

The crystal structure of köttigite

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Abstract

Köttigite, $(\text{Zn}_{2.44}\text{Co}_{0.42}\text{Ni}_{0.14})(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, from the type locality (Schneeberg, East Germany) crystallizes in space group $C2/m$ with $a = 10.241(3)$, $b = 13.405(3)$, $c = 4.757(2)\text{Å}$, $\beta = 105.21(2)^\circ$, and $Z = 2$. Isotypy with vivianite is confirmed: the hydrogen atoms have been located and the crystal structure refined using 812 Zr-filtered $\text{MoK}\alpha$ data to an R value of 0.054 ($R_w = 0.057$). The transition metals are randomly distributed over insular single and double (edge-sharing) octahedral groups of O atoms and H_2O molecules connected by AsO_4 tetrahedra to form complex slabs parallel to (010). These sheets are held together by hydrogen bonding alone, thereby accounting for the perfect {010} cleavage of the mineral. Shortening of the shared edge relative to the unshared edges within the octahedral dimer (0.139Å) is well within the rather wide range of values observed in other Zn compounds containing shared octahedral edges.

Introduction

The mineral köttigite, ideally $\text{Zn}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$, has long been recognized as a member of the vivianite group of minerals with the general formula $M_3(\text{TO}_4)_2 \cdot 8\text{H}_2\text{O}$. The monoclinic members of this family include the phosphates vivianite ($M = \text{Fe}$), bobierrite (Mg), and bariçite (Mg,Fe), and the arsenates köttigite, parasymphesite (Fe), hoernesite (Mg), annabergite (Ni), and erythrite (Co). In addition, both vivianite and parasymphesite have been observed in a closely-related triclinic modification as the minerals metavivianite and symphesite (Ritz *et al.*, 1974).

The topology of the monoclinic structure type was shown by Mori and Ito (1950)² to consist of octahedral edge-sharing dimers, $M_2\text{O}_6(\text{H}_2\text{O})_4$, and insular octahedra, $\text{MO}_2(\text{H}_2\text{O})_4$, linked by TO_4 tetrahedra into complex sheets parallel to (010). However, the atomic coordinates were not refined, and the details of this interesting structure remain in doubt. The structure of the triclinic dimorph is still unknown.

The structural analysis of köttigite was initiated as

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² Note that monoclinic $\text{Fe}_3(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ is (incorrectly) referred to as symphesite rather than parasymphesite by Mori and Ito (1950).

part of a continuing study of Zn stereochemistry and, in particular, of the characteristics of Zn octahedron shared-edge shortening. Material from the type locality in Schneeberg, East Germany, was kindly made available for study by B. D. Sturman of the Royal Ontario Museum (ROM specimen number M15537).

Experimental

The crystal selected for data collection was a pale red transparent platelet displaying well-developed {010} faces, and having the dimensions $0.098 \times 0.093 \times 0.037$ mm. Detailed morphological, optical, chemical and X-ray data for the material have been reported by Sturman (1976); the chemical composition determined in that study has been included in the abstract. The crystal was oriented with the c^* axis slightly displaced from the ϕ axis of a Picker FACS 1 four-circle diffractometer. Unit-cell parameters were refined by least-squares methods to give the best fit between calculated and observed angles 2θ , χ , and ϕ , measured at $25 \pm 2^\circ\text{C}$ with $\text{MoK}\alpha_1$ radiation ($\lambda = 0.70926\text{Å}$), for 30 automatically centered reflections in the range $2\theta = 30\text{--}45^\circ$. The resultant cell dimensions $a = 10.241(3)$ ³, $b = 13.405(3)$, $c = 4.757(2)\text{Å}$, $\beta = 105.21(2)^\circ$ [unit-cell volume = $630.2(2)\text{Å}^3$] agree well with values reported by Sturman (1976).

³ E.s.d.'s, given in parentheses, refer to the last decimal place.

	H	FD	FC	AC	BC	H	FD	FC	AC	BC	H	FD	FC	AC	BC	H	FD	FC	AC	BC				
K=0	141	139	-119	72	136	1	812	797	-795	-53	12	707	710	703	97	6	812	761	-759	-48	449	445	442	37
L=0	108	1579	1513	136	108	2	197	568	-49	-7	197	187	187	187	187	7	243	272	-183	-39	243	272	187	187
K=1	141	139	-119	72	136	3	812	797	-795	-53	13	707	710	703	97	8	812	761	-759	-48	449	445	442	37
L=0	108	1579	1513	136	108	4	197	568	-49	-7	197	187	187	187	187	9	243	272	-183	-39	243	272	187	187
K=2	141	139	-119	72	136	5	812	797	-795	-53	14	707	710	703	97	9	812	761	-759	-48	449	445	442	37
L=0	108	1579	1513	136	108	6	197	568	-49	-7	197	187	187	187	187	10	243	272	-183	-39	243	272	187	187
K=3	141	139	-119	72	136	7	812	797	-795	-53	15	707	710	703	97	11	812	761	-759	-48	449	445	442	37
L=0	108	1579	1513	136	108	8	197	568	-49	-7	197	187	187	187	187	12	243	272	-183	-39	243	272	187	187
K=4	141	139	-119	72	136	9	812	797	-795	-53	16	707	710	703	97	13	812	761	-759	-48	449	445	442	37
L=0	108	1579	1513	136	108	10	197	568	-49	-7	197	187	187	187	187	14	243	272	-183	-39	243	272	187	187
K=5	141	139	-119	72	136	11	812	797	-795	-53	17	707	710	703	97	15	812	761	-759	-48	449	445	442	37
L=0	108	1579	1513	136	108	12	197	568	-49	-7	197	187	187	187	187	16	243	272	-183	-39	243	272	187	187
K=6	141	139	-119	72	136	13	812	797	-795	-53	18	707	710	703	97	17	812	761	-759	-48	449	445	442	37
L=0	108	1579	1513	136	108	14	197	568	-49	-7	197	187	187	187	187	18	243	272	-183	-39	243	272	187	187
K=7	141	139	-119	72	136	15	812	797	-795	-53	19	707	710	703	97	19	812	761	-759	-48	449	445	442	37
L=0	108	1579	1513	136	108	20	197	568	-49	-7	197	187	187	187	187	20	243	272	-183	-39	243	272	187	187
K=8	141	139	-119	72	136	21	812	797	-795	-53	20	707	710	703	97	21	812	761	-759	-48	449	445	442	37
L=0	108	1579	1513	136	108	22	197	568	-49	-7	197	187	187	187	187	22	243	272	-183	-39	243	272	187	187
K=9	141	139	-119	72	136	23	812	797	-795	-53	21	707	710	703	97	23	812	761	-759	-48	449	445	442	37
L=0	108	1579	1513	136	108	24	197	568	-49	-7	197	187	187	187	187	24	243	272	-183	-39	243	272	187	187

H	FD	FC	AC	BC	H	FD	FC	AC	BC	H	FD	FC	AC	BC	H	FD	FC	AC	BC
-7	522	511	506	70	1	889	813	808	88	-5	586	583	578	75	-9	158	211	211	8
K=16	L=3				-3	329	278	278	-5	-9	166	47	-46	-11	-11	637	614	607	96
0	519	548	519	79	-3	1185	1110	1163	120	0	551	542	-538	-69	0	140	89	-85	28
-2	182	229	219	37	-2	1089	1171	1195	36	-2	312	307	305	-35	-2	1796	156	-155	-84
-4	513	493	493	-71	-7	710	725	714	20	-4	204	202	18	-3	-4	286	290	-288	-15
K=0	L=4				K=12	L=4				K=4	L=5			K=12	L=5				
0	410	325	325	-3	658	682	683	-64	-54	0	584	550	544	77	1	1018	910	906	81
-2	783	828	820	11	594	621	619	51	51	K=13	L=4			K=5	L=5				
-4	419	482	477	11	364	369	365	10	10	-1	136	136	136	-82	-1	449	494	489	-66
-6	184	834	831	73	170	166	166	-46	-46	-3	679	616	611	110	-1	452	498	496	-49
-8	951	1010	1004	10	428	438	436	-12	-12	-3	677	685	687	110	-1	249	201	-199	-28
-10	1006	1027	1019	12	453	432	430	-47	-47	-5	413	465	467	106	-3	463	468	467	-38
-12	348	392	390	39	481	490	486	-29	-29	-7	713	697	689	101	-9	258	250	-244	-54
K=1	L=4				K=14	L=4				K=6	L=5			K=1	L=6				
1	70	31	26	17	203	221	219	34	34	0	482	500	496	-68	0	414	343	339	51
-3	513	529	524	-77	343	339	337	-56	-56	-2	122	160	158	-53	-2	422	402	396	-68
-5	349	370	369	-78	478	424	420	-36	-36	-4	445	444	444	-53	-4	159	156	156	-44
-7	581	597	595	-50	327	337	332	-58	-58	-4	339	346	346	-59	-4	566	587	581	-44
-9	442	475	474	-27	491	513	509	-65	-65	-8	470	477	477	-66	-8	215	124	124	-66
-11	439	382	379	-25	87	186	185	-10	-10	-10	149	177	176	-30	-10	198	129	129	-30
-13	453	424	421	-55	502	490	486	-27	-27	K=3	L=6			K=3	L=6				
K=2	L=4				K=8	L=4				K=7	L=5			K=1	L=6				
0	521	463	463	-43	202	103	102	-10	-10	0	1235	1097	1092	109	0	287	194	193	-14
-2	761	798	754	-78	780	722	715	103	103	1	787	721	715	-20	-2	225	382	377	-21
-4	407	422	421	-76	1253	1226	1222	-59	-59	-3	110	110	110	-13	-3	110	103	103	-13
-6	425	440	439	-34	634	630	627	62	62	-9	145	52	-50	-50	-9	145	52	-50	-50
-8	251	212	210	-27	112	89	70	33	33	K=4	L=6			K=4	L=6				
-10	562	582	575	-93	802	812	804	-116	-116	0	270	238	235	96	0	270	238	235	96
-12	136	61	60	-118	224	212	212	116	116	K=8	L=5			K=8	L=5				
K=3	L=4				K=9	L=4				K=1	L=5			K=1	L=5				
1	783	724	720	-75	80	62	62	7	7	0	951	854	849	96	0	287	194	193	-14
-3	83	750	738	-75	280	232	232	-79	-79	-2	448	382	377	-21	-2	448	382	377	-21
-5	169	119	117	-70	437	423	423	-80	-80	-4	109	108	108	-51	-4	109	108	108	-51
-7	974	915	969	-108	266	250	244	-34	-34	-8	343	319	315	-49	-8	343	319	315	-49
-9	83	1034	1031	-104	442	440	439	-40	-40	0	97	186	186	109	0	97	186	186	109
-11	200	798	798	-27	312	277	275	40	40	K=10	L=5			K=10	L=5				
-13	97	711	708	-98	40	277	275	40	40	1	479	447	441	8	1	479	447	441	8
K=4	L=4				K=10	L=4				K=1	L=5			K=1	L=5				
0	984	896	891	-91	88	49	49	-21	-21	0	765	730	726	82	0	765	730	726	82
-2	444	413	412	-30	563	554	547	88	88	-3	120	117	116	-37	-3	120	117	116	-37
-4	174	206	204	-27	324	320	316	-29	-29	-5	387	372	369	-44	-5	387	372	369	-44
-6	709	746	743	-71	412	410	407	48	48	-2	320	276	273	-43	-2	320	276	273	-43
-8	814	860	856	-74	108	87	87	-87	-87	-4	786	777	771	-95	-4	786	777	771	-95
-10	314	355	351	-73	205	205	205	97	97	K=11	L=5			K=11	L=5				
-12	225	223	221	-30	369	355	351	47	47	-1	267	290	286	43	-1	267	290	286	43
K=5	L=4				K=11	L=4				K=11	L=5			K=11	L=5				
5	225	223	221	-30	369	355	351	47	47	-1	267	290	286	43	-1	267	290	286	43
-10	177	189	182	-51	211	152	148	-36	-36	-2	682	634	626	102	-2	682	634	626	102
-12	225	223	221	-30	369	355	351	47	47	-1	267	290	286	43	-1	267	290	286	43
K=5	L=4				K=11	L=4				K=11	L=5			K=11	L=5				
5	225	223	221	-30	369	355	351	47	47	-1	267	290	286	43	-1	267	290	286	43