

## The crystal structure of rhodizite

By **KARLHEINZ J. TAXER**<sup>1</sup> and **MARTIN J. BUERGER**

Massachusetts Institute of Technology, Cambridge, Massachusetts

*Dedicated to Prof. Dr. G. Menzer on the occasion of his 70th birthday*

(Received April 12, 1967)

### Auszug

Rhodizit zeigt, nach der Präzessionsmethode untersucht, keine systematischen Auslöschungen; zusammen mit der piezo- und pyroelektrischen Ansprechbarkeit führt das zur Raumgruppe  $P\bar{4}3m$ . Die Gitterkonstante ist  $a = 7,319 \pm 0,001$  Å. Für die Strukturbestimmung wurden die Intensitäten der Reflexe an einem kugelförmig geschliffenen Kristall mit dem Szintillationszähler gemessen. Die Struktur wurde etwas indirekt durch Interpretierung eines Schweratombildes in der Pattersonfunktion, kombiniert mit Fouriersynthesen der Elektronendichte bei schrittweiser Lokalisierung der Atomlagen, ermittelt. Die ideale Struktur hat die Formel  $\text{CsBe}_4\text{B}_{12}\text{Al}_4\text{O}_{28}$ ; sie wurde bis zu einem  $R$ -Wert von  $9,1\%$  verfeinert. Es ist jedoch zu vermuten, daß eine mit der Analyse übereinstimmende und chemisch annehmbare Formel  $\text{CsBe}_4\text{B}_{12-x}\text{Al}_4\text{O}_{28}\text{H}_2$ , mit  $x = 1$ , wahrscheinlicher ist. Eine weitere Verfeinerung ist so lange nicht gewährleistet, als die chemische Zusammensetzung nicht besser bekannt ist.

### Abstract

Rhodizite, examined by the precession method, has diffraction symbol  $m\bar{3}mP$  - - which, taken together with its piezoelectric and pyroelectric response, fixes the space group as  $P\bar{4}3m$ . The cell edge is  $a = 7.319 \pm .001$  Å. For solving the structure, reflection intensities from a spherical specimen were measured with a scintillation counter. The structure was solved somewhat indirectly by interpretation of a heavy-atom image in the Patterson function, combined with successive Fourier syntheses of the electron density as successive sets of atoms were located. The ideal structure has a formula  $\text{CsBe}_4\text{B}_{12}\text{Al}_4\text{O}_{28}$ , and this has been refined to an  $R$  value of  $9.1\%$ . It has been suggested that a more realistic composition, consistent with the analysis and chemically more acceptable, would be  $\text{CsBe}_4\text{B}_{12-x}\text{Al}_4\text{O}_{28}\text{H}_2$ , where  $x = 1$ . Further refinement is not warranted until the chemical composition is better established.

<sup>1</sup> Present address: 629 Weilburg/Lahn, Taunusstraße 21, Germany.

### Introduction

The chemical composition of the mineral rhodizite is described by DANA's System<sup>2</sup> as a complex borate of beryllium, aluminum and the alkalis. STRUNZ determined the cell and symmetry<sup>3,4</sup> of the mineral, and interpreted an analysis of PISANI, quoted by LACROIX<sup>5</sup>, as providing a composition  $\text{NaKLi}_4\text{Al}_4\text{Be}_3\text{B}_{10}\text{O}_{27}$ . FRONDEL and ITO recently studied well crystallized specimens from Manjaka, Madagascar<sup>6</sup>; they confirmed STRUNZ's cell and space group, and interpreted their new analysis (Table 1) as  $\text{AAl}_4\text{Be}_4\text{B}_{11}\text{O}_{25}(\text{OH})_4$ , or possibly  $\text{AAl}_4\text{Be}_4\text{B}_{12}\text{O}_{27}(\text{OH})_3$ , where A is a mixture,  $(\text{Cs}_{.44}\text{Rb}_{.16}\text{K}_{.31}\text{Na}_{.03})$ , of alkalis.

Table 1. *Chemical analysis of rhodizite from Manjaka, Madagascar*  
(from FRONDEL and ITO<sup>6</sup>)

Oxide	Weight per cent	Number of atoms	
		Based on 29 oxygen atoms	Based on molecular weight = 811
Li <sub>2</sub> O		Li	
Na <sub>2</sub> O	0.12%	Na	.03
K <sub>2</sub> O	1.79	K	.31
Rb <sub>2</sub> O	1.83	Rb	.16
Cs <sub>2</sub> O	7.54	Cs	.44
BeO	12.20	Be	4.03
Al <sub>2</sub> O <sub>3</sub>	24.41	Al	3.96
Fe <sub>2</sub> O <sub>3</sub>	0.12	Fe	.01
B <sub>2</sub> O <sub>3</sub>	46.82	B	11.1
SiO <sub>2</sub>	0.45		
Ign.	4.10	H	3.8
Rem.	0.53	O	29.0
Total	99.92		

<sup>2</sup> CHARLES PALACHE, HARRY BERMAN and CLIFFORD FRONDEL, The system of mineralogy of JAMES DWIGHT DANA and EDWARD SALISBURY DANA; Vol. 2, seventh edition (John Wiley and Sons, New York) 329–330.

<sup>3</sup> H. STRUNZ, Gitterkonstante und Raumgruppe von Rhodizit und Jeremjewit. *Naturwissenschaften* **26** (1938) 217.

<sup>4</sup> H. STRUNZ, Die Struktur von Rhodizit. *Naturwissenschaften* **31** (1943) 68.

<sup>5</sup> M. A. LACROIX, Nouvelles observations sur les minéraux des pegmatites de Madagascar. *Bull. Soc. franç. Minéralog. Cristallogr.* **33** (1910) 37–53, especially 42.

<sup>6</sup> CLIFFORD FRONDEL and JUN ITO, Composition of rhodizite. *Tschermaks mineral. petrogr. Mitt.* **10** (1965) 409–412.

### Symmetry and cell

Professor FRONDEL kindly supplied us with some of his Manjaka material for the purposes of a structural investigation. Our preliminary study confirmed the earlier work of STRUNZ<sup>3</sup> and the recent work of FRONDEL and ITO<sup>6</sup>. We found the material optically isotropic and with a positive piezoelectric response. We investigated the cell and symmetry by the precession method and determined the diffraction symmetry to be  $m\bar{3}mP$  ---. The piezoelectric response, the positive pyroelectric characteristic reported by RIES and ROSE<sup>7</sup>, and the tetrahedral crystal habit shown by DANA<sup>2</sup>, fix the space group as  $P\bar{4}3m$ . The precession photographs yielded the cell edge  $a = 7.32 \text{ \AA}$ , which is consistent with the results of STRUNZ<sup>3</sup> (7.30 kX) and of FRONDEL and ITO (7.317  $\text{\AA}$ ). We refined our value with the aid of a precision back-reflection Weissenberg photograph to  $a = 7.319 \pm 0.001 \text{ \AA}$ . Using FRONDEL and ITO's observed density 3.44 g/cm<sup>3</sup>, the cell would contain one unit of FRONDEL and ITO's formulas  $AA_4Be_4B_{11}O_{25}(OH)_4$  or  $AA_4Be_4B_{12}O_{27}(OH)_3$ , with  $A = Cs_{.44}Rb_{.16}K_{.13}Na_{.03}$ , which sums to  $A = .94$  alkali atoms per cell.

### Intensity measurements

Because of the conchoidal fracture of rhodizite, corrections of the measured intensities for absorption by the specimen could not be exactly made unless the specimen was ground to a sphere. Due to the great hardness of rhodizite, we found we could not prepare a sphere in the ordinary sphere grinder, but Dr. C. T. PREWITT kindly prepared several for us in a diamond-impregnated grinder. The one selected for this use had a radius of  $0.097 \pm 0.002 \text{ mm}$ .

This sphere was mounted for rotation about a crystallographic axis. The intensity data were collected with the aid of a single-crystal diffractometer designed for equi-inclination geometry. Filtered  $MoK\alpha$  x-radiation was employed, and the reflections received by a scintillation detector. Of the 760 reflections in the asymmetric Friedel field of the  $MoK\alpha$  sphere, 504 were found to have measureable intensities. These intensities were corrected for background, Lorentz, polarization and absorption effects.

<sup>7</sup> P. RIES and GUSTAV ROSE, Ueber die Pyroelektrizität der Mineralien. Ann. Physik Chem. 59 (1843) 353–390, especially 382.

### Structure determination

Since the cell of the Manjaka rhodizite contains several kinds of alkali atoms whose sum is nearly one, the alkali presumably occupies one of the two 1-fold equipoints of  $P\bar{4}3m$ , namely  $1a$  or  $1b$ . Since these are similar equipoints, the choice is immaterial, so we tentatively assigned the alkali to  $1a$  at the origin. This location is then the site of the collection of alkalis ( $\text{Cs}_{.44}\text{Rb}_{.18}\text{K}_{.31}\text{Na}_{.03}$ ) which, taken together, have the scattering power of an atom with 36 electrons. The remaining atoms in the cell have a total of 360 electrons. Thus one tenth of the scattering matter is concentrated at the origin, and the rest is distributed through the cell, but with no location having a concentration exceeding 10 electrons. These characterizations do not make the structure suitable for a straight-forward application of the ordinary heavy-atom method. On the other hand, the self-image of the structure is dominated by the image of the structure from the alkali, because this image is some  $3\frac{1}{2}$  times heavier than any other. Accordingly we attempted to solve the structure by assuming that the important peaks of the Patterson function were located at the positions of the atoms in the cell as seen from the origin.

In our first attempt to interpret the heavy-atom image of the structure, we attributed the fairly strong peaks near the origin to oxygen atoms surrounding the alkali position. This seemed especially reasonable because these occupied equipoint  $12i$  with  $xzx \approx \frac{1}{4}\frac{1}{4}0$ ; this provided the Cs atom with twelve nearest oxygen atoms at about 3.17 Å. We continued to assign atoms to Patterson peaks at increasing distances from the origin and thus derived a tentative structure, but this could not be refined.

We suspected that our failure was due to an enhancement of certain Patterson peaks due to a substructure. We found substantiating evidence for this by tabulating the values of  $|F_{hkl}|$  in reciprocal-lattice array; those reflections near the origin were strong which were at the points of a body-centered reciprocal lattice having a cell with double the edge of the reciprocal-lattice cell of the crystal. This suggested a substructure consisting of atoms at points of a face-centered lattice whose cell was a cube having half the edge of the crystal cell. (After solving the structure we found that this was a subcell of close-packed oxygen atoms.)

Faced with a substructure, we began to consider other hints suggested by the Patterson function, by a Fourier synthesis phased on the heavy alkali atom at the origin, and by other Fourier syntheses

suggested by the first false model. All of these showed strong peaks at  $4e$ , coordinates  $xxx$ ,  $x \approx \frac{3}{8}$ , as well as another set of peaks at  $4e$  with  $x \approx \frac{5}{8}$ . This suggested two sets of atoms which, together, occupy the corners of a cube whose edge is  $\frac{1}{4}a = 1.83 \text{ \AA}$ ; each such set would have a tetrahedral arrangement. This cube-edge distance accords well with the sum of the radii of aluminum and oxygen, namely  $R(\text{Al}) + R(\text{O}) = 0.57 + 1.32 = 1.89 \text{ \AA}$ .

If this is the interpretation of these peaks, there is indicated a set of 4 Al atoms in  $4e$  with  $x \approx \frac{3}{8}$  (or  $\frac{5}{8}$ ), and four oxygen atoms in  $4e$  with  $x \approx \frac{5}{8}$  (or  $\frac{3}{8}$ ). These oxygen atoms should be the central part of four sets of oxygen atoms, each octahedrally surrounding the 4 Al atoms. This would imply a cluster of four Al octahedra centered at  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ , each octahedron sharing each of three adjacent edges with an edge of another octahedron of the cluster, as seen in Fig. 2. The entire cluster of octahedra would then have a composition  $\text{Al}_4\text{O}_{16}$ . We found peaks on the Patterson function consistent with the additional 12 oxygen atoms required; these were located in  $12i$  at  $xxz \approx \frac{3}{8}\frac{3}{8}\frac{1}{8}$ .

With this new start, we computed a Fourier synthesis phased on the heavy alkali at the origin plus the limited  $\text{Al}_4\text{O}_4$  group centered at  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ , and found peaks at positions where the additional 12 oxygen atoms were expected in  $12i$  at  $\frac{3}{8}\frac{3}{8}\frac{1}{8}$ . Adding these additional atoms for phasing purposes, we computed another Fourier synthesis, and found additional atoms. We continued to repeat this cycle, at each stage adding an additional shell of atoms to the growing central cluster. Each such addition was acceptable from a point of view of appropriate coordination, and was consistent, in a general way, with the formula derived by FRONDEL and ITO from the chemical analysis. The general nature of the resulting structure is described in Table 2.

Table 2. Idealized description of the structure of rhodizite,  
 $P\bar{4}3m$ ,  $a = 7.319 \text{ \AA}$

Atom	Equipoint	Symmetry	Coordinates	
			General	Ideal
Cs	$1a$	$\bar{4}3m$	000	000
B	$12h$	2	$x\frac{1}{2}0$	$\approx \frac{1}{4}\frac{1}{2}0$
Be	$4e$	$3m$	$xxx$	$\approx \frac{3}{4}\frac{3}{4}\frac{3}{4}$
Al	$4e$	$3m$	$xxx$	$\approx \frac{3}{8}\frac{3}{8}\frac{3}{8}$
O(1)	$4e$	$3m$	$xxx$	$\approx \frac{5}{8}\frac{5}{8}\frac{5}{8}$
O(2)	$12i$	$m$	$xxz$	$\approx \frac{3}{8}\frac{3}{8}\frac{1}{8}$
O(3)	$12i$	$m$	$xxz$	$\approx \frac{5}{8}\frac{1}{8}\frac{1}{8}$

## Refinement

The rough structure outlined by Table 2 was, of course, partially refined by the successive Fourier syntheses required to establish it. The final stages of refinement were carried out by the full-matrix least-squares program written by C. T. PREWITT for the IBM computer 7090/94.

Table 3. *Observed and computed structure factors*

<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>obs</sub>	<i>F</i> <sub>cal</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>obs</sub>	<i>F</i> <sub>cal</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>obs</sub>	<i>F</i> <sub>cal</sub>	<i>h</i>	<i>k</i>	<i>l</i>	<i>F</i> <sub>obs</sub>	<i>F</i> <sub>cal</sub>
2	0	0	48.08	43.74	7	5	1	21.47	23.37	9	8	7	12.17	10.62	12	6	0	10.89	14.40
2	1	0	52.29	48.19	7	5	2	20.31	20.23	9	9	2	17.02	22.17	12	6	1	12.17	11.81
2	1	1	88.23	85.34	7	5	4	14.00	13.85	9	9	3	14.20	12.23	12	6	4	10.15	8.53
2	2	0	37.58	34.40	7	6	1	12.89	17.00	9	9	5	14.83	11.67	12	6	2	10.76	9.49
2	2	1	37.90	41.23	7	6	2	17.37	15.85	10	1	0	17.83	20.45	12	6	4	15.32	8.87
2	2	2	147.86	152.31	7	6	3	22.01	22.05	10	1	1	30.63	32.66	12	7	0	14.90	13.78
3	0	0	108.23	109.01	7	6	4	18.75	21.19	10	2	1	10.93	11.58	12	7	1	11.32	9.40
3	2	0	29.53	26.02	7	6	5	25.86	27.14	10	2	2	22.88	25.26	12	7	3	11.06	9.25
3	2	1	53.56	51.84	7	7	0	54.28	55.95	10	3	1	15.05	14.80	12	7	5	14.30	11.41
3	2	2	36.00	34.45	7	7	2	11.17	18.15	10	3	2	12.03	13.96	12	8	1	16.67	11.95
3	3	0	75.12	75.85	7	7	3	30.00	32.21	10	3	3	21.84	24.12	12	8	2	16.26	10.23
3	3	1	10.90	9.99	7	7	4	32.33	32.40	10	4	0	21.56	26.98	12	8	4	27.84	27.79
3	3	2	55.60	54.39	7	7	5	16.06	17.08	10	4	2	11.32	23.31	12	8	6	14.78	12.86
3	3	3	62.22	61.76	7	7	6	14.06	15.10	10	4	3	18.45	18.53	12	8	8	13.80	16.15
4	0	0	133.10	136.02	7	7	7	12.92	11.09	10	5	0	12.00	11.32	12	9	1	16.32	15.37
4	1	0	79.80	79.19	8	0	0	117.24	122.47	10	5	1	14.63	11.45	12	9	3	16.77	14.04
4	1	1	46.86	47.01	8	1	1	35.04	32.39	10	5	3	26.39	27.45	12	9	5	12.23	8.94
4	1	2	37.53	36.00	8	2	0	15.83	19.60	10	5	4	15.48	10.32	12	10	2	11.06	7.92
4	2	0	31.27	29.44	8	2	1	28.20	26.04	10	5	5	21.76	21.08	12	10	4	14.30	9.68
4	2	2	37.30	36.10	8	2	2	20.60	21.56	10	6	0	14.78	5.53	12	10	6	10.65	5.75
4	3	0	21.39	21.81	8	3	0	39.00	40.12	10	6	1	14.55	12.89	12	10	8	10.31	6.01
4	3	1	46.14	43.89	8	3	1	23.06	23.98	10	6	2	20.37	17.90	12	12	0	11.93	16.93
4	3	2	52.07	52.55	8	3	2	16.15	18.02	10	6	6	11.75	14.25	12	12	2	14.60	8.06
4	3	3	28.57	28.83	8	3	3	30.40	28.01	10	7	0	17.07	18.18	12	12	6	10.25	6.21
4	4	0	183.60	202.14	8	4	0	21.99	22.97	10	7	1	19.93	21.34	12	12	8	15.49	16.51
4	4	2	25.47	25.51	8	4	1	32.66	32.62	10	7	3	10.09	13.83	13	3	2	11.07	12.82
4	4	3	58.27	61.55	8	4	2	20.85	19.85	10	7	6	12.95	8.98	13	5	2	14.68	17.67
4	4	4	48.61	51.39	8	4	4	85.27	83.78	10	8	1	12.05	11.35	13	5	5	11.25	9.72
5	0	0	63.32	64.89	8	5	0	28.43	25.03	10	8	4	12.89	12.53	13	6	1	10.91	10.88
5	1	1	48.31	48.41	8	5	1	29.86	32.09	10	8	6	12.36	11.14	13	6	2	10.47	6.84
5	2	0	30.07	27.66	8	5	2	18.38	19.07	10	8	8	11.61	10.07	13	7	6	12.56	9.98
5	2	1	35.73	34.99	8	5	3	26.28	24.02	10	9	1	14.68	17.80	13	8	3	13.21	10.13
5	2	2	32.44	32.86	8	5	5	22.80	21.26	10	9	7	17.27	15.33	13	8	5	10.75	7.51
5	3	0	16.94	14.34	8	6	0	15.18	16.50	10	9	9	11.07	10.70	13	9	1	15.07	18.49
5	3	1	13.32	12.59	8	6	1	11.53	13.54	10	10	6	13.74	13.02	13	10	0	13.88	8.47
5	3	2	46.80	45.46	8	6	2	20.04	18.88	11	0	0	31.24	34.42	13	13	2	15.46	19.17
5	3	3	34.67	35.00	8	6	3	15.18	17.56	11	1	0	13.04	30.64	14	0	0	23.41	28.12
5	4	1	25.66	25.30	8	6	4	15.01	15.21	11	1	1	20.87	18.28	14	1	1	11.70	8.94
5	4	2	28.24	27.88	8	6	5	17.04	15.38	11	2	0	17.04	15.38	14	1	3	11.42	11.40
5	4	3	23.30	23.13	8	6	6	11.74	12.80	11	2	2	10.70	11.28	14	3	1	15.60	19.66
5	4	4	33.65	35.50	8	7	1	19.85	18.52	11	3	2	11.75	15.56	14	3	3	12.60	10.71
5	5	1	16.78	17.46	8	7	2	11.54	12.90	11	3	3	21.53	23.45	14	4	4	18.46	17.45
5	5	2	30.40	31.39	8	7	3	16.68	14.17	11	4	0	15.29	11.31	14	5	1	19.93	17.28
5	5	3	31.29	30.84	8	7	4	25.69	26.14	11	4	3	22.63	20.48	14	5	4	10.22	6.84
5	5	4	26.93	26.49	8	7	5	23.14	25.83	11	4	4	23.81	26.03	14	6	6	11.57	9.94
5	5	5	32.71	31.28	8	8	0	63.05	61.42	11	5	1	10.45	9.87	14	7	4	12.54	9.71
6	0	0	48.13	42.66	8	8	2	18.52	17.10	11	5	2	14.11	15.28	14	7	5	14.97	13.72
6	1	0	15.74	15.22	8	8	3	20.89	21.98	11	5	3	11.18	12.80	14	7	7	12.26	10.63
6	1	1	38.39	35.35	8	8	4	12.52	14.18	11	5	5	10.95	8.41	14	8	0	10.91	11.35
6	2	0	22.67	20.90	8	8	5	17.39	16.62	11	6	0	17.71	14.57	14	8	8	10.68	5.20
6	2	1	27.45	26.99	8	8	6	12.41	11.85	11	6	1	17.18	16.44	14	9	0	13.29	8.07
6	2	2	48.27	54.26	8	8	8	38.33	34.74	11	6	2	10.61	9.13	14	9	3	12.19	12.18
6	3	0	33.51	35.65	9	0	0	13.95	13.08	11	6	5	10.77	9.68	14	9	5	13.44	8.33
6	3	1	47.06	49.82	9	1	0	10.61	4.84	11	7	0	35.17	33.22	15	1	0	10.60	11.73
6	3	2	19.59	18.30	9	1	1	12.81	13.10	11	7	1	15.44	17.88	15	2	1	12.89	9.75
6	3	3	29.96	30.72	9	2	0	16.69	15.43	11	7	2	10.45	11.22	15	3	0	19.05	15.90
6	4	0	11.97	11.92	9	2	1	22.13	23.31	11	7	3	10.97	8.69	15	3	1	12.51	11.18
6	4	1	28.91	29.33	9	2	2	20.29	20.04	11	7	4	34.97	33.98	15	3	2	11.40	8.62
6	4	2	20.41	22.32	9	3	0	14.13	14.99	11	7	5	16.22	19.03	15	4	0	14.36	16.71
6	4	3	11.21	10.24	9	3	1	21.68	19.65	11	8	0	18.68	19.48	15	4	3	18.98	17.99
6	4	4	29.00	27.12	9	3	2	17.82	18.11	11	8	3	17.24	14.32	15	6	3	11.57	8.99
6	5	0	22.34	21.32	9	3	3	19.94	12.55	11	8	7	18.82	16.43	15	6	5	12.43	9.37
6	5	1	39.72	39.05	9	4	0	18.19	16.72	11	8	1	10.48	12.45	15	7	0	25.84	26.72
6	5	2	22.41	22.27	9	4	1	18.83	19.53	11	9	6	14.52	12.10	15	7	4	20.94	19.16
6	5	3	21.44	19.39	9	4	2	16.73	16.02	11	10	3	10.17	7.60	15	8	3	10.89	7.02
6	5	4	15.95	16.89	9	4	3	12.72	13.08	11	10	5	14.13	13.42	15	8	7	14.93	14.62
6	6	0	15.00	17.45	9	5	0	14.60	6.50	11	10	7	10.57	8.22	15	11	0	22.59	23.14
6	6	2	31.71	23.70	9	5	1	22.54	20.69	11	11	0	36.84	36.45	15	11	4	18.98	22.47
6	6	3	20.18	20.72	9	5	2	15.10	16.77	11	11	3	12.90	15.47	16	0	0	20.67	18.65
6	6	4	17.96	16.70	9	5	4	14.82	11.79	11	11	4	28.67	26.96	16	1	1	20.14	14.29
6	6	5	13.77	15.73	9	5	5	11.67	9.30	11	11	7	16.75	8.28	16	3	1	14.68	13.91
6	6	6	24.04	24.15	9	6	0	16.20	15.62	11	11	8	19.58	20.30	16	3	3	14.23	10.69
7	0	0	26.25	21.95	9	6	1	12.01	11.49	12	0	0	11.55	5.91	16	4	4	17.88	13.75
7	1	0	38.19	39.27	9	6	2	13.37	11.80	12	1	0	16.20	16.69	16	5	1	13.32	14.48
7	1	1	12.03	12.17	9	6	3	22.48	23.62										

Table 4. Final parameters of rhodizite  
( $R = 9.1\%$ )

Atom	Coordinates	Positional parameters			Thermal parameters						Equivalent average B	
		$x$	$z$		$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$		
Cs	000				0.0048 (02)	$= \beta_{11}$	$= \beta_{11}$	0	$= \beta_{12}$	$= \beta_{12}$	$= \beta_{12}$	1.02 (.04)
B	$x\frac{1}{2}0$	0.2469 (11)					not refined					.8
Be	$zzz$	0.749 (02)			0.0068 (13)	$= \beta_{11}$	$= \beta_{11}$	0.0003 (13)	$= \beta_{12}$	$= \beta_{12}$	$= \beta_{12}$	1.4 (.3)
Al	$zzz$	0.3603 (04)			0.0026 (03)	$= \beta_{11}$	$= \beta_{11}$	0.0002 (04)	$= \beta_{12}$	$= \beta_{12}$	$= \beta_{12}$	0.55 (.06)
O (1)	$zzz$	0.6203 (09)			0.0015 (06)	$= \beta_{11}$	$= \beta_{11}$	0.0017 (07)	$= \beta_{12}$	$= \beta_{12}$	$= \beta_{12}$	0.51 (.14)
O (2)	$zzz$	0.3643 (06)	0.1001 (07)		0.0013 (03)	$= \beta_{11}$	0.0020 (05)	0.0011 (04)	-0.0003 (04)	$= \beta_{12}$	$= \beta_{12}$	0.32 (.06)
O (3)	$zzz$	0.1342 (07)	0.5996 (09)		0.0029 (04)	$= \beta_{11}$	0.0048 (07)	0.0024 (06)	0.0001 (05)	$= \beta_{12}$	$= \beta_{12}$	0.75 (.09)

A correction for anomalous dispersion, specifically  $\Delta f' = -0.3e$ ,  $\Delta f'' = 1.9e$ , was applied to scattering by the alkali atom. Corrections were also applied for the contributions from general-radiation streaks to more distant points in the same central reciprocal-lattice row. In the first four cycles the weighting scheme was  $w = 1/\sigma^2 = |F_{\text{obs}}|/10,000$ .

Table 1 shows that the alkali position appears to be occupied by 0.94 atoms. Refinement of this occupancy was attempted, but this proved to be difficult due to interaction with the temperature coefficient.

Eight cycles of refinement, including positional parameters and isotropic temperature factors, reduced the discrepancy index,  $R$ , to 10.1%, and the occupancy of the alkali was reduced from 1.0 to 0.85. Two further cycles of refinement with anisotropic temperature factors reduced  $R$  to 9.1%, at which point the shifts of positional parameters were smaller than the standard deviations. A difference map showed no suggestion of hydrogen positions. The observed and computed  $|F|$ 's are given in Table 3. The refined parameters are given in Table 4.

### The structure

The general nature of the structure was reported in a preliminary paper<sup>8</sup>. The ideal positions of the atoms are indicated in Fig. 1.

The structure can be most easily described from the center of the cell outward. The center of the cell is the location of the center of the cluster whose composition is  $\text{Al}_4\text{O}_{16}$ , shown in Fig. 2. This consists of four  $\text{AlO}_6$  octahedra, each sharing an edge with three others so as to form a cluster having tetrahedral symmetry. The four inner oxygen atoms are O(1), the 12 outer oxygen atoms are O(2).

These clusters are held together across the cell faces by boron atoms. The outer O(2) oxygen atoms provide each boron atom with two neighbors, and a third oxygen atom, O(3), shown in Fig. 3, adds two more neighbors, giving each boron tetrahedral coordination. The beryllium atoms are in tetrahedral voids between sets of one O(1) and three O(3) atoms.

As a result of this arrangement, a band of tetrahedra, filled alternately with B and Be atoms, can be distinguished parallel to [110] directions on levels  $z = \frac{1}{4}$  and  $\frac{3}{4}$ , as seen in Fig. 4. In these bands, the Be atoms are on the mirror planes.

<sup>8</sup> MARTIN J. BUEGER and KARLHEINZ TAXER, Rhodizite: structure and composition. *Science* **152** (1966) 500–502.



The rhodizite structure can also be described as based upon a set of cubic close-packed oxygen atoms, which comprise the sub-structure mentioned earlier. The edges of the cell of the close-packed

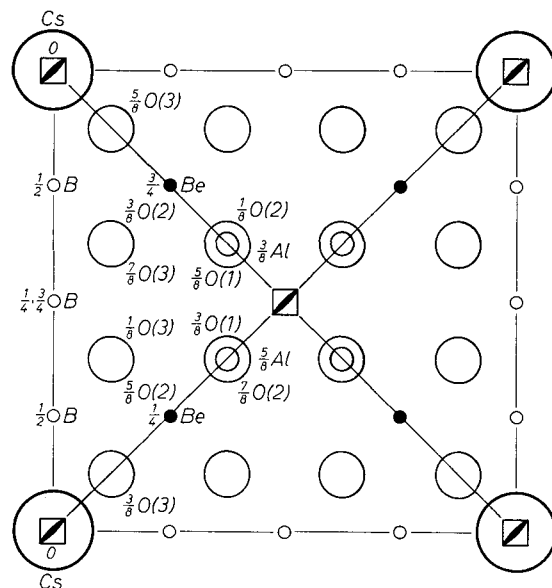


Fig. 1. Idealized positions of atoms in the cell of rhodizite. In the triangle outlined by the cell edge and two mirrors, atoms are labeled and the idealized z coordinate of each is indicated by a fraction

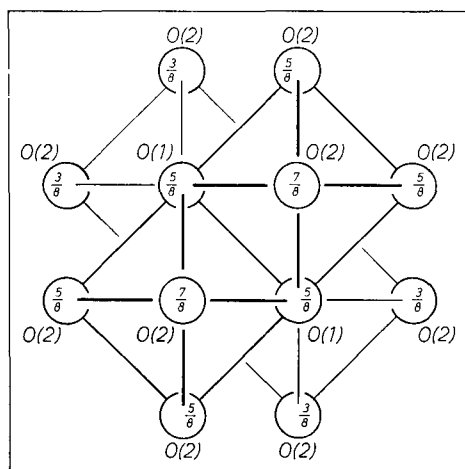


Fig. 2. The arrangement of the four AlO<sub>6</sub> octahedra to form the Al<sub>4</sub>O<sub>16</sub> cluster in the center of the rhodizite cell

set are parallel to the edges of the rhodizite cell, but are only half as long. If the cubic close-packed set were complete, the rhodizite cell would contain 32 atoms. Four atoms of the complete set are omitted

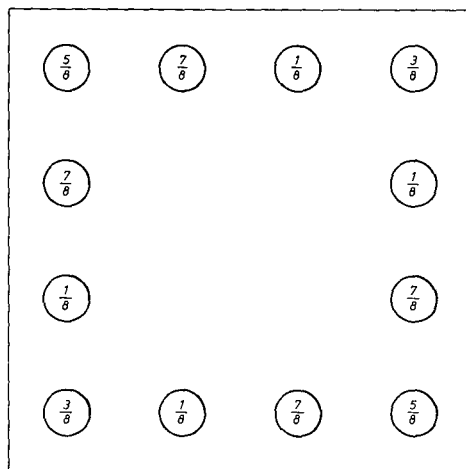


Fig. 3. The locations of the O(3) atoms

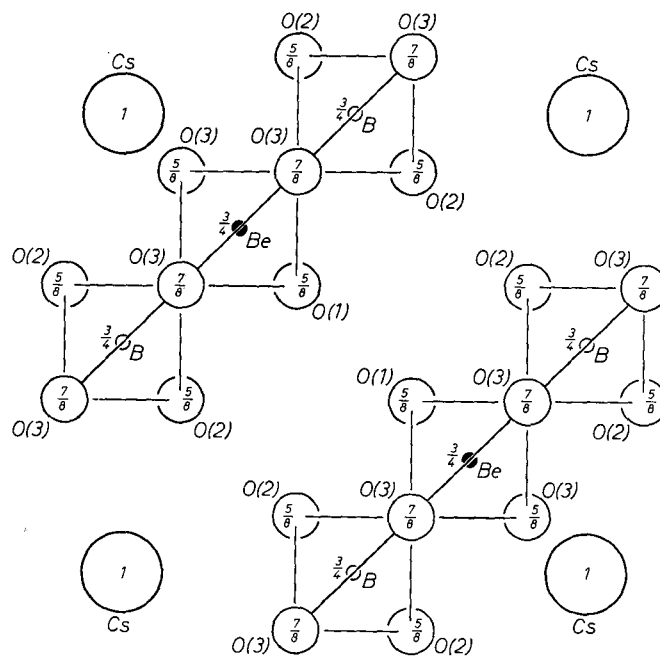


Fig. 4. The chains of tetrahedra parallel to  $[1\bar{1}0]$  at level  $\frac{3}{4}$ . Equivalent chains parallel to  $[110]$  occur at level  $\frac{1}{4}$

about the origin, however, providing a tetrahedral void within which the alkali is located. The small B and Be atoms occupy tetrahedral interstices in the close-packed oxygen set, while the 4 Al atoms occupy the octahedral voids between the oxygen atoms nearest the center of the cell.

### Interatomic distances and bond angles

The interatomic distances and bond angles in rhodizite are recorded in Tables 5 and 6. The octahedral and tetrahedral coordination groups about the small metal atoms are slightly distorted. The shared edges of the octahedra are shorter than the other edges. The B—O distances compare well with those found in other borates, and the Al—O, Be—O and Cs—O distances are comparable with those found in other inorganic structures. The Al—Al distances, however, are slightly longer than those found in metallic aluminum.

Table 5. *Interatomic distances in the structure of rhodizite*

Atoms	Interatomic distance	Standard deviation
Octahedron about Al		
Al —O (1)	1.915 Å	0.007 Å
Al —O (2)	1.905	0.005
O (1)—O (1)	2.497	0.005
O (1)—O (2)	2.777	0.005
O (2)—O (2)	2.735	0.009
Tetrahedron about Be		
Be —O (1)	1.63	0.03
Be —O (3)	1.630	0.009
O (3)—O (3)	2.755	0.012
O (3)—O (1)	2.546	0.011
Tetrahedron about B		
B —O (2)	1.504	0.006
B —O (3)	1.475	0.005
O (2)—O (3)	2.422	0.006
O (2)—O (2)	2.468	0.006
O (3)—O (3)	2.446	0.011
Al—Al	2.892	0.008
Cs—O (3)	3.243	0.008
Cs—Be	3.187	0.02

Table 6. *Bond angles in the structure of rhodizite*

Atoms	Bond angle	Standard deviation
BeO <sub>4</sub> tetrahedron		
O (3)—Be —O (3)	115.4°	1.3°
O (3)—Be —O (1)	102.6	0.2
O (1)—O (3)—O (3)	57.2	0.3
O (3)—O (1)—O (3)	65.5	0.3
O (3)—O (3)—O (1)	57.2	0.3
BO <sub>4</sub> tetrahedron		
O (2)—B —O (3)	108.8	0.4
O (3)—B —O (3)	112.0	0.4
O (2)—B —O (2)	110.3	0.4
O (2)—O (2)—O (3)	59.4	0.2
O (3)—O (3)—O (2)	59.6	0.3
O (2)—O (3)—O (2)	61.3	0.3
O (3)—O (2)—O (3)	60.7	0.3
AlO <sub>6</sub> octahedron		
O (1)—Al —O (2)	93.2	0.3
O (1)—Al —O (1)	81.3	0.4
O (2)—Al —O (2)	91.7	0.3
O (2)—Al —O (1)	172.8	0.4
O (2)—O (1)—O (1)	92.5	0.2
O (1)—O (2)—O (2)	87.5	0.2
O (2)—O (1)—O (2)	45.8	0.2
Al <sub>4</sub> O <sub>16</sub> cluster		
Al —Al —O (1)	84.1	0.2
Al —O (1)—Al	98.0	0.3
O (1)—Al —O (1)	81.3	0.4
O (2)—Al —Al	88.76	0.05
O (1)—O (1)—Al	96.1	0.1
O (1)—Al —Al	41.0	0.2
Bonds belonging to two different polyhedra		
Be —O (1)—Al	119.2	0.6
Al —O (2)—B	119.2	0.4
Be —O (3)—Cs	73.2	0.6
Be —O (3)—B	112.8	0.7
B —O (3)—Cs	114.5	0.3
B —O (3)—B	120.0	0.6
Al —O (1)—Al	98.0	0.4

### Thermal motion

The thermal motions are described by the parameters given in Table 4. The atoms Al, Be and O(1), all on equipoint  $4e$  with symmetry  $3m$ , vibrate in a similar manner but with different amplitudes. The motion of Al is nearly isotropic. The motion of Be is nearly isotropic, but with a large mean-square displacement, possibly due to its small mass. The thermal parameters of boron were not refined.

### Composition of rhodizite

A circumstance which plagues those who attempt to determine the crystal structures of minerals is lack of ideal material: Many minerals, especially those deposited at elevated temperatures, are solid solutions, and display other evidences of disorder. Sometimes this feature is aggravated by difficulties in the chemical analysis.

An exact understanding of the structure of rhodizite is hindered by these complications. For example, the analysis records four different alkalis whose sum is not quite sufficient to fill the one-fold equipoint. Should the sum actually total unity? Are all the recorded alkalis actually present in the one-fold equipoint, and in the amounts shown by the analysis? Unless the exact alkali composition is known, the occupancy of the alkali site (and how it scatters x-rays) contributes a complicating variable which has a strong correlation with the temperature factors of that site; this unknown feature, in itself, prevents attaining the lowest  $R$  value permitted by the intensity data. Furthermore, FRONDEL and ITO proposed two chemical formulae to interpret their analyses<sup>6</sup> as follows (the first being preferred):  $\text{CsB}_{11}\text{Be}_4\text{Al}_4\text{O}_{25}(\text{OH})_4$  and  $\text{CsB}_{12}\text{Be}_4\text{O}_{27}(\text{OH})_3$ . The hydrogen content of their formula was established by ignition. The interpretation of the analyses was based upon 29 oxygen atoms per cell (Table 1) while the structure deduced here has only 28.

In the preliminary report<sup>8</sup> of the structure, it was pointed out that, if each equipoint is occupied by the atom ideally assigned to it in the ideal structure, the chemical formula for rhodizite would be  $\text{CsBe}_4\text{B}_{12}\text{Al}_4\text{O}_{28}$ . The electrostatic-valence bonds to the several oxygen atoms are then

$$\begin{aligned} \text{O(1):} & \quad 3 \times \frac{1}{2} (\text{Al}) + \frac{1}{2} (\text{Be}) = 2, \\ \text{O(2):} & \quad \frac{1}{2} (\text{Al}) + 2 \times \frac{3}{4} (\text{B}) = 2, \\ \text{O(3):} & \quad \frac{1}{2} (\text{Be}) + 2 \times \frac{3}{4} (\text{B}) = 2. \end{aligned}$$

Thus the electrostatic-valence bonds summed on each oxygen satisfy PAULING's second rule<sup>9</sup>, and the part of the formula  $\text{Be}_4\text{B}_{12}\text{Al}_4\text{O}_{28}$  appears to be neutral, thus leaving Cs apparently neutral. Adding hydrogen merely aggravates the valence balance, so it was suggested that, perhaps the loss on ignition was not all hydrogen, but may have been due to loss of other constituents, possibly boron and alkali. In an answering note<sup>10</sup>, GABRIELLE DONNAY *et al.*, suggested that an alternate interpretation of the analysis could be had by omitting one boron of the 12 required for equipoint  $12h$ , and omitting one or two of the original 3 or 4 hydrogen atoms interpreted from the loss on ignition, thus giving a chemical composition  $\text{CsBe}_4\text{B}_{12-x}\text{Al}_4\text{O}_{28}\text{H}_2$ , where  $x = 1$ .

We feel that, with this set of uncertainties in the interpretation of the analysis, it is undesirable at this time to attempt to reduce  $R$  below 9.1%.

This investigation was supported by a grant from the National Science Foundation. The calculations were carried out in the M.I.T. Computation Center. We are indebted to Dr. CHARLES T. PREWITT for preparing the spherical specimen from which the reflection intensities were collected, and for testing the material for piezoelectric effect.

<sup>9</sup> LINUS PAULING, The principles determining the structure of complex ionic crystals. *J. Amer. Chem. Soc.* **51** (1929) 1010–1026.

<sup>10</sup> GABRIELLE DONNAY, A. N. THORPE, FRANK E. SENFLE and R. SIODA, Absence of neutral alkali atoms in rhodizite. *Science* **154** (1966) 889–890.