Kettnerite in Pmmn

h,k,l, Fc-squared, Fo-squared, sigma(Fo-squared) and status flag

2	0	0	30811.65	34553.97	202.02	o
4	0	0	10179.85	10202.59	135.28	o
1	1	0	21719.02	19653.21	127.25	o
3	1	0	10494.80	10965.16	143.47	o
5	1	0	3237.02	3226.41	42.64	o
0	2	0	30408.81	28564.93	315.67	o
2	2	0	15876.26	14860.76	158.46	o
4	2	0	6826.32	6806.32	93.56	o
1	3	0	10568.79	10961.33	158.14	o
3	3	0	6390.66	6148.26	86.36	o
0	4	0	10148.65	10241.48	141.74	o
2	4	0	6868.07	6885.44	99.19	o
1	5	0	3225.43	3229.60	46.70	o
1	0	1	5045.87	5073.17	51.69	o
2	0	1	6112.08	6271.29	81.52	o
3	0	1	2127.38	2173.46	30.04	o
4	0	1	2127.99	2141.89	30.72	o
5	0	1	1080.12	1058.11	16.56	o
0	1	1	5208.91	5262.05	77.31	o
1	1	1	8946.34	8568.50	83.24	o
2	1	1	5237.36	5426.24	66.75	o
3	1	1	3690.21	3724.08	54.13	o
4	1	1	1709.07	1621.81	24.02	o
5	1	1	1213.81	1229.08	18.79	o
0	2	1	6166.07	6772.00	94.96	o
1	2	1	5278.78	5458.70	72.05	o
2	2	1	4590.85	4487.40	62.36	o
3	2	1	2321.85	2245.23	33.35	o
4	2	1	1756.36	1731.13	25.11	o
0	3	1	2136.27	2214.72	34.48	o
1	3	1	3677.56	3830.63	52.26	o
2	3	1	2280.94	2332.65	34.07	o
3	3	1	1889.09	1821.45	26.60	o
4	3	1	928.98	895.27	16.21	o
0	4	1	2131.94	2137.11	34.78	o
1	4	1	1696.87	1695.98	26.59	o
2	4	1	1749.86	1768.75	26.96	o
3	4	1	932.53	925.10	16.93	o
0	5	1	1100.50	1064.44	32.78	o
1	5	1	1215.93	1203.66	22.48	o
1	0	2	8975.73	9176.30	75.91	o
2	0	2	3663.54	3756.61	52.67	o
3	0	2	4679.05	4794.26	65.67	o
4	0	2	957.59	957.72	14.37	o
5	0	2	1400.99	1397.97	21.37	o
1	1	2	776.20	759.00	10.72	o
2	1	2	4809.61	4685.43	63.51	o
3	1	2	455.18	422.22	8.10	o
4	1	2	2311.46	2308.63	32.94	o
5	1	2	294.37	305.66	12.12	o
1	2	2	4785.70	4655.66	70.67	o
2	2	2	3132.67	3087.55	43.99	o
3	2	2	2979.79	2875.91	42.73	o
4	2	2	995.99	984.44	15.46	o
0	3	2	4670.63	4887.90	70.93	o
1	3	2	443.53	449.43	9.94	o
2	3	2	3007.20	2959.10	42.73	o
3	3	2	224.82	238.41	9.55	o

4	3	2	1489.46	1532.61	21.75	o
0	4	2	965.43	1006.75	30.21	o
1	4	2	2320.19	2393.09	35.52	o
2	4	2	983.51	1028.60	16.21	o
3	4	2	1487.24	1462.51	21.03	o
0	5	2	1387.44	1341.13	38.70	o
1	5	2	297.14	313.72	16.17	o
1	0	3	29443.72	30903.53	167.08	o
2	0	3	640.70	600.08	8.84	o
3	0	3	12346.97	12617.15	154.80	o
4	0	3	74.15	59.10	7.71	o
5	0	3	3932.13	3902.70	56.85	o
1	1	3	835.75	934.20	13.67	o
2	1	3	15215.18	15684.28	150.25	o
3	1	3	192.45	183.69	6.99	o
4	1	3	6266.54	6199.44	86.33	o
5	1	3	103.77	94.71	10.64	o
1	2	3	15175.91	15421.86	171.38	o
2	2	3	647.81	697.77	11.05	o
3	2	3	8179.14	8444.36	118.64	o
4	2	3	130.77	129.62	9.18	o
1	3	3	185.53	190.65	8.81	o
2	3	3	8226.66	8378.80	108.83	o
3	3	3	55.00	59.47	8.45	o
4	3	3	4089.09	3921.34	55.77	o
1	4	3	6280.19	6206.12	93.10	o
2	4	3	126.43	123.37	10.64	o
3	4	3	4083.56	4188.94	56.88	o
1	5	3	105.38	105.38	15.79	o
1	0	4	5476.08	5482.58	73.67	o
2	0	4	6248.35	6598.23	93.04	o
3	0	4	2061.72	2125.29	29.64	o
4	0	4	2451.35	2441.67	35.54	o
5	0	4	883.10	874.48	16.55	o
1	1	4	17329.37	17470.11	158.81	o
2	1	4	4973.45	4989.27	72.10	o
3	1	4	6735.95	6535.22	97.12	o
4	1	4	1493.14	1483.76	21.77	o
5	1	4	2398.77	2363.84	35.48	o
1	2	4	5009.01	5040.47	74.75	o
2	2	4	4872.86	4720.02	71.36	o
3	2	4	2107.17	2087.46	30.36	o
4	2	4	2071.19	2032.47	29.94	o
1	3	4	6716.20	6711.12	98.24	o
2	3	4	2071.90	2034.26	30.73	o
3	3	4	3556.26	3492.11	48.30	o
4	3	4	755.16	764.50	16.20	o
1	4	4	1482.44	1525.41	24.34	o
2	4	4	2065.21	1997.68	28.46	o
3	4	4	757.84	789.90	17.29	o
1	5	4	2401.86	2354.25	34.01	o
1	0	5	634.36	709.51	10.32	o
2	0	5	7388.27	7227.97	104.52	o
3	0	5	228.84	241.74	7.34	o
4	0	5	3172.08	3219.05	44.93	o
5	0	5	68.05	68.27	11.01	o
1	1	5	6987.27	7077.13	90.52	o
2	1	5	379.11	382.86	7.35	o
3	1	5	4288.50	4276.43	58.68	o
4	1	5	123.89	129.62	9.18	o

5	1	5	1261.36	1219.56	19.17	o
1	2	5	378.74	367.79	9.19	o
2	2	5	3925.93	3808.77	55.69	o
3	2	5	160.89	171.50	8.46	o
4	2	5	1970.13	1944.06	29.55	o
1	3	5	4328.35	4321.63	58.69	o
2	3	5	160.52	147.65	9.18	o
3	3	5	2744.05	2678.17	39.27	o
4	3	5	67.63	62.41	11.39	o
1	4	5	124.01	139.54	13.95	o
2	4	5	1989.91	1991.83	28.83	o
3	4	5	67.90	69.02	12.11	o
1	5	5	1254.88	1243.50	29.47	o
1	0	6	659.04	641.72	9.97	o
2	0	6	8654.17	9044.75	125.30	o
3	0	6	244.25	259.39	7.71	o
4	0	6	3750.69	3878.70	56.90	o
5	0	6	177.69	138.09	12.11	o
1	1	6	18820.72	18466.11	212.40	o
2	1	6	991.31	1028.21	14.77	o
3	1	6	8711.38	8596.80	120.54	o
4	1	6	283.76	290.98	10.65	o
1	2	6	1004.35	1074.41	15.12	o
2	2	6	6838.06	6944.15	97.57	o
3	2	6	414.90	380.11	10.66	o
4	2	6	3143.60	3097.58	44.88	o
1	3	6	8699.44	8757.59	123.58	o
2	3	6	401.08	384.87	11.75	o
3	3	6	5006.63	4918.03	71.29	o
4	3	6	120.69	105.39	12.48	o
1	4	6	279.69	283.98	17.64	o
2	4	6	3134.94	3112.31	46.71	o
3	4	6	121.83	105.39	13.23	o
0	0	7	1257.18	1104.92	16.31	o
1	0	7	14399.97	14515.81	197.76	o
2	0	7	1748.67	1781.89	25.56	o
3	0	7	7094.09	7051.64	94.83	o
4	0	7	608.14	643.29	13.25	o
1	1	7	2096.40	2240.92	30.86	o
2	1	7	8496.74	8615.73	116.95	o
3	1	7	1001.00	1009.38	15.47	o
4	1	7	3826.52	3810.37	54.29	o
1	2	7	8473.07	8654.16	126.48	o
2	2	7	1742.20	1711.78	27.38	o
3	2	7	4829.74	4863.51	69.86	o
4	2	7	646.59	662.04	15.07	o
1	3	7	986.53	1009.67	21.74	o
2	3	7	4856.79	4707.80	68.76	o
3	3	7	512.51	545.25	14.72	o
2	4	7	638.50	637.01	18.76	o
0	0	8	418.52	438.68	10.29	o
1	0	8	9512.05	9475.61	123.12	o
2	0	8	564.77	574.13	9.95	o
3	0	8	4934.71	4861.83	68.87	o
4	0	8	118.84	111.98	9.92	o
2	1	8	5638.55	5659.61	80.96	o
3	1	8	7.04	2.93	7.71	o
4	1	8	2467.50	2503.45	34.79	o
2	2	8	573.46	597.12	13.26	o
3	2	8	3264.11	3251.63	46.78	o

4	2	8	177.71	157.16	12.11	o
2	3	8	3287.98	3298.34	46.06	o
3	3	8	2.44	29.73	11.39	o
2	4	8	173.20	174.42	16.51	o
0	0	9	1022.78	978.73	14.03	o
2	0	9	1026.16	1032.15	15.11	o
3	0	9	4374.89	4479.35	61.19	o
4	0	9	468.37	469.80	13.59	o
0	1	9	9255.14	8265.68	110.10	o
2	1	9	7619.07	7581.79	103.53	o
3	1	9	745.39	758.58	13.98	o
4	1	9	3018.20	3100.50	44.11	o
2	2	9	927.48	916.91	16.94	o
3	2	9	3970.06	4035.15	57.69	o
4	2	9	422.80	413.46	15.06	o
2	3	9	3933.76	3947.58	56.93	o
3	3	9	396.47	380.36	15.81	o
2	4	9	421.00	403.90	20.96	o
0	0	10	15821.58	14807.06	225.50	o
2	0	10	9668.00	10119.09	138.73	o
3	0	10	467.62	547.45	12.87	o
4	0	10	4742.01	4860.27	67.09	o
0	1	10	841.00	762.92	13.63	o
2	1	10	645.21	655.45	14.73	o
3	1	10	4311.45	4362.80	58.52	o
4	1	10	314.51	330.30	14.33	o
0	2	10	9564.98	8920.41	131.01	o
2	2	10	6209.89	6165.89	85.29	o
3	2	10	373.16	435.49	14.71	o
4	2	10	3354.59	3389.56	47.84	o
2	3	10	372.34	402.41	19.12	o
3	3	10	2986.93	2892.76	41.13	o
0	0	11	5396.10	5104.72	73.01	o
2	0	11	4233.47	4351.88	61.22	o
3	0	11	537.08	547.55	14.35	o
4	0	11	1860.80	1864.80	27.33	o
0	1	11	1306.14	1229.14	18.45	o
2	1	11	1280.83	1327.29	22.14	o
3	1	11	2856.18	2874.08	41.15	o
4	1	11	470.51	499.88	16.53	o
0	2	11	4249.86	4035.53	56.75	o
3	2	11	624.67	580.02	18.01	o
0	3	11	539.29	506.74	16.54	o
3	3	11	1683.63	1718.15	29.51	o
0	0	12	5379.25	4975.01	73.64	o
3	0	12	1434.51	1517.81	22.51	o
4	0	12	1889.22	2056.30	30.28	o
0	1	12	2482.15	2367.48	32.28	o
3	1	12	1738.33	1804.97	26.20	o
4	1	12	772.80	792.08	20.23	o
0	2	12	4553.00	4203.89	60.51	o
3	2	12	954.18	954.27	23.19	o
0	3	12	1431.70	1352.19	22.51	o
0	4	12	1896.68	1898.35	29.53	o
0	0	13	543.00	491.44	13.26	o
3	0	13	4860.36	4858.44	67.87	o
0	1	13	7679.45	7434.11	100.22	o
3	1	13	187.61	229.15	17.26	o
0	2	13	259.16	246.16	12.12	o
0	3	13	4858.01	4790.53	63.78	o

0	0	14	1204.64	1208.74	19.56	o
0	1	14	2957.92	2831.58	41.20	o
0	2	14	1077.79	1063.99	18.79	o
0	3	14	1657.25	1613.23	24.34	o
0	0	15	2950.92	2895.15	43.42	o
1	0	15	1187.01	1171.01	21.02	o
0	1	15	1188.97	1197.56	18.05	o
0	2	15	1852.79	1867.66	27.69	o
0	3	15	728.62	773.99	18.76	o
0	0	16	4637.60	4678.19	65.64	o
1	0	16	21.44	22.03	11.39	o
0	1	16	19.99	19.09	10.64	o
1	1	16	5910.34	5961.33	80.10	o
0	2	16	3752.05	3821.77	56.46	o
1	2	16	1.40	13.57	12.85	o
0	0	17	1990.24	1962.88	29.55	o
1	0	17	2162.53	2490.09	36.60	o
0	1	17	2154.57	2114.51	31.42	o
1	1	17	2085.78	2111.98	30.68	o
0	2	17	1779.19	1839.43	27.32	o
1	2	17	1611.24	1582.00	25.08	o
0	0	18	169.22	133.66	12.49	o
1	0	18	1598.46	1634.08	27.31	o
0	1	18	1589.72	1662.81	24.71	o
1	1	18	365.21	363.76	15.43	o
0	0	19	80.75	134.36	13.57	o

The Canadian Mineralogist
Vol. 37, pp. 923-927 (1999)

CRYSTAL-STRUCTURE DETERMINATION OF TWINNED KETTNERITE

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Abstract

The crystal structure of kettnerite, $CaBi(CO_3)OF$, *a* 3.7976(5), *b* 3.7976(5), *c* 13.569(4) Å, *V* 195.71(8) Å^3, space group *Pmmn*, *Z* = 2, has been refined to an *R* index of 0.016 on the basis of 265 unique, observed reflections. Although the cell and the distribution of diffraction intensities obey tetragonal symmetry, kettnerite is optically biaxial, and attempts to solve the structure with tetragonal symmetry led to stereochemical nonsense. Introduction of a twin plane *via* reflection on {110} for orthorhombic symmetry simulates tetragonal diffraction-intensity distribution for the merohedral twin, and gives a structure with sensible stereochemistry. Both large cations, Ca and Bi, have [8]-coordination, and Bi^{3+} shows stereoactive lone-pair behavior. The kettnerite structure is layered with a Ca–F layer, a Bi–O layer, and a CO_3 layer with the plane of the (CO_3) group orthogonal to the plane of the layer. Oxy-carbonate minerals are rare relative to hydroxy- and hydrated-carbonate minerals. The only cations that can satisfy the bond-valence requirements for a non-carbonate oxygen atom are those for which there is an electronic driving mechanism to produce a marked asymmetrical distribution of bond valences, such as for the uranyl group, $(UO_2)^{2+}$, and for large cations with stereoactive lone-pairs of electrons, *e.g.*, Bi^{3+}, Pb^{2+}. In this regard, all oxy-carbonate minerals contain such cations.

Keywords: kettnerite, crystal structure, merohedral twin, stereoactive lone-pair of electrons.

Sommaire

Nous avons affiné la structure cristalline de la kettnerite, $CaBi(CO_3)OF$, *a* 3.7976(5), *b* 3.7976(5), *c* 13.569(4) Å, *V* 195.71(8) Å^3, groupe spatial *Pmmm*, *Z* = 2, jusqu'à un résidu *R* de 0.016 en utilisant 265 réflexions observées. Quoique la maille et la distribution des intensités de raies diffractées répondent à une symétrie tétragonale, la kettnerite est biaxe dans ses propriétés optiques, et les essais d'une ébauche de la structure dans cette symétrie n'ont donné que des résultats sans aucun sens stéréochimique. L'introduction d'un plan de macle selon une réflexion sur {110} en symétrie orthorhombique mène à une simulation d'une distribution tétragonale des intensités pour une macle méroédrique, et à une structure stéréochimiquement correcte. Les deux cations de taille importante, Ca et Bi, possèdent une coordinence [8], et le Bi^{3+} fait preuve d'un comportement stéréoactif typique de la présence d'une paire isolée d'électrons. La structure, en couches, comporte un niveau Ca–F, un niveau Bi–O, et un niveau de carbonates dont le plan des groupes CO_3 est perpendiculaire aux couches. Les minéraux oxy-carbonatés sont rares en comparaison des minéraux carbonatés hydroxylés ou hydratés. Les seuls cations à pouvoir satisfaire aux exigeances en valences de liaison d'un atome d'oxygène non lié à un groupe carbonate sont ceux pour lesquels il existe un mécanisme électronique favorisant une distribution fortement assymétrique des valences de liaison, par exemple le groupe uranyle, $(UO_2)^{2+}$, et les cations de taille importante contenant une paire isolée d'électrons stéréoactifs, par exemple, Bi^{3+} et Pb^{2+}. Ainsi, tous les minéraux oxy-carbonatés contiennent de tels cations.

(Traduit par la Rédaction)

Mots-clés: kettnerite, structure cristalline, macle méroédrique, paire isolée d'électrons stéréoactifs.

Introduction

Kettnerite from Krupke, northwestern Bohemia, Czech Republic, was first reported as tetragonal, *P4/nmm*, by Žák & Syneček (1956). Syneček & Žák (1960) later reported the crystal structure of this material to be orthorhombic, *Cmma*, *a* 5.36(2), *b* 5.36(2), *c* 13.59(3) Å and *Z* = 4. Although this structure correctly located the Ca, Bi, F and non-carbonate O sites, the carbonate group was described as a tetragonal pyramid, which

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