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The crystal chemistry of rhodizite: a re-examination

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ABSTRACT. The crystal chemistry of rhodizite was re-examined using data from high-resolution electron microscopy (HREM), magic angle spinning nuclear magnetic resonance (MASNMR), a single crystal X-ray structure refinement, and a new chemical analysis. The analysis calculates to the formula: $(K_{0.46}Cs_{0.36}Rb_{0.06}Na_{0.02})_{\Sigma 0.90}Al_{3.99}Be_4(B_{11.35}Be_{0.55}Li_{0.02})O_{28}$. The distribution of alkali cations was shown to be truly random by HREM images and computer image simulations. The distribution of boron and beryllium was monitored by MASNMR, the spectra for both elements gave only single resonances indicating that all beryllium and boron atoms are located in chemically equivalent sites. The structure of rhodizite was refined by single crystal X-ray diffraction techniques. The mineral is cubic $a = 7.318(1)$ Å, space group $P\bar{4}3m$. A full matrix least-squares refinement using 152 unique observed reflections $[F > 3\sigma(F)]$ converged to $R = 0.0344$. The refinement confirmed the basic structure as determined by Taxer and Buerger (1967), 4 beryllium atoms of the unit cell were found to occupy a $4e$ special position, the remaining 0.5 being randomly distributed with the 11.35 boron atoms over the $12h$ sites.

KEYWORDS: rhodizite, crystal chemistry, high-resolution electron microscopy, magic angle spinning nuclear magnetic resonance.

THE year 1984—the one hundred and fiftieth anniversary of the description of the mineral rhodizite—offered a timely opportunity to re-examine the crystal chemistry of this unusual mineral. Rhodizite is a relatively rare mineral and one of the few which contains significant amounts of caesium. The exact chemical composition of the mineral has, however, remained problematical since its description by the German mineralogist and chemist, Gustav Rose (Rose, 1834, 1836). Rhodizite was first found as minute crystals on rubellite tourmaline in the lithia-rich pegmatites around the villages of Sarapulsk and Shaitansk, both near Mursinsk, north of Sverdlovsk (then Ekaterinburg), USSR. The mineral has since been found in crystals up to 2 cm on edge at several localities in Madagascar, including Antandrokomby near Mt Bity and at Manjaka and Ampakita in the Sahatany valley (Lacroix, 1922).

Early attempts at chemical analysis of rhodizite were hindered by the small amount of material available (see section 3). Many crystalline specimens were obtained from Madagascar in the early 1960s and using material from this source for analysis, Frondel and Ito (1965) proposed the formula $CsAl_4Be_4B_{11}O_{25}(OH)_4$. A structure determination of rhodizite was subsequently undertaken by Buerger and Taxer, 1966 (see also Taxer and Buerger 1967). They assigned the space group as $P\bar{4}3m$ (as did Strunz, 1938) on the basis of diffraction symmetry, positive pyro- and piezoelectric characteristics and crystal habit. A structure solution was obtained using Patterson methods and the structure was refined to 9.1%; the structure is described in detail in the next section.

From their studies Buerger and Taxer (1966) obtained a structural formula $CsAl_4Be_4B_{12}O_{28}$, which is at variance with their analysis in requiring an additional boron, one less oxygen and no hydrogen atoms. This formula also requires the caesium to be neutral in order to maintain charge balance. However, Donnay *et al.* (1966) showed by electron spin resonance (ESR) and magnetic susceptibility measurements that caesium is present in its unipositive state and proposed the alternative formula $CsAl_4Be_4B_{11}O_{26}(OH)_2$. This formula is consistent with the analytical data of Frondel and Ito—and with the density measurements and a structure of Taxer and Buerger—if a randomly disordered boron vacancy is introduced and two hydroxyl groups are randomly substituted for oxygen. In the light of the findings of Donnay *et al.* (1966) and due to the uncertainties in the interpretation of the chemical analysis, Taxer and Buerger (1967) decided to curtail their refinement at 9.1%, leaving certain aspects of the crystal chemistry unclear. The exact occupation of the

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alkali site remained uncertain. Earlier workers (Frondel and Ito, 1965; Duparc *et al.*, 1911) found that other alkali elements substitute for caesium, the total occupancy from the chemical analyses being slightly less than unity. It was left unclear whether this value should be unity and whether the alkali substitution is random or ordered. Similarly, uncertainties remained as to the locations of the proposed boron vacancy and the two hydroxyl groups suggested by Donnay *et al.* (1966). Since the thermal parameters for boron were not refined, the assignment of boron and beryllium into the 12*h* and 4*e* sites is open to question.

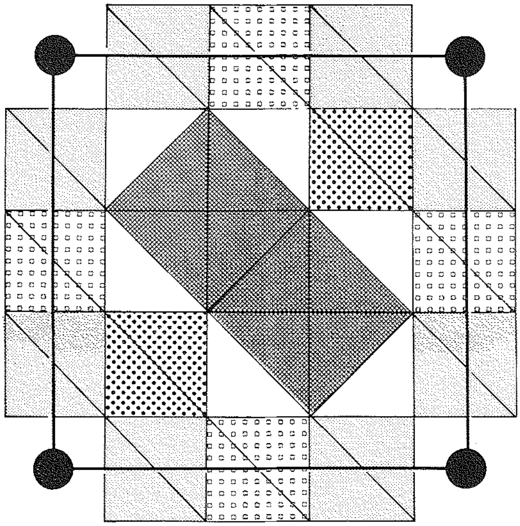

FIG. 1. Schematic diagram showing the upper half of the rhodizite cell. Alkali ions (black circles) are positioned at the cubic cell corners. The edge-sharing pair of AlO_6 octahedra are shown finely crosshatched. The tetrahedra containing beryllium (at $z = \frac{3}{4}$), which lie on the mirror planes, are shaded with large dots and the set of tetrahedra containing boron (also at $z = \frac{3}{4}$) are shaded with squares. The other tetrahedral sites, lightly shaded, contain boron at height $z = \frac{1}{2}$.

We carried out a structural investigation of rhodizite using electron diffraction, HREM and MASNMR. A full chemical analysis of the material studied was also undertaken. The initial results obtained using these techniques raised several new questions regarding the crystal chemistry of rhodizite, in particular the site assignment of boron and beryllium. Therefore, a crystal structure refinement by single crystal X-ray diffraction was carried out in an attempt to clarify these points. In this paper, accounts of the structural imaging, chemical analysis and the structure refinement are given, together with a brief discussion of the MASNMR data. A preliminary account of the structural imaging has been given elsewhere. (Pring *et al.*, 1983) and a full account of the MASNMR data will be presented later.

The structure of rhodizite

The general structure of rhodizite, as determined by Buerger and Taxer (1966) is shown schematically in fig. 1. It is built around a central tetrahedral cluster of four edge-sharing AlO_6 octahedra, these clusters being linked through the cell faces by BO_4 tetrahedra. Beryllium and boron atoms occupy rows of tetrahedral sites parallel to {110}, with the four beryllium atoms assigned to a set of 4*e* type special positions which lie on the mirror planes. The alkali ions occupy large 12-coordinate sites, of approximately tetrahedral geometry, at the cell origins. The idealized atomic arrangement is illustrated in fig. 2.

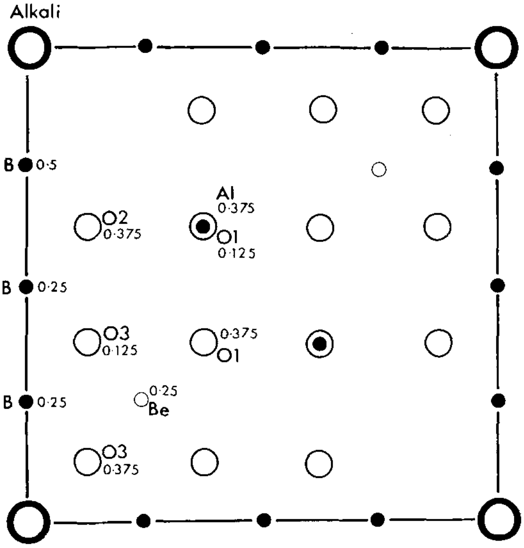

FIG. 2. Idealized atomic arrangement in the lower half of the rhodizite unit cell.

Taxer and Buerger also provide an alternative description of the structure based on an incomplete array of cubic close-packed oxygen atoms. If the close-packed set were complete, the rhodizite cell would contain 32 oxygens; however, 4 atoms about the origin are omitted, resulting in the large tetrahedral 12-coordinate alkali site. An oxygen subcell is evident within the structure, its cell edges parallel to those of the rhodizite cell but only half the length. The 4 Al atoms occupy the octahedral intersites between the oxygen atoms nearest to the centre of the rhodizite cell, with the boron and beryllium atoms occupying tetrahedral voids in the close-packed oxygen array.

Chemical analysis

Several rhodizite crystals from Ambatofinandrahana, in the Ankarata Mts, Madagascar (20° 33′ S., 46° 49′ E.), were obtained from Mr G. Binns of Hastings, England. A preliminary electron microprobe examination of a rhodizite crystal fragment and the X-ray powder pattern of the material prepared for analysis showed quartz to be the only significant impurity. Consequently all Si was assumed to be present as quartz and the analytical results were recalculated accordingly. For the analyses, fragments taken from a single rhodizite crystal were finely powdered in an agate mortar (some additional SiO_2 may have been introduced by this process) and the resultant powder was dried at 110° for 2 hours prior to semi-microanalysis, according to the procedures described. Analytical grade reagents were used except where otherwise specified.

A portion of 49.7 mg of the powdered material was fused with spectrographic grade Li_2CO_3 and the cold fusion product was dissolved in 2 ml of 4M HCl. The solution was made up to volume with deionized water and analysed for Al, Be, Ca, Cs, Fe, K, Na, Rb, and Si by atomic absorption spectrophotometry (AAS). Li was also determined by AAS on a separate aliquot of 132.4 mg of sample fused with NaOH then dissolved in 3M H_2SO_4 and made up to standard volume as before. A separately prepared crystal fragment (4.12 mg) was used for the determination of B by inductively coupled plasma emission spectrometry (ICPES). The powdered sample was fused with NaOH and the fusion product was dissolved in 4M HNO_3 and made up to standard volume for analysis. Si was also determined in this solution in order that the measured B concentration could be corrected for quartz impurity. The AAS and ICPES instruments were calibrated using standards prepared to match closely the analyte solutions. H_2O+ and CO_2 were determined on a 27.5 mg sample using a CHN elemental analyser (Din and Jones, 1978).

Our full chemical analysis of the Ambatofinandrahana material is presented in Table I together with the analyses reported by Frondel and Ito (1965) and earlier workers. The cell contents listed in Table I were calculated on the basis of 28 oxygens per cell. There are several differences between our analysis and that of Frondel and Ito. For example, potassium was found to exceed caesium as the principal alkali cation rather than the contrary. However, the two most important differences between the analyses, from a structural viewpoint, are the much lower water and the higher beryllium contents of the material we studied. The formula $(K,Cs)_{0.9}Al_4Be_{4.5}B_{11.35}O_{28}$ was obtained, compared to $CsAl_4Be_4B_{11}O_{26}(OH)_2$ as proposed by Donnay *et al.* (1966) on the basis of Frondel and Ito's analysis. The former formula matches the structural formula of Buerger and Taxer with $Be+B = 15.85$ (Buerger and Taxer, $Be+B = 16$) and at the same time achieves charge neutrality without the boron deficiency and hydroxyl substitution required by the formula proposed by Donnay *et al.* It is proposed that the additional (0.5 atom) beryllium is randomly disordered over the 12 boron sites and there is 0.15 boron site vacancy.

Three early analyses of rhodizite appear in the literature, but of these only the material analysed by Duparc *et al.* (1911), although contaminated by albite, yields a structurally meaningful composition. Duparc *et al.* (1911) obtained the formula $(Li,K,Cs,Rb,Na,H)_4Al_6Be_7B_{14}O_{39}$. However, if this analysis is recalculated assuming all silicon present is from the albite impurity (4.63 %), the formula obtained is $(Na_{0.33}K_{0.25}Rb_{0.20}Cs_{0.20})Al_{4.24}Be_{4.92}Li_{0.37}B_{10.26}H_{1.28}O_{28}$. Sodium is the dominant alkali while potassium, rubidium, and caesium are approximately equal. It is also notable that there are 4.92 Be atoms per cell, the excess Be and Al, together with the Li can be assigned to the 12 boron sites. There are 11.79 cations assigned to the boron sites, excluding the protons, and only 0.21 of a boron vacancy is required. The structural ramifications of the higher Be content and the possible role of water or hydroxyl groups are discussed below. The most widely quoted of the early analyses is that of Pisani (Lacroix, 1910), whose sample was heavily contaminated with spodumene ($LiAlSi_2O_6$). On the basis of this analysis Lacroix (1910, 1922) proposed the formula $(Cs,Rb,K,Na,H)_8Be_4Al_6B_{12}O_{35}$. Also based on Pisani's analysis and with a knowledge of the cell, Strunz (1938) proposed the stoichiometry $NaKLi_4Al_4Be_3B_{10}O_{27}$ and later (Strunz, 1943) suggested a structural model for the mineral which was subsequently shown to be incorrect. The earliest rhodizite analysis is that by Damour (1882) of material from the type locality in the Urals. Since he unfortunately overlooked Be and did not determine the alkali elements individually, the type Russian rhodizite is chemically very poorly defined; to rectify this situation a modern analysis on Urals material has been initiated.

Table I. Analytical Data

	% Oxides by weight					Cations per 28 oxygens for analysis 1		
	1	2	3	4	5			
Li_2O	0.03		0.68	7.30		Li	0.02	
Na_2O	0.06	0.12	1.78	3.30	1.62	Na	0.02	0.90
K_2O	2.77	1.79	1.41			K	0.46	
Rb_2O	0.73	1.83	2.29	5.90	12.00	Rb	0.06	
Cs_2O	6.4	7.54	3.47			Cs	0.36	
Al_2O_3	25.8	24.41	27.40	30.50	41.40	Al	3.99	
BeO	14.3	12.20	14.93	10.10		Be	4.51	
B_2O_3	50.2	46.82	[43.33]	40.60	33.93	B	11.35	
H_2O+	0.32	4.10	1.42	0.45	2.96			
CO_2	0.15							
Rem	0.28	1.10	3.29	1.36	3.49			
TOTAL	101.0	99.91	100.00	99.51	95.40			

(1) Ambatofinandrahana, Madagascar. Sample weight for main analysis: 49.7mg contained 6.23% SiO_2). Sample weight for boron determination: 4.12mg (contained 3.75% SiO_2). The data are for material dried at 110°C and are calculated to a SiO_2-free basis. 'Rem' is the sum of FeO (0.09%), CaO (0.18%), and MgO (0.01%). The estimated analytical error is ±5% relative for Cs_2O and oxides < 1% by weight and ±1% relative for other components. Analyst V.K. Din.

(2) Manjaka, Madagascar. Sample weight 5g. The data are from Frondel and Ito (1965). 'Rem' is SiO_2 (0.45%); Fe_2O_3 (0.12%); Sn (0.1%); H_2O (0.43%). Analysts Ito and Haramura.

(3) Manjaka, Madagascar. Sample weight 2.5g. Analysis by Duparc et al. (1911). 'Rem' is MgO (0.11%) and SiO_2 (3.18%). Contained albite admixed.

(4) Antandrokomby, Madagascar. Sample weight 1.25g. The data are from Lacroix (1910). 'Rem' is SiO_2 (1.36%). Contained spodumene admixed. Analyst F. Pisani.

(5) Urals, Russia. Sample weight 0.135g. The data are from Damour (1882), beryllium was overlooked. 'Rem' is CaO (0.74%), MgO (0.82%) and Fe_2O_3 (1.93%).

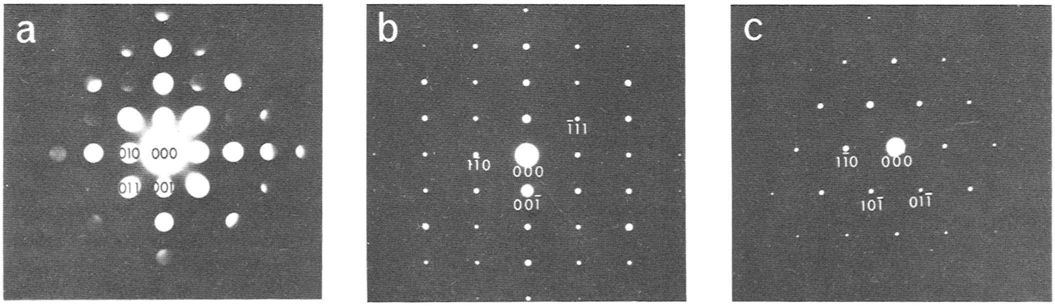

FIG. 3. Electron diffraction of rhodizite: (*a*) [100]; (*b*) [110]; (*c*) [111].

Electron optical studies

Imaging and diffraction. All electron microscopy was performed using a JEOL JEM 200Cx electron microscope operating at 200 kV with a standard tungsten hairpin filament and a beam current of typically 40 μA. A ±25° side-entry eucentric goniometer stage was used and the spherical and chromatic aberration coefficients of the objective lens were Cs = 2.5 mm and the nominal Cc = 2.7 mm, giving an optimum defocus (the so-called Scherzer defocus (Scherzer, 1949) of −950 Å). The point to point-to-point resolution at this defocus was 2.9 Å.

Thin fracture fragments of rhodizite for EM study, obtained by crushing the mineral under acetone in an agate pestle and mortar, were deposited on to holey carbon support films from suspension. Electron diffraction patterns were recorded with the beam parallel to zone axes [100], [110], and [111] of this cubic mineral (fig. 3*a–c*). They show no evidence of supercell ordering of the alkali ions or of the proposed boron vacancies.

High resolution lattice images of sections perpendicular to these three zones were recorded (fig. 4*a–c*). Images viewed down [100] (fig. 4*a*), show square arrays of bright spots 7.3 Å apart, corresponding to the cubic cell *a* repeat. At the centre of these nets are weaker-contrast white dots, the intensities of which increase with crystal thickness. The image is slightly distorted at the crystal edge indicating that the crystal was tilted slightly off the exact zone orientation. Fig. 4*b* is a lattice image viewed down [110], showing a rectangular 7.3 × 5.2 Å motif, while the [111] zone image (fig. 4*c*) shows a repeat pattern of black hexagons, a projection consistent with the threefold symmetry axis along [111]. These lattice images show large regions of perfect lattice and neither point defects nor dislocations were observed.

Computer image simulations. Simulations of the high resolution lattice images were generated using computer programs, written by one of us (D.A.J.), based on the multislice method of Goodman and Moodie (1974) (see also Cowley and Moodie, 1957). Calculations were performed using the electron optical parameters of the JEOL 200Cx as described above. The final atomic parameters of Taxer and Buerger (1967) were used in all calculations; image simulations were completed before the new structure refinement was undertaken (the minor changes in atomic coordinates that resulted would not affect these simulations). Images were calculated over a range of defocus (Δf) from 0 to −1600 Å and for crystal thicknesses (ΔH) 2.5 to 200 Å. It should be noted that in the course of these image simulations the effects of beam tilt were not considered. The recent work of Smith, Saxton *et al.* (1983) demonstrated that beam alignment can have a marked effect on image detail, particularly in materials with small unit cells.

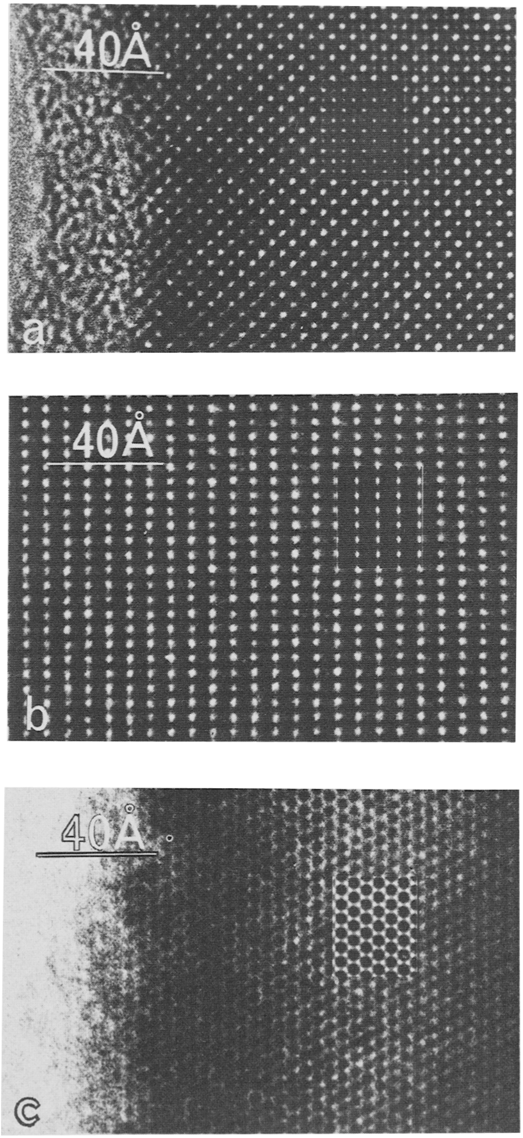

FIG. 4. Lattice projections of rhodizite viewed down: (*a*) [100], image defocus −700 Å, crystal thickness approximately 50 Å. (*b*) [110], image defocus −450 Å, crystal thickness approximately 100 Å. (*c*) [111], image defocus −500 Å, crystal thickness approximately 150 Å. The inserts show matching image simulations for an average alkali (36 electron scatterer).

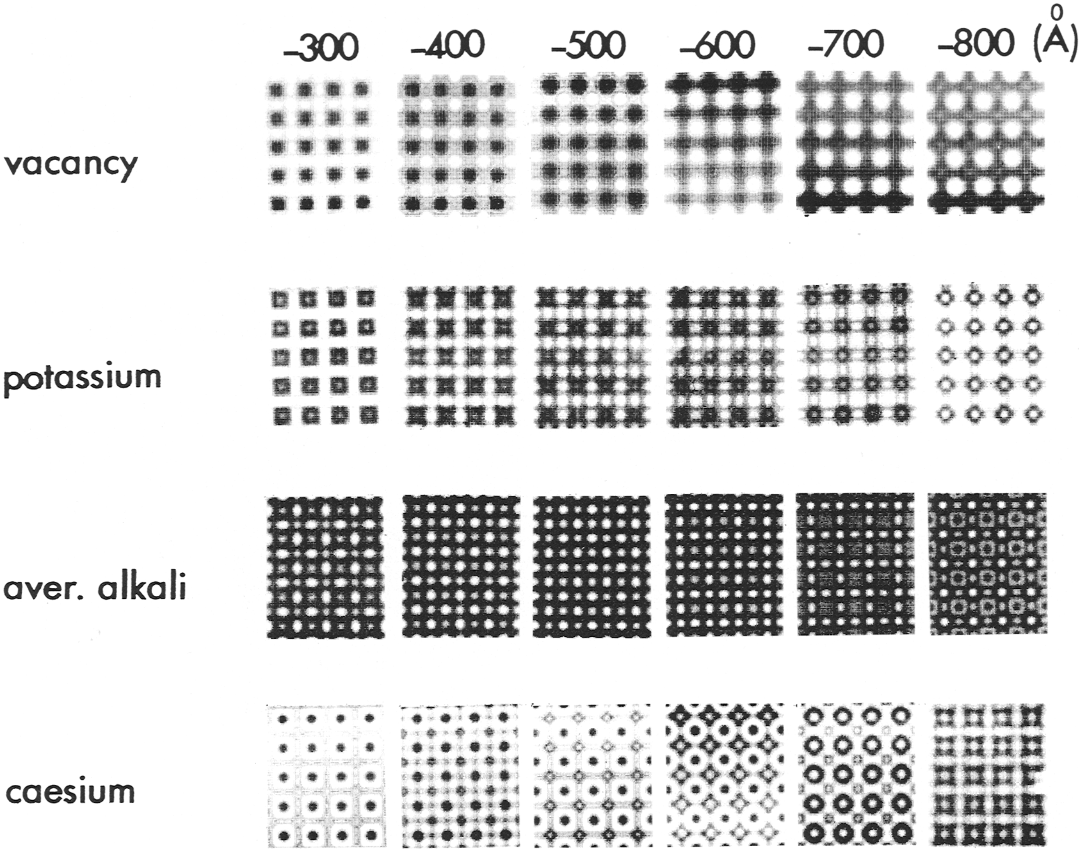

FIG. 5. Series of image simulations for rhodizites, [100] zone, with different alkali site occupancies, viz: vacant, potassium, average alkali, and caesium. The crystal thickness for the calculations is 50 Å.

The alkali ions are the strongest scatterers in the structure (accounting for about 10% of the total electrons) and their effect on the image detail was investigated by simulation of a series of [100] images. Fig. 5 shows a set of through-focus series calculated with four different scatterers occupying the alkali sites, viz: a vacancy, potassium, the 'average alkali' (used by Buerger and Taxer in their refinements), and caesium. The average alkali was calculated from the earlier alkali analysis of Frondel and Ito (1965) and corresponds to an atom with the scattering power of 36 electrons. The images simulated using the average alkali provide the best match for the [100] image shown in fig. 4*a*. The image match was also sustained in through-thickness calculations (see fig. 6). Matching image simulations for each of the three zones, calculated with the 36 electron scatterer, are shown as inserts in the lattice images (fig. 4*a*–*c*).

Overall the agreement between the observed and calculated image is good and can be taken as confirmation of Buerger and Taxer's structure. The homogeneity of the image detail for a given crystal thickness in the lattice images indicates the absence of any highly ordered domains rich in a particular alkali. However, it was not possible to draw any conclusions regarding the distribution of the lighter boron and beryllium atoms using image simulation techniques owing to the lack of sensitivity of the method to small changes in electron density.

Magic angle spinning NMR

Rhodizite is ideally suited to study using multinuclear MASNMR as the principal cations are responsive to the technique by which it is possible to probe the site coordination and distribution of the responsive cations (Fyfe *et al.*, 1982, 1983). A series of MASNMR spectra of rhodizite were kindly recorded by Dr C. A. Fyfe and his colleagues

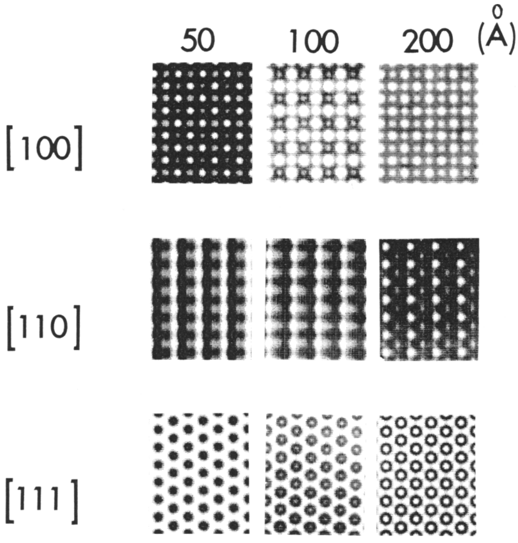

FIG. 6. Through-thickness series of image calculations for rhodizite using the average alkali data. The image defocus values are −700 Å, −450 Å and −500 Å respectively for the [100], [110], and [111] zones.

at the University of Guelph, Ontario, Canada, and the results were made available for the present study.

The ^{133}Cs spectrum showed that caesium is present in its unipositive oxidation state and thus confirmed the earlier findings of Donnay *et al.* (1966). The spectra for aluminium and boron are consistent with the expected site symmetries for these ions; octahedral and tetrahedral respectively. The MASNMR ^{9}Be spectrum showed only a single resonance at −3.11 ppm with respect to beryl, indicating that all Be is present in chemically equivalent sites. In the Buerger and Taxer structure all the Be is assigned to the 4*e* special position. However, analysis 1 in Table I shows that there are 4.5 Be atoms per cell, thus 0.5 Be atoms must be assigned to the 12*h* sites occupied by the 11.35 boron atoms. Since there is only a single resonance in the ^{9}Be and ^{11}B spectra the 4*e* and 12*h* sites must be chemically equivalent. It is therefore probable that the beryllium and boron atoms are randomly distributed over all sixteen available sites. In an attempt to resolve this point and to clarify the overall understanding of the crystal chemistry of rhodizite a structure refinement, reported in the following section, was undertaken.

Structure refinement

Collection of intensity data. The single crystal X-ray diffraction data used in the structure refinement were collected on a Stoe four-circle diffractometer with graphite-monochromated Mo-$K\alpha$ radiation using a small irregular crystal fragment approximately 0.1 × 0.1 × 0.1 mm. Unit cell dimensions were determined from the angular measurement of forty-two strong reflections with $15° < 2\theta < 25°$. A total of 612 reflections were collected in the range $5° < 2\theta < 60°$ using 24-step ω–φ scan techniques. The step width was set at 0.05° and the scan rate varied between 0.5 and 2s per step. A set of three standard reflections was monitored every hour throughout the data collection and showed no significant variation.

Lorentz polarization corrections were applied to the data and equivalent reflections were averaged to give 152 unique observed reflections $[F > 3\sigma(F)]$. Owing to the irregular shape of the rhodizite fragment and its low mass absorption coefficient ($\mu = 26.93$ cm^{-1}) no absorption correction was applied. The neutral atom scattering factors used in the refinement were taken from Doyle and Turner (1968).

Initial data reduction was performed on the dedicated Nova 3 computer at the Chemical Laboratory, Cambridge, using programs written by Dr W. Clegg. The structure refinement was carried out using programs written by Prof. G. W. Sheldrick; the initial stages of the refinement were carried out on the University of Cambridge IBM 370/165 computer and the refinement was completed using the Australian National University Univac 1100 Computer.

Crystal data. Space group $P\bar{4}3m$ (No. 215); $a = 7.318(1)$ Å; V = 391.90 Å^3; no systematic absences; $F(000) = 383.95$; Z = 1; μ (Mo-$K\alpha$) = 26.93 cm^{-1}; Mo-$K\alpha$ radiation $\lambda = 0.71069$ Å; $D_{\text{meas.}} = 3.36$ g cm^{-3} (flotation in Clerici's solution and water) $D_{\text{calc.}} = 3.345$ g cm^{-3}.

Refinement. The final atomic parameters of Taxer and Buerger (1967) were used as a starting model for the refinement. In the initial stages of the refinement 12 boron atoms were assigned to the 12*h* sites, 4 Be atoms to the 4*e* sites and an average alkali atom of 36 electrons was employed. After four cycles of least-squares refinement of all positional parameters and isotropic temperature factors, the discrepancy index, *R*, was 4.01 %. At this point the average alkali was replaced by the mixture of alkali ions according to the determined distribution. The occupancy factors for each alkali species were fixed and two further cycles of refinement reduced *R* to 3.8 %.

The distribution of the boron and beryllium between the 12*h* and the 4*e* sites was then refined, using a single thermal parameter for each site. It was not possible to refine the site occupancy while still employing the fixed analytical composition, so several structural models with fixed occupancies were refined. During these refinements, site occupancies were fixed at their analytical values but the positional and thermal parameters on all atoms were freed. Details of the beryllium and boron assignments for the three models together with their final discrepancy indices are presented in Table II.

The Taxer and Buerger (1967) model, with the boron atoms assigned to the 12*h* sites, full beryllium occupancy of the 4*e* sites and the remainder of the beryllium in the 12*h* sites, gave the best agreement between the observed and calculated structure factor with $R = 3.44\%$. It also provided the 'flattest' difference Fourier map (no peak or trough greater than one electron). Refinements of the other two models were marked by rapid increases in the thermal parameter of the 4*e* site together with an increase in the discrepancy index.

The final atomic and thermal parameters from the successful refinement are presented in Table III. This refinement resulted in only minor changes in the atomic parameters from those of Taxer and Buerger; however the position of the 4*e* site occupied by beryllium did change significantly. The effect of this shift is most evident when the bond

Table II. Occupancy Models for B and Be in Rhodizite

	MODEL		
	TAXER & BUERGER	DISORDERED	INVERSE TAXER & BUERGER
12h SITE	11.35B + 0.5Be	8.80B + 3.375Be	7.35B + 4.50Be
4e SITE	4.0Be	2.850B+ 1.125Be	4.00B
DISCREPANCY INDEX %	3.44	3.80	4.01

Table III. Final Atomic and Thermal Parameters

		Parameters		
		Atomic		Thermal
Atom	Site	x	z	B
Alkali	1a 000			0.02500 (7)
Be	4e xxx	0.7429 (9)		0.0059 (20)
B	12h x 1/2 0	0.2482 (8)		0.0036 (9)
Al	4e xxx	0.3600 (2)		0.0015 (5)
O(1)	4e xxx	0.6189 (5)		0.0024 (13)
O(2)	12i xxz	0.3637 (4)	0.0997 (4)	0.0038 (7)
O(3)	12i xxz	0.1347 (4)	0.6013 (4)	0.0036 (7)

Table IV. Bond Lengths for Rhodizite

Interatomic Distances

BeO_4 tetrahedron	
Be - O(01)	1.571(5)Å.
Be - O(3)	1.636(4)Å.
O(3) - O(3)	2.731(6)Å.
O(3) - O(1)	2.553(6)Å.
BO_4 tetrahedron	
B - O(2)	1.497(4)Å.
B - O(3)	1.487(4)Å.
O(2) - O(3)	2.428(6)Å.
O(2) - O(2)	2.472(6)Å.
O(3) - O(3)	2.468(6)Å.
AlO_6 octahedron	
Al - O(1)	1.907(5)Å.
Al - O(2)	1.905(4)Å.
O(1) - O(1)	2.461(12)Å.
O(2) - O(2)	2.732(6)Å.
Al - Al	2.895(5)Å.
Cs - O(3)	3.234(3)Å.
Cs - Be	3.259(12)Å.

Table V. Selected Bond Angles for Rhodizite

	Bond Angles
BeO_4 tetrahedron	
O(3) - Be - O(3)	112.9(1)°
O(3) - Be - O(1)	105.6(2)°
O(1) - O(3) - O(3)	57.7(1)°
O(3) - O(1) - O(3)	64.6(2)°
O(3) - O(3) - O(1)	57.7(1)°
BO_4 tetrahedron	
O(2) - B - O(3)	108.9(2)°
O(3) - B - O(3)	111.6(5)°
O(2) - B - O(2)	111.3(4)°
O(2) - O(2) - O(3)	59.7(1)°
O(3) - O(3) - O(2)	59.6(1)°
O(2) - O(3) - O(2)	61.1(2)°

lengths and angles from the two refinements are compared (see Table IV and V). While the bond lengths in the current refinement show a greater degree of variation; Be–O(1) 1.571 Å and Be–O(3) 1.630 Å, compared with 1.630 Å for both sets of bonds in the earlier refinement, the tetrahedral angles in the current refinement more closely approach 109° 28′. Overall the current refinement has resulted in a reduction in the difference in size of the boron and beryllium sites and confirmation of the analytical formula as a realistic representation of the crystal chemistry of rhodizite.

Discussion

The chemical analysis of the material studied revealed potassium as the dominant alkali ion. It is likely that fairly extensive solid solution may exist involving the various alkali ions, the material examined by Frondel and Ito being caesium-rich and that examined by Duparc *et al.*, sodium-rich. In spite of the large variation in radii of the ions (Na = 1.39, K = 1.64, Rb = 1.72, Cs = 1.88 Å; Shannon, 1976), their distribution, as revealed by HREM, is random. There was no evidence of alkali ion ordering or domain formation within the crystals examined. The alkali ion content, from the analysis is 0.90 per cell, similar to the values 0.90 and 0.98 per cell reported by Frondel and Ito (1965) and Duparc *et al.* (1911), respectively. The incomplete occupancy of the alkali site was one of the features of the rhodizite structure left unresolved by Taxer and Buerger (1967). With the total alkali content per cell close to unity, the alkali, boron and beryllium contents are balanced to achieve charge neutrality and minimize the number of vacant sites within the structure.

The structure refinement confirmed that the formula derived from the analysis $(K,Cs)_{0.9}Al_4Be_{4.5}B_{11.35}O_{28}$ is an accurate representation of the crystal chemistry of rhodizite. The calculated density of 3.345 is in good agreement with the measured value 3.36 g cm^{-3} and also lies toward the centre of the range of reported values, 3.22 to 3.44 g cm^{-3}. It should be noted that this range may reflect the variation in alkali content rather than experimental inaccuracy. The calculated density of rhodizite varies markedly between 3.2 for the pure potassium compound and 3.62 g cm^{-3} for the caesium end member.

Charge neutrality in the material studied is achieved via the partial substitution of boron by beryllium, while in the material studied by Frondel and Ito, 1965 (and also used by Buerger and Taxer for their structure determination), hydrogen ions may, in some part, play this role. However, it is interesting to note that if the analyses of Frondel and Ito and Duparc *et al.* are recalculated to a water and to a hydroxide-free basis respectively, the following formulae are obtained:

$$(Cs_{0.45}K_{0.32}Rb_{0.16}Na_{0.03})Al_4Be_4(B_{11.5}Be_{0.15}Al_{0.08})O_{28}$$

and

$$(Na_{0.33}K_{0.25}Rb_{0.21}Cs_{0.21})Al_4Be_4(B_{10.6}Be_{1.03}Li_{0.4}Al_{0.4})O_{28}.$$

These are close to the composition obtained for the Ambatofinandrahana material. The composition from the recalculation of Frondel and Ito's analysis is fully consistent with the structure, while the composition from Duparc *et al.* has an excess of cations due to the high Al and Li contents.

The role of water within the rhodizite structure remains unclear. Only very minor amounts of water were detected in the sample studied and water clearly is not an essential component of rhodizite. Hydronium ions (H_3O^+) commonly substitute for alkali ions in a wide variety of compounds (see for example Gatehouse and Pring, 1981). Water (or hydronium ions), if present in rhodizite, could reside in the large 12-coordinate alkali site and may thus play a role in the reduction of vacant sites. Full substitution of alkali ions by water would yield a structural formula very similar to that originally proposed by Buerger and Taxer (1966), i.e. $H_2O\,Al_4Be_4B_{12}O_{28}$. However, none of the published rhodizite analyses shows alkali occupation lower than 0.9 and, in this respect, rhodizite analyses indicate a very small compositional range.

To date, we are aware of five published full chemical analyses of rhodizite only three of which yield structurally meaningful formulae. Thus a much larger pool of analytical data is required before the compositional limits of rhodizite can be firmly established, particularly the limits of beryllium substitution for boron.

The site symmetry and chemical environment of the beryllium and boron in rhodizite were monitored by MASNMR; as noted earlier, the spectra for both elements show only a single resonance corresponding to the ions in tetrahedral coordination with oxygen. The structure refinement shows that beryllium occupies two crystallographically distinct sites (12*h* and 4*e*) which are chemically equivalent at the level of sensitivity afforded by MASNMR. The final atomic coordinates from the structure refinement reveal a considerable difference in the cation–oxygen contacts between the two sites. The beryllium ions which occupy 12*h* sites are surrounded much more closely by oxygen atoms than those in the 4*e* sites. However, it should be remembered that these bond lengths represent only the mean distance and that the 12*h* contact is greatly shortened by the dominance of the smaller boron ion in this site. While the technique of MASNMR has been used widely in the study of silicates (Smith, Kirkpatrick *et al.*, 1983) it has not been applied so extensively in the study of ordering of lighter elements. Further MASNMR studies have been initiated on the sensitivity of the position of ^{9}Be and ^{11}B resonances to chemical environment.

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Note. A full listing of structure factors for the rhodizite refinement may be obtained from the Mineral Library, British Museum (Natural History), London SW7 5BD.

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