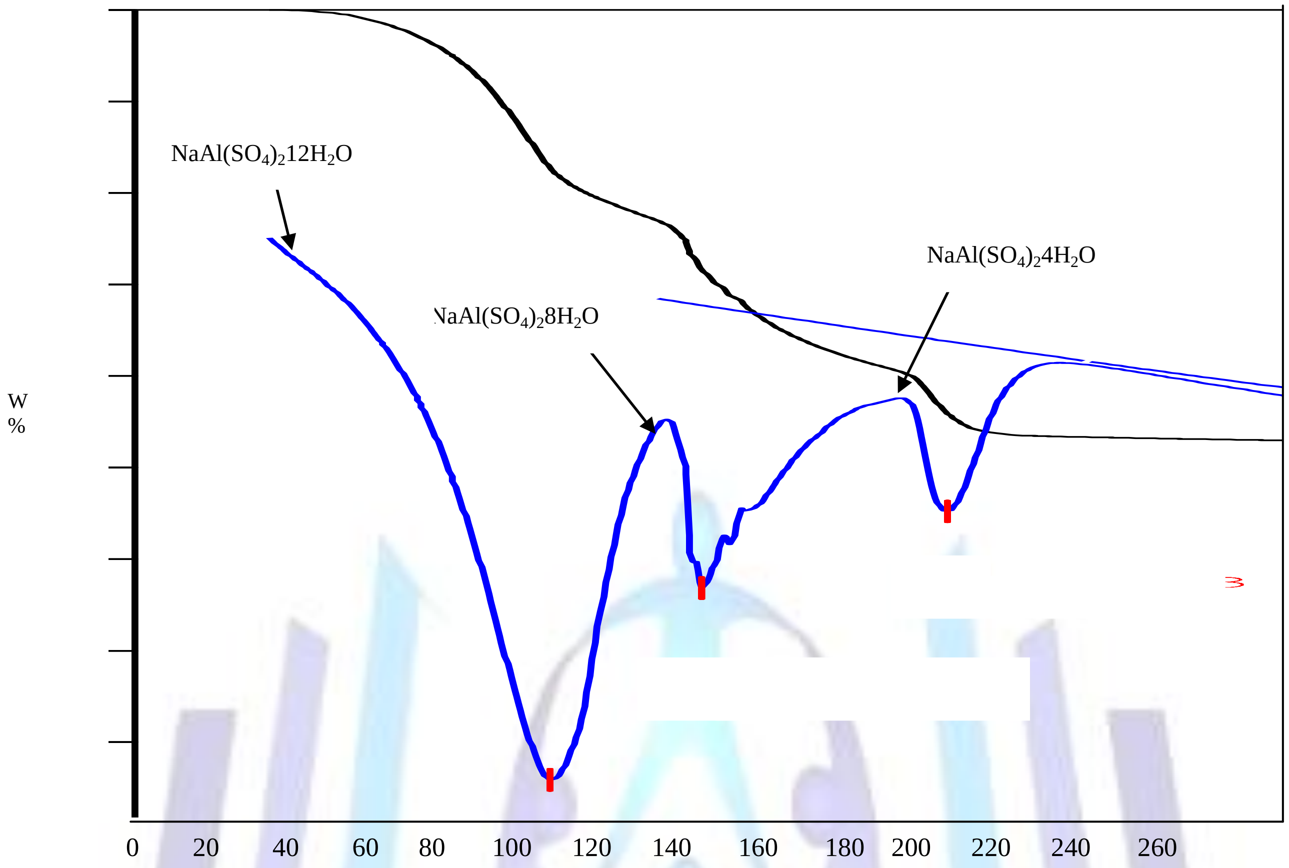


Figure. 1. Differential thermal analysis curves of $NaAl(SO_4)_2.12H_2O$.

III- ab-initio structure determination of $NaAl(SO_4)_2$

A. Structure solution

The alum $NaAl(SO_4)_2$ compound is characterized by space group P 3 2 1 and has the trigonal, anhydrous alum type structure. The cell constants and atomic parameters of the starting model were taken from the X-ray structure determination of the pure potassium alum $KAl(SO_4)_2$ [13], space group P 3 2 1. After refinement, the structural model indicators converged to $R_p = 0.15$ and $R_{WP} = 0.16$, with a high thermal parameter of the O2 and a characteristic difference is obtained between observed and calculated intensities of the (300) reflection (fig. 2a). The large *B* value of O2 led us to suppose that this site is partially occupied. The refinements of occupancy site 4e of oxygen atoms show 50% occupation of these sites. A difference Fourier applied to the observed intensities (extracted from the X-ray data by the program FULLPROF (Le Bail method)) using SHELXL-97 [11] was carried out to check a possible oxygen atom positions C3 at approximately 1.6 Å from sulfur at (0.6, 0.95, 0.35) O3. Suggest the existence of disordered sulfate ions in this structure. After refinement, the occupancies of O2 and O3 are respectively 70% and 30%. The final refinement gave a much better description of the (300) peak shape (fig. 2b). Generally, the effect of the disordered structure was an improvement of the fit to the diffraction peaks (fig. 3) and lowering of Rp and Rwp by 0,189 / 0.188 to 0,14/0,14.

Fig. 3 shows the powder X-Ray diffraction pattern and the difference between the calculated and the observed pattern. The crystallographic parameters and atomic coordinates are presented in table 1 and 2. Final atomic coordinates, isotropic displacement parameters, bond distances and angles are reported in table 3. Projection of the structure is set in Fig 4.

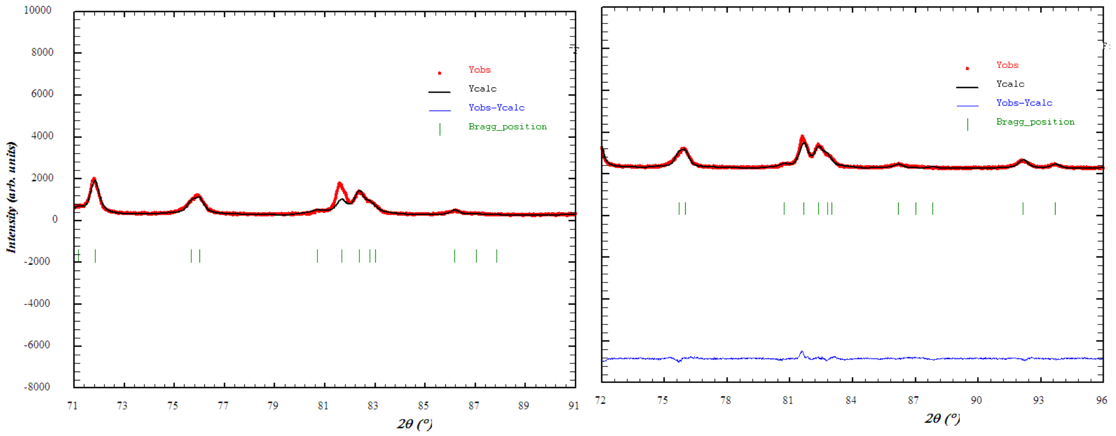


Figure.2. Experimental data and the fit through X-ray powder diffraction spectra around the (300) reflexion taken from Rietveld refinement of the ordinate structure (a) leading to Rp = 0.19 for the complete pattern. (b) With old disordered structure, leading to Rp = 0.14

B. Structure description

The view of the structure along the a-axis in fig. 4 visualises the two possible orientations of SO_4^{2-}. In the two configurations, the atomic arrangement can be described in term of two different layers parallel to (001): the first layer is composed of corner-linked AlO_6 octahedra and SO_4 tetrahedra, with $[Al(SO_4)_2]^-$ formulation, which alternates with a second layer built on ion Na^+. Thus the individual layers are joined along the c axis by the interaction between monovalent atoms Na^+ and the O1 top oxygens of the tetrahedra in are layer that point down with those in the next layers which point up and so forth.

The corner-linkage between AlO_6 octahedral and SO_4 tetrahedral in both compounds is topologically identical to ZrO_6-PO_4 layer in some Zirconium phosphates $KZr_2(PO_4)_3$[14], $Zr_2(NaPO_4)_4.6H_2O$[15] $ZrMH(PO_4)_2$, where M = K or Na [16]. The ,α-$Zr(HPO_4)_2.H_2O$[17], and Na Al $Zr(PO_4)_2(OH)_2.H_2O$[18].

In first S-O_4 Tetrahedral(p_1= 0.70), the average S-O_4 distance is (1.496 Å; values range from 1.467 to 1.584 Å) , the angle of the base oxygen, sulphur and the top oxygen is 110,6and that of the base oxygen, sulphur and base oxygen is 105,1°. In the second S-O_4 Tetrahedral (30%), the average S-O distance is 1.577 Å; ranges from 1.575 to 1.584 Å. The angle formed by O_1-S-O_2 is 105,1and that of the O_2-S-O_2 is 113,4° (table 3). In $KAl(SO_4)_2$, the S-O distance range from 1.431 to1.442 Å, and the angle formed by the top oxygen sulfur and base oxygen is 110 and that of the base oxygen and sulfur is108,94° (Table 2).

The distance between aluminium and oxygen is 2.018(1) Å in the first orientation and Al-O bond length is 1.8(3) in the second. In the pure potassium KAl $(SO_4)_2$ [15] the Al-O bond length is 1.909(1) (Table 3).

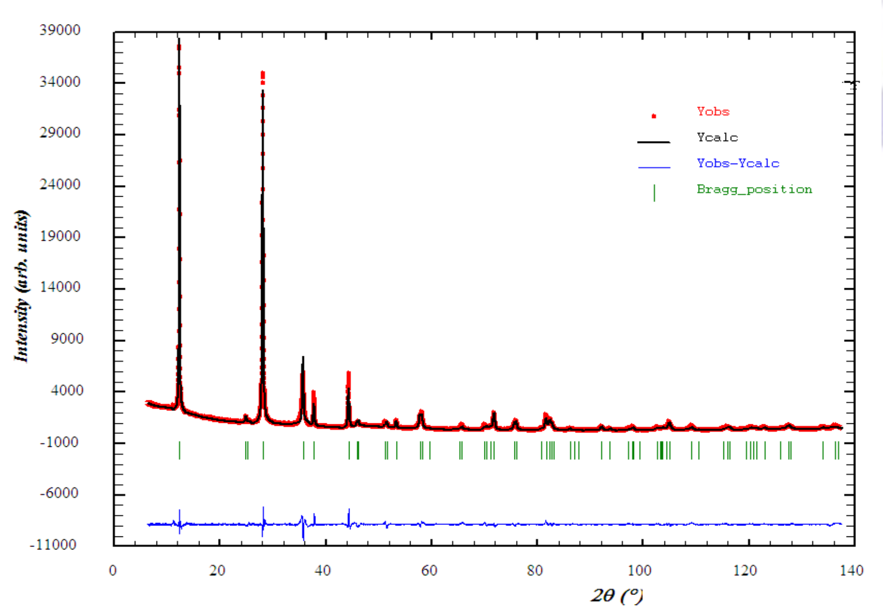


Figure. 3: Observed, calculated and difference curve of $NaAl(SO_4)_2$

Table 1: Conditions of X-ray data collection and crystallographic characteristics of $NaAl(SO_4)_2$

	$NaAl(SO_4)_2$
Diffractometer	Siemens D 5001
Radiation	Cobalt
Angular range [°2θ]	5-140
Step scan increment [°2θ]	0.017
Count time [sec/step]	17
Miscellaneous	Room temperature
Space group	P 3 2 1
Cell parameters	a = 4.749(19) c = 8.306(9)
Volume (Å), Z	162.249(6), Z = 1
Number of reflections	104
Number of refined parameters	23
Halfwidth parameters	U = 0.0592(2), V = 0.2175(3), W = 0.0009(3)
Zero point	0.1403(4)
Reliability factors	R_B = 4.124, R_F =6.334, $R_{p\,=}$ 15.3 $R_{wp\,=}$ 16

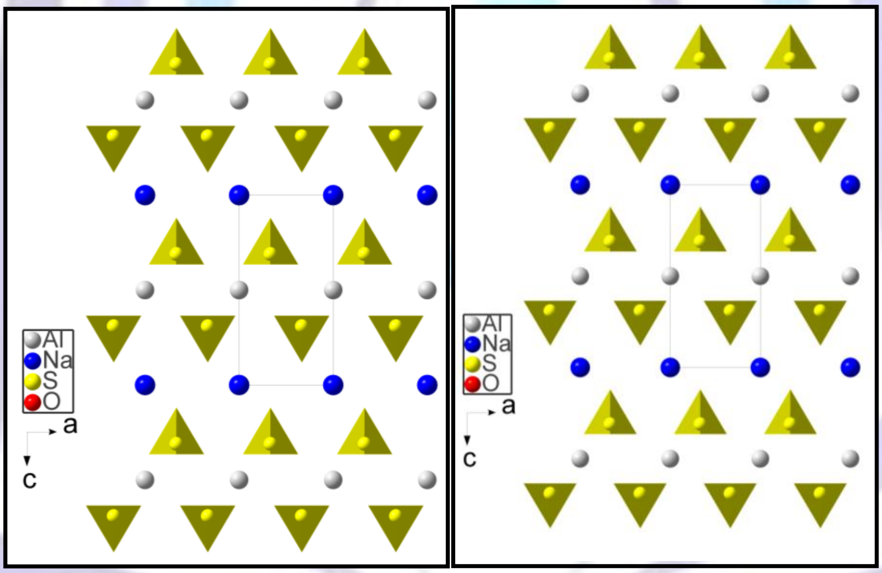
Table2: Selected bond distances (Å) and angles (°) in $NaAl(SO_4)_2$ for the two orientations possible of SO_4^{2-}

70%	30%
SO_4 tetrahedron S—O_1 1.584(5) S—O_3 ×3 1.575(5) O2—S—O2 ×2 113.40(1) O1—S—O2 105.10(2) AlO_6 octahedron Al—O ×6 1.800(5)	SO_4 tetrahedron S—O_1 1.584(5) O3—S—O3 ×2 110.6(1) O3—S—O1 ×2 108.2(2) AlO_6 octahedron Al—O3 ×6 2.018(1)

Table 3. The refined structural parameters for $NaAl(SO_4)_2$ and equivalent isotropic displacement parameters

Atomes	X	Y	Z	Biso($Å^2$)
Al	0	0	0.5	0.0695(16)
Na	0	0	0	0.395(8)
S	1 /3	2 / 3	0.3098(4)	0.0391(10)
O_1	1 / 3	2 / 3	0.1191(5)	0.0241(10)
O_2*	0.253(11)	0.939(14)	0.3593(7)	0.0241(10)
O_3*	0.628(3)	0.959(4)	0.3651(18)	0.0241(10)

* rate of occupation(O_2 = 70% . O_3 = 30% for the Rietveld refinement of $NaAl(SO_4)_2$



P = 70 %

P = 30%

Figure 4: Projection of the $NaAl(SO_4)_2$ disordered structure in the (011) plan, showing the two possible orientation of SO_4^{2-} tetrahedral

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