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Studies on synthetic galloalunites $AGa_3(SO_4)_2(OH)_6$: Synthesis, thermal analysis, and X-ray characterization

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ABSTRACT

Stoichiometric end member galloalunites of the general formula $AGa_3(SO_4)_2(OH)_6$, with $A = Na^+$, K^+ , Rb^+ , H_3O^+ , and NH_4^+ have been synthesized under hydrothermal conditions. These galloalunites were characterized by chemical methods, thermal analysis (DSC, TG coupled with mass spectroscopy), and powder X-ray diffraction (XRD).

The stages of thermal decomposition of sodium, potassium and rubidium galloalunite show a common decomposition mechanism forming β -Ga₂O₃ and A₂SO₄ (A = Na⁺, K⁺, and Rb⁺) while ammonium and oxonium galloalunite decompose under formation of pure β -Ga₂O₃. The thermogravimetric results confirmed the analytical results on the galloalunites and thereby verified the stoichiometry of these synthetic products.

Galloalunites with different monovalent cations in A site (i.e. Na^+ , K^+ , Rb^+ , H_3O^+ and NH_4^+) crystallize in the rhombohedral space group $R\overline{3}m$ (#166). The effects of substitution on the unit cell parameters are rationalized in terms of the structural arrangements in galloalunites. The unit cell parameter *c* increases with increasing effective ionic radii of the cation in the A site, whereas the parameter *a* changes to a much lesser degree.

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1. Introduction

Minerals of the alunite-jarosite group have the general formula $AB_3(SO_4)_2(OH)_6$, where *A* is H_3O^+ , Na^+ , K^+ , Rb^+ , Ag^+ , Tl^+ , NH_4^+ , $1/2Ca^{2+}$ or 1/2 Pb²⁺ and *B* is Al³⁺ (alunite group) or Fe³⁺ (jarosite) [1–4]. Members of this group are isostructural, belonging to the hexagonal space-group R³m [5,6].

The basic gallium sulfate $(H_3O)Ga_3(SO_4)_2(OH)_6$ described some time ago, is not a naturally occurring mineral but its structure is isostructural with alunite [7]. Gallium accompanies Fe³⁺ and Al³⁺ in their compounds and recently natural jarosite samples with approximately 1000–3000 ppm Ga³⁺ replacing Fe³⁺ in the *B* site were described [8]. The isomorphous substitution of Al³⁺ and Ga³⁺ ions in the alunite structure of synthetic compounds were described as well [9]. These chemically and thermally stable materials are of wide interest in metallurgy [10] and for fixation of toxic or radioactive ions for depositional purposes [11]. Furthermore, jarosite has been detected on Mars and because hydroxyl ions are present in its structure its occurrence at Meridiani Planum

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is mineralogical evidence for aqueous processes on Mars, probably under acid-sulfate conditions [12]. Jarosite also plays an important role as an antiferromagnetic material with interesting magnetic behaviour [13]. These are but a few reasons to study compounds of this assemblage.

In this paper, we deal exclusively with members of the galloalunite group $AGa_3(SO_4)_2(OH)_6$ expanding on our study on synthetic alunites [14]. The synthetic alunites and jarosites [14–16] are prone to form nonstoichimetric products on both the A and B sites. Oxonium ions commonly replace alkali metal ions in the A site, while deficiencies in the *B* site of Al^{3+} are charge balanced by protonation of the hydroxyl groups to form water. This leads to occupancy of the Al³⁺ site that is typically in the 82–97% range. Therefore, special care was taken in applying synthesis conditions that allow production of stoichiometric products [14,15]. After our studies on synthetic alunites [14] we advance further to the investigation of galloalunite end members with oxonium, Na⁺, K⁺, Rb⁺ and ammonium as monovalent cations (A(I)). Galloalunite, KGa₃(SO₄)₂(OH)₆ sensu stricto, is the end member of gallium bearing alunites but, for clarity, we will name it potassium galloalunite. The stoichiometry of these galloalunite compounds has been determined by chemical methods and thermal analysis. Structural studies have been carried out using powder X-ray diffraction and Rietveld refinement.

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Table 1

Synthesis conditions for galloalunite end members (oxonium galloalunite (H₃O-Ga-alunite), D₃O-galloalunite (d-Ga-alunite-d6), Na-galloalunite, K-galloalunite, NH₄galloalunite, Rb-galloalunite, and K-galloalunite-d6).

Run no. Ga alunite Sample	Starting solutio m A2SO4#/g	on compositions m Ga2(SO4)3/g	m H ₂ O _{total/} g*	рН	Synthesis c ϑ (°C)	onditions <i>p</i> /bar	Time (h)	Yield (g)	pH super-natant
G01	0.147	1.617	29.215	0.89	170	15	904	1.19	0.30
H₃O-Ga-alunite G02 D₂O-Ga-alunite-d6	0.102	1.605	28.620	-	170	12.9	904	1.13	-
G03	0.715	1.936	15.450	0.85	150	12.9	344	1.627	0.21
Na-Ga-alunite G04 K. Ca alunita	0.805	1.983	14.850	0.87	150	12.9	344	1.583	0.12
G05	0.725	2.010	22.200	0.87	150	12.9	344	1.482	0.11
G06 Rb-Ga-alunite	1.590	1.860	14.100	0.86	150	12.9	342	3.866	0.12
G07 K-Ga-alunite-d6	0.760	1.956	14.100	-	150	12.9	324	1.550	-

A2SO4-G01: H2SO4; G02: D2SO4; G03: Na2SO4; G04: K2SO4; G05: (NH4)2SO4; G06: Rb2SO4; G07: K2SO4.

 $^{*}\text{D}_{2}\text{O}$ was used in case of compound # G02 and # G07.

2. Experimental

2.1. Synthesis of galloalunite samples

Synthesis conditions are important in producing stoichiometric samples and the hydrothermal synthesis applied has been published in some detail elsewhere [14]. Galloalunites were prepared from commercial grade $Ga_2(SO_4)_3 \cdot 18H_2O$ after further purification: $Ga_2(SO_4)_3$ · 18H₂O was precipitated with p.a. ethanol from the aqueous solution, dried over $CaCl_2$ and used to prepare a $Ga_2(SO_4)_3$ stock solution. The Ga³⁺ and sulfate content of the stock solution were determined as described in detail by Rudolph and Pye [17]. The stock solution was filtered through a 0.45 µm Millipore filter. The concentration of the stock solution was 0.98 mol/L (1.012 mol/kg). Commercial-grade RbSO₄, K₂SO₄, Na₂SO₄, and (NH₄)₂SO₄ (all salts of p.a. quality, Merck, Darmstadt) were used for synthesis. The starting solutions for galloalunite synthesis were prepared by weight. The pH values of the sulfate solution prior to the precipitation of galloalunite were about 0.90, but after complete precipitation, the pH had dropped to between 0.30 and 0.10 in the supernatants (Table 1) with the lowest pH for the alkali metal galloalunite end members and a higher value for the H₃O-galloalunite end member.

A fully deuterated D_3O^+ -galloalunite-d6 has been synthesized from a $Ga_2(SO_4)_3/D_2O$ stock solution in D_2O (99.9 wt% D; Merck, Darmstadt) with ca. 0.1 g 96 wt% D_2SO_4 (99 wt% D; Aldrich) yielding a product with a deuteration degree better than 95%. A deuterated potassium galloalunite, $KGa_3(SO_4)_2(OD)_6$ has been synthesized from potassium sulfate and a $Ga_2(SO_4)_3/D_2O$ solution in D_2O . The potassium galloalunite-d₆ had a deuteration degree better than 98%.

The synthesis was carried out under hydrothermal conditions in quartz ampoules containing ca. 15 ml solution. The optimal temperature conditions for producing stoichiometric galloalunite *inter alia* alunite were determined and described in detail previously [14] and therefore only a brief account is given. Synthesis temperatures of 150–160 °C were chosen and the synthesis was maintained for up to approximately 340 h in order to improve crystallinity and to reach equilibrium. After quenching the reaction vessel in ice water, the crystalline galloalunite samples were isolated and washed with bi-distilled water and dried. In contrast, the deuterated galloalunite samples were washed with D₂O. From preliminary thermal analysis studies, it became clear that the drying procedure is crucial to eliminate the remaining amounts of adsorbed or occluded water. It is known that oxonium alunite, for instance, adsorbs a few wt.-% of water, which is responsible for the anomalous proton conduction [18]. The galloalunites were dried for 12–14 h in a vacuum apparatus under the following temperatures: oxonium galloalunites at 190 °C, ammonium galloalunites at 220 °C, potassium galloalunites, sodium galloalunites and rubidium galloalunites at 250 °C. After this drying procedure, the galloalunites contained only minute amounts of excess water (<0.2 wt %). The solid products were cooled in a desiccator and stored for further investigation. The synthesis conditions for all of the galloalunites are given in Table 1.

Syntheses of oxonoium galloalunite $((H_3O)Ga_3(SO_4)_2(OH)_6)$ and potassium-galloalunites $(KGa_3(SO_4)_2(OH)_6)$ were carried out twice in order to check the synthesis procedure as well as the whole analytical procedure (from acid digestion to analytical procedure) and to make sure stoichiometric compounds were produced.

2.2. Analytical methods

The chemical analysis of galloalunite species was carried out on samples digested in 4 mol/L HCl (Baker, ultrapure) in a Teflon lined beaker mantled with a steel jacket at 120 °C for 12 h. The gallium, potassium, sodium, rubidium and sulfur contents were determined with inductively coupled plasma optical emission spectroscopy (ICP-OES). The instrument used for all analyses of Ga, S, Na, K, and Rb was an ARL 3520 sequential ICP-OES. Further details about the wet chemical procedure and ICP-OES analysis may be found in Ref. [14].

The thermogravimetric (TG) and thermal analysis (DSC) was carried out in a simultaneous thermal analyser (STA 409 Luxx) manufactured by NETZSCH. The gas outlet of the thermogravimetric analysis device was directly coupled with a mass spectrometer (Äolos, NETZSCH; $(m/z)_{max}$ = 300). Measurements were carried out in the temperature range from ϑ = 25 to 1100 °C with a heating rate of 10K/min in an atmosphere of air. The decomposition temperature, derived from the first decomposition step, was determined at the onset of the corresponding thermal effect, where the material starts to decompose into new solids and gaseous products. This temperature has been reported to be the decomposition temperature which is lower than the maximum of the thermal peak of the DSC curve; the decomposition temperatures of the galloalunites are given below. The analysis of the gaseous products carried out with the mass-spectrometer has been used to verify the sequence of decomposition. The composition of the gas phase has been detected in a first measurement run with an overall scan in the mass range m/z = 1, ..., 300 and the fragments of the gaseous species with m/z = 14 (N⁺), 15 (NH⁺) for the ammonium compound in addition to $m/z = 16 (O^+, NH_2^+), 17 (OH^+, NH_3^+), 18 (H_2O^+), 48 (SO^+), 64 (SO_2^+)$



Fig. 1. Comparison of TG-curves of the thermal decomposition of galloalunites $AGa_3(SO_4)_2(OH)_6$ (A = Na⁺, K⁺, Rb⁺, NH4⁺, and H₃O⁺) (*NETZSCH* STA 409 Luxx + Äolos, atmosphere: air, heating rate: 10 K min⁻¹).

and 80 (SO₃⁺) for all the galloalunites have been detected. No carbon containing species (CH_x, CO, and CO₂) could be ascertained. A second run of the TG–MS measurement has been performed for all samples in order to detect the temperature dependent intensities of the corresponding fragments of the species.

Powder XRD patterns of the solid products of synthesized compounds were collected with a *SIEMENS* D5000 X-ray diffractometer using Cu K_{α} -radiation (reflexion mode) using an accelerating voltage of 40 kV and a filament current of 25 mA. The diffractometric scans were obtained over the 2 Θ range between 5° and 110° at a scan speed of 0.875°/min. The crystal structure parameters and lattice constants have been refined using the program package Powder Cell [19].

3. Results

Details on starting solutions and hydrothermal synthesis conditions used for the preparation of these end members: (H₃O)Ga₃(SO₄)₂(OH)₆, KGa₃(SO₄)₂(OH)₆, NaGa₃(SO₄)₂(OH)₆, $(NH_4)Ga_3(SO_4)_2(OH)_6$, and $RbGa_3(SO_4)_2(OH)_6$ are presented in Table 1. Analytical results of the end member galloalunites and the determined stoichiometries are presented in Table 2. Thermal data on these galloalunites are presented in Tables 3-7 for Na⁺-, K⁺-, Rb⁺-, H₃O⁺-, and NH₄⁺-galloalunites respectively. Fig. 1 depicts representative TG curves for comparison of thermal decomposition temperatures of different phases. Figs. 2-6 show always the complete data set of thermal analysis for Na⁺, K⁺, Rb⁺, H₃O⁺, and NH4⁺ galloalunites including TG curves, DSC measurements and mass spectrometric (MS) traces of species resulting from water (m/z=17, 18) and sulfurous species (m/z=48, 64, 80). XRD patterns of gallo-alunites with $A =: Na^+, K^+, Rb^+, NH_4^+$, and H_3O^+ are presented in Fig. 7. The progress of reflexion positions is marked for reflexes with hkl-indexes (003), (006), (009), (110), and (220).

Unit cell parameters for the galloalunite end members are presented in Table 8 and Fig. 8.

3.1. Chemical characterization and thermal analysis studies on galloalunites

Examination of the SEM photographs shows that the galloalunite samples are polycystalline particles, ranging in size from 9 to 12 μ m [11]. The absence of unidentified peaks in powder XRD indicates that no other crystalline phases are present in the precipitate at detectable levels and only a single solid phase was



Fig. 2. TG-curve of the thermal decomposition of Na[Ga₃(SO₄)₂](OH)₆ (*NETZSCH* STA 409 Luxx + Äolos, atmosphere: air, heating rate: 10 K min⁻¹), measurement of thermal effects (DSC) during the decomposition and MS trace of the ion current of fragments of water (m/z = 18 (H_2O^+); m/z = 17 (OH⁺)) and of sulfur oxide species (m/z = 48 (SO⁺); m/z = 64 (SO₂⁺); m/z = 80 (SO₃⁺)).



Fig. 3. TG-curve of the thermal decomposition of $K[Ga_3(SO_4)_2](OH)_6$ (*NETZSCH* STA 409 Luxx + Äolos, atmosphere: air, heating rate: 10 K min⁻¹), measurement of thermal effects (DSC) during the decomposition and MS trace of the ion current of fragments of water (m/z = 18 (H_2O^+); m/z = 17 (OH⁺)) and of sulfur oxide species (m/z = 48 (SO⁺); m/z = 64 (SO⁺); m/z = 80 (SO₃⁺)).



Fig. 4. TG-curve of the thermal decomposition of Rb[Ga₃(SO₄)₂](OH)₆ (*NETZSCH* STA 409 Luxx + Åolos, atmosphere: air, heating rate: 10 Kmin^{-1}), measurement of thermal effects (DSC) during the decomposition and MS trace of the ion current of fragments of water (m/z = 18 (H_2O^+); m/z = 17 (OH⁺)) and of sulfur oxide species (m/z = 48 (SO⁺); m/z = 64 (SO₂⁺); m/z = 80 (SO₃⁺)).

Table 2

Analytical results (ICP-OES) for the end-members and the galloalunite.

Sample	<i>m</i> % Ga	m% S	m% A	<i>m</i> % Ga	<i>m</i> % S	m% A	Formula (OH and excess H ₂ O from TGA) ^a
	Theoretical	Theoretical	Theoretical	Experiment	Experiment	Experiment	
G01 H₃O-Ga-alunite	40.042	12.277	3.642	40.30	12.30	-	(H ₃ O)Ga _{3.02} (SO ₄) _{2.00} (OH) _{6.00} <0.05 H ₂ O
G03 Na-Ga-alunite	20.537	16.271	4.827	20.50	16.20	-	Na _{1.00} Ga _{2.99} (SO ₄) _{1.99} (OH) _{6.10} <0.05 H ₂ O
G04 K-Ga-alunite	19.542	15.482	9.44	19.45	15.40	9.40	K _{1.00} Ga _{2.99} (SO ₄) _{1.99} (OH) _{6.04} <0.10 H ₂ O
G05 NH4-Ga-alunite	20.589	16.311	4.588	20.60	16.30	-	(NH ₄)Ga _{2.97} (SO ₄) _{2.00} (OH) _{6.20} <0.05 H ₂ O
G06 Rb-Ga-alunite	20.333	16.108	5.775	20.25	16.09	5.75	Rb _{1.00} Ga _{2.98} (SO ₄) _{2.00} (OH) _{6.04} <0.20 H ₂ O

^a The formula represent the experimental values and allow an error estimation for the stoichiometry (they are therefore not stoichiometrically balanced). The error in determining the OH content (and water content) from the TGA curves is unrealistically high because of the error in separating the individual steps. In TA experiments the total weight loss with respect to the stoichiometric formula is more meaningful. We have carried out two or three independent TA experiments in order to verify our experimental results and OH content and given is an average.

Table 3

TG results for decomposition reaction of sodium-galloalunite - NaGa₃(SO₄)₂(OH)₆; all temperatures in °C.

Product	Decomposition step	T_{onset} (DSC)	T_{peak} (DSC)	T_{peak} (DTG)	TG range (°C)	Theor. step (%)	Exp. step (%)
$\begin{array}{l} Na[Ga_3(SO_4)_2](OH)_6 \\ 1/2Na_2SO_4 + 1/2Ga_2(SO_4)_3 + Ga_2O_3 \\ 1/2Na_2SO_4 + 3/2Ga_2O_3 \end{array}$	-3.0 H ₂ O -1.5 SO ₃	380(2) 587(2)	457(2) 653(2)	456(2) 653(2)	370–490 580–850	-10.3 -22.8 -33.1	-10.0(3) -23.0(3) -33.0(6)

Table 4

TG results for decomposition reaction of potassium-galloalunite - KGa₃(SO₄)₂(OH)₆; all temperatures in °C.

Product	Decomposition step	T _{onset} (DSC)	T _{peak} (DSC) (DSC)	T _{peak} (DTG) (DTG)	TG range (°C)	Theor. step (%)	Exp. step (%) /%
K[Ga3(SO4)2](OH)6	-3.0 H ₂ O	395(2)	482(2)	480(2)	390-520	-10.0	-10.3(3)
$KGa(SO_4)_2 + Ga_2O_3$	-1.5 SO ₃	$576(2)_{exo}$ 622(2)	595(2) _{exo} 685(2)	687(2)	600-850	-22.1	-22.4(3)
1/2K ₂ SO ₄ +3/2Ga ₂ O ₃						-32.1	-32.7(6)

Table 5

TG results for decomposition reaction of Rb-galloalunite - RbGa₃(SO₄)₂(OH)₆; all temperatures in °C.

Product	Decomposition step	T_{onset} (DSC)	T_{peak} (DSC)	T_{peak} (DTG)	TG range (°C)	Theor. step (%)	Exp. step (%)
Rb[Ga3(SO4)2](OH)6	$-3.0 H_2 O$	382(2)	453(2)	446(2)	370-495	-9.2	-9.5(5)
$RbGa(SO_4)_2 + Ga_2O_3$	-1.5 SO ₃	589(2) _{exo}	602(2) _{exo}		590-850	-20.4	-21.0(5)
		643(2)	704(2)	705(2)			
$1/2Rb_2SO_4 + 3/2Ga_2O_3$						-29.6	-30.5(10)

Table 6

TG results for decomposition reaction of oxonium-galloalunite - H₃O[Ga₃(SO₄)₂](OH)₆; all temperatures in °C.

Product	Decomposition step	T_{onset} (DSC)	T_{peak} (DSC)	T_{peak} (DTG)	TG range (°C)	Theor. step (%)	Exp. step (%)
$H_3O[Ga_3(SO_4)_2](OH)_6$	-3.5 H ₂ O	207(2) 405(2)	361(2) 427(2)	360(2) 424(2)	200-470	-12.1	-12.0(2)
7/6Ga ₂ O ₃ + 2/3Ga(HSO ₄) ₃	-1.0 H ₂ O -0.5 SO ₃	485(2)	675(2) 690(2)	671(2) 685(2)	470-710	-11.1	-12.0(2)
$Ga_2O_3 + 1/2Ga_2(SO_4)_3$ Ga_2O_3	-1.5 SO ₃	749(2)	779(2)	772(2)	740-820	-23.0 -46.2	-22.0(2) -46.0(6)

produced (Fig. 7). The analytical and thermal results on these end member galloalunites (see Table 2) show that only a minute amount of additional water is present in the synthetic galloalunites. A water content ~0.2 wt% was detected. Thus the drying procedure was crucial in order to obtain stoichiometric galloalunites thereby driving off all occluded water. The thermal analysis shows that adsorbed/occluded water driven off from the galloalunites at temperatures of about 250 °C up to max. 340 °C for Na⁺-, K⁺- and Rb⁺-galloalunite can be carried out without destroying the structure, i.e. resulting in stoichiometric galloalunites without significant "free" water content. An exception applying such high drying temperatures constitutes the oxonium galloalunite which would decompose at this temperature. Therefore this sample has to be dried at temperatures not higher than $190 \,^{\circ}$ C. The ammonium galloalunite has been dried at $220 \,^{\circ}$ C. Besides the minute amount of excess water, the ratio A(I): Ga:S shows that our synthetic galloalunites are stoichiometric and no gallium deficient compounds resulted.

In contrast to our results Tananaev et al. [20] reported chemical analysis data on galloalunites which showed severe nonstoichiometric composition with respect to the *A* site and lack of full gallium occupancy resulting in compounds with additional water. Our synthetic basic gallium sulfate of the alunite type compares well with the synthetic product described by Johansson [7]. However, non-stoichiometric compositions have been described for synthetic alunites by Ripmeester et al. [21].

Table	7

TG results for decom	position reaction of a	ammonium-galloalunite –	$NH_4[Ga_3(SO_4)_2](O$	H)6: all temperatures in °C.
			71 7/21	70,

Product	Decomposition step	Tonset (DSC)	T_{peak} (DSC)	T_{peak} (DTG)	TG range (°C)	Theor. step (%)	Exp. step (%)
$NH_4[Ga_3(SO_4)_2](OH)_6$	-3.0 H ₂ O -1.0 NH ₃	325(2)	426(2)	425(2)	320-490	-13.6	-13.5(4)
Ga_2O_3 + $GaSO_4(HSO_4)$	-0.5 H ₂ O -0.5 SO ₃	510(2)	579(2)	579(2)	490-610	-9.4	-7.0 ^a
$Ga_2O_3 + 1/2$ $Ga_2(SO_4)_3$	-1.5 SO ₃	615(2)	675(2) 737(2) 781(2)	674(2) 740(2) 782(2)	610-820	-23.0 -32.4	-25.9 -32.9(6)
Ga_2O_3						-46.0	-46.8(10)

^a Incomplete decomposition step; overlapped with next step.

Table 8

Unit cell parameters and the crystal data for the end member galloalunites.

Sample	Run no.	a (Å)	<i>c</i> (Å)	$V(Å^3)$	c/a	$D(x)(g/cm^3)$
H ₃ O-Ga-alunite	G01	7.184(1)	17.169(2)	767.59(6)	2.3896	3.390
Na-Ga-alunite	G03	7.140(1)	16.729(2)	738.58(6)	2.3430	3.550
K-Ga-alunite	G04	7.138(1)	17.324(2)	764.42(6)	2.4270	3.535
NH ₄ -Ga-alunite	G05	7.162(1)	17.751(6)	788.32(6)	2.4785	3.295
Rb-Ga-alunite	G06	7.164(1)	17.823(2)	792.18(6)	2.4879	3.703



Fig. 5. TG-curve of the thermal decomposition of $H_3O[Ga_3(SO_4)_2](OH)_6$ (*NETZSCH* STA 409 Luxx + Äolos, atmosphere: air, heating rate: 10 K min⁻¹), measurement of thermal effects (DSC) during the decomposition and MS trace of the ion current of fragments of water (m/z = 18 (H_2O^+); m/z = 17 (OH⁺)) and of sulfur oxide species (m/z = 48 (SO⁺); m/z = 64 (SO⁺); m/z = 80 (SO⁺)).



Fig. 6. TG-curve of the thermal decomposition of NH₄[Ga₃(SO₄)₂](OH)₆ (*NETZSCH* STA 409 Luxx + Äolos, atmosphere: air, heating rate: 10 K min⁻¹), measurement of thermal effects (DSC) during the decomposition and MS trace of the ion current of fragments of water and ammonia (m/z = 18 (H₂O⁺); m/z = 17 (OH⁺; NH₃⁺)) and of sulfur oxide species (m/z = 48 (SO⁺); m/z = 64 (SO₂⁺); m/z = 80 (SO₃⁺)).



Fig. 7. XRD pattern (*SIEMENS* D5000; Cu K α ; reflexion mode) of gallo-alunites $A[Ga_3(SO_4)_2](OH)_6$ with A = alkali metal ions: Na⁺, K⁺, Rb⁺ and NH₄⁺, and H₃O⁺. The progress of reflexion positions is marked for reflexes with h k l-indexes (003), (006), (009) and (110), (220).



Fig. 8. Progress of lattice constants of gallo-alunites $A[Ga_3(SO_4)_2](OH)_6$ with $A = alkali metal ions: Na^+, K^+, Rb^+ and NH_4^+, H_3O^+.$

The thermogravimetric measurements of dried powder samples reinforce the analytical results in that there are no problems of "non-stoichiometry" concerning "excess water" and lack of gallium occupancy in the *B* site. The decomposition of galloalunites shows two steps with the exception of oxonium and ammonium galloalunite. The decomposition of the latter two galloalunite compounds will be discussed separately. The first step reflects the theoretical amount of water resulting from the OH-groups for all galloalunite samples, according to Eq. (1). The second step reflects the loss of sulfur oxides. The processes of thermal decomposition will be discussed in detail later but first the total mass loss of the galloalunite decompositions will be discussed because it allows one to draw conclusions about the stochiometry of the synthetic compounds.

The experimental total mass loss of H₂O, (NH₃), and SO₃ reported in Tables 3-7 confirms the composition of the initial products in accordance with their stoichiometry $AGa_3(SO_4)_2(OH)_6$ $(A = Na^+, K^+, Rb^+, H_3O^+ and NH_4^+)$. For Na-galloalunite a weight loss of 33.0(6) wt% was detected which compares well with the theoretical value of 33.1 wt%; similarly for K-galloalunite the experimental value of 32.7(6) wt% compares well with the theoretical value of 32.1; for Rb-galloalunite the found value is 30.5(10) and the theoretical value is 29.6 wt%. For oxonium-galloalunite which decomposes in a more complicated manner than the alkali metal galloalunites the found the value at 46.0(8) wt% and compares favorably with its theoretical value of 46.2 wt%. The same is true for ammonium-galloalunite with a measured value of 46.8(10) wt% and a theoretical one at 46.0 wt%. Therefore, the weight losses compare favorably with the theoretical values of the galloalunite compounds within the experimental uncertainty again verifying the stoichiometry of the compounds.

The alkalimetal galloalunites ($A = Na^+$, K^+ , Rb^+ ; see Figs. 1–4; Tables 3–5) decompose in two steps similar to the alunite counterparts [14]. In the first step, the dehydration step, release of water from the OH⁻ groups and formation of A_2SO_4 , $Ga_2(SO_4)_3$ and Ga_2O_3 (1) is observed (Tables 3–5). The detected massspectrometric fragments of the molecule $H_2O_{(g)}$ are OH⁺ (m/z = 17) and H_2O^+ (m/z = 18); Figs. 2–4. The onset temperatures of the first (endothermic) step taken from the DSC curve occurs at $380(2) \degree C$ for Na-galloalunite, at $395(2) \degree C$ for K-galloalunite, and at $382(2) \degree C$ for Rb-galloalunite. The formal decomposition reaction may be summarized by Eq. (1):

$$\begin{split} &A[Ga_3(SO_4)_2](OH)_6 \rightarrow \ 1/2A_2(SO_4)_{(s)} + 1/2Ga_2(SO_4)_{3(s)} \\ &+ Ga_2O_{3(s)} + 3H_2O_{(g)} \quad (A = Na, \ K, \ Rb) \end{split} \tag{1}$$

In the cases of potassium and rubidium the intermediate phases $A_2SO_{4(s)} + Ga_2(SO_4)_{3(s)}$ combine in an exothermic reaction to form $AGa(SO_4)_2$ (A = K, and Rb respectively [22]). The corresponding thermal effect has been observed at $\vartheta = 576(2)$ °C for KGa(SO₄)₂ (Fig. 3, Table 4) and $\vartheta = 589(2)$ °C for RbGa(SO₄)₂ (Fig. 4, Table 5) and the phases formed have been identified by powder XRD. The XRD measurements were taken after halting the thermal analysis after the first decomposition step. These measurements were carried out in an independent TG measurement. Similar exothermic effects have been determined in the same manner for the alunite phases containing potassium and rubidium [14,23]. The analogous compound is unknown for sodium; accordingly no exothermic effects could be detected for this system (Fig. 2, Table 3).

The second steps occur from $587(2)^{\circ}$ C for Na-galloalunite, $622(2)^{\circ}$ C for K-galloalunite, and $643(2)^{\circ}$ C for Rb-galloalunite. In the process the decomposition of intermediate phases $Na_2SO_{4(s)} + Ga_2(SO_4)_{3(s)}$ or rather $AGa(SO_4)_2$ (A = K, Rb) proceeds under release of sulfoxides ($SO_{3(g)}$, $SO_{2(g)}$) and the formation of stable products A_2SO_4 and Ga_2O_3 (see Eq. (2a) for sodium, Eq. (2b) for potassium, rubidium). The detected fragments are SO⁺ (m/z = 48), SO₂⁺ (m/z = 64) and small amounts of SO₃⁺ (m/z = 80) (Figs. 2–4). The actual ratio of molecules of decomposition cannot be experimentally quantified from the ratio of the sulfoxide-species in the mass-spectrometer due to their fragmentation in the ionization chamber. The equilibrium constant $K_p = 0.6$ (at T = 1000 K) can be obtained from thermodynamic equilibrium calculations using the data from [24], and a theoretical ratio $p(SO_2) \approx 2 \cdot p(SO_3)$ results (3). Furthermore, the signal m/z = 80 is accompanied by the signal m/z = 18 which may suggest the formation of H₂SO₄. The mass spectrum of H₂SO₄ contains also m/z = 80.

The presence of SO in the gas is originated from the destruction of SO₂ molecules in the ionisation chamber of the mass spectrometer. Although the release of SO_(g) as a primary product of the decomposition of potassium alunite K[Ga₃(SO₄)₂](OH)₆ was discussed [25], thermodynamic calculations substantiate, that the equilibrium constant of the formation of SO_(g) = $(2/3SO_{2(g)} = 2/3SO_{(g)} + 1/3O_{2(g)}$: $K_p \approx 10^{-7}$) is very low.

Finally, sublimation of alkali metal sulfates could not be detected within the investigated temperature range; the equilibrium partial pressures are calculated for compound data [24]: $p(A_2SO_4)_{1300} < 10^{-5}$ bar.

$$\begin{split} &1/2Na_2SO_{4(s)} + 1/2Ga_2(SO_4)_{3(s)} + Ga_2O_{3(s)} \rightarrow \ 1/2Na_2SO_{4(s)} \\ &+ 3/2Ga_2O_{3(s)} + 3/2SO_{3(g)}(SO_{2(g)} + 1/2O_{2(g)}) \end{split} \tag{2a}$$

$$\begin{aligned} AGa(SO_4)_{2(s)} + Ga_2O_{3(s)} &\rightarrow 1/2A_2SO_{4(s)} + 3/2Ga_2O_{3(s)} \\ + 3/2SO_{3(g)}(SO_{2(g)} + 1/2O_{2(g)}) \quad (A = K, Rb) \end{aligned} \tag{2b}$$

$$2/3SO_{3(g)} \rightarrow 2/3SO_{2(g)} + 1/3O_{2(g)}$$
 (3)

The decomposition of oxonium-galloalunite and ammoniumgalloalunite shows notably an earlier effect due to the thermodynamic gain from the formation of the gaseous products such as H_2O and NH_3 , respectively; see Fig. 1. The onset temperatures of the first (endothermic) step lie at 207(2) °C for H_3O^+ -galloalunite and 325(2) °C for NH_4^+ -galloalunite. Basically, the decomposition steps for $(H_3O)Ga_3(SO_4)_2(OH)_6$ and $NH_4Ga_3(SO_4)_2(OH)_6$ are more strongly structured although the two steps characteristic of the galloalunite decomposition, dehydration and de-sulfation are still separated from each other. Dealing first with oxonium galloalunite (Fig. 5, Table 6) reveals that the decomposition can be divided into three steps:

$$H_{3}O[Ga_{3}(SO_{4})_{2}](OH)_{6} \rightarrow 7/6Ga_{2}O_{3} + 2/3Ga(HSO_{4})_{3} + 7/2H_{2}O_{(g)}$$
(4)

$$\begin{aligned} &7/6Ga_2O_3 + 2/3Ga(HSO_4)_3 \rightarrow \ Ga_2O_3 + 1/2Ga_2(SO_4)_3 + H_2O_{(g)} \\ &+ 1/2SO_{3(g)}(SO_{2(g)} + 1/2O_{2(g)}) \end{aligned} \tag{5}$$

$$Ga_2O_3 + 1/2Ga_2(SO_4)_3 \rightarrow 3/2Ga_2O_3 + 3/2SO_{3(g)}(SO_{2(g)} + 1/2O_{2(g)})$$

(6)

In the first step of the oxonium-galloalunite decomposition ranging from 200 to 470 °C, of which the first interval is broad and smeared out while the second one is sharp and 3.5 mole water are lost resulting in the formation of Ga₂O₃ and Ga(HSO₄)₃. The second step, directly preceding the third step, is actually a double peak with maxima at 675 and 690 °C (DSC) resulting in the loss of one mole of water simultaneously with small amounts of SO₂/SO₃

(Figs. 5 and 6) stemming from 1/2 mole of SO₃ (5). In the process Ga(HSO₄)₃ decomposes forming the solid products Ga₂O₃ and 1/2 mol Ga₂(SO₄)₃. Finally in the third step (6), starting above 740 °C the remaining Ga₂(SO₄)₃ is decomposed completely to form Ga₂O₃ and gaseous products SO_{3(g)}, SO_{2(g)}, and O_{2(g)}.

In the case of ammonium-galloalunite - NH₄[Ga₃(SO₄)₂](OH)₆ - three decomposition regions containing submaxima are observed (Fig. 6; Table 7). The first broad peak (320-490°C) for the first decomposition step (7) occurs under release of stoichiometric amounts of ammonia and water (dehydration and de-ammoniation, respectively) namely 3H₂O and one NH₃ and the intermediate products (8) formed are Ga₂O₃ and GaSO₄(HSO₄). The second decomposition region (containing two peaks between 490 and $610 \,^{\circ}$ C) reflects the incomplete decomposition of GaSO₄(HSO₄) leading to the formation of anhydrous gallium sulfate $Ga_2(SO_4)_3$ under release of water and SO₃ (SO₂ + $1/2O_2$). Above 610 °C three peaks appear marking the third decomposition region (peaks at 675, 737 and 781 °C, DSC). In this decomposition step the completion of the second step occurs and also the release of 1.5 mole SO₃ $(SO_2 + 1/2O_2)$ under formation of Ga_2O_3 (see Fig. 6). The following process is proposed:

$$NH_{4}[Ga_{3}(SO_{4})_{2}](OH)_{6} \rightarrow Ga_{2}O_{3} + GaSO_{4}(HSO_{4}) + 3H_{2}O_{(g)} + NH_{3(g)}$$
(7)

$$\begin{split} & Ga_2O_3 + GaSO_4(HSO_4) \rightarrow \ Ga_2O_3 + 1/2Ga_2(SO_4)_3 \\ & + 1/2H_2O_{(g)} + 1/2SO_{3(g)}(SO_{2(g)} + 1/2O_{2(g)}) \end{split} \tag{8}$$

$$Ga_2O_3 + 1/2Ga_2(SO_4)_3 \rightarrow 3/2Ga_2O_3 + 3/2SO_{3(g)}(SO_{2(g)} + 1/2O_{2(g)})$$
(9)

In the case of oxonium and ammonium galloalunite independent X-ray powder diffraction experiments identified the stable final product namely Ga_2O_3 as β - Ga_2O_3 [26] while in the case of the alkali metal galloalunites, alkali metal sulfates, A_2SO_4 ($A = Na^+$, K⁺, and Rb⁺) and β - Ga_2O_3 are formed.

3.2. X-ray analysis and determination of unit cell parameters

The powder XRD patterns of all galloalunites presented (Fig. 7) show phase pure samples with characteristic reflexes of the alunite/jarosite type (rhombohedral space group R3m; #166). The reflexes shift due to different unit cell parameters of the galloalunites in correlation to the ionic radii of the alkali metal-, oxoniumor ammonium-cation. Noticeably, reflexes with *Miller* indices (*hk* 0) are almost not displaced while those with indices (00l) shift considerably from the highest diffraction angles (lower d-values) to the lowest in the sequence: sodium - oxonium - potassium - ammonium and rubidium. Hence the *c* parameter is changed significantly (ca. 7%) by isomorphous replacement of the univalent cation ($\Delta r(A)$) ca. 21%). Changes in the *a* parameter, although in the same direction, are much smaller (ca. 0.4% difference between Na-galloalunite and Rb-galloalunite). Oxonium galloalunite, which has the highest a parameter is slightly out of sequence. The unit cell parameters a and c, the ratio c/a, the volume of the unit cell and the crystallographic densities are presented in Table 8 for the galloalunite end members. In Fig. 8 the progression of the lattice constants a and *c* are given for the galloalunites as function of the ionic radius for 12-fold coordination.

Substituting the trivalent cation Al^{3+} for Ga^{3+} in oxonium galloalunite, results in the end member, oxonium alunite. Comparable unit cell parameters have been recently published by Rudolph et al. [14]. Comparing H₃O⁺-galloalunite with the H₃O⁺-alunite for instance shows that there is only a slight increase in c parameter (ca. 0.2%) but a significant decrease in a parameter (ca. 2.5%).

4. Discussion

4.1. Chemical composition and thermal analyses

Our synthesis conditions (Table 1) were designed to produce stoichiometric galloalunites: very long reaction times and optimal temperature ranges were applied. Recently, stoichiometric alunites and jarosites with respect to the complete filling of the *A*(I) site as well as avoiding the deficiency in the *B* site were reported. Rudolph et al. [14] described the synthesis of stoichiometric alunites and Baciano and Peterson [15] reported the synthesis of stoichiometric jarosites.

The thermal analysis of the synthetic galloalunites was undertaken to determine the stoichiometry and purity of the synthetic products. From TG analysis of the end member galloalunites (cf. Tables 3–7) it could be established that the galloalunites are stoichiometric and show the typical decomposition mechanism also found in alunites [14,24]. Among the alkali metal galloalunites, potassium galloalunite is most thermally stable, while Na-galloalunite and Rb-galloalunite are less stable. Clearly, potassium fits most favorably in the galloalunite structure. NH₄⁺galloalunite and, even less so, the oxonium galloalunite are the least stable members of the end member galloalunites, Fig. 1.

Thermal analysis for the end members $A[Ga_3(SO_4)_2](OH)_6$ with $A = H_3O^+$, NH_4^+ , Na^+ , K^+ , and Rb^+ supply proof for an almost common decomposition sequence of all prepared galloalunites: two primary endothermic reactions occurred during the thermal decomposition of galloalunites: first the dehydration, and second the desulfurization. The regions could be assigned using coupled mass spectrometry. A small exothermic step starting directly before the second endothermic step occurs for potassium and rubidium galloalunites. This step is due to the formation of double sulfates such as KGa(SO₄)₂ and RbGa(SO₄)₂, respectively. The respective decomposition of analogous alunite has been discussed recently by Rudolph et al. [14]. The thermal decomposition data for oxonium galloalunite reinforces the existence of the oxonium ion in these structures. Thermal analysis on these pure galloalunites has not yet been described in the literature.

4.2. Structural arrangements and unit cell parameters of galloalunites

In order to facilitate discussion of the chemical and unit cell parameter data we present a brief discussion of the alunite structure. The first crystal structure of alunite was assigned to the acentric space group R3m (C_{3v}^5) on the basis of a positive pyroelectric test by Hendricks [27], although the reported structural coordinates displayed a centre of symmetry. Later, crystal structure refinement data revealed that the space group for the alunite-jarosite structure has to be assigned to a centrosymmetric space group R $\overline{3}m$ (D_{3d}^5) [5,28] with Z=3 (in the hexagonal unit cell).

The basic structure consists of layers of two-dimensional cornershared octahedra of GaO_6 and isolated, distorted icosahedra AO_{12} between these layers. The icosahedra are formed with the alkali metal-, oxonium- or ammonium-cations surrounded by twelve anions, consisting of six sulfate- (O2) and six OH-groups (O3; Fig. 9) which are nearly at the same distance from the cation. In contrast the slightly distorted GaO_6 -octahedra are coordinated by two sulfate- (O2) and four OH-groups (O3; Fig. 9). Each gallium atom lies in a centre of symmetry.

The sulfur atoms lie on the trigonal axis and are surrounded by three basal oxygen atoms (O(2)) and the apical oxygen (O(1)) which



Fig. 9. (a) Crystal structure of gallo-alunites $A[Ga_3(SO_4)_2](OH)_6$ with A = alkali metal ions: Na⁺, K⁺, Rb⁺ and NH₄⁺, H₃O⁺. (b) Octahedral coordination of gallium atoms and linkage with sulfate groups via O(2) position. (c) Icosahedral coordination of A ions and linkage with sulfate groups via O(2) position.

also lies on the threefold axis. The apical oxygen, O(1) is not shared with coordination polyhedra of other cations and forms H-bonds to OH (cf. Ref. [5]). Wang et al. [28] described this S–O bond as almost doubly bonded. This apical oxygen atom (O(1)) of sulfate groups show alternate orientations (+/-) along the *c*-axis.

There have been few measurements of galloalunite unit cell parameters published in the past [7,20]. Our results for end member galloalunites of sodium, potassium, ammonium and oxonium are presented in Table 8 and Fig. 8.

Considering the data for potassium galloalunite Tananaev et al. [20] reported a parameter a of 7.24 Å and a parameter c of 17.24 Å. For Na-galloalunite the authors reported: a = 7.13 Å and c = 16.66 Å; for ammonium galloalunite: a = 7.21 Å and c = 17.78 Å; and for Rbgalloalunite: a = 7.21 Å and c = 17.05 Å. Comparison of our unit cell parameters with the ones published by Tananaev et al. [20] shows that their data were collected on material that was synthesized under conditions that would not lead to a stoichiometric product (e.g. Rb-galloalunite has an unusually low c parameter). It is noteworthy that in samples which were grown under conditions chosen to produce a stoichiometric alunite, and in which stoichiometry was confirmed by chemical analysis, the results are consistent [29]. The most common problem encountered in producing stoichiometric alunite inter alia galloalunite is a lack of the cation in the A site and a lack of gallium in the B site according to ideal stoichiometry and subsequent incorporation of water. The importance of synthesis conditions on resulting stoichiometric alunite products and consequently on obtaining reliable unit cell parameters as well as Raman and infrared spectra has to be stressed.The following data sets on oxonium galloalunite were reported by Tananaev et al. [20]: a = 7.18 Å and c = 16.96 Å; while Johansson reported: a = 7.18 Å and c = 17.17 Å. Our unit cell parameters on oxonium galloalunite are presented in Table 8 and compare favorably with the values reported by Johannson [7]. As described above, we took care to remove excess water by heating the samples to drive off slight amounts of non-stoichiometric water. It is noteworthy that the oxonium galloalunite is one of the few examples where the existence of H_3O^+ is unambiguous. (About the problem of identifying oxonium ions in minerals see e.g. Ref. [30]).

The data plot (data from Table 8) in Fig. 8 of the unit cell parameters a and c dependent on the ionic radii of the monovalent cations shows a straight line with a correlation coefficient of 0.9962. This implies an almost complete substitution of the alkali metal cations in the A(I) site of the galloallunite structure and again underlying the stoichiometry of the formed galloalunites.

The significant shift of *c* parameter results from the structural arrangement: the isomorphous replacement in *A* position (Na⁺, K⁺, NH₄⁺, Rb⁺ and H₃O⁺) resulting in a anisotropic widening of the 12-fold coordination polyhedra. Since the AO_{12} icosahedra are linked in the *ab* plane by six O(2) oxygen atoms of the sulfate groups (and six O(3) from OH⁻) a flexible stacking of layers and a subsequent increase of the inter-sheet distance only becomes possible along *c* where the terminal oxygen atoms (O1) of the sulfate group lies. Thus, the unit cell parameter *c* follows the increasing size of the ionic radii of the cations in twelvefold coordination (Na⁺ = 1.39 Å [31], H₃O⁺ = 1.70 Å [33], K⁺ = 1.64 Å [32], NH₄⁺ = 1.85 Å [31] and Rb⁺ = 1.86 Å [32]). The influence on the length of *a* parameter is only slight.

The comparison of the unit cell parameters for galloalunites with unit cell parameters of alunite [14] and jarosites [15] allows the study of the influence of different B site cations, namely Ga^{3+} , Al^{3+} or Fe³⁺. Comparing H₃O⁺-galloalunite with the H₃O⁺-alunite for instance shows that there is only a slight increase in *c* parameter (ca. 0.2%) but a significant decrease in *a* parameter (ca. 2.5%). If *B* is Al^{3+} , the parameter *a* is 7.008(1)Å, while it lengthens to 7.170(2)Å if B is occupied by Ga^{3+} (compare our unit cell data in Table 8). Comparing the data of H₃O⁺-galloalunite with the data reported for H_3O^+ -jarosite we observe a still larger widening of a parameter for H₃O⁺-jarosite namely a = 7.355 Å [15]. This observation is due to the different B-O bond lengths, namely the largest bond length is to be found for Fe–O(3)H (1.992 Å) [15] but a smaller for Ga–O(3)H (1.952 Å) bond length and smallest for Al–O(3)H (1.879 Å). On the other hand, together with the B-OH variation the bond length B-O(2) also varies, namely Al–O(2)=1.947 Å, Ga–O(2)=2.017 Å and Fe–O(2)=2.015 Å [15]. This means that the size effect of substituting the B^{3+} cations results mainly by widening and tilting of the BO_6 octahedra along the *ab* plane via the oxygen O(3).

These results suggest that the substitutions in the *A* and *B* site can be distinguished on the basis of their effects on the unit cell parameters. Values in unit cell parameters react very sensitively on change in chemical composition which has been recently found in the case for alkali metal alunite compounds [14].

5. Conclusions

- 1. Careful synthesis and chemical analysis are required in order to prepare and characterize stoichiometric end member galloalunites.
- 2. The stages of thermal decomposition of these galloalunites show a common decomposition mechanism for all end members (two main decomposition stages). Taking into account the final products of decomposition: Ga_2O_3 (for galloalunites with $A = H_3O^+$ and NH_4^+) or Ga_2O_3 and A_2SO_4 (with $A = Na^+$, K⁺, and Rb⁺ for the respective galloalunites) the composition of the samples may be derived from the decomposition steps of the thermogravimetry.
- 3. The thermogravimetric results confirmed the analytical results on the end member galloalunites and showed that these galloalunites are stoichiometric.
- 4. Galloalunite, the pure potassium end member, shows the highest decomposition temperature ($\vartheta_{ons} = 395 \,^{\circ}C$) while sodium galloalunite ($380 \,^{\circ}C$) and rubidium galloalunite ($382 \,^{\circ}C$) are less stable followed by ammonium alunite ($325 \,^{\circ}C$) and oxonium alunite ($207 \,^{\circ}C$).
- 5. With the increase of the effective ionic radius of the cation occupying the *A* site in the series from Na⁺, K⁺, H₃O⁺, NH₄⁺ to Rb⁺ there is a large increase in *c* unit cell parameter accompanied by only a slight increase in *a* parameter.

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