

The crystal structure of nigerite-24R

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Abstract

A 24R nigerite polytype was discovered in tin-bearing skarns at Mt. Garnet in northern Queensland. Its space group is $R\bar{3}m$, with rhombohedral lattice parameters $a_r = 18.826(10)\text{Å}$, $a_r = 17.508(3)^\circ$. The corresponding hexagonal lattice parameters are $a_{\text{hex}} = 5.730(3)$, $c_{\text{hex}} = 55.60(3)\text{Å}$. Its formula, determined from microprobe analysis (combined with information from the structure determination) is $\text{Al}_{14.69}\text{Sn}_{2.01}\text{Fe}_{2.76}\text{Zn}_{1.42}\text{Ca}_{0.28}\text{Mn}_{0.06}\text{Si}_{0.21}\text{O}_{30}(\text{OH})_2$. The correct structural model was obtained using crystallochemical reasoning based on structural principles established from an analysis of the related structures of spinel, nolanite, and others. The structure was refined to an R value of 0.044 for 448 symmetry-independent reflections with $F^2 \geq 3\sigma[F^2]$, collected using $\text{MoK}\alpha$ radiation. The model is based on a close packed anion framework (oxygens and hydroxyls) with a 24-layer mixed stacking sequence along c_{hex} given by ACBABCBCBACBACBACBACBCABC... (cchcccch...) and with an alternation of three types of metal atom layers in the sequence (...OT₁OT₁OT₂OT₂...), where O and T₂ represent the all-octahedral and the mixed octahedral-tetrahedral (111) metal atom layers found in spinel (with composition M_3O_4), and T₁ represents the mixed octahedral-tetrahedral metal atom layer found in nolanite, $\text{Zn}_2\text{Mo}_3\text{O}_8$, $\text{Co}_2\text{Mn}_3\text{O}_8$, etc. (with composition M_3O_4 , and one less tetrahedral metal per unit-cell layer than the T₂ type). The interlayer articulation of the various polyhedra is controlled by the oxygen stacking sequence and is such that tetrahedra share only corners with octahedra, and octahedra share edges and corners. The ...OT₂OT₂... part of the structure represents a 4-layer spinel block, with ordering of Al into the octahedral sites and divalent Fe and Zn into the tetrahedral sites. The Sn atoms are fully ordered into the octahedral sites in the T₁ layers, whereas the tetrahedral sites in these layers contain predominantly Al.

The structural principles which were used to derive the nigerite-24R structure have been applied to predict the structures of related minerals such as nigerite-6H, högbomite-8H, and the taaffeite polytypes.

Introduction

Nigerite, a tin-bearing oxide mineral, was discovered by Jacobson and Webb (1947) in 1944 during an investigation of the tin-bearing pegmatites of Kabba Province, central Nigeria. A subsequent study of the physical and chemical properties of the mineral by Bannister *et al.* (1947) showed that the mineral had symmetry $\bar{3}m$, with $a = 5.72$, $c = 13.86\text{Å}$. The ideal unit-cell composition was given by the formula $(\text{Zn},\text{Mg},\text{Fe}^{2+})(\text{Sn},\text{Zn})_2(\text{Al},\text{Fe}^{3+})_{12}\text{O}_{22}(\text{OH})_2$. The mineral was often found as overgrowths on (111) planes

of gahnite, and Bannister *et al.* noted the structural correspondence in (111) close-packed oxygen layers in gahnite being parallel to equivalent (0001) layers in nigerite. A close structural relationship between nigerite, högbomite, and taaffeite polytypes has been suggested by McKie (1963). The minerals all have trigonal or hexagonal symmetry, with similar a values and values of c that are multiples of about 2.3Å , the separation between closest-packed oxygen layers. According to McKie's nomenclature, in which a double oxygen layer is taken as a repeat layer, nigerite is designated as a 3H polytype (H for hexagonal

H	K	L	F OBS	F CALC
0	1	1	46.67	48.96
-1	0	1	182.77	180.63
-1	1	1	33.26	29.08
-1	-1	2	138.62	139.56
-2	0	2	337.88	329.15
-1	0	2	17.05	14.02
0	0	2	30.74	33.44
-1	1	2	30.60	35.69
1	1	2	59.53	62.21
-2	2	2	31.02	28.43
0	2	2	162.51	161.11
1	2	2	75.18	72.39
-2	-1	3	111.37	108.74
-3	0	3	107.88	103.37
-1	0	3	32.28	32.87
-2	1	3	28.93	30.73
0	1	3	86.22	83.45
1	1	3	32.00	32.66
-3	2	3	30.46	23.46
-1	2	3	41.78	43.60
0	2	3	50.44	48.70
2	2	3	72.94	73.68
-2	3	3	51.28	60.98
-1	3	3	38.43	36.97
2	3	3	45.69	44.57
3	3	3	33.12	32.79
-2	-2	4	181.80	180.59
-3	-1	4	81.89	75.68
-1	-1	4	32.84	24.14
-4	0	4	145.74	147.85
-2	0	4	26.27	24.36
0	0	4	129.12	124.19
0	1	4	44.86	44.47
-2	2	4	96.56	96.75
-1	2	4	45.83	46.84
0	2	4	14.25	11.68
1	2	4	40.66	42.78
-2	3	4	27.81	29.94
0	3	4	48.35	49.63
1	3	4	28.79	28.09
2	3	4	14.67	10.15
3	3	4	47.65	48.62
-1	4	4	31.58	27.40
0	4	4	27.11	24.57
2	4	4	38.57	33.68
4	4	4	34.79	39.31
-1	0	5	42.20	40.52
0	0	5	35.91	35.43
-2	1	5	48.35	46.85
-1	1	5	36.89	35.24
-2	2	5	32.70	29.86
0	2	5	50.58	51.01
1	2	5	35.77	34.80

H	K	L	F OBS	F CALC
2	2	5	30.18	28.43
0	3	5	29.07	28.29
1	3	5	25.15	24.19
2	3	5	32.28	33.38
3	3	5	81.47	72.14
0	4	5	24.45	18.94
1	4	5	29.48	31.74
3	4	5	188.36	187.94
4	4	5	19.42	17.31
0	5	5	20.03	22.14
1	5	5	35.07	35.10
2	5	5	178.58	173.60
3	5	5	64.56	60.66
4	5	5	47.37	51.15
-1	0	6	30.04	30.44
0	1	6	32.42	32.99
-1	2	6	25.15	26.36
0	2	6	25.99	25.37
1	3	6	31.58	31.94
2	3	6	15.51	9.91
3	3	6	137.92	137.75
2	4	6	31.30	33.64
3	4	6	13.83	10.97
4	4	6	107.74	106.02
-1	5	6	26.55	21.68
0	5	6	17.61	12.86
1	5	6	108.85	107.97
3	5	6	45.69	47.27
5	5	6	192.56	199.03
0	6	6	22.22	23.63
2	6	6	61.20	63.82
4	6	6	45.27	35.47
5	6	6	89.85	88.58
0	2	7	24.73	22.66
1	2	7	23.20	20.80
0	3	7	21.24	18.77
1	3	7	25.57	24.56
2	3	7	127.02	126.25
3	3	7	29.07	28.93
1	4	7	104.66	104.05
3	4	7	37.03	38.54
4	4	7	25.99	22.40
0	5	7	96.84	97.70
1	5	7	19.98	18.58
2	5	7	31.86	31.24
4	5	7	158.74	158.18
5	5	7	120.54	117.23
1	6	7	32.00	31.85
3	6	7	128.00	127.79
4	6	7	83.56	82.55
5	6	7	19.00	19.89
6	6	7	55.34	58.80
2	7	7	106.06	105.86

H	K	L	F OBS	F CALC
3	7	7	78.25	75.81
4	7	7	21.38	22.63
5	7	7	102.15	101.01
6	7	7	126.88	126.66
2	2	8	32.00	27.50
1	3	3	73.50	75.51
3	3	8	32.14	34.58
2	4	8	45.41	48.21
1	5	8	28.79	30.34
3	5	8	117.24	115.85
4	5	8	63.58	63.37
3	6	8	52.40	51.30
5	6	8	61.20	61.55
1	7	8	72.94	72.18
2	7	8	50.03	48.74
4	7	8	47.93	48.43
5	7	8	131.35	130.97
6	7	8	54.64	52.84
7	7	8	34.24	34.91
3	8	8	45.97	45.93
5	8	8	49.05	45.66
6	8	8	63.44	60.31
7	8	8	20.68	18.05
2	3	9	27.53	25.31
3	4	9	87.47	85.91
4	4	9	52.12	58.03
2	5	9	82.72	83.95
3	5	9	56.45	57.22
4	5	9	21.94	16.66
5	5	9	64.42	65.27
2	6	9	46.95	47.23
4	6	9	31.58	34.14
5	6	9	91.81	90.86
6	6	9	38.71	40.60
3	7	9	48.91	49.00
4	7	9	63.86	64.36
5	7	9	17.89	17.46
6	7	9	32.98	31.62
2	8	9	30.04	30.22
3	8	9	72.94	71.80
4	8	9	33.12	35.16
5	8	9	25.99	24.98
7	8	9	29.90	30.84
6	9	9	23.48	26.11
8	9	9	38.99	41.97
3	4	10	38.57	38.29
4	5	10	43.32	42.57
5	5	10	90.13	93.60
3	6	10	39.58	39.88
5	6	10	41.22	38.82
6	6	10	43.60	41.09
3	7	10	72.52	72.97
4	7	10	38.71	36.69

H	K	L	F OBS	F CALC
5	7	10	22.22	20.60
6	7	10	17.47	12.64
7	7	10	34.38	34.17
3	8	10	33.54	31.44
4	8	10	32.42	32.24
5	8	10	21.80	19.49
6	8	10	45.27	46.00
8	8	10	49.89	50.16
3	9	10	21.52	15.83
5	9	10	19.84	22.00
7	9	10	38.01	38.90
9	9	10	90.27	92.76
4	10	10	40.80	44.38
6	10	10	42.06	41.93
8	10	10	226.51	230.91
9	10	10	66.93	67.11
10	10	10	22.22	28.33
4	5	11	45.13	44.92
4	6	11	23.06	26.48
5	6	11	27.11	20.13
4	7	11	19.56	19.76
6	7	11	23.34	17.45
7	8	11	33.40	33.84
6	9	11	31.16	30.07
8	9	11	53.80	54.85
9	9	11	99.35	103.60
5	10	11	21.38	28.06
7	10	11	66.23	66.44
8	10	11	64.00	63.17
9	10	11	22.08	24.90
10	10	11	54.78	57.08
6	11	11	31.72	30.00
7	11	11	76.02	73.19
10	11	11	106.20	107.81
8	11	11	26.83	26.31
9	11	11	88.87	89.93
11	11	11	83.56	85.27
6	6	12	45.69	43.62
5	7	12	23.76	23.99
7	7	12	28.65	30.26
6	8	12	32.42	35.02
8	8	12	162.09	163.69
5	9	12	29.20	26.85
7	9	12	69.87	69.63
8	9	12	54.78	53.45
6	10	12	129.95	129.96
7	10	12	38.29	41.11
8	10	12	25.01	22.22
9	10	12	57.01	57.97
13	10	12	246.77	254.27
6	11	12	44.16	43.35
7	11	12	21.24	15.30
8	11	12	44.86	43.71

H	K	L	F OBS	F CALC	H	K	L	F OBS	F CALC
9	11	12	81.33	81.85	11	13	14	44.58	45.83
10	11	12	58.55	58.76	13	13	14	47.65	51.18
11	11	12	23.76	19.55	8	14	14	33.68	29.62
7	12	12	42.62	45.07	9	14	14	26.13	23.45
8	12	12	181.94	180.11	13	14	14	51.56	50.22
9	12	12	59.81	60.67	14	14	14	40.52	40.35
10	12	12	46.81	45.20	9	9	15	52.40	46.90
11	12	12	45.41	47.01	8	10	15	31.72	27.27
12	12	12	58.55	59.99	10	10	15	32.98	34.63
6	7	13	29.48	24.53	11	11	15	24.17	30.09
7	8	13	38.99	41.87	8	12	15	34.38	28.44
8	8	13	45.69	45.20	10	12	15	33.54	31.45
6	9	13	30.60	30.08	11	12	15	40.24	42.22
7	9	13	53.94	56.36	12	12	15	19.56	18.84
8	9	13	17.89	21.34	9	13	15	30.04	28.24
9	9	13	67.49	66.78	10	13	15	40.66	40.52
6	10	13	41.78	39.24	11	13	15	19.56	18.86
7	10	13	20.54	17.60	12	13	15	47.09	49.16
8	10	13	37.31	35.84	9	14	15	30.46	31.58
9	10	13	81.89	81.80	11	14	15	44.72	46.24
10	10	13	39.27	41.52	12	14	15	31.86	36.58
6	11	13	20.68	19.78	13	14	15	35.91	34.12
7	11	13	56.73	53.20	14	14	15	55.34	59.53
8	11	13	73.64	73.67	10	15	15	33.54	37.43
9	11	13	64.98	64.80	12	15	15	22.08	27.17
10	11	13	23.34	20.39	13	15	15	23.48	17.64
7	12	13	58.13	57.61	14	15	15	117.66	116.97
8	12	13	35.21	36.79	15	15	15	55.20	57.96
9	12	13	17.89	16.14	10	10	16	32.56	32.79
10	12	13	42.06	42.46	10	11	16	20.12	19.22
11	12	13	17.47	17.43	11	11	16	32.84	34.08
12	12	13	37.17	37.99	9	12	16	21.24	19.81
7	13	13	41.22	44.37	9	13	16	25.99	29.65
11	13	13	32.70	29.16	11	13	16	38.43	37.71
12	13	13	53.24	55.10	12	13	16	38.01	37.21
8	9	14	34.10	35.46	13	13	16	35.63	35.53
9	9	14	49.75	49.87	11	14	16	42.20	37.73
7	10	14	37.31	36.66	12	14	16	30.04	32.44
8	10	14	138.48	139.85	13	14	16	42.90	44.90
9	10	14	45.55	48.04	10	15	16	25.57	23.44
10	10	14	28.23	30.27	11	15	16	26.27	30.52
7	11	14	42.48	44.88	12	15	16	44.02	43.49
8	11	14	40.10	39.86	13	15	16	89.29	88.03
10	11	14	32.84	32.89	14	15	16	65.26	66.81
11	11	14	27.81	26.24	11	16	16	29.20	31.12
7	12	14	36.05	42.17	13	16	16	57.57	59.47
8	12	14	26.69	23.24	15	16	16	50.06	53.56
9	12	14	28.51	31.24	16	16	16	86.22	84.00
10	12	14	52.68	49.94	11	12	17	39.41	40.40
11	12	14	30.46	29.61	12	12	17	24.17	22.55
8	13	14	20.37	25.57	12	13	17	22.36	24.35
9	13	14	22.78	21.24	11	14	17	27.39	25.95
10	13	14	29.20	28.01	12	14	17	42.90	45.63

H	K	L	F OBS	F CALC
13	14	17	87.61	89.76
14	14	17	64.70	61.15
11	15	17	24.17	18.04
12	15	17	90.69	91.25
13	15	17	45.69	47.01
15	15	17	51.98	54.53
11	16	17	59.95	60.03
12	16	17	49.75	49.23
14	16	17	46.11	51.73
15	16	17	65.54	65.66
16	16	17	89.85	91.10
13	17	17	36.47	42.93
14	17	17	56.45	54.03
15	17	17	58.69	59.19
16	17	17	47.09	48.17
17	17	17	36.89	35.30
12	13	18	28.09	28.56
13	13	18	59.67	58.07
13	14	18	48.07	48.12
12	15	18	39.82	43.27
14	15	18	45.83	45.66
15	15	18	64.28	64.56
13	16	18	37.45	37.87
14	16	18	58.55	57.58
15	16	18	79.51	78.56
16	16	18	50.44	48.70
12	17	18	49.89	39.61
14	17	18	72.10	72.38
15	17	18	39.96	41.88
16	17	18	33.26	35.29
17	17	18	40.38	40.29
13	18	18	59.11	59.56
14	18	18	30.57	40.06
15	18	18	34.93	34.79
18	18	18	50.44	53.70
14	14	19	39.27	40.70
13	15	19	34.65	35.36
14	15	19	41.78	39.94
15	15	19	48.35	48.95
13	16	19	31.72	34.90
14	16	19	62.74	67.80
15	16	19	39.13	39.01
16	16	19	28.93	27.97
13	17	19	39.13	43.77
14	17	19	34.10	37.15
15	17	19	31.44	27.35
16	17	19	25.01	22.74
14	18	19	22.64	25.75
15	18	19	29.76	30.40
17	18	19	42.48	44.75
18	18	19	21.94	28.75
16	19	19	39.68	39.20
17	19	19	21.66	24.29

H	K	L	F OBS	F CALC
19	19	19	66.37	64.58
15	15	20	35.21	32.22
14	16	20	39.27	34.64
15	16	20	31.16	30.17
14	17	20	25.85	27.67
15	17	20	38.57	33.22
17	17	20	43.18	43.72
16	18	20	40.80	45.31
17	18	20	24.87	19.80
18	18	20	64.00	66.34
15	19	20	37.45	38.11
16	19	20	26.55	23.99
17	19	20	23.20	27.09
18	19	20	38.71	39.62
16	20	20	57.85	58.77
17	20	20	31.16	29.39
18	20	20	28.51	25.07
19	20	20	25.85	32.06
20	20	20	108.85	109.52
16	17	21	34.51	34.76
17	17	21	22.22	18.83
16	18	21	26.55	25.01
17	18	21	22.64	17.56
18	18	21	45.13	42.62
16	19	21	21.24	14.77
17	19	21	48.49	52.47
19	19	21	74.20	69.24
16	20	21	35.77	35.88
18	20	21	26.97	28.17
19	20	21	22.22	16.98
20	20	21	68.33	70.34
17	21	21	56.45	55.55
19	21	21	99.07	100.92
20	21	21	24.87	25.59
21	21	21	49.61	53.74
17	18	22	31.16	26.40
18	19	22	30.32	29.48
17	20	22	30.74	27.05
18	20	22	86.36	86.33
19	20	22	67.49	66.33
20	20	22	42.76	46.95
18	21	22	63.58	61.69
19	21	22	27.53	25.11
20	21	22	50.86	49.93
18	22	22	36.61	38.90
19	22	22	54.08	52.50
20	22	22	79.09	83.07
21	22	22	28.09	26.27
22	22	22	45.41	45.75
19	19	23	80.91	83.15
18	20	23	57.15	54.57
19	20	23	23.89	22.21
20	20	23	40.66	41.13

<u>H</u>	<u>K</u>	<u>L</u>	<u>F ORS</u>	<u>F CALC</u>
19	21	23	45.55	47.02
21	21	23	27.39	29.68
20	22	23	25.01	21.99
21	22	23	55.61	52.56
20	23	23	49.47	51.02
22	23	23	28.65	28.81
20	20	24	67.63	64.49
20	21	24	29.48	22.56
21	21	24	44.44	46.49
20	22	24	37.17	40.09
21	23	24	32.70	35.89
23	23	24	31.30	29.88
21	24	24	23.20	15.62
22	24	24	25.01	21.61
23	24	24	31.30	30.17
22	23	25	25.71	26.82
22	24	25	28.65	25.03
24	24	25	51.84	53.63
23	25	25	34.38	37.66
25	25	25	38.85	36.51
24	25	26	49.47	51.77
25	25	26	26.13	23.36
25	26	26	54.36	55.45
26	26	26	35.49	41.16