American Mineralogist, Volume 88, pages 1331–1335, 2003

The crystal structure of chromian kassite from the Saranovskoye deposit, Northern Urals, Russia

I.E. GREY,[1,]* W.G. MUMME,[1] I.V. PEKOV,[2] AND D.YU. PUSHCHAROVSKY[2]

[1]CSIRO Minerals, Box 312 Clayton South, Victoria 3169, Australia
[2]Geology Department, Moscow State University, Vorobievy Gory 119899, Moscow, Russia

ABSTRACT

The crystal structure of kassite, ideally $Ca[Ti_2O_4(OH)_2]$, containing 2 wt% Cr_2O_3, from the Saranovskoye chromite deposit, Perm' district, Northern Urals, has been determined and refined to $R1 = 0.06$ using single crystal X-ray diffraction data. The crystals have monoclinic symmetry, $P2_1/a$, with $a = 5.275(1)$, $b = 9.009$ (2), $c = 9.557$ (2) Å, $\beta = 90.43°$. A pronounced sub-structure for the mineral, conforming to space group $I2/a$, is related to the $I2/a$ structure for lucasite-(Ce), $Ce[Ti_2O_5(OH)]$. It comprises (001) layers of gibbsite-like fused hexagonal rings of edge-shared $Ti(O,OH)_6$ octahedra with the Ca atoms sandwiched between pairs of opposing rings and displaced from the center of the rings along [010]. Ordering of the protons in chromian kassite lowers the symmetry to $P2_1/a$. Kassite, $CaTi_2O_4(OH)_2$, and cafetite, $CaTi_2O_5(H_2O)$, are identical chemically but significantly different in their crystal structures.

INTRODUCTION

Kassite was first mentioned as an unknown hydrous calcium titanate in association with cafetite in specimens from the Afrikanda alkaline-ultrabasic massif in the Kola Peninsula, Russia, by Kukharenko et al. (1959). These authors subsequently described kassite as a new mineral species with composition $CaTi_2O_4(OH)_2$, and having orthorhombic symmetry, $a = 8.99$, $b = 9.55$, $c = 5.26$ Å (Kukharenko et al. 1965). It occurred as blocky aggregates of pale yellow platy crystals, in contrast to the associated cafetite, another hydrous oxide of Ca and Ti, which was described as forming tangled fibrous aggregates or radial-fibrous aggregates of acicular crystals. Both minerals were found in cavities of pegmatoid jacupirangite with Ti-magnetite, titanite, chlorite, calcite, and goethite (Kukharenko et al. 1959, 1965).

Rudashevsky et al. (1977) discovered a compound having an X-ray powder pattern identical to kassite among products obtained from bauxite using the Bayer method. It had the composition $(Ca_{0.79}Na_{0.11}Mn_{0.05})_{\Sigma 0.95}(Ti_{1.15}Al_{0.59}Mg_{0.16}Fe^{3+}_{0.15})_{\Sigma 2.05}O_{2.80}(OH)_{3.33}$ and orthorhombic cell parameters $a = 9.05$, $b = 9.58$, $c = 5.27$ Å. These authors also prepared a synthetic form and studied its physical properties (Rudashevsky et al. 1977).

The findings of Kukharenko and colleagues were disputed by Evans et al. (1986), who studied new specimens of a calcium titanate mineral from the Magnet Cove alkalic intrusion in Hot Spring County, Arkansas. They found two types of occurrences of the mineral, as brownish-pink platey rosettes and yellow spherules. A semi-quantitative energy dispersive X-ray analysis of the rosettes showed Ca and Ti as principal constituents in a 1:2 atomic ratio, with traces of Na, Nb, and Fe as the only other elements, linking the mineral compositionally to kassite. However, a Gandolfi powder X-ray diffraction (XRD) pattern of a rosette matched the published powder data for cafetite in Kukharenko et al. (1965). Evans et al. (1986) indexed precession photos of single crystals with an *A*-centered orthorhombic cell having $a = 12.1$, $b = 31.65$, $c = 4.95$ Å, consistent with the cell reported for cafetite (Kukharenko et al. 1959) except for interchange of *a* and *b*. Evans et al. (1986) concluded that the crystallographic data for kassite and cafetite were inadvertently interchanged in the original description, and described the Magnet Cove specimen as kassite. The entries for the two minerals were then interchanged in a subsequent update (Set 39 in 1989) of powder diffraction data by the International Centre for Diffraction Data.

The findings of Evans et al. (1986) were contested by Self and Buseck (1991) in a paper reporting transmission electron microscopy (TEM) studies on a specimen from Josephine Creek, Oregon. The specimen contained micrometer-sized grains of a calcium titanate mineral which had been previously analyzed by Burton (1982), giving a composition close to $CaTi_2O_4(OH)_2$. The TEM analysis showed that the mineral had a *B*-centered orthorhombic cell with $a = 9.08$, $b = 4.78$ and $c = 5.23$ Å, consistent with the cell reported for kassite by Kukharenko et al. (1965), except for a halving of the *b* parameter, but in disagreement with the cell assignment reported by Evans et al. (1986). Self and Buseck (1991) concluded that Kukharenko et al. (1965) probably did not intermix their samples and they proposed that kassite and cafetite should be distinguished by their different crystallographic properties rather than by the iron content. Self and Buseck (1991) obtained a good calculated match to the intensity distribution in the powder XRD pattern of a synthetic sample of kassite, with a model based on the trigonal $PbSb_2O_6$ structure (Magneli 1941; Hill 1987). They noted that the kassite structure is closely related to that of lucasite-(Ce), $CeTi_2O_5(OH)$ (Nickel et al. 1987).

The kassite/cafetite controversy has been largely resolved by the recent work of Krivovichev et al. (2003) on the characterization of a cafetite holotype specimen supplied originally

---

* E-mail: ian.grey@csiro.au

0003-004X/03/0809–1331$05.00

by A.A. Kukharenko to the Mineralogical Museum, St. Petersburg State University. The orthorhombic cell parameters matched those reported by Kukharenko et al. (1959) but electron microprobe analyses on large crystals gave a Ca:Ti atomic ration of 1:2, and an iron analysis of only 0.3 wt%, expressed as FeO. From the low analysis total it was estimated that the cafetite sample had the same water content as kassite, making the compositions almost identical for the two minerals. However, a single crystal structure determination showed that cafetite contains molecular water, bonded only to Ca, giving the formula $CaTi_2O_5(H_2O)$, whereas the water in kassite is incorporated structurally, as hydroxyl ions.

I.V. Pekov and I.M. Kulikova conducted microprobe analyses on holotype specimens of both cafetite and kassite from Afrikanda deposited in the Mineralogical Museum of St. Petersburg State University (Pekov 1998) and concluded, as did Krivovichev et al. (2003), that the analyses for cafetite reported by Kukharenko et al. (1959) were probably made on a specimen that contained fine-scale admixtures of iron oxide minerals. The major remaining aspect of these two minerals to be clarified is the detailed structure of kassite. Self and Buseck's (1991) Rietveld powder XRD refinement was done using a synthetic sample and the slight distortion of the unit cell from hexagonal geometry could not be resolved, thus preventing them from elucidating the structure details.

Kassite was found recently at the Saranovskoye chromite deposit, Perm' district, Northern Urals, Russia, and was described by Popova et al. (1998). At this locality, it is present as a chromian variety (~2 wt% Cr_2O_3). Its chemical composition was given as: Na_2O 0.09, MgO 0.57, CaO 20.85, FeO 0.01, Al_2O_3 0.80, Cr_2O_3 2.34, SiO_2 0.16, TiO_2 60.34, Cl 0.21, –O = Cl_2 0.05, total 85.32 wt% (Popova et al. 1998), which corresponds to the formula $(Ca_{0.93}Mg_{0.04}Na_{0.01})_{\Sigma 0.98}(Ti_{1.90}Cr_{0.10}Al_{0.04}Si_{0.01})_{\Sigma 2.05}O_4(OH)_{2.00}Cl_{0.01}\cdot 1.03H_2O$. We obtained a sample of kassite from Saranovskoye from A.A. Kanonerov, re-studied its chemical composition, and isolated a small single crystal for a structure determination. The crystallographic study showed that chromian kassite has the same unit-cell parameters as reported by Kukharenko et al. (1965), but that the symmetry is monoclinic rather than orthorhombic. We report here the structure determination and refinement for chromian kassite.

OCCURRENCE AND CHEMICAL COMPOSITION

The Saranovskoye (Biserskoye) chromium deposit is situated within the Saranovsky layered gabbro-ultrabasic massif. Rich chromite ore bodies are localized in dunite intrusions. The Saranovskoye deposit is well-known because of numerous remarkable findings of hydrothermal chromian minerals occurring in fractures cross-cutting massive chromite ore. It is the type locality for uvarovite and shuiskite and is famous for its occurrences of large crystals of Cr-bearing varieties of some minerals including deep-green gem titanite and vesuvianite, color-changing amesite, clinochlore, and diaspore.

Chromian kassite was found on the walls of fractures in the chromite body. It forms tabular and platy crystals and rosette-like aggregates. It has a bright green color, which is unusual for kassite from other known localities but typical for Cr^{3+}-bearing varieties of many minerals. Chromian kassite is transparent and its luster is diamantine. It is associated with pink Cr-bearing clinochlore, deep-green Cr-bearing titanite (~1.2 wt% Cr_2O_3), orange anatase, and colorless calcite. Kassite mainly occurs on titanite without clear signs of replacement.

Wavelength-dispersive electron-microprobe analyses of the chromian kassite sample were conducted using a Camebax SX 50 instrument with an operating voltage of 15 kV and an estimated beam current of 30 nA. The standards used were diopside (Ca, Mg), albite (Al), andradite (Fe), $MnTiO_3$ (Mn, Ti), chromite (Cr), and vanadinite (V). The average of eight point analyses gave the following values: MgO 0.52, CaO 22.94, MnO 0.08, Al_2O_3 0.50, V_2O_3 0.25, Cr_2O_3 2.24, Fe_2O_3 0.37, TiO_2 64.18, total 91.08 wt%. The corresponding formula is $Ca_{0.97}(Ti_{1.91}Cr_{0.07}Mg_{0.03}Al_{0.02}Fe_{0.01}V_{0.01})_{\Sigma 2.05}O_{3.97}(OH)_{2.03}\cdot 0.16H_2O$ (H_2O content was calculated by difference). The Na, Si, and Cl noted by Popova et al. (1998) and also K, Sr, Zn, Zr, Nb, and F were not found in our sample. The analysis sum is significantly higher than reported for kassite from Saranovskoye by Popova et al. (1998) and closer to the ideal value: CaO 23.98, TiO_2 68.32, H_2O 7.70, total 100.00 wt% for $CaTi_2O_4(OH)_2$.

CRYSTALLOGRAPHY AND CRYSTAL STRUCTURE

A grain of the chromian kassite was crushed and the fragments were examined in a microscope under polarized light. We found that sharply extinguishing "single crystals" only occurred as small, very thin flakes, typically 0.01 to 0.02 mm thick. A suitably small fragment was studied using a precession camera. The approximately orthogonal lattice and cell dimensions reported by Kukharenko et al. (1965) were confirmed as $a \sim 5.25$, $b \sim 9.0$ ($\sim\sqrt{3}a$), and $c \sim 9.5$ Å (after permutation of axes, *cab*). Reciprocal lattice zones perpendicular to **c** displayed strong pseudo-trigonal character. The precession patterns showed mirror symmetry perpendicular to **b** only, indicating that the symmetry was monoclinic, rather than orthorhombic as reported by Kukharenko et al. (1965). However, the departure of the monoclinic angle from 90° was too small to be reliably measured from the precession photos. The diffraction patterns displayed a strong subset of reflections consistent with $I2/a$ extinctions, as in lucasite-(Ce) (Nickel et al. 1987), together with much weaker reflections that suggested a primitive cell.

Inspection of larger crystals, including those which extinguished cleanly in polarized light, showed that twinning was common, by twofold rotation about the pseudo-trigonal axes. Because of the near orthogonality of the unit cell and the high symmetry of the strong reflections, the twinning was only evident in the distribution of the weak P cell reflections in $(h\ k\ n)$ upper level zones with n odd. A crystal suitable for data collection that was free of such twinning was selected for structure analysis.

DATA COLLECTION AND STRUCTURE ANALYSIS

Single-crystal intensity data were collected using a Nonius Kappa diffractometer employing a CCD area detector. The data collection was made at 293 K and included a phi scan (180° in 1° steps) and a set of omega scans. Long counting times of 180 sec per frame were employed because of the very small crystal size. The crystal-to-detector distance was 25 mm. The data were corrected numerically for absorption using the Nonius software and converted to F^2, which were used with SHELXL (Sheldrick 1993) for the structure solution and refinement. The data collection and processing details are summarized in Table 1.

The structure determination strategy was to first obtain a fit to the $I2/a$ subset of strong reflections, using the lucasite $I2/a$ structure (Nickel et al. 1987) as a model, and then to analyze the refined parameters in the average structure to obtain information on the perturbations giving rise to the much weaker P cell reflections.

Averaging of the intensity data set in $I2/a$ gave 551 unique reflections with $R_{\text{merg}} = 0.06$, of which 444 reflections had $F > 4\sigma_F$. The coordinates for lucasite-(Ce) (Nickel et al. 1987) were used to commence the refinement, which readily converged using isotropic displacement parameters to $R1 = 0.09$. Refinement with anisotropic displacement parameters then gave convergence at $R1 = 0.056$ for the 444 observed reflections. The refined coordinates are given in Table 2, where they are compared with the ideal coordinates based on perfect hexagonal closest packing of the anions, and with the coordinates for lucasite-(Ce) (Nickel et al. 1987). The average model comprises (001) layers of gibbsite-like fused hexagonal rings of edge-shared octahedra with the larger cations sandwiched between pairs of opposing rings. The refinement gave Ca-O bond lengths in the range 2.31 to 2.41 Å (<Ca-O> = 2.37 Å), and Ti-O bond lengths in the range 1.91 to 2.05 Å (<Ti-O> = 1.97 Å). Both the bond length ranges and the average values are typical for six-coordinated Ca and Ti, for example in cafetite (Krivovichev et al. 2003). This eliminates the possibility of mixed Ca/Ti occupancy of the octahedral rings as a cause of the primitive symmetry.

TABLE 1. Crystallographic data for chromian kassite

$Ca(Ti,Cr)_2O_4(OH)_2$	$a = 5.275(1)$, $b = 9.009(2)$,
Monoclinic, $P2_1/a$	$c = 9.557(2)$ Å, $\beta = 90.43(1)°$, $z = 4$
Platelet, 0.075 × 0.045 × 0.015 mm	$D_{\text{calc}} = 3.38$ g/cm^3, $\mu = 4.59$ mm^{-1}
Nonius Kappa CCD diffractometer	ϕ and ω scans, $2\theta_{\max} = 56°$
Mo$K\alpha$ radiation, $T = 293$ K	$h = -7 \rightarrow 6$, $k = -11 \rightarrow 12$, $l = -11 \rightarrow 11$
Absorption correction	3648 independent reflections
Numerical, face indexed	1093 unique reflections
$T_{\min} = 0.79$, $T_{\max} = 0.91$, $R_{\text{int}} = 0.074$	714 with $F > 4\sigma_F$
Refinement of F^2, 83 parameters	$R1 = 0.06$ for $F > 4\sigma_F$
$Dr_{\max} = 0.94$ eÅ^{-3}	$R1 = 0.10$ for all data, $S = 0.98$

TABLE 2. Average structure parameters from refinement in $I2/a$, compared with ideal coordinates (hexagonal close packing) and those for lucasite

Atom	x	y	z	U_{eq}, Å^2
Ideal hcp				
Ca	1/4	1/4	0	
Ti	1/4	11/12	1/4	
O1	5/8	1/4	1/8	
O2	3/8	1/12	3/8	
O3	1/8	1/12	1/8	
Refined				
Ca	1/4	0.2317(2)	0	0.021(1)
Ti	0.2523(2)	0.9206(1)	0.2501(1)	0.024(1)
O1	0.6324(8)	0.2476(4)	0.1334(4)	0.019(1)
O2	0.4365(8)	0.0652(5)	0.3726(4)	0.020(1)
O3	0.0591(8)	0.0624(5)	0.1471(4)	0.021(1)
lucasite*				
Ce	1/4	0.1894(1)	0	0.013(1)
Ti	0.2187(3)	0.9154(2)	0.2651(2)	0.013(1)
O1	0.6007(13)	0.2541(8)	0.1411(7)	0.014(3)
O2	0.4083(13)	0.0799(8)	0.3692(8)	0.016(3)
O3	0.9976(13)	0.0450(8)	0.1402(7)	0.014(3)

* From Nickel et al. (1987).

A feature of the average structure refinement in $I2/a$ was high anisotropic displacement parameters ($U_{\text{ij}} \sim 0.02$–0.03 Å^2) for all atoms. This suggested that the weak P reflections are due to displacement rather than compositional modulations of the $I2/a$ structure. The largest anisotropic displacement parameters were along [010] for Ti and Ca. The magnitudes and directions of the principal mean square displacements for Ti and Ca were used to establish starting models for refinement of the full reflection data. To avoid any bias, the models were constructed in $P1$. Models with all possible combinations of the major displacements, e.g., $+\Delta y$ and $-\Delta y$ for each Ti atom were tested, accepting or discarding individual displacements based on the R factor calculated with only the scale refined.

An inspection of the model comprising the combination of displaced Ca and Ti atoms that gave the best fit to the intensity data showed that the displacements conformed to the symmetry of space group $P2_1/a$. This was confirmed by using ADDSYMM in Platon (Speck 2001). The model was then fully refined in $P2_1/a$, resulting in convergence at $R1 = 0.06$ for 714 reflections with $F > 4\sigma(F)$. $R1$ was 0.10 for all 1093 reflections. The refined atomic coordinates and displacement parameters are reported in Table 3.

DESCRIPTION OF STRUCTURE

As suggested by Self and Buseck (1991), the kassite structure is closely related to the trigonal ($P\overline{3}1m$) structure of $PbSb_2O_6$ (Magneli 1941; Hill 1987). This is a common structure type for oxides, hydroxides, and fluorides with general composition AM_2X_6 (DeBoer et al. 1994). It is based on a distorted hexagonal closest packing of anions, with alternate (001) layers of octahedral interstices that are two thirds occupied by M atoms and one-third occupied by A atoms respectively. The MX_6 octahedra share edges in a honeycomb arrangement as in gibbsite or corundum, giving a layer composition $[M_2X_6]^{n-}$. The A atoms sit above and below the empty octahedral sites in the M_2X_6 layers, resulting in the AO_6 octahedra corner-sharing with three MX_6 octahedra from the hexagonal rings on either side. The $[Ti_2O_4(OH)_2]^{2-}$ layers and the location of the Ca atoms in chromian kassite is illustrated in Figure 1.

Chromian kassite has a small monoclinic distortion of the ideal trigonal $PbSb_2O_6$ structure, together with a doubling of the **c** parameter. These cell modifications result from displacements of the Ca atoms along [010] from their ideal positions in the centers of the double hexagonal rings of octahedra. These

TABLE 3. Structure parameters from refinement in $P2_1/a$

Atom	x	y	z	* U_{eq}, Å^2
Ca	0.0063(3)	0.4821(2)	0.2505(2)	0.0244(5)
Ti1	0.0056(3)	0.1605(1)	0.4927(1)	0.0229(5)
Ti2	0.0010(3)	0.1815(2)	0.9920(1)	0.0239(5)
O1	0.380(1)	0.4973(6)	0.3866(6)	0.023(1)
O1a	0.885(1)	0.9971(6)	0.8784(6)	0.024(1)
O2	0.683(1)	0.8167(6)	0.1211(6)	0.023(1)
O2a	0.189(1)	0.3144(7)	0.6238(6)	0.024(1)
O3	0.807(1)	0.3105(6)	0.3955(6)	0.026(1)
O3a	0.310(1)	0.8144(6)	0.8994(6)	0.024(1)

* Anisotropic displacement parameters are available from the authors.

displacements can be described in space group *I*2/*a*, and are analogous to those which occur for Ce in lucasite-(Ce). In the structure of the latter mineral, illustrated in Figure 2, the Ce atoms undergo large displacements of 0.53 Å along [010] to form bonds to two additional O atoms, giving bisdisphenoid coordination (Nickel et al. 1987). In chromian kassite the displacement of Ca along [010] is much smaller, 0.16 Å, and the Ca remains octahedrally coordinated, as shown by the bond distances in Table 4.

The anions layers in chromian kassite are considerably distorted relative to ideal hexagonal closest packing. The opposing triangular faces of the TiO_6 octahedra are rotated relative to one another by ~13° relative to the fully staggered configuration. This is a direct result of repulsions of the high-valency Ti atoms across the shared octahedral edges. The rotation of the triangular faces brings about increased shielding of the Ti atoms by a shortening of the shared octahedral edges (DeBoer et al. 1994). In the structurally related compound Li_2ZrF_6 (Brunton 1973), in which low valence Li^+ ions are ordered in the hexagonal rings, the Li-Li repulsions are weak and the anion layers are close to ideal hexagonal closest packing. A comparison of Figures 1 and 2 shows that the anion layers are considerably more distorted in lucasite than in chromian kassite. This is particularly evident from the shape of the projected empty sites in the honeycomb layers, which are in the form of regular hexagons in kassite but which are strongly deformed hexagons in lucasite. The extra distortion in lucasite is in the form of tilting of octahedra about the shared edges to accommodate the bonding requirements of the eight-coordinated Ce atoms.

TABLE 4. Selected bond lengths (Å) for chromian kassite

Ti1-O1	1.865(6)	Ca-O3a	2.302(6)
Ti1-O3	1.865(6)	Ca-O3	2.331(6)
Ti1-O3	1.943(6)	Ca-O1	2.358(6)
Ti1-O1	1.960(6)	Ca-O2	2.388(6)
Ti1-O2a	2.100(6)	Ca-O1a	2.402(6)
Ti1-O2a	2.108(6)	Ca-O2a	2.425(6)
Ti2-O3a	1.869(6)	Ca-Ti2	3.665(2)
Ti2-O2	1.892(6)	Ca-Ti1	3.707(2)
Ti2-O3a	1.947(6)	Ti1-Ti1	2.894(3)
Ti2-O2	1.992(6)	Ti1-Ti1	3.092(2)
Ti2-O1a	2.073(6)	Ti2-Ti2	2.912(1)
Ti2-O1a	2.115(6)	Ti2-Ti2	3.273(3)

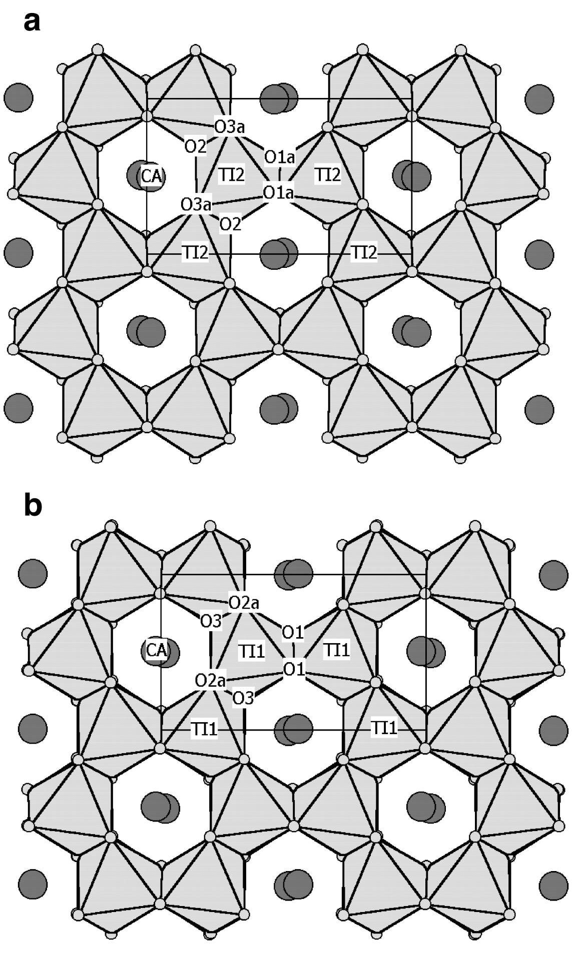

FIGURE 1. Polyhedral $[Ti_2O_4(OH)_2]^{2-}$ layers in chromian kassite. Ca atoms are shown as filled circles. (**a**) layer centered at *z* ~ 0, (**b**) layer centered at *z* ~ 0.5. Unit cell outline shown with **b** horizontal.

Chromian kassite differs from lucasite in a lowering of the symmetry from *I*2/*a* to the subgroup $P2_1/a$, which gives rise to extra weak reflections in the diffraction patterns. The lower symmetry in kassite is considered to arise from an ordering of H atoms. Although the quality of the diffraction data from the very tiny crystal was not adequate to resolve the positions of the H atoms, their location can be determined from bond valence calculations. The bond valence parameters of Brese and O'Keeffe (1991) were used to calculate the valence sums at each of the atom sites in both the average *I*2/*a* and the complete $P2_1/a$ structures. The results are given in Table 5. In the average *I*2/*a* structure, the valence sums indicate that O3 is an O atom site and that the H atom is statistically distributed over the O1 and O2 sites. In $P2_1/a$, O1 and O2 each split into two independent anion sites, labeled O1, O1a and O2, O2a. The valence sum calculations show clearly that one of each of the sites, O1 and O2, contains O atoms while the other pair, O1a

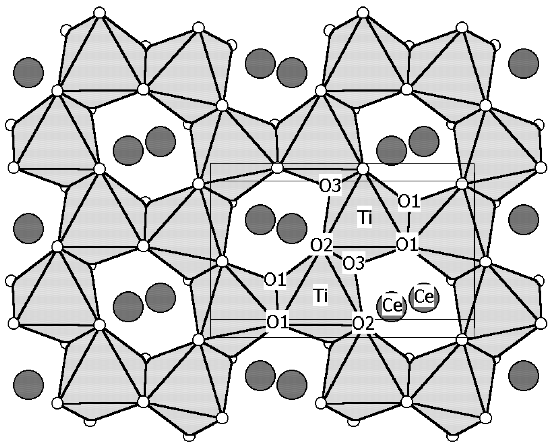

FIGURE 2. Polyhedral $[Ti_2O_5(OH)]^{3-}$ layer in lucasite-(Ce). Ce atoms are shown as filled circles.

TABLE 5. Valence sums for chromian kassite from average structure ($I2/a$) and complete structure ($P2_1/a$) refinements

Atom	$I2/a$ average Valence sum	$P2_1/a$ complete Valence sum
Ca	2.04	2.05
Ti1	3.92	4.09
Ti2		3.88
O1	1.54	1.93
O1a		1.23
O2	1.44	1.74
O2a		1.21
O3	1.96	1.96
O3a		1.94

and O2a, contain hydroxyl ions. The displacements of the Ti and Ca atoms needed to satisfy the local valence requirements of the ordered O and OH anions break the *I*-centering and give rise to the weak *P* cell reflections.

The results from this study on the refinement of the structure for chromian kassite, together with the recent full refinement of the cafetite structure (Krivovichev et al. 2003), support the original crystallographic descriptions given by Kukharenko et al (1959, 1965). The proposal by Evans et al. (1986) to interchange the crystallographic assignments, and the resulting changes to the ICDD powder diffraction database should be reversed. Pekov (1998) and Krivovichev et al. (2002) suggest that the problems most likely arose from the analysis of an impure cafetite sample being reported by Kukharenko et al. (1959). In fact cafetite and kassite have the same chemical analysis, ideally $CaTi_2O_5(H_2O)$, but the water is incorporated as molecular water in cafetite, $CaTi_2O_5(H_2O)$, and as hydroxyl ions in kassite, $CaTi_2O_4(OH)_2$. Our study shows that, at least for chromian kassite, the protons are structurally ordered.

ACKNOWLEDGMENTS

We are grateful to A.A. Kanonerov for providing a sample of chromian kassite from the Saranovskoye deposit. We thank G. Fallon for collecting the CCD intensity data set and L. Cranswick for applying Platon to check for missing symmetry. Thanks to G. Sparrow for reviewing the manuscript. This work was supported in part by the Russian Scientific Foundation (grants 03-05-64054) and by the Russian Universities Program.

REFERENCES CITED

Brese, N.E. and O'Keeffe, M. (1991) Bond-valence parameters for solids. Acta Crystallographica, B47, 192–197.

Brunton, G. (1973) Li_2ZrF_6. Acta Crystallographica, B29, 2294.

Burton, J.H. (1982) An extraordinary specimen derived from the earth's mantle. M.Sc. thesis, Cornell University, Ithaca, New York.

DeBoer, B.G., Young, R.A., and Sakthivel, A. (1994) X-ray Rietveld structure refinement of Ca, Sr and Ba meta-antimonates. Acta Crystallographica, C50, 476–482.

Evans, H.T.E. Jr., Dwornik, E.J., and Milton, C. (1986) Kassite from the Diamond Jo quarry, Magnet Cove, Hot Spring County, Arkansas: the problem of cafetite and kassite. American Mineralogist, 71, 1045–1048.

Hill, R.J. (1987) Structure of $PbSb_2O_6$ and its relationship to the crystal chemistry of PbO_2 in antimonial lead-acid batteries. Journal of Solid State Chemistry, 71, 12–18.

Krivovichev, S.V., Yakovenchuk, V.N., Burns, P.C., Pakhomovsky, Y.A., and Menshikov, Y.P. (2003) Cafetite, $Ca[Ti_2O_5](H_2O)$: crystal structure and revision of chemical formula. American Mineralogist, 88, 424–429.

Kukharenko, A.A., Kondratyeva, V.V., and Kovyazina, V.M. (1959) Cafetite, a new hydrous titanate of calcium and iron. Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva, 88, 444–453.

Kukharenko, A.A., Orlova, M.P., Bulakh, A.G., Bagdasarov, E.A., Rimskaya-Korsakova, O.M., Nefedov, Ye.I., Ilinskiy, G.A., Sergeyev, A.S., and Abakumova, N.B. (1965) The Caledonian complex of ultrabasic alkalic rocks and carbonatites of the Kola peninsula and northern Karelia. Nedra, Moscow, 368–375.

Magneli, A. (1941) The crystal structure of $PbSb_2O_6$ and isomorphous compounds. Arkiv foer Kemi Mineralogi och Geologi, 15B, 3, 1–6.

Nickel, E.H., Grey, I.E., and Madsen, I.C. (1987) Lucasite-(Ce), $CeTi_2(O,OH)_6$, a new mineral from the Western Australia: its description and structure. American Mineralogist, 72, 1006–1010.

Pekov, I.V. (1998) Minerals First Discovered on the Territory of the Former Soviet Union. OP, Moscow, 369 pp.

Popova, V.I., Popov, V.A., and Kanonerov, A.A. (1998) Chromium-bearing kassite, $CaTi_2O_4(OH)_2$, from the Saranovskoye deposit—a first finding on the Urals. Miass, 2, 75–77.

Rudashevsky, L.S., Firfarova, I.B., and Tsekhovolskaya, D.I. (1977) Synthetic analogue and refinement of properties of kassite and hydrokassite. Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva, 106, 114–120.

Self, P.G. and Buseck, P.R. (1991) Structure model for kassite, $Ca_2Ti_2O_4(OH)_2$. American Mineralogist, 76, 283–287.

Sheldrick, G.M. (1993) SHELX93, A Program for the Refinement of Crystal Structures. University of Gottingen, Germany.

Speck, A.L. (2001) PLATON, A Multipurpose Crystallographic Tool. Utrecht University, Utrecht, The Netherlands.

MANUSCRIPT RECEIVED OCTOBER 27, 2002
MANUSCRIPT ACCEPTED MARCH 24, 2003
MANUSCRIPT HANDLED BY PETER BURNS