Refinement of NiYb$_2$Be$_2$Si$_2$O$_{10}$, a gadolinite-type structure

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Auszug

Die Kristallstruktur eines synthetischen Gadolinits, NiYb$_2$Be$_2$Si$_2$O$_{10}$, der die Raumgruppe $P2_1/c$ und die Gitterkonstanten $a = 4,664$, $b = 7,385$, $c = 9,866$ Å, $\beta = 90,02°$ hat, wurde mittels der Methode der kleinsten Quadrate unter Verwendung von 595 mit dem Diffraktometer gemessenen Intensitäten bis zu $R = 0.073$ verfeinert. Die Struktur läßt sich von der des Datoliths ableiten, wenn darin Ca, B und OH durch Yb, Be und O ersetzt und Ni im Koordinatenursprung in oktaedrischer Umgebung untergebracht wird. Sie besteht aus Schichten von vier- und achtgliedrigen Ringen aus abwechselnden SiO$_4$- und BeO$_4$-Tetraedern; die Schichten sind durch Ni- und Yb-Atome miteinander verbunden. Die Gesamtzahl der von einem Sauerstoffatom empfangenen Valenzbindungen, $\zeta(O)$, kann für die Zuordnung der Bindungslängen im Ni-Tetraeder benutzt werden. Mullikens Bindungsüberlappungs-Dichte ist dagegen besser geeignet für die Einordnung der Bindungslängen in den SiO$_4$- und BeO$_4$-Tetraedern.

Abstract

The structure of synthetic gadolinite, NiYb$_2$Be$_2$Si$_2$O$_{10}$, space group $P2_1/c$ with $a = 4.664$, $b = 7.385$, $c = 9.866$ Å, and $\beta = 90.02°$ has been refined ($R = 0.073$) by least-squares methods using 595 intensities measured with a diffractometer. The structure can be derived from that of datolite, CaBSiO$_4$(OH), by replacing Ca by Yb, B by Be, OH by O, and by placing Ni in octahedral coordination at the origin. It is based on sheets of four- and eight-membered rings of alternating SiO$_4$ and BeO$_4$ tetrahedra with the sheets bonded together by Ni and Yb atoms. The sum of valence-bond numbers received by oxygen, $\zeta(O)$, can be used to order bond lengths in the Ni octahedron while Mulliken bond-overlap populations can be better used to order bond lengths in the SiO$_4$ and BeO$_4$ tetrahedra.

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Introduction

The structural relationship between gadolinite, $FeY_2Be_2(SiO_4)_2O_2$, and datolite, $CaB(SiO_4)OH$, was first pointed out by ITO and MORI (1953) when they proposed that the gadolinite structure could be derived from that of datolite by replacing Ca by Y, B by Be, OH by O and by placing Fe at the origin. In support of their proposal they cited the general agreement between calculated structure factors and observed structure amplitudes obtained by visual estimation of line intensities recorded on x-ray powder photographs. PAVLOV and BELOV (1959) verified this proposal when they determined the structure of gadolinite using direct methods. In their analysis of the coordination of Fe in gadolinite, they used coordinates obtained from c-axis projection data in conjunction with the z coordinates of datolite. However, their analysis resulted in a set of Fe—O bond distances that could not be ordered by the sum of the valence bond numbers, $\zeta(O)$, received by the coordinating oxygen atoms (SMITH, 1953; BAUR, 1970).

ITO (1965, 1966, 1967) undertook an extensive examination of the crystal chemistry and stability relations of synthetic materials with the gadolinite type structure. He showed that substituents such as Mg, Ni, Co, Zn, Cu, Mn, Cd, and La, Sm, Yb, Ce, Nd, Dy, Gd, Er, Tm, and Lu were capable of isomorphously replacing Fe and Y, respectively. A dependency of the lattice constants (especially β) on the variation in size of the substituient ions was also observed (ITO, 1965).

In the present study, the structure of a synthetic gadolinite of composition $NiYb_2Be_2Si_2O_{10}$ was refined first, to verify the structural relationship between synthetic and natural gadolinite and datolite and second, to examine bond length variations in both the octahedral (Ni) and the tetrahedral (Si, Be) portions of the structure in terms of valence-bond numbers received by oxygen, $\zeta(O)$, (PANT and CRUICKSHANK, 1967) and Mulliken bond overlap populations, respectively.

Crystallographic data

The $NiYb_2Be_2Si_2O_{10}$ crystal used in our study was selected from a number synthesized and kindly supplied by Dr. J. ITO of Harvard University. A bright green euhedral, equant crystal measuring 0.1 mm in maximum dimension was mounted along the b axis. The space group determined from the Friedel symmetry and systematic presences

on Weissenberg and precession photographs is $P2_1/c$, which is consistent with that of natural gadolinite (ITO and MORI, 1953). The lattice parameters determined from multiple measurements of the 4θ values of axial reflections using a four-circle single crystal x-ray diffractometer are $a = 4.664(4)$, $b = 7.385(4)$, $c = 9.866(8)$ and $\beta = 90.02°$. The β angle is in close agreement with that reported by ITO (1965) for a synthetic gadolinite of this composition.

Intensity data

More than 720 nonequivalent intensities within the limit $(\sin\theta)/\lambda = 0.63$ were measured using Nb-filtered MoKα radiation and a scintillation counter mounted on an automated Picker single-crystal diffractometer. The data were corrected for Lorentz and polarization factors but absorption effects were neglected because of the small size of the crystal $(\mu R = 1.2)$.

Refinement

The refinement was undertaken using ORFLS, a Fortran IV, full-matrix least-squares program written by BUSING, MARTIN and LEVY (1962), and 660 observed structural amplitudes. Sixty-one amplitudes which were either unobserved or were less than five times the standard deviations obtained from counting statistics were not included in the refinement. The starting parameters were those of datolite (FOIT, PHILLIPS and GIBBS, 1973) with Ni placed at the origin. The scattering factor tables were constructed from the values given in *International tables for x-ray crystallography* for neutral atoms and the data were weighted according to a scheme presented by HAN-

Table 1. NiYb₂Be₂Si₂O₁₀ *atom coordinates and isotropic temperature factors with standard errors in parentheses*

Atom	M	x	y	z	B
Yb	4	0.9990(2)	0.1082(1)	0.3271(1)	0.34(3) Å²
Ni	2	0	0	0	0.25(6)
Si	4	0.4859(12)	0.2819(8)	0.0785(5)	0.39(8)
Be	4	0.538(7)	0.422(4)	0.341(3)	1.0(4)
O(1)	4	0.238(4)	0.420(2)	0.027(2)	0.8(2)
O(2)	4	0.697(4)	0.293(2)	0.455(2)	0.9(2)
O(3)	4	0.704(4)	0.347(2)	0.197(1)	0.8(2)
O(4)	4	0.296(4)	0.108(2)	0.137(2)	0.7(2)
O(5)	4	0.204(4)	0.410(2)	0.333(2)	0.8(2)

Table 2. *Observed and calculated structure factors*

Panel 1

h	k	l	F_o	F_c
0	0	4	54.1	47.3
		6	176.7	191.8
		8	103.4	101.5
		12	117.2	114.5
1	0	-12	91.5	88.8
		-10	21.8	18.1
		-8	47.5	44.5
		-6	158.5	201.4
		-4	35.9	52.6
		-2	59.5	79.2
		2	101.4	104.9
		4	70.7	62.4
		6	185.3	200.2
		8	78.8	75.1
		10	15.3	11.6
		12	100.2	97.8
2	0	-10	15.1	12.4
		-8	85.0	88.7
		-6	111.8	133.5
		-4	50.2	50.8
		-2	63.0	78.5
		0	118.7	179.6
		2	42.5	38.6
		4	39.0	33.0
		6	127.5	123.2
		8	77.5	73.0
		10	11.4	8.6
3	0	-10	21.2	16.9
		-8	60.6	64.3
		-6	127.3	161.9
		-4	31.3	33.2
		-2	46.2	60.6
		0	130.3	172.1
		2	62.7	75.3
		4	12.2	3.5
		6	154.3	162.6
		8	50.6	47.0
		10	23.4	17.9
4	0	-8	54.4	57.3
		-6	101.8	117.1
		-4	30.6	32.8
		-2	30.8	31.7
		0	149.4	195.8
		2	38.1	43.0
		4	24.7	25.9
		6	120.0	128.1
		8	87.2	85.5
5	0	-6	114.3	130.2
		-4	14.7	9.1
		-2	40.1	39.8
		0	94.7	104.4
		2	58.0	64.7
		4	19.2	18.5
		6	113.9	123.5
0	1	3	116.2	149.5
		4	118.4	117.8
		5	68.2	63.5
		6	24.8	22.1
		7	23.5	17.2
		8	88.2	80.4
		9	108.8	103.4
		10	70.0	62.2
		11	60.6	56.5
		12	35.4	29.5
1	1	-12	34.4	30.6
		-11	50.3	44.0
		-10	94.5	91.7
		-9	107.5	109.2
		-8	53.3	50.2
		-7	27.2	21.0
		-6	31.5	30.3
		-5	62.3	61.4
		-4	93.8	102.5
		-2	84.3	133.1
		2	106.8	130.1
		3	173.8	183.2
		4	81.4	70.1
		5	56.5	48.1
		6	22.4	18.0
		8	34.0	26.0
		9	119.1	114.5
		10	93.7	85.2
		11	53.0	46.8
		12	19.4	17.6
2	1	-11	50.0	46.5
		-10	51.1	49.2
		-9	102.0	106.3
		-8	58.2	59.1
		-7	17.1	12.2
		-6	23.6	20.9
		-5	28.3	25.5
		-4	96.1	119.6
		-3	124.4	174.1
		-2	60.9	73.2
		-1	42.4	53.0
		0	9.3	12.0
		1	17.6	11.9
		2	70.6	74.4
		3	157.2	179.0
		4	131.5	137.2

Panel 2

h	k	l	F_o	F_c
2	1	5	49.8	44.6
		6	14.2	8.4
		7	13.0	5.4
		8	73.4	69.9
		9	116.6	112.2
		10	52.6	46.9
		11	54.8	49.2
3	1	-10	66.9	70.2
		-9	95.8	105.0
		-8	30.8	28.9
		-6	13.5	15.7
		-5	50.6	53.3
		-4	36.9	40.5
		-3	112.0	152.4
		-2	70.6	90.4
		-1	21.1	23.3
		1	18.5	19.0
		2	70.8	84.4
		3	126.3	148.8
		4	44.5	48.6
		5	59.7	59.1
		6	41.3	40.4
		8	48.8	45.5
		9	97.6	94.2
		10	81.3	78.8
4	1	-9	80.4	86.2
		-8	67.3	67.9
		-6	16.3	14.4
		-5	40.7	43.2
		-4	81.6	92.2
		-3	93.2	113.0
		-2	39.9	45.2
		-1	21.3	20.4
		0	22.4	20.8
		1	35.8	40.5
		2	46.9	54.2
		3	92.0	104.6
		4	79.5	83.7
		5	41.2	41.2
		6	43.8	39.7
		9	85.7	82.8
5	1	-5	36.3	37.6
		-4	58.7	60.6
		-3	87.1	93.6
		-2	79.0	82.0
		-1	25.2	23.8
		0	12.9	6.8
		1	21.3	20.8
		2	62.8	65.7
		3	91.0	99.4
		4	61.1	61.1
		5	28.0	29.5
		6	21.2	20.6
0	2	1	134.8	136.3
		2	10.5	7.7
		3	35.2	29.8
		4	26.3	21.5
		5	134.6	137.9
		6	96.6	92.5
		7	111.5	108.2
		8	29.2	23.0
		9	31.9	29.9
		10	13.7	11.0
		11	66.5	57.7
		12	34.3	27.8
1	2	-12	50.5	47.4
		-11	73.2	67.1
		-10	27.5	24.5
		-9	51.4	48.3
		-8	17.8	14.8
		-7	120.5	127.2
		-6	36.3	31.7
		-5	103.3	112.5
		-3	49.0	44.2
		-2	30.2	28.7
		-1	116.1	173.8
		0	75.6	113.6
		1	140.4	173.2
		2	44.3	38.1
		3	74.7	67.3
		4	26.5	22.4
		5	110.0	102.2
		6	45.4	37.3
		7	142.6	137.8
		8	17.8	11.6
		9	56.2	52.0
		10	19.2	14.0
		11	68.3	60.7
		12	45.4	40.0
2	2	-11	53.7	49.3
		-9	30.2	28.6
		-7	121.6	144.1
		-6	69.7	74.3
		-5	88.9	99.5
		-4	41.6	42.3
		-3	31.8	33.5
		-1	102.3	151.5
		0	34.9	44.2
		1	116.5	156.5
		3	27.4	28.3

Panel 3

h	k	l	F_o	F_c
2	2	4	23.7	12.2
		5	102.8	100.5
		6	69.8	63.0
		7	143.2	143.0
		8	16.0	9.2
		9	47.3	44.5
		10	12.5	10.6
		11	45.7	43.4
3	2	-10	21.8	18.3
		-9	36.1	34.8
		-7	99.9	111.1
		-6	26.6	24.4
		-5	94.9	108.1
		-3	23.2	25.2
		-2	15.3	15.1
		-1	103.8	139.5
		0	51.4	64.7
		1	103.5	138.5
		2	21.3	20.0
		3	21.2	20.7
		5	102.4	103.9
		6	32.9	27.6
		7	111.2	109.7
		8	11.3	8.7
		9	34.0	32.1
		10	22.1	19.5
4	2	-8	14.5	4.3
		-7	87.5	92.9
		-6	48.9	55.6
		-5	85.6	93.8
		-4	12.5	13.7
		-3	11.4	11.2
		-1	84.0	94.1
		0	33.9	35.7
		1	89.0	108.0
		3	28.9	32.3
		4	19.9	21.1
		5	83.2	90.3
		6	55.4	61.9
		7	92.2	94.5
		8	23.3	17.1
5	2	-6	28.7	26.5
		-5	59.4	64.7
		-3	12.5	4.3
		-2	16.5	12.6
		-1	89.4	99.8
		0	59.9	62.4
		1	81.1	89.6
		2	17.4	17.1
		3	15.1	16.8
		4	13.9	12.5
		5	56.6	61.5
		6	24.7	24.1
0	3	1	80.9	75.5
		2	133.3	142.6
		3	60.7	56.0
		4	134.5	140.4
		5	79.1	74.0
		6	27.3	23.2
		7	21.3	19.8
		8	63.6	60.2
		9	32.2	28.5
		10	128.3	127.4
		11	70.1	67.9
1	3	-11	41.4	40.4
		-10	91.3	92.2
		-9	32.7	28.7
		-8	88.5	89.4
		-7	45.0	42.2
		-6	43.2	42.6
		-5	74.6	76.1
		-4	122.9	152.9
		-3	42.1	42.3
		-2	102.7	128.0
		-1	37.2	40.0
		0	38.0	46.9
		1	70.4	78.2
		2	102.8	96.3
		3	44.1	37.7
		4	147.4	149.0
		5	85.6	82.9
		6	17.6	11.7
		7	63.1	59.7
		9	89.6	82.3
		10	77.3	70.9
		11	53.9	51.1
2	3	-11	55.0	53.4
		-10	88.7	91.6
		-9	35.2	34.0
		-8	64.0	65.0
		-7	38.2	37.5
		-6	37.5	38.0
		-5	47.8	49.1
		-4	83.7	94.3
		-3	33.3	32.8
		-2	109.1	142.1
		-1	71.8	94.7
		1	60.1	74.2
		2	125.8	150.3

Panel 4

h	k	l	F_o	F_c
2	3	3	32.2	31.5
		4	92.1	93.8
		5	54.9	51.1
		6	38.2	35.4
		7	28.9	24.4
		8	80.9	73.4
		9	39.0	36.2
		10	100.3	96.8
		11	50.1	48.3
3	3	-9	24.6	25.2
		-8	67.7	68.3
		-7	39.2	42.0
		-6	14.5	15.0
		-5	68.7	75.8
		-4	98.1	113.1
		-3	39.5	40.3
		-2	53.5	61.1
		-1	41.1	50.1
		0	30.1	32.2
		1	26.8	28.6
		2	64.9	78.2
		3	45.6	48.7
		4	110.6	121.6
		5	71.1	71.7
		6	27.2	32.1
		7	33.6	33.1
		9	20.6	19.7
4	3	-8	51.1	51.0
		-7	15.1	14.2
		-6	15.9	11.1
		-5	40.7	43.4
		-4	86.6	95.3
		-3	36.9	40.0
		-2	95.9	108.8
		-1	40.6	43.7
		1	55.5	64.7
		2	79.5	91.8
		3	27.3	29.3
		4	79.9	85.3
		5	48.1	50.1
		6	31.3	29.4
		7	22.5	22.5
		8	49.8	46.1
5	3	-5	47.5	46.6
		-4	86.5	91.1
		-3	22.8	21.7
		-2	75.8	80.7
		-1	36.6	37.7
		1	31.2	32.3
		2	68.9	73.6
		3	25.2	29.4
		4	92.4	105.3
		5	40.5	44.2
0	4	0	91.4	135.9
		1	72.9	70.4
		2	131.2	139.4
		3	14.1	11.1
		4	85.4	81.2
		5	29.8	26.3
		6	123.4	127.4
		7	46.4	41.5
		8	94.4	92.5
		9	34.6	32.9
		10	37.1	32.2
		11	30.2	27.5
1	4	-11	15.6	14.6
		-10	20.3	19.3
		-9	102.1	106.3
		-8	53.8	50.3
		-7	71.8	66.3
		-6	50.4	48.1
		-5	71.4	72.4
		-4	19.0	18.5
		-3	84.4	100.1
		-2	38.7	41.4
		-1	92.6	132.8
		0	48.1	51.9
		2	94.8	94.4
		3	38.1	35.1
		4	87.2	84.5
		5	72.8	66.6
		6	97.1	91.5
		7	58.5	54.4
		8	117.3	114.5
		9	17.2	12.2
		10	36.9	35.5
		11	22.9	21.2
2	4	-10	36.5	34.0
		-9	24.2	22.5
		-8	87.3	91.8
		-7	42.8	41.8
		-6	97.9	103.9
		-5	38.9	36.4
		-4	53.0	54.1
		-3	22.3	21.0
		-2	88.7	104.2
		-1	51.7	62.2
		0	61.2	73.5
		1	44.7	49.7

Panel 5

h	k	l	F_o	F_c
2	4	2	93.4	103.0
		4	66.2	63.2
		5	26.1	22.8
		6	92.2	85.4
		7	52.4	47.3
		8	87.1	83.4
		9	24.0	24.0
		10	35.7	28.7
3	4	-9	13.9	6.0
		-8	86.7	90.4
		-7	66.1	63.0
		-6	74.2	75.9
		-5	49.5	49.9
		-4	76.2	81.0
		-3	22.8	23.6
		-2	75.7	88.0
		-1	47.4	51.5
		0	95.5	114.5
		1	51.9	59.1
		2	75.1	88.4
		3	10.0	7.9
		4	60.8	59.4
		5	46.2	45.1
		6	73.3	65.9
		7	56.9	51.4
		8	95.6	93.9
		9	11.2	2.5
4	4	-7	26.8	26.0
		-6	79.4	81.4
		-5	29.5	26.9
		-4	59.5	52.1
		-2	67.1	77.9
		-1	42.4	44.3
		0	74.1	83.9
		1	43.6	49.5
		2	77.6	95.1
		4	46.6	50.1
		5	28.3	26.2
		6	93.9	97.5
		9	35.8	38.4
5	4	-3	13.9	14.4
		-2	55.3	58.2
		-1	27.8	24.8
		0	79.9	83.7
		1	20.5	23.6
		2	54.4	58.5
		3	20.3	19.6
0	5	1	86.1	81.4
		2	33.8	28.5
		3	85.2	80.3
		4	11.6	6.9
		5	123.6	125.3
		7	59.5	52.7
		8	13.5	13.3
		9	80.0	73.4
		10	30.7	28.6
1	5	-10	24.8	23.3
		-9	83.2	79.4
		-8	37.3	33.0
		-7	58.5	54.0
		-5	98.1	102.5
		-4	53.2	51.8
		-3	104.3	110.0
		-2	27.5	28.4
		-1	96.1	114.7
		0	14.2	14.9
		1	97.6	105.4
		2	23.7	20.8
		3	121.6	115.9
		4	46.6	40.5
		5	91.3	80.2
		6	15.9	12.0
		7	31.7	20.0
		8	25.8	21.3
		9	91.8	83.3
2	5	-9	74.9	71.8
		-7	66.7	64.4
		-5	93.5	97.8
		-4	30.1	26.7
		-3	109.1	121.8
		-2	39.1	40.2
		-1	61.3	73.7
		1	48.0	53.8
		2	44.4	45.1
		3	121.7	126.7
		4	33.6	30.1
		5	117.8	118.4
		6	17.8	14.0
		7	66.4	63.5
		8	13.3	10.8
		9	73.9	71.1
3	5	-8	27.2	23.3
		-7	22.8	19.7
		-6	11.4	6.9
		-5	75.5	74.6
		-4	29.6	31.5
		-3	90.0	100.9
		-1	78.2	91.1
		1	83.3	99.4
		2	13.9	17.7

Table 2. *(Continued)*

h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c	h k l	F_o	F_c
3 5 3	82.3	86.5	1 6 -2	62.5	64.6	3 6 -2	48.6	54.6	1 7 1	12.1	3.1	0 8 3	37.5	31.7
4	39.5	39.6	-1	64.9	67.0	-1	69.2	79.0	2	103.3	103.7	4	21.8	12.8
5	87.5	92.6	0	38.7	47.7	0	29.8	33.5	3	25.7	24.3	5	79.2	71.7
7	38.7	34.6	1	91.3	99.9	1	66.4	75.0	4	103.7	99.0	6	82.1	78.2
8	24.6	25.5	2	80.6	77.6	2	49.5	57.2	5	35.6	32.8	1 8 -6	75.9	71.2
4 5 -5	98.5	102.6	3	40.5	39.3	3	15.5	18.7	6	23.0	17.4	-5	43.3	40.8
-4	13.4	14.3	4	48.9	43.7	4	35.6	36.1	7	30.0	24.2	-3	22.7	17.9
-3	70.0	72.1	5	90.8	80.9	5	72.4	75.9	8	68.8	64.6	-2	25.3	21.6
-2	35.5	34.7	6	56.9	46.4	6	47.4	45.9	2 7 -6	22.5	20.3	-1	80.8	84.0
-1	56.8	57.8	7	95.0	88.9	7	80.5	78.8	-4	98.1	96.7	0	74.3	92.3
1	52.2	57.9	8	65.1	62.0	4 6 -4	49.1	48.6	-3	19.6	20.6	1	72.1	72.4
2	19.7	19.6	9	27.3	22.2	-2	37.3	38.1	-2	86.8	93.7	2	31.0	23.2
3	75.0	82.0	2 6 -8	71.7	69.5	-1	71.0	77.4	-1	29.4	31.7	5	56.2	51.4
5	78.5	82.0	-7	72.9	74.2	0	55.8	57.3	1	30.6	32.2	6	89.0	86.6
6	15.1	12.2	-6	35.5	35.3	1	74.8	83.6	2	89.3	93.4	2 8 -3	16.9	16.0
0 6 0	67.0	82.6	-5	63.4	64.6	2	40.7	49.8	3	19.6	17.5	-2	17.1	15.3
1	108.4	109.1	-4	33.9	41.0	4	32.1	28.2	4	103.6	100.2	-1	48.2	53.0
2	61.5	57.7	-2	69.6	75.7	0 7 1	35.1	29.0	5	9.8	4.7	0	76.6	86.7
3	22.2	18.6	-1	86.0	106.2	2	99.4	95.7	6	21.5	20.4	1	59.4	64.9
4	60.5	57.8	0	44.2	52.5	3	44.8	40.6	3 7 -5	24.8	25.5	2	20.5	17.8
5	63.9	59.9	1	75.6	89.0	4	122.4	118.9	-4	82.9	87.7	3	21.2	22.7
6	58.5	53.4	2	57.1	58.2	6	35.2	28.0	-3	17.4	19.9	3 8 -1	75.2	79.5
7	91.0	84.0	4	51.0	53.7	8	70.9	65.1	-2	78.7	84.2	0	75.2	84.3
8	71.4	62.7	5	62.5	60.0	1 7 -8	68.3	65.2	0	12.1	11.6	1	73.1	79.3
9	32.6	31.8	6	39.7	34.2	-7	36.0	34.0	1	11.2	2.5	0 9 1	36.5	34.5
1 6 -9	16.6	12.5	7	82.2	80.1	-6	31.0	30.2	2	70.8	79.8	2	23.0	17.9
-8	61.4	60.0	8	71.3	67.1	-5	28.7	26.9	3	11.4	10.0	3	104.3	105.6
-7	87.6	88.8	3 6 -7	87.9	86.0	-4	102.0	107.6	4	85.2	93.5	1 9 -2	15.6	11.3
-6	64.0	58.4	-6	41.6	37.1	-3	20.2	18.9	5	16.7	15.5	-1	20.3	20.3
-5	85.2	86.2	-5	69.3	68.4	-2	95.5	102.0	0 8 0	73.3	86.4	0	15.5	8.9
-4	41.7	39.6	-4	45.2	43.0	-1	14.4	13.9	1	69.8	65.3	1	23.0	17.5
-3	33.9	29.3	-3	24.3	20.1	0	16.9	17.1	2	32.9	29.1	2	16.3	16.5

son (1965). The weighting coefficients were adjusted during the course of the refinement so as to make $W\Delta F^2$ constant for ten equal sized groups of increasing F_0, consistent with the criteria for a good weighting scheme. Twenty cycles, varying positional and isotropic thermal parameters, reduced the unweighted residual, R to 0.102 for 660 $|F_0|$'s. A comparison of the observed and calculated structural amplitudes at this stage reveal a marked secondary extinction effect limited primarily to the intense reflections having small values of 2θ. During subsequent refinement 65 of these reflections were removed from the data set. This resulted in a reduction of the unweighted residual to 0.073 for 595 reflections and more reasonable isotropic temperature factors. The differences in the positional parameters before and after the removal of these reflections were well within the estimated standard deviations. The refined thermal and positional parameters and structure factors are given in Tables 1 and 2, respectively. The bond distances shown in Table 3 were calculated using the Fortran function and error program written by BUSING, MARTIN and LEVY (1964).

Discussion

The structure of gadolinite is based on alternating sheets parallel to (100) of corner-sharing Si- and Be-containing tetrahedra (Fig. 1 a) and of edge-sharing Ni-containing octahedra and Yb-containing tetragonal antiprisms (Fig. 1 b). The sheet of tetrahedra is topologically identical to that found in datolite (FOIT et al., 1973) and

Table 3. *Interatomic distances and angles with standard errors in parentheses*

Si—O(1)	1.62(2) Å	O(1) —Si—O(2)'*	113.5(8)°
Si—O(2)'*	1.66(2)	O(1) —Si—O(3)	119.0(9)
Si—O(3)	1.62(2)	O(1) —Si—O(4)	102.6(9)
Si—O(4)	1.67(2)	O(2)'*—Si—O(3)	104.9(8)
		O(2)'*—Si—O(4)	108.3(8)
Mean Si—O	1.64	O(3) —Si—O(4)	108.1(8)
O(1) —O(2)'*	2.75(2)	Mean O—Si—O	109.4
O(1) —O(3)	2.80(2)		
O(1) —O(4)	2.57(2)		
O(2)'*—O(3)	2.61(2)		
O(2)'*—O(4)	2.70(2)		
O(3) —O(4)	2.66(2)		
Mean O—O	2.68		
Be—O(2)	1.65(3)	O(2) —Be—O(3)	100(2)
Be—O(3)	1.71(3)	O(2) —Be—O(4)″	101(2)
Be—O(4)″	1.59(4)	O(2) —Be—O(5)	117(2)
Be—O(5)	1.56(4)	O(3) —Be—O(4)″	100(2)
		O(3) —Be—O(5)	113(2)
Mean Be—O	1.63	O(4)″—Be—O(5)	123(2)
O(2) —O(3)	2.57(2)	Mean O—Be—O	109
O(2) —O(4)″	2.50(2)		
O(2) —O(5)	2.73(2)		
O(3) —O(4)″	2.52(2)		
O(3) —O(5)	2.73(2)		
O(4)″—O(5)	2.77(2)		
Mean O—O	2.64		
Yb—O(1)″*	2.29(2)	Si—O(2)'*—Be'*	115(2)
Yb—O(1)'*	2.27(2)	Si—O(3) —Be	114(2)
Yb—O(2)	2.33(2)	Si—O(4) —Be″*	117(1)
Yb—O(3)	2.58(2)		
Yb—O(3)″*	2.39(2)	Mean Si—O—Be	115
Yb—O(4)*	2.33(2)		
Yb—O(5)*	2.42(2)		
Yb—O(5)″*	2.36(2)		
Mean Yb—O	2.37		
Ni—O(2)'*, O(2)″*	2.13(2)		
Ni—O(4), O(4)‴	2.09(2)		
Ni—O(5)″*, O(5)'*	2.01(2)		
Mean Ni—O	2.08		

$' = x, \frac{1}{2} - y, \frac{1}{2} + z$; $'' = \bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$; $''' = \bar{x}, \bar{y}, \bar{z}$: transformations relating coordinates to those of Table 1.

* = positioned in adjacent unit cells.

consists of alternating BeO_4 and SiO_4 tetrahedra linked so as to form four- and eight-membered rings. The coordination polyhedra containing Ni and Y are located directly above the centers of the four- and eight-membered rings, respectively. Edge-sharing is common among the coordination polyhedra containing Yb, Ni and Be and occurs according to the scheme presented in Table 4. In each of these coordination polyhedra, the shared edges are the shortest as expected from bonding considerations (PAULING, 1929).

As in many substances in which the bonding is appreciably covalent, there is a high correlation between the bond lengths and the sum of valence bond numbers, $\zeta(O)$, received by the oxygen atoms (SMITH, 1953; BAUR, 1961, 1970; GIBBS et al., 1972; LAGER and GIBBS, 1973).

Table 4. *Edge sharing of polyhedra*

Polyhedra sharing edges		Edges shared	Number of edges
Yb	Ni	O(2) —O(5)	1
		O(4) —O(5)″	1
	Be	O(2) —O(3)	1
		O(3) —O(4)″	1
		O(1)′ —O(1)″	1
	Yb	O(3)″—O(5)″	1
		O(3) —O(5)	1
		Total edges shared by Yb antiprism	7
Ni	Be	O(2)″—O(4)	2*
	Yb	O(2)″—O(5)″	2*
		O(4) —O(5)″	2*
		Total edges shared by Ni octahedron	6
Be	Yb	O(2)—O(3)	1
		O(3)—O(4)″	1
	Ni	O(2)—O(4)″	1
		Total edges shared by Be tetrahedron	3

* Ni positioned on a center of symmetry.
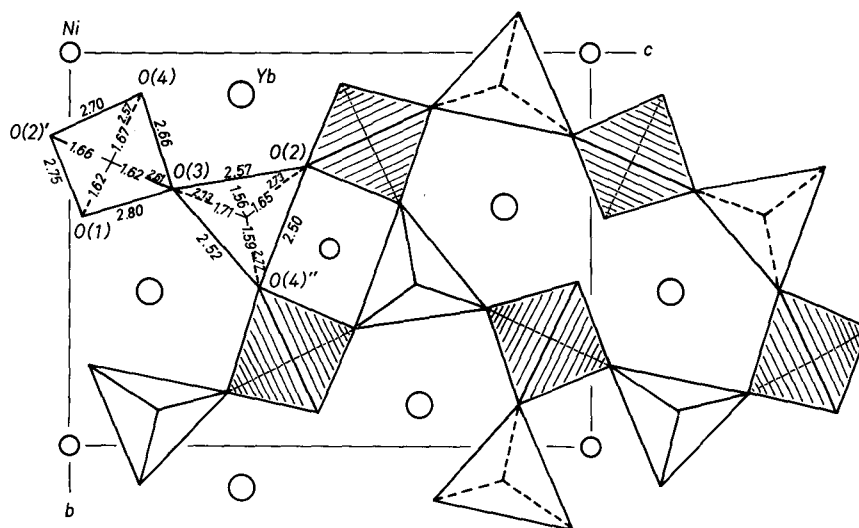
Fig. 1 a

Fig. 1. The structure of $NiYb_2Be_2Si_2O_{10}$ projected down [100] showing (a), the four- and eight-membered rings of alternating SiO_4 (shaded) and BeO_4 tetrahedra (unshaded) and (b), the sheet of edge-sharing antiprisms containing Yb and octahedra containing Ni

However, as ZACHARIASEN (1963) and BAUR (1970) have pointed out, this type of analysis cannot be expected to unfailingly account for all bond-length variations because it neglects the effects of nearest-neighbor interactions and shared edges. Assuming valence bond numbers of 1.0 for Si—O, 0.5 for Be—O, 0.33 for Ni—O and 0.75 for Yb—O, (PAULING, 1947), we find that two of the oxygen atoms in gadolinite, O(1) and O(5), are underbonded whereas the remaining three, O(2), O(3) and O(4), are overbonded (Table 5). With the exception of the Yb—O(5) distance which averages 2.39 Å and the Si—O(3) distance of 1.62 Å, the bonds to the undersaturated oxygen atoms are appreciably shorter than those to the oversaturated ones. Unlike the Fe—O bond distances reported by PAVLOV and BELOV (1959) for natural gadolinite, $FeY_2Be_2Si_2O_{10}$, the Ni—O bond distances in synthetic gadolinite can be ordered on the basis of ζ(O).

If the datolite (FOIT et al., 1973) and gadolinite structures are compared, there is observed a correlation between the range of bond lengths and ζ(O) for a given type of coordination polyhedron. The

Fig. 1b

coordination polyhedra of datolite containing Ca and Si show a greater range in both bond distances and $\zeta(O)$ than do the ones in synthetic gadolinite containing Yb and Si. Likewise the spread in both of these parameters is greater in the BeO_4 tetrahedron of gadolinite than for the BO_4 tetrahedron of datolite.

Table 5. *Sum of the valence-bond numbers received by oxygen in synthetic* $NiYb_2Be_2Si_2O_{10}$, *natural gadolinite*, $FeY_2Be_2Si_2O_{10}$, *and datolite*, $CaBSiO_4(OH)$

	$NiYb_2Be_2Si_2O_{10}$ and $FeY_2Be_2Si_2O_{10}$			$CaBSiO_4(OH)$		
			$\zeta(O)$			$\zeta(O)$
O(1)		$1 + 2(\frac{3}{8})$	$= 1.75$		$1 + 2(\frac{1}{4})$	$= 1.50$
O(2)	$1 + \frac{1}{2} + \frac{1}{3} + \frac{3}{8}$		$= 2.21$	$1 + \frac{3}{4} + \frac{1}{4}$		$= 2.00$
O(3)	$1 + \frac{1}{2} + 2(\frac{3}{8})$		$= 2.25$	$1 + \frac{3}{4} + 2(\frac{1}{4})$		$= 2.25$
O(4)	$1 + \frac{1}{2} + \frac{1}{3} + \frac{3}{8}$		$= 2.21$	$1 + \frac{3}{4} + \frac{1}{4}$		$= 2.00$
O(5)	$\frac{1}{2} + \frac{1}{3} + 2(\frac{3}{8})$		$= 1.58$	$1 + \frac{3}{4} + 2(\frac{1}{4})$		$= 2.25$

Table 6. *Mulliken bond-overlap populations calculated using extended Hückel molecular-orbital theory, constant bond lengths and observed valence angles*

			n(Si—O)				n(Be—O)
Si—O(1)	=	1.62 Å	0.497	Be—O(5)	=	1.56 Å	0.372
Si—O(3)	=	1.62	0.495	Be—O(4)	=	1.59	0.345
Si—O(2)	=	1.66	0.490	Be—O(2)	=	1.65	0.342
Si—O(4)	=	1.67	0.481	Be—O(3)	=	1.71	0.337

Finally, Mulliken bond-overlap populations calculated for the tetrahedral ions in synthetic gadolinite (Table 6) can be used to order the observed tetrahedral bond lengths, shorter bonds involving larger
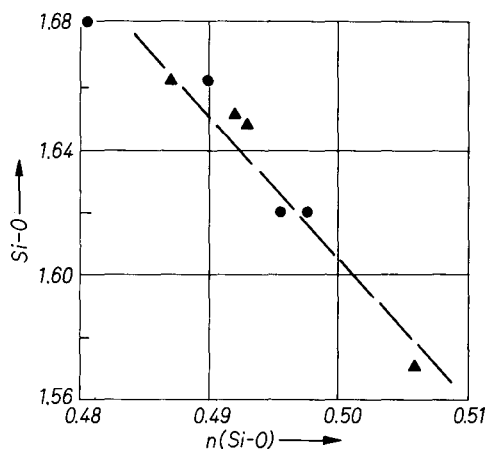
Fig. 2. A plot of observed Si—O bond lengths for gadolinite (circles) and datolite (triangles) versus Mulliken bond-overlap populations, n(Si—O). The calculations were carried out neglecting the nontetrahedral cations and sp basis functions and using the observed valence angles with the Si—O bond lengths clamped at 1.63 Å

overlap populations [see Gibbs *et al.* (1972) for details of the calculations]. This assertion is evidenced for the silicate tetrahedron by Fig. 2 where the bond-overlap populations, n(Si—O), calculated for gadolinite and datolite are plotted against the observed lengths of the Si—O bonds. Despite the relatively large estimated standard deviations associated with the bond lengths observed for gadolinite, the correlation, $r = -0.94$, is surprisingly good and in close correspondence

with that obtained earlier for datolite (FOIT *et al.*, 1973). The correlation between bond-overlap population, $n(Be-O)$, and observed bond length for the tetrahedron containing Be in gadolinite is not as well-developed as that for the silicate tetrahedron. Nevertheless, shorter bonds do involve larger $n(Be-O)$ values as expected. Accordingly, the steric details of both the gadolinite and the datolite structures and their interrelationships seem to fit the requirements of a model involving appreciable covalent bonding.

Acknowledgements

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