Alvanite from Kazakhstan, U.S.S.R.: new crystallographic and chemical data

PETE J. DUNN

Department of Mineral Sciences, Smithsonian Institution, Washington, DC 20560

ANDREW C. ROBERTS

Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario, Canada K1A OE8

AND

FRANZ PERTLIK

Institut für Mineralogie und Kristallographie, Universitat Wien, A-1010 Wien, Austria

Abstract

Alvanite is monoclinic $P2_1/n$, with $a = 17.808(8)$, $b = 5.132(3)$, $c = 8.881(4)$Å, and $\beta = 92.11(3)^0$. The density is 2.49 g/cm^3 (meas), 2.492 g/cm^3 (calc). Microprobe analysis yielded Al_2O_3 34.2, FeO 0.3, ZnO 7.6, NiO 4.2, V_2O_5 27.5, H_2O (by difference) 26.2, total = 100.0 wt.%. This leads to the idealized formula $(Zn,Ni)Al_4(VO_3)_2(OH)_{12}.2H_2O$ with $Z = 2$.

KEYWORDS: alvanite, crystallography, Kazakhstan, U.S.S.R.

Introduction

ALVANITE was first described from several mines in the Kurumsak and Balasauskandyk oil fields of the U.S.S.R. by Ankinovich (1959). The unit cell was not determined, and there were some ambiguities in the chemical composition. Accordingly, we undertook a re-investigation of alvanite in order to determine the crystallographic parameters and the chemical composition of the mineral. The studied specimen is labelled as being from Kazakhstan, U.S.S.R. and is catalogued under NMNH no. 139831 in the Smithsonian Institution. It consists of light blue–green crystals of alvanite encrusting a brown fine-grained matrix, which is mostly mica and possibly roscoelite.

Chemical composition

Alvanite was analysed using an ARL-SEMQ electron microprobe utilizing an operating voltage of 15 kV and a sample current of 0.025 μA, measured on brass. The standards used were: synthetic anorthite (An_{80}) for Al, hornblende for Fe, synthetic ZnO and NiO for Zn and Ni, respectively, and synthetic V_2O_3 for V. The data were corrected using a modified version of the MAGIC-4 program. The resultant analysis yielded Al_2O_3 34.2, FeO 0.3, ZnO 7.6, NiO 4.2, V_2O_5 27.5, H_2O (by difference) 26.2, total = 100.0 wt.%. The water content by difference is very similar to those given in the original analyses (Ankinovich, 1959), namely 25.6, and 25.2 wt.%H_2O^+, and its presence and amount is supported by the crystal structure determination of our material (Pertlik and Dunn, 1990). The density of the studied specimen, determined using heavy-liquid techniques, is 2.49 g/cm^3, compared with the theoretical value, 2.492 g/cm^3, calculated using the idealized formula derived from the crystal-structure analysis (Pertlik and Dunn, 1990) and a Zn:Ni ratio of 1.70:1 derived from the microprobe analysis.

The original chemical analyses of alvanite (Ankinovich, 1959) yielded CaO 0.5; MgO 0.5; ZnO 0.5; NiO 2.7; Al_2O_3 39.6, 39.4; Fe_2O_3 trace; V_2O_3 not detected; V_2O_4 3.7, 3.8; V_2O_5 24.1, 24.3; SiO_2 1.8; H_2O^- 0.4, 0.6; H_2O^+ 25.6, 25.2; total = 99.4 wt.%. Thus, presuming the type material was in fact very similar in composition to the material studied here, the analysis given

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Table 1. X-ray powder diffraction data for alvanite.

I(est)	d(meas)	d(calc)	hkl	I(est)	d(meas)	d(calc)	hkl
90	8.91	8.90	200	*20	2.283	2.285	$\bar{3}21$
80	7.85	7.83	101	20	2.223	2.223	420
50	5.02	5.02	$\bar{3}01$			2.221	022
100	4.46	4.45	400	20	2.194	2.193	612
30	4.32	4.33	$\bar{1}11$			2.191	413
		4.29	111	*10	2.110	2.112	$\bar{5}13$
25	4.01	4.00	$\bar{2}11$	10	2.050	2.054	$\bar{7}12$
35	3.88	3.88	310			2.049	513
3	3.60	3.59	$\bar{3}11$	*40	1.973	1.971	$\bar{6}13$
5	3.524	3.525	311	*30	1.940	1.941	620
*30	3.363	3.357	012	*35	1.910	1.909	613
*45	3.287	3.282	112	*10	1.833	1.834	$\bar{7}13$
3	3.195	3.201	$\bar{4}02$	*10	1.806	1.806	720
		3.173	$\bar{4}11$	10	1.777	1.779	$\bar{7}21$
*30	3.118	3.112	212			1.777	713
*45	2.957	2.957	$\bar{3}12$	*10	1.707	1.707	$\bar{8}13$
*20	2.901	2.901	103	*30	1.682	1.681	820
*15	2.692	2.687	$\bar{3}03$	5	1.655	1.654	813
*25	2.648	2.645	412	5	1.615	1.612	$\bar{5}05$
		2.566	020	5	1.589	1.592	$\bar{1}32$
3	2.557	2.563	013	10	1.538	1.543	804
		2.548	$\bar{1}13$			1.536	332
5	2.522	2.526	113	3	1.517	1.515	531
		2.509	$\bar{6}02$	3	1.501	1.502	524
*25	2.485	2.484	$\bar{2}13$			1.498	515
5	2.468	2.468	$\bar{7}01$	50	1.481	1.481	033
		2.466	220			1.479	006
*10	2.442	2.442	213	20	1.466	1.468	$\bar{2}06$
3	2.411	2.409	512			1.462	1020
*10	2.381	2.381	$\bar{3}13$	*15	1.440	1.440	1013
*30	2.353	2.355	320	5	1.421	1.419	$\bar{4}06$
*20	2.327	2.326	313	15	1.413	1.413	$\bar{6}32$
						1.413	$\bar{4}33$
				*15	1.399	1.400	$\bar{4}25$

114.6 mm Gandolfi camera.

Cu-radiation; Ni-filtered ($\lambda CuK\alpha$ = 1.54178Å).

* - used in unit cell refinement.

Intensities estimated visually; no internal standard.

Indexed on a = 17.808, b = 5.132, c = 8.881 Å, β = 92.11°.

by Ankinovich (1959) is very low in Zn and slightly low in Ni, with a surfeit of Al.

Calculation of unit-cell contents using the data presented herein and a density of 2.49 g/cm^3, yields: $Al_{8.18}Fe_{0.05}Zn_{1.14}Ni_{0.68}V_{3.68}H_{35.38}O_{40.99}$. This yields the idealized formula $(Zn,Ni)Al_4(VO_3)_2(OH)_{12}.2H_2O$, with Z = 2. The presence of the (VO_3) group has been verified by the crystal-structure determination (Pertlik and Dunn, 1990).

X-ray crystallography

Two crystal fragments were examined by precession single-crystal methods using Zr-filtered Mo radiation. One fragment was oriented such that c^* was parallel to the dial axis and the other fragment mounted such that b^* was parallel to the dial axis. Levels collected were: $h0l$, $h1l$, $0kl$, $\rightarrow 2kl$, and $hk0 \rightarrow hk2$. Alvanite is monoclinic with measured (and calculated) unit-cell parameters: $a = 17.89$, $b = 5.131$, $c = 8.906$ Å, $\beta = 92.17^0$. The mineral is twinned by rotation about a^* as noted on the $h0l$ precession film. This twinning, coupled with the small beta angle, produced extensive nodal overlap for hkl and $\bar{h}kl$ reflections. Interpretation of upper-level precession films was difficult but not impossible. Systematic absence conditions: (1) $h0l$ with $h+l \neq 2n$ and (2) $0k0$ with $k \neq 2n$, dictate that the unique space group is $P2_1/n$ (14). The fully indexed powder pattern is given in Table. 1. The refined unit-cell parameters, based on 23 reflections between 3.363 and 1.399 Å for which unambiguous indexing was possible, are: $a = 17.808(8)$, $b = 5.132(3)$, $c = 8.881(4)$ Å, $\beta = 92.11(3)^0$, $V = 811(1)$ Å^3, $a:b:c = 3.470:1:1.731$. All reflections were visually examined on precession films. This unit cell is in its reduced form as determined by a unit-cell reduction program.

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