In Search of the True Structure of the Sodium Chromium Alum: Crystal Growth and Structure of the Double Salt $NaCr(SO_4)_2(H_2O)_6$

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The cubic structure of the sodium chromium alum $[NaCr(SO_4)_2(H_2O)_{12}]$ has been published in 1968 with a lattice parameter a which is by 0.17 Å larger than the one of the potassium chromium alum. In order to investigate this "lattice parameter anomaly", the growth of Na-Cr alum crystals was attempted with the aim to re-determine their structure. However, instead of cubic alum crystals, monoclinic crystals of composition $NaCr(SO_4)_2(H_2O)_6$ were obtained. Their structure consists of one-dimensionally infinite $[Na(SO_4)_2]^{3-}$ chains and "isolated" $[Cr(H_2O)_6]^{3+}$ complexes, held together by electrostatic attraction and numerous hydrogen bonds. The compound is erroneously addressed as the sodium chromium alum in the Powder Diffraction File PDF-2.

Key words: Chromium Alums, Double Salt, Crystal Growth, Crystal Structure

Introduction

As a "lattice parameter anomaly" (LPA) we define a case where one or more of the crystallographic lattice parameters a, b, c in a "crystal-chemically isotypic series" [1] *de*creases while the atomic size of the variable chemical element in the series *in*creases. Two such anomalies can be found (and have been rationalized) in the series BiSX (X = Cl, Br, I) [1] and AEO_2 [E = Sb, Bi (for A = K, Rb, Cs)] [2]. In order to find more LPAs, the 2008/1 version of the Inorganic Crystal Structure Database ICSD [3a] was systematically searched for such cases by the FORTRAN program FINDIS [4, 5]. One of the numerous LPAs retrieved affects the cubic lattice parameter of the alkali chromium alum series $ACr(SO_4)_2(H_2O)_{12}$ (A = Na, K, Rb, Cs) (Table 1). The published single-crystal value for a(Na-Cr alum) [6] is by 0.17 Å larger than that of a(K-Cr alum) [7]. (Note: in this work the term "alum" is used exclusively for the *dodeca*hydrates of the corresponding double salts).

FINDIS retrieved also a similar, though less pronounced, LPA for the Na-Al and K-Al alums with a(Na-Al alum) = 12.21 [8] and a(K-Al alum) = 12.16 Å [7]. In this case, a quick "excuse" for the anomaly can be found in the fact that there are small differences in the structures of the two isotypic compounds: the Na-Al alum is, by the orientation and coordination of the different building blocks, a "γ-alum", while the K-Al alum is an α-alum [9]. In the case of the two chromium alums, however, this reasoning does not hold, as both have been classified as α-alums. Therefore another explanation had to be sought here.

A closer look at the different A-Cr alum structures in the ICSD [3b] revealed that the structure model of $NaCr(SO_4)_2(H_2O)_{12}$ [6], obtained from 2D Weissenberg data, shows, besides the large lattice parameter comparable to the one of the Cs-Cr alum (Table 1), some shortcomings (according to modern standards) like high R value (0.165), missing standard deviations and severely distorted octahedral coordination for the Cr hexaquo complex (O–Cr–O (*cis*) = 78 and 102°). Thus, before trying to explain the lattice parameter anomaly, we decided to first re-determine the structure of the Na-Cr alum which meant, in the first instance, to grow crystals of the compound.

The Na-Cr alum is mentioned several times in the literature (*e. g.* in refs. [10 – 13]). In a number of cases the information given is restricted to the statement that the compound resp. crystals of it could not be obtained

FINDIS program output					Explanation
KAl(SO4)2(H2O)12		(K Al H24 S2 O20)			structure type
1	[Na K Rb Cs]	Cr H24 S2 O20			1st retrieved isotypic series of this type
	36082	280552	280320	201211	ICSD reference codes ("best" structures)
	1968	2000	2000	1981	publication years
	X C	X C	X C	X C	all structures are X-ray and single-crystal
	0.2000	0.0465	0.0424	0.0320	R values, 0.20 = 'not given'[a]
	Pa-3	Pa-3	Pa-3	Pa-3	space groups
	12.400	12.231	12.296	12.413	lattice parameters a (Å)
		-0.17	0.07	0.12	$\Delta a = a_{n+1} - a_n$
			-0.4	1.8	$\Delta a_{m+1}/\Delta a_m$

[a] Actually specified as 0.165 in ref. [6].

Table 1. The isotypic alkali chromium alum series as retrieved from the ICSD [3a] by FINDIS [4], plus explanations for the meanings of the different rows.

(*e. g.* refs. [14, 15]) or may be unstable [16]. On the other hand, there is the (although questionable) single-crystal structure in the ICSD as well as an experimental powder pattern assigned to the Na-Cr alum in the Powder Diffraction File PDF-2 [17]. From this pattern, a cubic a of 12.12 Å was derived (see also ref. [18]), a value which would fit much better into the series of a values in Table 1 (but see below).

No information regarding the synthesis and crystal growth is given for the single-crystal structure analysis of the Na-Cr alum [6]. In the powder case the standard procedure for the synthesis of chromium alums had been used: reduction of A_2CrO_4 in sulfuric acid, usually by ethanol, in this case by SO_2 at a temperature below 5 °C, and with A = Na [17]. Based on information given in ref. [13], we used another approach in the attempt to synthesize the Na-Cr alum: crystallization from solutions of $Na_2SO_4/Cr_2(SO_4)_3(H_2O)_x$ mixtures in a water/methanol solvent. See Experimental Part for details.

Results and Discussion

Instead of cubic alum crystals our crystallization experiments yielded bunches of thin pale violet crystalline platelets (Fig. 1) which turned out to belong to the monoclinic crystal system. A structure analysis showed them to consist of the title compound, $NaCr(SO_4)_2(H_2O)_6$, with a composition very similar to that of the expected alum but containing only 6 water molecules per formula unit, instead of 12. The existence of a compound of this composition has been postulated from the results of thermodynamic investigations [12]. The powder diffractogram of our monoclinic crystals as well as a theoretical diffractogram calculated from the single-crystal structure both match the experimental PDF-2 pattern which – erroneously

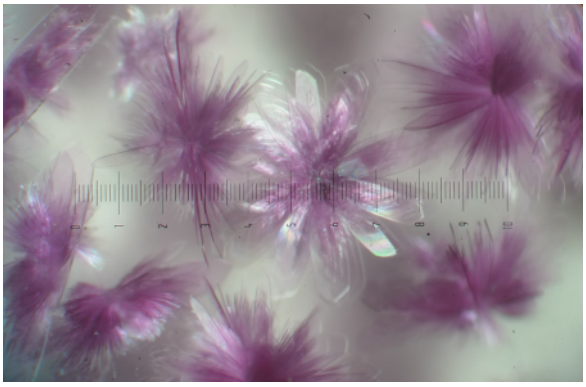

Fig. 1 (color online). Crystals of $NaCr(SO_4)_2(H_2O)_6$. The scale covers a distance of 2.5 mm.

– had been assigned to the cubic Na-Cr alum [17, 18] (see Experimental Part).

In the only other Na-containing alum to be found in the ICSD [3b], $NaAl(SO_4)_2(H_2O)_{12}$, both metal atoms, the mono- and the trivalent one, are octahedrally coordinated by water [8]. This is a characteristic feature of a γ-alum. In α- and β-alums like K-Cr [7] and Cs-Cr alum [6, 19] the monovalent cation is also coordinated by six water molecules but additionally by two (α-alum) or six (β-alum) sulfate O atoms. In $NaCr(SO_4)_2(H_2O)_6$, however, only Cr^{3+} forms a hexaaquo complex. Na^+ is indeed also coordinated sixfold by O atoms, in this case however the latter are provided exclusively by four surrounding sulfate ions. Fig. 2 shows the four independent building blocks of the title compound (one $[Cr(H_2O)_6]^{3+}$ complex and one Na^+ cation with two $[SO_4]^{2-}$ anions) plus two additional $[SO_4]^{2-}$ ions which are, like the other two, coordinated to the Na^+ ion. Fig. 3 visualizes a "packing diagram" of the building blocks in the unit cell including hydrogen bonds but neglecting Na–O bonds.

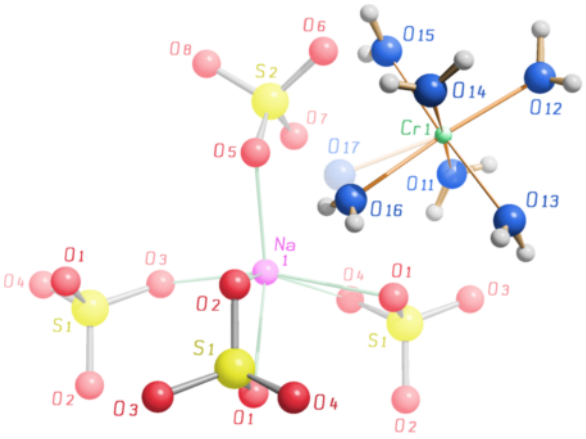

Fig. 2 (color online). The structure model of the asymmetric unit of $NaCr(SO_4)_2(H_2O)_6$ plus two additional SO_4^{2-} groups as seen from approximately [001]. Atoms more distant to the viewer are drawn paler. Besides this, O17 is drawn pale as its site occupancy factor is only 0.12.

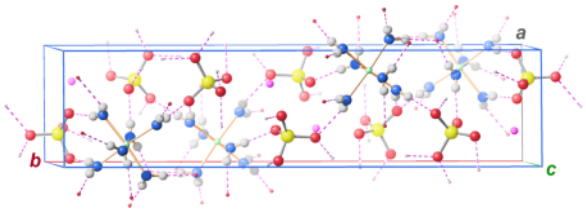

Fig. 3 (color online). A view of the crystal structure of $NaCr(SO_4)_2(H_2O)_6$ including hydrogen bonds (dashed sticks) as seen from approximately [001]. The atom O17 with s. o. f. 0.12 has been omitted here.

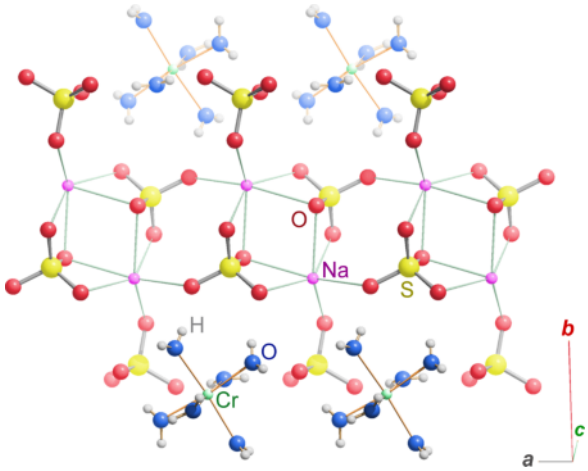

Fig. 4 (color online). A section of a one-dimensionally infinite $[Na(SO_4)_2]^{3-}$ rod plus accompanying $[Cr(H_2O)_6]^{3+}$ complexes as seen from $[1\bar{1}6]$. The atom O17 (s. o. f. 0.12) has been omitted here.

In the Cr complex, the Cr–O bond lengths (except Cr–O17, see below) are in the range 1.95 to 1.98 Å (Table 2) which includes the corresponding bond length of 1.96 Å in the K-Cr alum [7]. Most O–Cr–O angles differ by less than 5° from the ideal ones for an octahedral coordination. However, when O16 (Fig. 2) is involved, larger deviations occur (*e. g.* O16–Cr–O12 = 172°). The reason is that the O16 position is split (→ O16/O17) with a refined weight ratio of 0.88 : 0.12. Both O positions show short distances of 2.67 and 2.72 Å (O16)/2.74 and 2.93 Å (O17) to two neighboring sulfate O atoms O4, O2 (O16)/O2, O5 (O17) indicating the formation of hydrogen bonds which probably are responsible for the distortion/splitting. For Na, the coordination polyhedron is a severely distorted octahedron with Na–O distances from 2.28 to 2.54 Å (*cf.* sum of ionic radii: 2.42 Å) and O–Na–O (*cis*) angles ranging from 57 to 116° due to the fact that two O atom pairs each belong to one and the same sulfate ion (Fig. 2). By the coordinative Na–O bonds, Na^+ and the S1 sulfate form one-dimensionally infinite $[NaSO_4]^-$ rods parallel [100] with additional S2 sulfate "side chains" alternatingly pointing towards [010] and $[0\bar{1}0]$. The space between these rods is occupied by "isolated" $[Cr(H_2O)_6]^{3+}$ complexes (Fig. 4). A simple crystal-chemical formula [20] could therefore be $\{^1_\infty\}[Na(SO_4)_2]\,\{g\}[Cr(H_2O)_6]$. This formula does not account for the "2nd order connectivity" generated by the numerous hydrogen bonds in the structure. Actually, each of the water H atoms in the Cr complex and each of the sulfate O atoms is involved in at least one hydrogen bond (Fig. 3).

Conclusion

Our attempts to grow Na-Cr alum crystals led to crystals of a composition similar to the expected one but with 6 water molecules less per formula unit. The monoclinic phase obtained had erroneously been assigned to the Na-Cr alum in the literature [17, 18].

We presently are investigating crystals of a different kind with similar, but hitherto not fully known composition which were grown at slightly lower temperatures by a similar method as described here. The powder X-ray pattern of these crystals is again very different from those of the known alums, thus, more efforts will be necessary to get an answer to the question whether the

lattice parameter anomaly in the alkali chromium alum series is actually an artifact or not.

Experimental Part

15 mg of the chromium sulfate hydrate $Cr_2(SO_4)_3(H_2O)_x$ (Strem Chemicals) used for the following experiment was heated under Ar on a Netzsch STA 449 DSC/TG apparatus from room temperature to 1000 °C. The residue (24.4 wt.-%) was identified as Cr_2O_3 by powder diffractometry. From the weight loss, x was determined to be approx. 12.

$NaCr(SO_4)_2(H_2O)_6$ (sodium hexaquachromium disulfate)

To 93 mg (0.15 mmol) of $Cr_2(SO_4)_3(H_2O)_{12}$ was added 1.3 mL of H_2O. The rapidly formed solution was separated by means of a pipette from most of a small unsolved residue (< 1 %) and filled into a 15 mL specimen glass with a screw cap. The open glass was put into a 250 mL ice bath. 56 mg (0.4 mmol) of Na_2SO_4 (5 N, Strem Chemicals) was dissolved in the chromium sulfate solution. During about 5 min, 1.6 mL methanol (pre-cooled in the ice bath) was added dropwise to the solution. When the solution turned cloudy at the end, a drop of water was added to re-establish clarity of the solution. The closed specimen glass was positioned with its lower part in a water bath with a temperature of 19–20 °C (not higher!). After three days, bunches of blue-violet crystalline platelets had grown at the bottom of the specimen glass (Fig. 1). The mother liquor was removed, the air-stable crystals were washed rapidly with 1 mL of methanol and dried in air. Yield: 31 mg (0.08 mmol, 27 %).

A fragment of one of the platelets was measured on a Bruker SMART APEX II diffractometer equipped with a CCD detector at room temperature. The structure was solved and refined with SHELXTL [21]. A geometrical distortion of the $[Cr(H_2O)_6]^{3+}$ complex (see Results and Discussion) and a comparatively large peak in the difference Fourier map, close to O16, led to a splitting of the latter (→ O16/O17) with a refined weight relation of 0.88 to 0.12. Water H atoms, except those bound to O17, were located from the final difference Fourier maps. Free refinement of their positions yielded not surprisingly mostly too small O–H bond lengths in the range 0.71 to 0.92 Å. A similar range

Table 2. Bond lengths (Å) for $NaCr(SO_4)_2(H_2O)_6$.

Bond	Length	Bond	Length
Cr1–O11	1.9621(11)	Na1–O4[a]	2.4068(15)
Cr1–O12	1.9626(11)	Na1–O5	2.3340(15)
Cr1–O13	1.9538(13)	S1–O1	1.4807(12)
Cr1–O14	1.9588(12)	S1–O2	1.4831(12)
Cr1–O15	1.9586(13)	S1–O3	1.4704(12)
Cr1–O16	1.9825(15)	S1–O4	1.4661(12)
Cr1–O17	1.944(13)	S2–O5	1.4639(12)
Na1–O1[a]	2.5403(14)	S2–O6	1.4730(11)
Na1–O1[b]	2.5098(14)	S2–O7	1.4736(12)
Na1–O2[b]	2.4702(15)	S2–O8	1.4790(12)
Na1–O3[c]	2.2803(14)		

Symmetry transformations used to generate equivalent oxygen atoms: [a] $x, y, z-1$; [b] $-x+1, -y, -z+1$; [c] $x-1, y, z-1$.

Table 3. Crystal structure data for $NaCr(SO_4)_2(H_2O)_6$.

Empirical formula	$CrH_{12}NaS_2O_{14}$
M_r	374.21
Crystal size, mm^3	$0.25 \times 0.12 \times 0.02$
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	6.1228(1)
b, Å	25.4694(3)
c, Å	7.4222(1)
β, deg	94.798(1)
V, Å^3	1153.93(3)
Z	4
D_{calcd}, g cm^{-3}	2.16
μ(Mo K_α), cm^{-1}	14.6
$F(000)$, e	764
hkl range	±9, ±41, ±12
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.8121
Refl. measured/unique/R_{int}	35 919/5121/0.0339
Param. refined	216
$R(F)/wR(F^2)$[a] (all refls.)	0.0447/0.0863
GoF (F^2)[b]	1.063
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.64/−0.57

[a] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [b] $\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

Table 4. Atomic coordinates and isotropic displacement parameters (Å^2) for $NaCr(SO_4)_2(H_2O)_6$.

Atom	x	y	z	U(eq)	s. o. f.
Cr1	0.8215(1)	0.1447(1)	0.3603(1)	0.015(1)	
O11	0.8631(2)	0.1267(1)	0.1084(2)	0.022(1)	
O12	1.0902(2)	0.1871(1)	0.3762(2)	0.022(1)	
O13	1.0118(2)	0.0866(1)	0.4439(2)	0.029(1)	
O14	0.7696(2)	0.1631(1)	0.6095(2)	0.026(1)	
O15	0.6494(2)	0.2052(1)	0.2676(2)	0.032(1)	
O16	0.5669(3)	0.0971(1)	0.3700(3)	0.029(1)	0.88(1)
O17	0.5280(20)	0.1156(7)	0.3170(20)	0.028(3)	0.12(1)
Na1	0.3028(1)	0.0527(1)	−0.1168(1)	0.026(1)	
S1	0.7488(1)	0.0201(1)	0.7950(1)	0.018(1)	
O1	0.7056(2)	0.0372(1)	0.9794(2)	0.025(1)	
O2	0.7611(2)	−0.0380(1)	0.7965(2)	0.026(1)	
O3	0.9586(2)	0.0417(1)	0.7459(2)	0.029(1)	
O4	0.5681(2)	0.0377(1)	0.6672(2)	0.028(1)	
S2	0.2885(1)	0.1833(1)	−0.1418(1)	0.016(1)	
O5	0.2604(2)	0.1390(1)	−0.0199(2)	0.030(1)	
O6	0.4529(2)	0.2198(1)	−0.0571(2)	0.026(1)	
O7	0.3594(2)	0.1642(1)	−0.3150(2)	0.031(1)	
O8	0.0774(2)	0.2111(1)	−0.1774(2)	0.027(1)	

Table 5. Anisotropic displacement parameters (Å^2) for $NaCr(SO_4)_2(H_2O)_6$. The anisotropic displacement factor exponent takes the form: $-2\pi^2\ [h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cr1	0.014(1)	0.016(1)	0.015(1)	−0.004(1)	0.002(1)	−0.001(1)
O11	0.024(1)	0.023(1)	0.019(1)	−0.006(1)	0.006(1)	−0.004(1)
O12	0.020(1)	0.021(1)	0.025(1)	0.002(1)	−0.003(1)	−0.005(1)
O13	0.041(1)	0.021(1)	0.027(1)	0.007(1)	0.013(1)	0.011(1)
O14	0.017(1)	0.040(1)	0.019(1)	−0.011(1)	0.003(1)	−0.004(1)
O15	0.038(1)	0.036(1)	0.020(1)	−0.008(1)	−0.009(1)	0.022(1)
O16	0.027(1)	0.038(1)	0.023(1)	−0.001(1)	−0.001(1)	−0.017(1)
Na1	0.021(1)	0.028(1)	0.030(1)	−0.002(1)	0.003(1)	0.001(1)
S1	0.017(1)	0.018(1)	0.019(1)	−0.001(1)	0.002(1)	−0.001(1)
O1	0.032(1)	0.023(1)	0.022(1)	−0.006(1)	0.006(1)	−0.006(1)
O2	0.032(1)	0.018(1)	0.030(1)	−0.003(1)	0.006(1)	0.001(1)
O3	0.019(1)	0.039(1)	0.029(1)	0.011(1)	0.002(1)	−0.006(1)
O4	0.022(1)	0.036(1)	0.027(1)	0.004(1)	−0.002(1)	0.002(1)
S2	0.014(1)	0.016(1)	0.019(1)	−0.001(1)	0.001(1)	−0.002(1)
O5	0.033(1)	0.019(1)	0.038(1)	0.006(1)	0.009(1)	−0.004(1)
O6	0.028(1)	0.025(1)	0.023(1)	0.005(1)	−0.008(1)	−0.012(1)
O7	0.022(1)	0.051(1)	0.022(1)	−0.011(1)	0.003(1)	0.004(1)
O8	0.020(1)	0.024(1)	0.037(1)	−0.009(1)	−0.004(1)	0.004(1)

(0.69 – 0.89 Å) can be found, *e. g.*, in the comparatively recently determined structure model of the K-Al alum [7]. From the final refinements the reflection 020 was excluded as it had been identified by the program CHECKCIF [22] as affected by the beamstop. Crystal data, measurement parameters, bond lengths and atomic parameters are given in Tables 2 to 6.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; E-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/request_for_deposited_data.html) on quoting the deposition number CSD-424987.

Table 6. Hydrogen coordinates and isotropic displacement parameters (Å^2) for $NaCr(SO_4)_2(H_2O)_6$.

Atom	x	y	z	U_{eq}
H111	0.972(5)	0.1332(11)	0.081(4)	0.048(8)
H112	0.817(4)	0.0954(11)	0.058(3)	0.041(7)
H121	1.088(4)	0.2200(11)	0.367(4)	0.045(7)
H122	1.173(4)	0.1797(10)	0.448(4)	0.037(7)
H131	1.073(5)	0.0646(12)	0.353(4)	0.057(8)
H132	0.985(5)	0.0688(14)	0.522(4)	0.066(10)
H141	0.849(5)	0.1781(12)	0.670(4)	0.053(8)
H142	0.657(4)	0.1631(10)	0.634(3)	0.031(6)
H151	0.597(4)	0.2270(11)	0.327(4)	0.042(7)
H152	0.589(5)	0.2056(12)	0.173(4)	0.055(8)
H161	0.493(6)	0.0920(17)	0.293(5)	0.058(11)
H162	0.583(6)	0.0753(15)	0.455(5)	0.059(11)

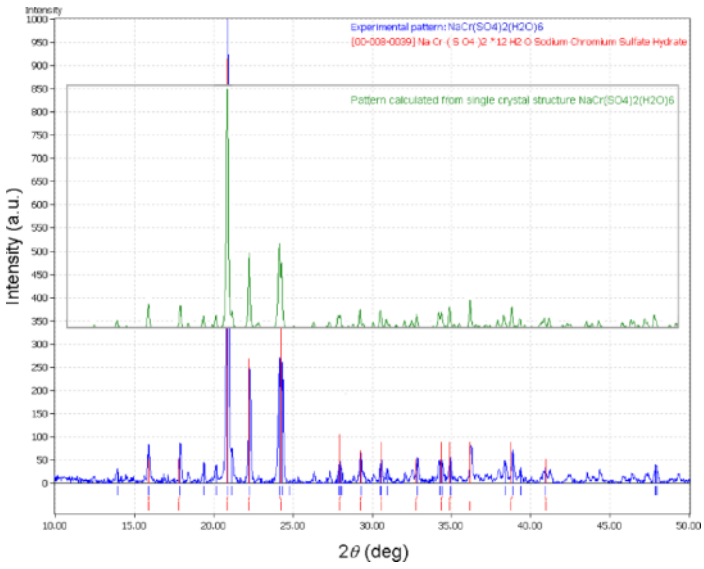

Fig. 5 (color online). Experimental (blue) and calculated (green, in the inset) powder diffraction pattern of the title compound and the peak positions (red vertical lines) for the alleged Na-Cr alum as retrieved by MATCH! [23] from the PDF-2 [17]. The calculated pattern was generated by WINXPOW [24] from the single-crystal structure.

The positions and intensities of the most dominant peaks in the experimental and calculated powder diffraction patterns of the title compound match those of the experimental pattern referenced in the PDF-2 [17, 18] for the Na-Cr alum, as can be seen from Fig. 5.

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