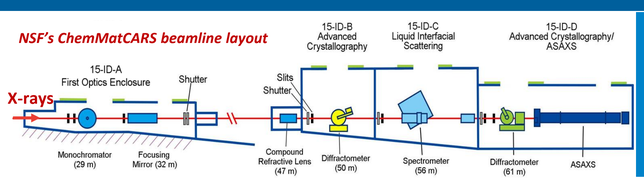
ESRP: Determination of the Effect of Temperature on Potassium Aluminum Sulfate



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ABSTRACT

Potassium aluminum sulfate, ($AlK(SO_4)_2{\cdot}12H_2O$), is an inorganic salt produced in the dodecahydrate form [11]. Potassium aluminum sulfate has an octahedral crystalline shape caused by the formation of its crystal lattice through its cations (K^+ and Al^{3+}) and anions (SO_4^{2-}). Using the APS, the crystalline system was determined to be cubic, with a space group of Pa-3. Temperature studies (250 K to 100 K) were performed to determine the effect of temperature on the bond length and volume of the ions in the unit cell. It was determined that as the temperature increased, the bond length and volume also increased in a linear model. Study of the effect of cation replacement on this compound has been limited. A tertiary purpose of this study was to determine if cation replacement of the Al^{3+} by other 3+ cations, specifically Cr^{3+}, results in different crystalline structures. In potassium aluminum sulfate, the aluminum was replaced with chromium (3+), and the possible changes in the structure, symmetry, and space group was attempted. The chromium 3+ cation is in period 4 of the periodic table, whereas aluminum is in period 3, suggesting the structure of the potassium aluminum crystal would change because of the different sizes of the cations. Potassium chromium sulfate has a hexagonal structure [3], differing from its cation partner potassium aluminum sulfate. The Sector 15 NSF's ChemMatCARS at Advanced Photon Source (APS) has played an important role in recent scientific advancements, and the Advanced Crystallography Program can illuminate small crystal samples to determine the crystal structure at atomic resolution level. Due to difficulties in the synthesis of the potassium chromium sulfate, the effect on the structural changes due to the change in cation was not determined. In this poster, only ($AlK(SO_4)_2{\cdot}12H_2O$) data have been presented. In addition, a temperature study (250 K to 100 K) was performed to understand the linear thermal expansion phenomenon in the crystalline.

BACKGROUND & PURPOSE

A crystal is an accumulation of matter that forms into a 3-dimensional figure with multiple variations and arrangements of ions, atoms, and molecules [4]. There are 7 types of crystal systems noted that form during the crystal growing process: cubic, tetragonal, orthorhombic, rhombohedral, hexagonal, monoclinic, and triclinic. The differentiation between each crystal is determined through the lattice parameters (Figure 1). The symmetry of the crystal is determined by the systematic absence of Miller Indices (Figure 2). A crystal can form into various shapes as there are over 230 space groups (the symmetrical 3D configuration groups a crystal can form into) [5]. Crystallography studies the patterns and structures of different crystals and their forms [13]. Crystal structures can be resolved and understood through the study of crystallography and using X-rays to understand diffraction patterns [6]. Crystal structures are extremely important to crystallography as they allow for atoms and molecules to be understood in different forms and allow scientists to understand the structures and workings of other molecules and matter [8, 15,16].

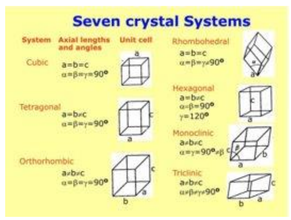


Figure 1. Seven crystal systems

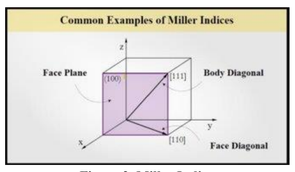


Figure 2. Miller Indices

The purpose of this study is primarily to determine the crystalline structure of potassium aluminum sulfate at 250 K. A secondary goal is to observe the effect of temperature change on the bond length and volume of the unit cell. As temperature is decreased from 250 K to 100 K, it is likely that the increase in kinetic energy of the ions would affect the structure. A tertiary purpose is to determine the effect of the crystalline structure if the Al^{3+} is replaced with other 3+ cations such as Cr^{3+}. Since aluminum is in period 3 and chromium is in period 4 of the periodic table, chromium is a smaller cation as compared to aluminum. Since the aluminum and chromium sulfate compounds being studied are ionic substances, it seems reasonable to see a difference if the 3+ cation is a difference size.

RESULTS

Table 1 Crystal data and structure refinement for Potassium Aluminum Sulfate

Identification code	100K	150K	200K	250K
Empirical formula	$Al_{0.5}H_{12}K_{0.5}O_{10}S$	$Al_{0.5}H_{12}K_{0.5}O_{10}S$	$Al_{0.5}H_{12}K_{0.5}O_{10}S$	$Al_{0.5}H_{12}K_{0.5}O_{10}S$
Formula weight	237.2	237.2	237.2	237.2
Temperature/K	100(1)	150(1)	200(1)	250(1)
Crystal system	Cubic	Cubic	Cubic	Cubic
Space group	Pa-3	Pa-3	Pa-3	Pa-3
a/Å	12.1281(5)	12.1375(3)	12.1467(5)	12.1587(4)
b/Å	12.1281(5)	12.1375(3)	12.1467(5)	12.1587(4)
c/Å	12.1281(5)	12.1375(3)	12.1467(5)	12.1587(4)
α/°	90	90	90	90
β/°	90	90	90	90
γ/°	90	90	90	90
Volume/Å^3	1783.9(2)	1788.08(13)	1792.2(2)	1797.47(18)
Z	8	8	8	8
ρ_{calc}g/cm^3	1.766	1.762	1.758	1.753
μ/mm^{-1}	0.16	0.159	0.159	0.159
F(000)	992	992	992	992
Crystal size/mm^3	0.1 × 0.06 × 0.04	0.1 × 0.06 × 0.04	0.1 × 0.06 × 0.04	0.1 × 0.06 × 0.04
Radiation	Synchrotron	Synchrotron	Synchrotron	Synchrotron
Wavelength/Å	λ = 0.41328	λ = 0.41328	λ = 0.41328	λ = 0.41328
2Θ range for data collection/°	3.382 to 34.328	3.38 to 34.3	3.378 to 34.332	3.374 to 34.298
Index ranges	-17 ≤ h ≤ 17, -16 ≤ k ≤ 17, -17 ≤ l ≤ 17	-17 ≤ h ≤ 17, -16 ≤ k ≤ 17, -17 ≤ l ≤ 17	-17 ≤ h ≤ 17, -16 ≤ k ≤ 17, -17 ≤ l ≤ 17	-17 ≤ h ≤ 17, -17 ≤ k ≤ 16, -17 ≤ l ≤ 17
Reflections collected	54015	55517	55379	55655
Independent reflections	918 [R_{int} = 0.0736, R_{sigma} = 0.0136]	918 [R_{int} = 0.0604, R_{sigma} = 0.0112]	922 [R_{int} = 0.0740, R_{sigma} = 0.0156]	922 [R_{int} = 0.0721, R_{sigma} = 0.0142]
Data/restraints/parameters	918/0/71	918/0/71	922/0/71	922/0/71
Goodness-of-fit on F^2	1.117	1.088	1.125	1.127
Final R indexes [I>=2σ (I)]	R_1 = 0.0165, wR_2 = 0.0530	R_1 = 0.0155, wR_2 = 0.0495	R_1 = 0.0172, wR_2 = 0.0552	R_1 = 0.0191, wR_2 = 0.0614
Final R indexes [all data]	R_1 = 0.0175, wR_2 = 0.0533	R_1 = 0.0168, wR_2 = 0.0501	R_1 = 0.0185, wR_2 = 0.0564	R_1 = 0.0208, wR_2 = 0.0626
Largest diff. peak/hole /eÅ^{-3}	0.24/-0.27	0.23/-0.26	0.21/-0.28	0.29/-0.23

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Potassium aluminum sulfate. Ueq is defined as 1/3 of the trace of the orthogonalised U_{ij} tensor

	100K				150K			
Atom	x	y	z	U(eq)	x	y	z	U(eq)
K1	5000	5000	5000	19.65(12)	5000	5000	5000	25.85(12)
Al1	5000	0	5000	7.96(12)	5000	0	5000	9.76(12)
O1	4797.6(5)	1519.4(4)	4788.6(4)	13.32(13)	4801.4(4)	1519.2(4)	4792.3(4)	15.83(12)
O2	6306.0(5)	3041.6(4)	4526.6(5)	16.29(14)	6310.7(5)	3038.6(4)	4529.8(5)	20.30(14)
S1A	3056.4(14)	3056.4(14)	3056.4(14)	7.8(5)	3070(3)	3070(3)	3070(3)	11.4(5)
O3A	3058.4(6)	2631.0(6)	4200.5(6)	16.7(2)	3064.8(5)	2630.5(6)	4198.6(6)	21.9(2)
O4A	2359.7(7)	2359.7(7)	2359.7(7)	21.3(3)	2363.4(7)	2363.4(7)	2363.4(7)	28.1(3)
S1B	3077(5)	3077(5)	3077(5)	14(2)	3036(11)	3036(11)	3036(11)	11.6(19)
O3B	2805.4(19)	1993.5(17)	3614.7(18)	11.9(6)	2811.6(19)	1999.5(18)	3616.7(19)	16.9(6)
O4B	3749.0(17)	3749.0(17)	3749.0(17)	15.9(8)	3747.4(18)	3747.4(18)	3747.4(18)	23.4(9)
H1A	4201(13)	1801(12)	4590(13)	44(4)	4206(12)	1800(11)	4589(12)	44(4)
H1B	5348(13)	2014(12)	4720(13)	44(4)	5355(13)	2017(11)	4724(12)	45(4)
H2A	6589(13)	2980(12)	3906(14)	32(3)	6582(13)	2974(12)	3901(14)	49(4)
H2B	6831(11)	2903(12)	4957(12)	43(4)	6831(11)	2889(11)	4952(12)	36(3)
	200K				250K			
Atom	x	y	z	U(eq)	x	y	z	U(eq)
K1	5000	5000	5000	32.31(15)	5000	5000	5000	38.93(17)
Al1	5000	0	5000	12.01(13)	5000	0	5000	14.86(15)
O1	4804.7(5)	1519.3(4)	4795.5(5)	19.03(14)	4808.5(6)	1518.9(5)	4798.4(5)	23.13(16)
O2	6317.6(5)	3034.6(5)	4532.0(6)	25.32(16)	6326.6(6)	3030.3(6)	4533.9(7)	31.38(19)
S1A	3079(4)	3079(4)	3079(4)	13.9(5)	3056(4)	3056(4)	3056(4)	18.8(8)
O3A	3073.3(6)	2633.8(8)	4200.0(7)	28.0(3)	3084.2(8)	2638.6(11)	4203.1(9)	35.9(4)
O4A	2370.7(8)	2370.7(8)	2370.7(8)	36.3(4)	2379.6(10)	2379.6(10)	2379.6(10)	46.9(6)
S1B	3020(14)	3020(14)	3020(14)	14.7(18)	3110(13)	3110(13)	3110(13)	15.7(13)
O3B	3749(2)	3749(2)	3749(2)	34.3(12)	2832(3)	2022(2)	3630(3)	33.9(9)
O4B	2818(2)	2009(2)	3625(2)	24.1(7)	3752(2)	3752(2)	3752(2)	50.7(16)
H1A	4231(13)	1792(12)	4593(13)	45(4)	4234(15)	1786(14)	4592(15)	50(4)
H1B	5363(14)	2023(13)	4733(14)	48(4)	5364(16)	2011(14)	4719(15)	51(4)
H2A	6585(15)	2975(13)	3913(16)	52(4)	6590(17)	2978(15)	3914(19)	61(5)
H2B	6830(12)	2882(13)	4944(13)	39(4)	6836(14)	2888(15)	4930(15)	48(5)

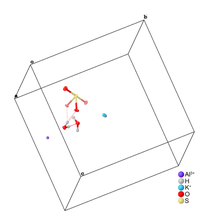


Figure 6. Molecule in asymmetric unit

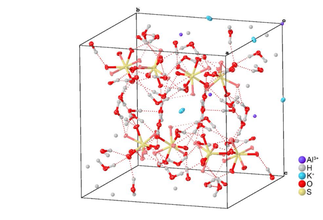


Figure 7. Molecules in one unit-cell
Potassium Aluminum Sulfate is a cubic structure with bond lengths ranging from 1.464 Å to 2.9120 Å in 4 temperatures' crystal structure results are shown in Table 3.

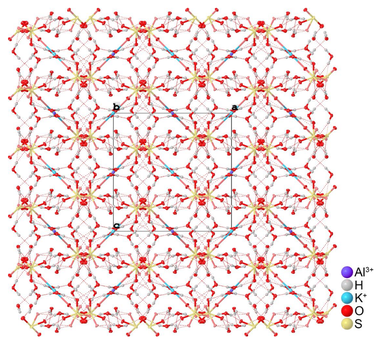


Figure 8. Packing diagram. This structure shows when Potassium Aluminum Sulfate is "packed" within Olex2, creating a larger and more complex structure compared to the original.

Table 3 Selected Bond Lengths for Potassium Aluminum Sulfate

	100K	150K	200K	250K
Atom	Length/Å			
K1-O2	2.9120(6)	2.9196(5)	2.9298(6)	2.9425(8)
K1-O4B	2.628(4)	2.633(4)	2.633(4)	2.629(5)
Al1-O1	1.8766(5)	1.8766(5)	1.8771(5)	1.8775(6)
S1A-O3A	1.4804(12)	1.485(7)	1.491(9)	1.484(4)
S1A-O4A	1.464(3)	1.470(2)	1.465(3)	1.425(10)
S1B-O3B	1.503(4)	1.49(2)	1.53(3)	1.505(11)
S1B-O4B	1.412(10)	1.468(8)	1.452(9)	1.35(3)

Table 4 Selected Bond Angles for Potassium Aluminum Sulfate

	100K	150K	200K	250K
Atom	Angle/°			
O2^1-K1-O2^2	112.959(9)	113.044(9)	113.141(10)	113.264(13)
O2^1-K1-O2	67.042(9)	66.957(9)	66.858(10)	66.736(13)
O4B-K1-O2^1	105.706(11)	105.606(11)	105.491(12)	105.344(15)
O4B-K1-O2	74.293(11)	74.393(11)	74.509(12)	74.656(15)
O4B-K1-O4B^2	180.00(8)	180.00(8)	180.00(9)	180.00(10)
O1^7-Al1-O1	89.31(2)	89.34(2)	89.37(2)	89.44(3)
O1^{10}-Al1-O1^6	180.00(3)	180.00(2)	180.00(3)	180
O1^6-Al1-O1	90.69(2)	90.66(2)	90.63(2)	90.56(3)
O3A^5-S1A-O3A	109.01(11)	109.0(2)	110.2(3)	111.0(3)
O4A-S1A-O3A	109.93(11)	109.0(2)	108.7(3)	107.9(4)
O3B-S1B-O3B^4	106.4(4)	109.0(9)	107.1(11)	105.5(11)
O4B-S1B-O3B	112.4(4)	110.0(9)	111.8(10)	113.2(9)
S1B-O4B-K1	180.0(4)	180.0(6)	180.0(5)	180.0(16)

[1]1-Y,1-Z,1-X; [2]1-X,1-Y,1-Z; [3]1-Z,1-X,1-Y; [4]+Z,+X,+Y; [5]+Y,+Z,+X; [6]1/2+Y,1/2-Z,1-X; [7]+Z,1/2-X,1/2+Y; [8]1-Z,-1/2+X,1/2-Y; [9]1-X,-Y,1-Z; [10]1/2-Y,-1/2+Z,+X

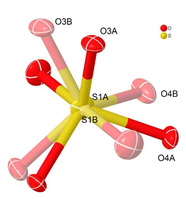


Table 5 Atomic Occupancy for Potassium Aluminum Sulfate

	100K	150K	200K	250K
Atom	Occupancy			
S1A	0.7721(19)	0.781(2)	0.768(2)	0.740(3)
S1B	0.2278(19)	0.219(2)	0.232(2)	0.260(3)
O3A	0.7721(19)	0.781(2)	0.768(2)	0.740(3)
O3B	0.2278(19)	0.219(2)	0.232(2)	0.260(3)
O4A	0.7721(19)	0.781(2)	0.768(2)	0.740(3)
O4B	0.2278(19)	0.219(2)	0.232(2)	0.260(3)

Figure 9. Disordered sulfate group. Different colors show different sulfate groups in each disorder position.
It is not uncommon for real crystals to have defects, but a crystal is considered to be disordered if the crystal lattice is able to accommodate various components. Competing environmental conditions is the main cause of a crystal being disordered.

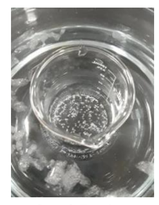
PROCEDURE

Synthetic method:

Potassium aluminum sulfate was synthesized by reacting sulfuric acid with aluminum foil at room temperature 20°C. Potassium hydroxide was added to the solution and the crystals were filtered and allowed to air dry (Figure 3). Potassium chromium sulfate was synthesized by dissolving potassium dichromate in distilled water, heating until the dichromate dissolved, adding sulfuric acid, then dropwise adding ethanol until a deep purple was obtained. The crystals were then filtered and air dried (Figure 4).

Figure 3. Synthesis of Potassium Aluminum Sulfate

Reaction of aluminum and sulfuric acid

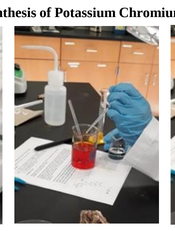


Crystals Forming

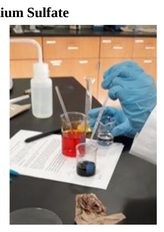
Filtering Crystals

Figure 4. Synthesis of Potassium Chromium Sulfate

Dissolution of Dichromate in Water



Addition of Sulfuric Acid



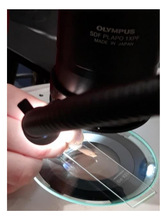
Addition of Ethanol

Single Crystal X-ray Diffraction:

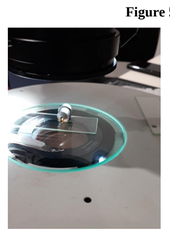
Crystal holders (glass fiber tips) were formed through a tiny glass rod, using the coil and gravity to pull fine tips of glass fiber. Using a microscope, transparent crystal was cut with size of 100×60×40 μm^3 and mounted on the fiber tip (Figure 5). The single crystal diffraction data collection was performed using a Huber 3-circle (Phi, Kappa, Omega) diffractometer at the temperatures of 250 K, 200 K, 150 K and 100 K, respectively. At each temperature, the data was collected using Phi-scan with 0.5° and 1s exposure time for each frame, with Kappa at 0° and 30°, respectively. Total 1440 frames were collected, and the data was indexed and integrated using Bruker APEX3 Suite [2]. The absorption correction for the integrated raw data was performed using SADABS [10]. The space group determination was using XPREP [11]. Finally, the modeling of the crystal structure was carried on with Olex2 [4].

Figure 5. Sample Prep

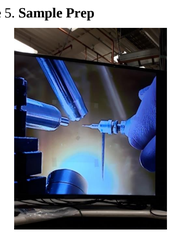
Preparing glass fiber



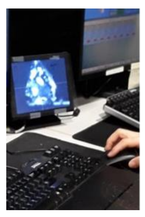
Cutting sample to proper size



Crystal Mounted on holder



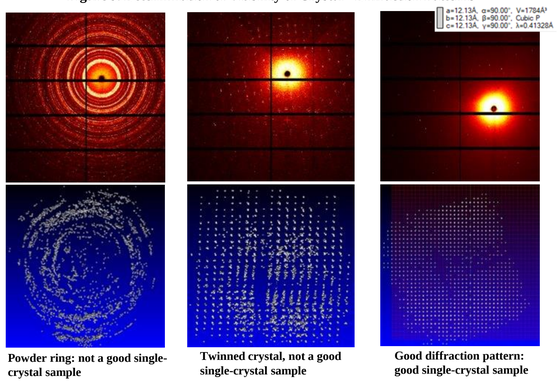
Mounting crystal on the diffractometer



Centering Crystal

DISCUSSIONS & CONCLUSIONS

Figure 9. Determination of Viability of Crystal - Diffraction Patterns



Powder ring: not a good single-crystal sample

Twinned crystal, not a good single-crystal sample

Good diffraction pattern: good single-crystal sample

This study investigated potassium aluminum sulfate in multiple aspects. Initially the diffraction patterns were observed to determine if a viable single crystal sample was used as seen in Figure 9. Too much scattering indicated either the sample was a powder or not a single crystal. In this case another crystal sample was needed for analysis.

The primary purpose was to determine the crystalline structure of the ionic compound. From Table 1, it was seen that the crystal system is cubic with a space group of Pa-3, indicating a Bravais primitive lattice [12]. Figures 6 and 7, illustrate the cubic shape and a body centered structure with aluminum as the center. The values for α = β = γ = 90°. From Figure 8, the repeated arrangement shows translational symmetry.

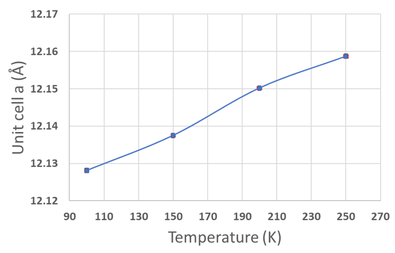


Figure 10. Unit cell vs temperature

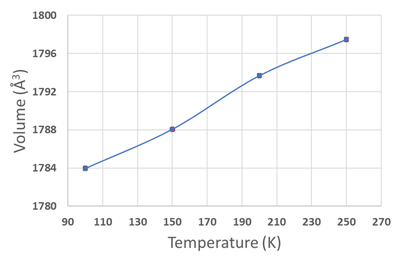


Figure 11. Volume vs temperature

The secondary purpose was to investigate the effect of temperature change on the unit cell. Temperature studies ranged from 250 K to 100 K in increments of 50 K. As can be seen from Table 1 and Figures 10 and 11, the lattice parameters (*a*, *b*, *c*) increased from 12.1281 Å to 12.1587 Å and the volume increased from 1783.9 Å^3 to 1797.43 Å^3. As temperature increases, the kinetic energy of the ions in the compound increases resulting in the ions moving further away from each other as demonstrated by the increase in the bond length and volume. From Table 1, the goodness-of-fit (GoF on F^2) ranged from 1.117 to 1.127 with values that are close to one, indicating that the crystalline model fits the data very well.

The tertiary purpose was to investigate the effect of cation replacement of Al^{3+} by Cr^{3+} to determine if the size of the 3+ cation affects the bond lengths and structure. The results were inconclusive since there were difficulties in the synthesis of the potassium chromium sulfate. Appropriately sized single crystals could not be obtained. The crystals seemed to be wet resulting in multiple water molecules being observed. In several runs, the structure did not indicate a chromium ion. In a single trial, that had an acceptable diffraction pattern, the structure was monoclinic, which is different from the potassium aluminum sulfate which indicates a possible effect. This needs further study to confirm.

FUTURE PLANS

In light of the issues with the results of the Cr^{3+} replacement synthesis, a next step would be to do more research into other syntheses to create an appropriate crystal which will yield results in proper crystalline form with the correct color and atomic arrangement. During the preparation of the potassium chromium sulfate, there was an issue with the proportions of ethanol and the dichromate used that caused a malformation of crystals and resulted in dichromate reformation. This can be solved by using different starting materials or different proportions of ethanol to dichromate. Another possibility would be the synthesis of compounds where the Al^{3+} would be replaced by Ni or Fe. The theoretical compounds would preferably be KFe^{3+}or KNi^{3+}, bonded to a hydrated double sulfate and grown in lab conditions from solution. The materials could include sulfuric acid to supply the sulfates, potassium ferricyanide for the iron compound, or K_2Ni^{2+} for the nickel compounds.

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