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X-RAY STUDY OF SYNTHETIC ALUNITE

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Synthetic alunite was obtained by two different synthesis methods. Powder data obtained with a standard Bragg-Brentano geometry of two analyzed samples are reported for a broad angular range. The chemical analysis as well as the unit-cell dimensions indicate that the analyzed alunite is K and Al deficient and contains excess water. A need for high resolution diffraction experiments is expressed.

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1. Introduction

Alunite, $KAl_3(SO_4)_2(OH)_6$, crystallizing in space group $R\bar{3}m$, is a mineral identified in numerous sites in the world. It belongs to a family of structurally related substances described by a general formula $AB_3(SO_4)_2(OH)_6$, where A may become Na^+ , K^+ , H_3O^+ , NH_4^+ or Ag^+ and B either Al^{3+} or Fe^{3+} . Natural and synthetic alunites have been subjects of extensive structural investigations employing single-crystal and powder X-ray techniques, NMR and other methods [1-16]. One of the reasons of this interest is a possibility of industrial applications of alunite and related minerals.

The composition of the natural alunite depends on the formation conditions and on the environment while that of a synthetic one is influenced by the way of synthesis. A number of recent papers [5, 6, 9, 13-16] deal with the problem of the composition of natural and synthetic alunite. The existing synthesis methods yield alunite of composition often differing from the stoichiometric one; the reported differences concern the deficiency in K and Al as well as the presence of "excess water". In our work the term "excess water" refers to various forms of water (e.g. H_3O^+ , H_2O) which may be present in alunite unit-cell except for stoichiometric OH^- ions. Due to differences in synthesis method and observed differences in composition, the published unit-cell dimensions vary within a range of about 0.05 Å

and 0.3 Å for lattice parameters a_0 and c_0 , respectively, which reflect the differences in chemical composition of the studied samples. In an early study [9], a conclusion has been drawn that a heat treatment of alunite in air up to 400°C does not influence the composition nor the unit-cell dimensions. Other works have shown that a heat treatment of synthesized alunite containing excess water leads to an expansion of the unit cell and a reduction of the water content [5, 14] (samples heated in air at 300°C), [16] (a sample heated in K_2SO_4 solution at 250°C).

2. Analyses and data collection

For the purpose of aluminum and potassium content determination, the alunite was dissolved in hot 12N HCl. The Al content was determined gravimetrically by precipitation with 8-hydroxyquinoline following the method described in Ref. [17]. The K content was determined by flame photometry. The sulfur content was determined with LECO SC132 sulfur analyzer. The grain size was determined by granulometry using SEDIGRAPH-5100 analyser and by scanning electron microscopy using Opton DSM-940 microscope. X-ray powder data were collected with a standard Bragg-Brentano arrangement and Co $K\alpha$ radiation. DRON-1 diffractometer with the beam path modernized to enable a fine alignment and a computer controlled work was used. To reduce the effect of preferred orientation, the loosely packed specimens were prepared by deposition of the non-ground powder obtained directly by the chemical reactions on a thin vaseline layer. The measurement conditions are given in Table I. The preliminary analysis of step scanned data was performed using the commercial DIIN-PDS system. The lattice constants were obtained by the least-squares method with a new version of the program SCANIX described in Refs. [18, 19].

3. Methods of synthesis

Two specimens of alunite were synthesized by different methods using analytically pure reagents. Alunite A was prepared by the hydrolysis of alum, $AlK(SO_4)_2 \cdot 12H_2O$, in a pressure reactor. The reactor was charged with 3.8 kg of alum and 2.2 dm³ of distilled water. The pressure during hydrolysis was kept at 12 bars and the solution temperatures ranged from 175 to 180°C. The run time was approximately 2 h. The obtained powder was filtered off, washed with distilled water and dried at 105°C for 12 h. Alunite B was synthesized by a modified version of the procedure described earlier in Ref. [11]. In the modified version (reported elsewhere [20]) the following synthesis conditions were applied. The amounts of 45 g of $Al_2(SO_4)_3 \cdot 18H_2O$ and 59 g of K_2SO_4 were dissolved in 150 cm³ of hot distilled water and subsequently refluxed for 3 h. The pH value of the refluxed solution was kept in the range 3.0–3.6 by periodic addition of solid KOH. The obtained precipitate was filtered off, washed with distilled water and dried at 105°C for 3 h. Both reactions yielded a white powder with the grain size of the dominant fraction ranging from 1 to 10 μm .

TABLE I

X-ray diffraction measurement conditions applied for alunite.

Power	495 watt (45 kV, 11 mA)
Radiation	Co $K\alpha$ radiation with a Fe filter at the diffracted beam
Diffractometer radius	180 mm
Monochromator	None
Sample rotation	Applied
Counter	Scintillation
Counting time	6 s
Temperature	$20 \pm 3^\circ\text{C}$
Two-theta scan range	16° – 130° , step 0.04°
Divergence slit	2°
Receiving slit	0.25 mm
Soller slits	2.5° slits employed at both the incident and the diffracted beam
α_2 stripping	Performed
Wavelength applied in calculations	1.788965 Å
Standard	None

4. Results and discussion

The results of the chemical analyses of both samples are presented in Table II. The observed differences related to the stoichiometric alunite are similar to those reported in literature [5, 9, 14]. The X-ray data collected in a wide angular range down to interplanar spacing equal 1 Å are shown in Table III. The samples were found to be a single-phase alunite with no trace of other phases. The obtained peak intensities agree with those reported for the low-angle region in Refs. [5, 10]. The unit-cell constants are $a_0 = 7.0140(7)$ Å, $c_0 = 17.139(9)$ Å (sample A) or $a_0 = 6.9979(5)$ Å, $c_0 = 17.115(5)$ Å (sample B).

The cell dimensions fall in the region of values (around $a_0 = 7.01$, $c_0 = 17.15$) reported in Refs. [4, 5, 14, 16] for synthetic alunite samples not subjected to a high-temperature treatment and containing some excess water. It has been concluded in Ref. [15] that the values of lattice constants cannot give detailed compositional information for alunite containing excess water because the a_0 and c_0 in such case tend to adopt similar values for a variety of compositions. In particular, the deficiency in K and Al (observed in our samples) does not affect much the lattice constants. However, a qualitative conclusion can be drawn from experimental unit-cell dimensions of samples A and B. The decrease in unit-cell

dimensions going from sample A to B correlates with the increase in H_2O content revealed by chemical analysis (see Table II). This observation agrees with the reported tendency of unit-cell contraction with increasing content of excess water [4, 5, 14, 16].

TABLE II
Results of chemical analyses of samples A and B. The H_2O content refers to the residual (not measured) water which may be present in the alunite unit cell in various forms (OH^- , H_3O^+ , H_2O).

Sample	Content [weight %]				
	K_2O	Al_2O_3	SO_3	H_2O (residual)	Total
Stoichiometric	11.37	36.92	38.66	13.05	100.00
Alunite A	10.43	30.95	39.90	18.72	100.00
Alunite B	8.65	30.94	36.41	24.00	100.00

TABLE III
Diffraction data for samples A and B. Peak height intensities are given. The choice of the Miller indices was guided by the structure factors calculated in Ref. [10]. Refined lattice constants and their standard deviations: for the sample A $a_0 = 7.0140(7)$ Å, $c_0 = 17.139(9)$ Å (rhombohedral cell $a_R = 7.003$ Å, $\alpha = 60.11^\circ$), for the sample B $a_0 = 6.9979(5)$ Å, $c_0 = 17.115(5)$ Å (rhombohedral cell $a_R = 6.991$ Å, $\alpha = 60.07^\circ$). Experimental 2θ values written in italics were applied in least-squares refinement assuming the starred (hkl)s.

Sample A				Sample B				$h k l$
d_{exp} [Å]	$2\theta_{\text{exp}}$ [deg]	$2\theta_{\text{calc}}$ [deg]	I_{exp}	d_{exp} [Å]	$2\theta_{\text{exp}}$ [deg]	$2\theta_{\text{calc}}$ [deg]	I_{exp}	
5.721	17.990	17.976 18.016	10.0	5.710	18.025	18.016 18.041	8.4	1 0 1 0 0 3
4.957	<i>20.790</i>	20.798	48.8	4.946	<i>20.837</i>	20.840	55.9	0 1 2*
3.506	<i>29.559</i>	29.554 34.807	28.9	3.500	<i>29.616</i>	29.623 34.889	28.4	1 1 0* 0 2 1
2.989	34.829	34.829 34.871	100.0	2.983	34.904	34.902 34.929	100.0	1 1 3 0 1 5
2.864	36.401	36.497	2.5	2.851	<i>36.564</i>	36.550	4.8	0 0 6*
2.478	<i>42.312</i>	42.323 46.343	3.1	2.473	<i>42.416</i>	42.412 46.437	2.4	0 2 4* 2 0 5

TABLE III (cont.)

Sample A				Sample B				<i>h k l</i>
d_{exp} [Å]	$2\theta_{\text{exp}}$ [deg]	$2\theta_{\text{calc}}$ [deg]	I_{exp}	d_{exp} [Å]	$2\theta_{\text{exp}}$ [deg]	$2\theta_{\text{calc}}$ [deg]	I_{exp}	
2.272	46.371	46.394	12.5	2.267	46.471	46.469	16.7	1 0 7*
2.218	47.576	47.575	5.1	2.213	47.690	47.688	5.3	1 2 2*
2.024	52.457	52.464	1.2	2.019	52.594	52.583	1.0	2 1 4
		52.556				52.641		0 1 8
1.9078	55.921	55.899	18.8	1.9043	56.033	56.033	20.6	0 3 3
		55.972				56.079		0 2 7
		56.031				56.116		0 0 9
1.7531	61.360	61.343	9.0	1.7496	61.493	61.499	11.9	2 2 0*
		61.453				61.569		2 0 8
1.6523	65.554	65.518	1.8	1.6483	65.732	65.685	1.4	3 1 2
		65.571				65.719		0 3 6
		65.677				65.786		1 0 10
1.5676	69.584	69.571	1.5	1.5643	69.755	69.745	1.4	1 3 4
		69.649				69.794		1 2 8
		72.504				72.696		4 0 1
1.5122	72.530	72.542	1.4	1.5093	72.692	72.721	1.6	3 1 5
		72.694				72.817		0 1 11
		73.483				73.677		0 4 2
		73.533				73.709		2 2 6
1.4943	73.541	73.634	6.1	1.4912	73.716	73.773	6.9	0 2 10
1.4309	77.380	77.354	1.2	1.4278	77.580	77.556	1.2	4 0 4*
		80.181				80.402		3 2 1
		80.218				80.426		0 4 5
1.3885	80.214	80.255	2.7	1.3852	80.444	80.449	2.6	1 3 7
		80.304				80.480		0 3 9
		80.365				80.519		2 0 11
1.3754	81.134	81.130	1.1	1.3719	81.384	81.353	1.7	2 3 2
		81.277				81.447		2 1 10
1.3260	84.840	84.880	1.0	1.3223	85.139	85.121	1.1	4 1 0*
		85.098				85.260		1 1 12
1.2909	87.725	87.695	2.9	1.2885	87.928	87.943	3.5	4 1 3

TABLE III (cont.)

Sample A				Sample B				<i>h k l</i>
d_{exp} [Å]	$2\theta_{\text{exp}}$ [deg]	$2\theta_{\text{calc}}$ [deg]	I_{exp}	d_{exp} [Å]	$2\theta_{\text{exp}}$ [deg]	$2\theta_{\text{calc}}$ [deg]	I_{exp}	
		87.756				87.982		4 0 7
		87.804				88.012		2 2 9
		87.937				88.097		1 0 13
1.2111	95.220	95.218	2.0	1.2086	95.477	95.479	1.9	3 2 7*
		96.086				96.377		5 0 2
1.2024	96.127	96.232	1.0	1.1992	96.475	96.470	1.1	1 3 10
		96.378				96.563		0 1 14
1.1678	99.80	99.844	1.1	1.1666	100.121	100.158	1.5	3 3 0
		99.869				100.173		0 5 4
		100.065				100.298		3 0 12
		102.696				103.026		2 4 1
1.1453	102.71	102.709	1.3	1.1427	103.036	103.034	1.5	3 3 3
		102.734				103.050		5 0 5
		102.957				103.191		2 1 13
1.1090	107.528	107.548	0.6	1.1069	107.826	107.899	0.9	2 4 4*
		107.751				108.028		2 2 12
1.0884	110.545	110.519	0.8	1.0863	110.864	110.885	0.9	4 2 5*
		110.610				110.943		4 1 9
		110.675				110.984		0 4 11
		118.727				119.157		1 5 5
		118.768				119.184		2 4 7
1.0392	118.879	118.976	0.6	1.0371	119.200	119.316	1.0	1 3 13
		124.145				124.644		6 0 0
1.0114	124.365	124.262	0.5	1.0099	124.679	124.719	1.0	4 2 8
		124.615				124.943		0 2 16

The rhombohedral angle close to 60° in both samples results in an FCC-like powder pattern with a strong peak overlap in the whole investigated angular range. This property is characteristic for alunite containing excess water but is not observed for other members of the alunite family where the rhombohedral angle differs from 60° by at least about 0.5° . High resolution diffraction experiments could be helpful in resolving the multiplets when the rhombohedral angle is close to 60° . The resolution of Guinier camera is not sufficient for this purpose [13].

The strong peak overlap implies that the lattice constants have to be computed on the basis of a limited number of mainly low-angle peaks. This condition limits the accuracy of the calculated lattice constants.

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