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Crystal structure of rasvumite, KFe_2S_3

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Abstract

Rasvumite, KFe_2S_3, isostructural with $BaFe_2S_3$ described by Hong and Steinfink (1972), is orthorhombic, *Cmcm*, $a = 9.049(6)$, $b = 11.019(7)$, $c = 5.431(4)$Å, $V = 541.5$Å^3, Z = 4, density (calc) = 3.029 g cm^{-3}. Least-squares refinement of 332 single-crystal *hkl* reduced the conventional residual to 0.081. The structure contains double edge-sharing chains of Fe–S tetrahedra parallel to *c* and face-sharing pairs of K–S polyhedra that also form double chains parallel to *c*. The average bond distances are: Fe–S = 2.264, Fe–Fe = 2.710, K–S = 3.515Å. By analogy to $BaFe_2S_3$, rasvumite has high-spin iron with delocalized electrons such that the average oxidation state is close to the 2.5+ indicated by the formula.

Introduction

Rasvumite was discovered at the Khibina massif, Kola Peninsula, USSR, and described by Sokolova *et al.* (1970). The chemical formula originally proposed, $K_3Fe_{19}S_{14}$, with Z = 1 in the orthorhombic cell, was not compatible with the symmetry. The correct formula, KFe_2S_3, was assigned by Czamanske *et al.* (1979) after discovery and study of rasvumite at Coyote Peak, Humboldt County, California.

The Coyote Peak rasvumite has not been found in crystals as excellent as those found in the Khibina massif. Through the courtesy of M. N. Sokolova, Academy of Sciences, Moscow, some of the original crystals were made available to us for study, and one of these was selected for structural analysis.

Comparison of the crystallographic data for rasvumite with those reported for synthetic $BaFe_2S_3$ by Hong and Steinfink (1972) left little doubt that the two are isostructural despite the differences in chemistry and formal valence. The isostructural relationship is confirmed by the results of our refinement for the rasvumite structure. A brief preliminary description was given by Clark *et al.* (1979).

Experimental data

Crystallography, collection of data

The crystallographic data for rasvumite given by Czamanske *et al.* (1979) were confirmed upon examination of the Khibina crystal selected for the structural study. That crystal was a prismatic fragment 0.5 mm long and 0.2 × 0.05 mm in cross-section. It was impossible to obtain a more nearly equant crystal because of its tendency, noted by Sokolova *et al.* (1970), to split into fine needles when pressed. A least-squares fit of the angular coordinates of 29 automatically centered reflections in the 2θ range 30° to 46° gave the values in Table 1. For comparison, the values reported by Sokolova *et al.* and by Czamanske *et al.* (1979) are also listed in Table 1, together with those for the isostructural synthetics, $BaFe_2S_3$ (Hong and Steinfink, 1972) and $CsCu_2Cl_3$ (Brink *et al.*, 1954).

A total of 458 reflections in the angular 2θ range of 5° to 60° was measured using an ω–2θ scan mode, a scan range of 2°, graphite-monochromatized Mo$K\alpha$ radiation, and a solid-state detector system. Two

Table 3.

COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS, RASVUMITE

An asterisk indicates a reflection with intensity less than $3\sigma(I)$; see text. Within each column, ℓ is at the left, F_o in the middle, and F_c at the right.

0,0,L

2	29	-26
4	235	211
6	0*	-6

0,2,L

0	141	176
1	11	-1
2	163	166
3	0*	1
4	104	94
5	0*	1
6	68	61
7	0*	-1

0,4,L

0	0*	10
1	53	62
2	244	258
3	38	-41
4	13	10
5	20	24
6	114	107
7	3*	-13

0,6,L

0	119	137
1	23	-31
2	106	111
3	15	23
4	77	78
5	7*	-14
6	56	53
7	23	7

0,8,L

0	140	159
1	35	-41
2	42	42
3	26	32
4	102	107
5	16	-21
6	22	18

0,10,L

0	95	109
1	27	30
2	42	47
3	20	-23
4	66	75
5	15	15

0,12,L

0	35	37
1	17	13
2	66	80
3	10*	-11
4	21	26

0,14,L

0	9*	13
1	0*	-8
2	58	76
3	3*	6

1,15,L

0	31	38
1	16	14

1,13,L

0	17	19
1	10*	17
2	38	42
3	0*	-14
4	14	14

1,11,L

0	23	21
1	32	-39
2	47	56
3	34	32
4	19	15
5	15	-23

1,9,L

0	84	90
1	16	-17
2	7*	15
3	0*	14
4	58	60
5	0*	-10
6	16	9

1,7,L

0	60	69
1	65	66
2	55	59
3	51	-51
4	44	45
5	41	35
6	20	25

1,5,L

0	36	41
1	16	-7
3	5*	2
4	29	25
5	9*	1
6	47	47
7	12*	-2

1,3,L

0	130	140
1	59	-54
2	60	56
3	41	37
4	80	70
5	22	-25
6	31	28
7	0*	15

1,1,L

0	101	109
1	2*	5
2	111	98
3	0*	-1
4	66	58
5	0*	-3
6	42	34
7	0*	4

2,0,L

0	35	-39
2	74	-62
4	24	-23
6	20	-21

2,2,L

0	90	-95
1	190	-177
2	14	-13
3	131	117
4	52	-48
5	87	-74
6	0*	-8
7	51	43

2,4,L

0	38	-37
1	18	17
2	54	-48
3	6*	-10
4	21	-21
5	11*	4
6	18	-20
7	25	-1

2,6,L

0	0*	15
1	77	79
2	75	-79
3	68	-63
4	16	7
5	45	44
6	29	-33

2,8,L

0	56	-62
1	6*	11
2	7*	-1
3	0*	-10
4	38	-38
5	15	8
6	0*	-3

2,10,L

0	36	-47
1	23	-31
2	10*	-1
3	24	27
4	26	-32
5	0*	-20

2,12,L

0	0*	-2
1	31	-32
2	20	-32
3	22	26
4	13	-3

2,14,L

0	20	-10
1	19	18
2	0*	-17
3	24	-16

3,15,L

0	28	-29

3,13,L

0	68	-82
1	19	18
2	17	-15
3	26	-15

3,11,L

0	69	-82
1	12	-10
2	41	-39
3	4*	8
4	51	-58
5	15	-6

3,9,L

0	11	-13
1	16	-11
2	127	-132
3	8*	9
4	0*	-9
5	0*	-7

Table 3 (continued).

COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS, RASVUMITE

	3,7,L	
0	91	-87
1	27	21
2	97	-101
3	6*	-16
4	64	-54
5	4*	11
6	54	-50
	3,5,L	
0	207	-207
1	30	-26
2	32	-34
3	19	17
4	139	-126
6	24	-15
	3,3,L	
0	139	-146
1	0*	3
2	128	-118
3	0*	-2
4	101	-90
5	0*	1
6	56	-44
7	0*	0
	3,1,L	
0	160	-110
1	49	47
2	181	-169
3	33	-30
4	0*	-60
5	11*	16
6	82	-72
7	16	-7
	4,0,L	
0	22	22
2	237	-219
4	12	9
6	100	-92
	4,2,L	

0	130	-129
1	26	-23
3	12	16
4	20	-74
5	7*	-10
7	0*	6
	4,4,L	
0	199	-196
1	36	40
2	12	-9
3	27	-29
4	67	-121
5	17	18
	4,6,L	
0	75	-78
1	14	-10
2	90	-83
3	0*	7
4	55	-53
5	16	-4
6	0*	-37
	4,8,L	
0	22	-34
1	21	-27
2	96	-97
3	15	21
4	20	-21
5	0*	-14
6	56	-51
	4,10,L	
0	34	-39
1	9*	16
2	61	-68
3	11*	-12
4	34	-27
5	0*	7
	4,12,L	
0	50	-61
1	13	5
2	0*	-25

3	21	-4
4	39	-46
	4,14,L	
0	48	-60
1	3*	-3
2	7*	-10
	5,13,L	
0	0*	4
1	0*	12
2	20	-4
	5,11,L	
0	16	-16
1	48	-51
2	17	14
3	40	43
4	18	-11
	5,9,L	
0	0*	5
1	14	-18
2	0*	-4
3	7*	15
4	0*	3
5	0*	-11
	5,7,L	
0	0*	-7
1	79	78
2	0*	6
3	66	-64
4	0*	-4
5	46	44
6	0*	2
	5,5,L	
0	5*	1
1	0*	13
2	9*	-2
3	7*	-12
4	7*	1
5	17	10

6	0*	-1
	5,3,L	
0	40	43
1	73	-68
2	41	-36
3	59	55
4	22	23
5	43	-38
6	23	-13
	5,1,L	
0	36	-36
1	24	-26
2	30	30
3	26	23
4	20	-20
5	20	-18
6	9*	11
7	0*	12
	6,0,L	
0	131	133
2	43	44
4	91	83
6	26	21
	6,2,L	
0	74	71
1	73	-73
2	92	93
3	61	58
4	52	47
5	45	-39
6	40	43
	6,4,L	
0	59	59
1	19	15
2	96	91
3	14	-11
4	42	38
5	14	6
6	45	45

	6,6,L	
0	83	94
1	37	35
2	51	42
3	36	-30
4	59	62
5	28	22
6	33	24
	6,8,L	
0	53	56
1	0*	-1
2	55	55
3	14	0
4	37	41
5	0*	0
	6,10,L	
0	28	42
1	17	-12
2	40	49
3	20	11
4	37	31
	6,12,L	
0	37	41
3	0*	12
	7,11,L	
0	30	32
1	16	3
2	49	56
3	0*	-3
	7,9,L	
0	109	117
3	10*	5
4	93	83
	7,7,L	
0	77	83
1	13	-1

Table 3 (continued).

COMPARISON OF OBSERVED AND CALCULATED STRUCTURE FACTORS, RASVUMITE

L	Fo	Fc
	7,7,L	
2	50	47
3	0*	1
4	63	59
5	15	-1
	7,5,L	
0	0*	8
1	16	-21
2	139	134
3	17	16
4	0*	6
5	0*	-10
	7,3,L	
0	70	69
1	15	18
2	95	95
3	21	-14
4	49	43
5	0*	9
6	56	50
	7,1,L	
0	135	136
1	38	36
2	45	41
3	30	-28
4	101	92
5	17	18
6	26	19
	8,0,L	
0	67	69
2	0*	-16
4	55	47

L	Fo	Fc
	8,2,L	
0	19	15
1	40	-42
2	34	31
3	37	35
4	10*	11
5	23	-24
	8,4,L	
0	12	-5
1	12	13
2	48	47
3	12	-10
4	0*	-4
5	0*	7
	8,6,L	
0	42	34
1	21	19
2	0*	7
3	20	-16
4	27	23
5	17	12
	8,8,L	
0	32	25
1	4*	-5
2	0*	9
3	0*	4
4	24	19
	8,10,L	
0	0*	16
1	15	-5
2	13*	13
3	0*	5

L	Fo	Fc
	8,12,L	
0	0*	10
	9,9,L	
0	21	-28
1	0*	-12
2	26	-25
3	15	10
	9,7,L	
0	37	-36
1	56	52
2	26	-26
3	43	-43
4	27	-26
	9,5,L	
0	38	-31
1	9*	12
2	37	-38
3	20	-11
4	25	-23
	9,3,L	
0	17	-17
1	44	-45
2	58	-56
3	40	38
4	19	-14
5	31	-27
	9,1,L	
0	63	-62
1	21	-22
2	21	-19
3	19	20
4	36	-43
5	9*	-15

L	Fo	Fc
	10,0,L	
0	9*	-1
2	104	-99
4	9*	-11
	10,2,L	
0	62	-64
1	14	-16
2	57	-50
3	9*	14
4	48	-46
	10,4,L	
0	92	-91
1	15	13
2	20	-19
3	3*	-10
4	72	-66
	10,6,L	
0	50	-47
1	14	3
2	47	-50
3	0*	-3
	10,8,L	
0	30	-29
1	17	-9
2	52	-56

L	Fo	Fc
	11,7,L	
0	16	-16
1	0*	3
	11,5,L	
0	61	-62
1	0*	-8
2	21	7
	11,3,L	
0	41	-39
1	12*	5
2	14	-18
3	9*	-4
	11,1,L	
0	18	-8
1	0*	13
2	47	-49
3	2*	-11
	12,0,L	
0	21	20
2	21	7
	12,2,L	
0	0*	7
1	36	-37
2	16	18
	12,4,L	
0	12*	11
1	0*	2