On the Structure of Rhodizite

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Ultra-high resolution (real-space) imaging combined with computer simulation sheds new light on the structure of the mineral rhodizite, the composition of which is $(K_{0.44}Cs_{0.36}Rb_{0.07})B_{11.3}Be_{4.5}Al_4O_{28}$.

Although rhodizite was first identified some 150 years ago,[1] its crystal chemistry is still a matter of considerable conjecture. Part of the reason for this state of affairs stems from the fact that it consists of at least four light elements (Al, Be, B, and O) so that, taken with its insolubility (it resists attack by cold concentrated acids, including HF) even its composition cannot be readily established. Three separate studies in the mid-sixties led to the following suggested stoicheiometries: $CsAl_4Be_4B_{11}O_{25}(OH)_4$,[2] $CsAl_4Be_4B_{12}O_{28}$,[3] and $CsAl_4Be_4B_{11}O_{26}(OH)_2$.[4]

X-Ray crystallographic studies[3] of rhodizite showed that it is cubic ($P\bar{4}3m$; a = 7.317 Å) and a general structure was established, the top half of the most plausible model for the unit cell being as shown in Figure 1(a). The centre of the unit cell is thought to contain a tetrahedral cluster of AlO_6, edge-sharing octahedra, these clusters being linked by BO_4 tetrahedra through the unit cell faces, Figure 1(b). In this model, Cs occupies 12 co-ordinate sites at the origin and the Be and B atoms occupy rows of tetrahedral sites aligned parallel to

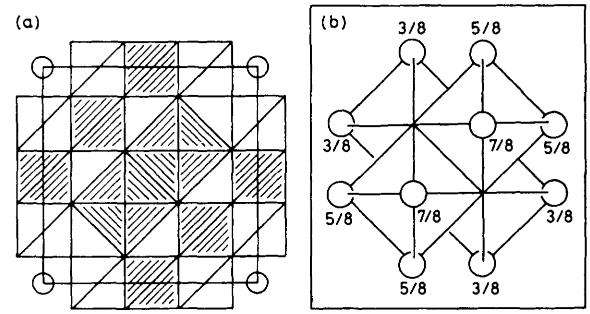


Figure 1. (a) Schematic diagram of the rhodizite structure. Only the top half of the unit cell is shown [based on ref. 3(b)]. (b) Diagram showing the tetrahedral cluster of four AlO_6 octahedra, the oxygen atoms, shown as open circles, are also part of BO_4 tetrahedra, the clusters being linked by these tetrahedra through the cell faces.

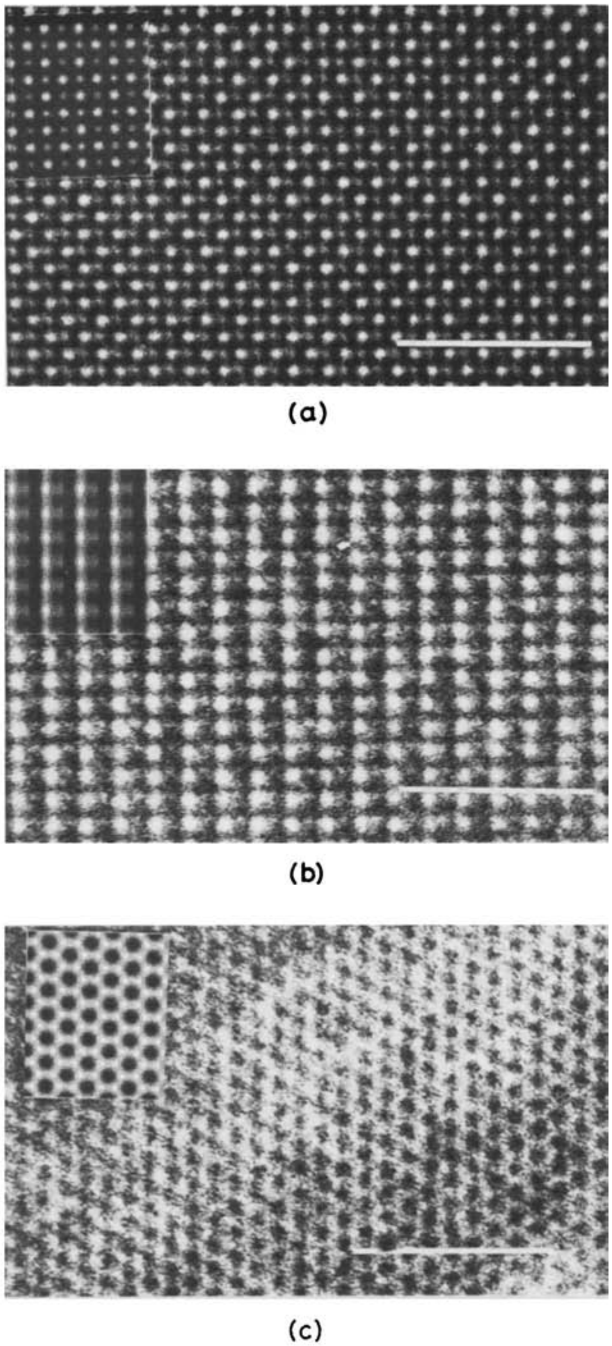
<110>; the Be atoms are thought to occupy, fully, the four 4*e* special positions lying on the mirror planes and the boron atoms are assigned to occupy all the twelve 12*h* sites. There is still much doubt as to the validity of this model, not least because it requires Cs to be present as neutral atoms.

In another model,[4] based on extra measurements which established the presence of unipositive Cs ions, additional structural features, including a boron vacancy randomly distributed amongst the 12*h* sites, were proposed.

Here we show that ultra-high resolution electron microscopy coupled with image simulation (computed images based on specific models) can shed much light on structural problems of this kind. Our work also takes into consideration very recent microanalytical and high-resolution solid-state n.m.r. data. The wet chemical analysis, kindly carried out by Mr. V. Din at the British Museum, gave a formula of $(K_{0.44}Cs_{0.36}Rb_{0.07})$ $(Be_{11.3}B_{4.5})Al_4O_{28}$, there being traces of Li^+ and Na^+ (Li_2O, 0.03; Na_2O, 0.06%). The sample emanated from Ambalalifotsy, Madagascar, and was supplied by Mr. G. Binns.

Selected area electron diffraction patterns down the principal zone axes [100], [110], and [111] of crushed specimens showed no sign of supercell ordering of the alkali ions or of the proposed boron vacancy. On the assumption that the 12-co-ordinated site was occupied by an average cation (Z = 36) rather than exclusively by Cs (Z = 55) or K (Z = 19), good correspondence between observed and calculated images was obtained for the three principal high symmetry zone axes (Figure 2).[5] Moreover, this correspondence was sustained both when specimen thickness was varied and for different settings of objective lens defocus. Our results, therefore, confirm the general correctness of the Buerger–Taxer model; but the high resolution electron microscopy test is not sufficiently sensitive to discriminate between our proposed formula, $(K,Cs,Rb)Al_4Be_{4.5}B_{11.3}O_{28}$ and $CsAl_4Be_4B_{11}O_{26}(OH)_2$.

Multinuclear magic-angle spinning n.m.r. spectroscopy sheds[6] further light on this problem. Apart from confirming the expected co-ordination of Al (octahedral) and B (tetrahedral), the single Be resonance at −3.11 p.p.m. with respect to beryl shows that Be ions occupy chemically equivalent sites. Similarly the single B resonance shows that all the boron occupies chemically equivalent 4-co-ordinate sites. Recalling that analysis shows 4.5 Be per cell and that there are only four 4*e* sites per cell, it follows that 0.5 Be atoms on average must be assigned to some of the 12*h* sites normally occupied by B. But since there is only one Be-resonance the two sites must be chemically equivalent. Hence we conclude that the B and Be ions are both randomly distributed over all sixteen available tetrahedral sites.


(a)

(b)

(c)

Figure 2. Lattice images of rhodizite taken down: (a) [100], crystal thickness approximately 50 Å and defocus −700 Å. (b) Down [110], crystal thickness approximately 100 Å and defocus −450 Å. (c) Down [110], crystal thickness approximately 150 Å and defocus −500 Å. (The white bar on each micrograph represents a length of 50 Å.)

In summary, therefore, the broad structural principles of the Buerger–Taxer model are vindicated. In addition, we see that Cs, Rb, K, and Li are all present as monovalent cations and distributed at random in the 12-co-ordinated sites, there being no domains rich in one or other of these alkali metals. The Be and B are probably randomly distributed over, and almost completely occupy, the sixteen available tetrahedral sites. Only a highly refined *X*-ray or neutron diffraction structure determination can tell whether Be ions do have some preference for the 4-fold special positions. Such a determination (now initiated), which will help to explain the exceptional efficacy with which the Cs^+ ion is incarcerated within the rhodizite structure, would be of value in clarifying the principles of the disposal of radioactive waste.

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