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REFINEMENT OF THE CRYSTAL STRUCTURE OF TADZHIKITE

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ABSTRACT

The crystal structure of tadzhikite, monoclinic, *a* 19.058(4), *b* 4.729(1), *c* 10.321(2) Å, ß 111.39(1)°, *V* 866.1(3) Å^3, Z = 2, space group *P*2/*a*, has been refined to an *R* index of 4.9% for 1702 observed reflections measured with Mo*K*α X-radiation. The crystal used to collect the X-ray-diffraction data was subsequently analyzed with an electron microprobe. Tadzhikite is isostructural with hellandite, but shows strong positional disorder of the *REE* cations that is presumably related to partial metamictization. Bond-valence analysis shows that the structure contains essential H as OH, and site populations were assigned on the basis of the refined site-scattering values and the results of electron-microprobe analysis. The general formula of tadzhikite can be written as $Ca_2(Ca,Y)_2(Ti^{4+},Fe^{3+})(R^{3+},\square)_2[B_4Si_4O_{16}(O,OH)_6](OH)_2$.

Keywords: tadzhikite, crystal-structure refinement, electron-microprobe analysis, hellandite, metamictization.

SOMMAIRE

Nous avons affiné la structure cristalline de la tadzhikite [monoclinique, *a* 19.058(4), *b* 4.729(1), *c* 10.321(2) Å, ß 111.39(1)°, *V* 866.1(3) Å^3, Z = 2, groupe spatial *P*2/*a*] jusqu'à un résidu *R* de 4.9% en utilisant 1702 réflexions observées mesurées avec rayonnement Mo*K*α. Le cristal qui a servi a ensuite été analysé avec une microsonde électronique. La tadzhikite est isostructurale avec la hellandite, mais elle fait preuve d'un désordre de position important impliquant les atomes de terres rares, que nous attribuons à une métamictisation partielle. Une analyse des valences de liaison montre que le minéral possède des atomes de H sous forme de groupes OH. Les atomes ont été répartis selon la dispersion affinée des rayons X associée aux divers sites et les résultats des analyses chimiques. On peut exprimer ainsi la formule générale de la tadzhikite: $Ca_2(Ca,Y)_2(Ti^{4+},Fe^{3+})(R^{3+},\square)_2[B_4Si_4O_{16}(O,OH)_6](OH)_2$.

(Traduit par la Rédaction)

Mots-clés: tadzhikite, affinement de la structure cristalline, données de microsonde électronique, hellandite, métamictisation.

INTRODUCTION

Tadzhikite is a borosilicate mineral first described by Efimov *et al.* (1970), who proposed that it is structurally related to hellandite. Mellini & Merlino (1977) solved the crystal structure of hellandite, assigned it the formula $[Ca_{5.5}(Y,REE)_{5.0}\square_{1.5}](Al,Fe^{3+})_2(OH)_4[Si_8B_8O_{40}(OH)_4]$, and suggested the formula $Ca_7(Y,REE)_5(Al,Ti)_2(OH)_4[Si_8B_8O_{44}]$ or $Ca_7(Y,REE)_5(Al,Ti)_2O_2[Si_8B_8O_{44}]$ for tadzhikite, noting that Efimov *et al.* (1970) reported tadzhikite as anhydrous. Tadzhikite is partly metamict owing to α-decay damage from small amounts of U in the structure. Chernitsova *et al.* (1983) heated tadzhikite to 700°C and then refined the crystal structure, subsequently assigning the formula $Ca_{6.36}(Y,REE)_{4.40}(Ti,Fe^{3+},Al)_{2.22}B_{8.08}(Si,Al)_8O_{44}$. This formula is anhydrous, but has a number of anions different from that in the anhydrous formula suggested by Mellini & Merlino (1977). It is not clear if this difference relates to the difficulty in dealing with such a chemically complicated mineral as tadzhikite, or if the difference relates to the fact that tadzhikite was heated prior to the X-ray investigation of Chernitsova *et al.* (1983). In a synthesis of the crystal chemistry of B-bearing minerals, Hawthorne *et al.* (1996) drew attention to this problem, and the current work on crystals from Dara-i-Pioz, Tadzhikistan, was done in order to resolve this issue.

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EXPERIMENTAL

Tadzhikite crystals examined vary in translucence; we assumed that this variation is due to the effect of metamictization, and selected the clearest crystal for collection of X-ray intensity data. The crystal was mounted on a Nicolet *R*3*m* (updated to Siemens *P*$\bar{4}$) automated four-circle diffractometer; twenty-nine reflections were aligned using Mo*K*α X-radiation. The cell dimensions were determined by least-squares refinement of the setting angles, and the values are given in Table 1. A total of 5237 intensities was collected over two asymmetric units with the index ranges $-25 \leq h \leq 24$, $0 \leq k \leq 6$, $0 \leq l \leq 14$ according to the procedures of Hawthorne & Groat (1985). A psi-scan absorption correction reduced *R*(azimuthal) from 9.4 to 4.4%, with the crystal modeled as a triaxial ellipsoid; application of this absorption correction to the intensity data, averaging into one asymmetric unit, and making the usual geometrical corrections, resulted in 2548 unique reflections, of which 1702 were considered as observed (greater than 5σ above background).

TABLE 1. TADZHIKITE: CRYSTAL DATA AND REFINEMENT INFORMATION

a (Å)	19.058(4)	Crystal size (mm)	0.13 x 0.21 x 0.31
b	4.729(1)	Radiation	Mo*K*α
c	10.321(2)	Total unique $\lvert F_o \rvert$	2548
β (°)	111.39(1)	No. $\lvert F_o \rvert > 5\sigma$	1702
V (Å^3)	861.1(3)	*R*(obs) %	4.9
Sp. Gr.	*P*2/*a*	*wR*(obs) %	5.7

Unit cell contents: $2[Ca_2(Ca,Y)_2(Ti^{4+},Fe^{3+})(R^{3+},\square)_2[B_4Si_4O_{18}(O,OH)_6](OH)_2]$
$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$
$wR = [\Sigma w(|F_o|-|F_c|)^2/\Sigma F_o^2]^{½}$, $w = 1$

All calculations were done with the SHELXTL PC(PLUS) system of programs; *R* indices are of the form given in Table 1. Using the atomic parameters of Chernitsova *et al.* (1983), the structure of tadzhikite was refined to an *R* index of 4.9%. All atoms were represented with anisotropic displacements except for the *REE*-sites (designated as *RE*-sites). The atoms at these sites show strong positional disorder, with site separations in the range 0.48–0.98 Å. As it was necessary to refine both positional and site-scattering parameters for these very close sites, it was necessary to use isotropic displacements and to constrain the isotropic displacements at all *RE*-sites to be identical; only in this way could variable correlation be damped sufficiently to obtain a stable refinement. Final positions and displacement parameters are listed in Table 2, selected interatomic distances are given in Table 3, and refined site-scattering values are given in Table 4; structure factors may be obtained from The Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

Subsequent to the collection of the X-ray intensity data, the crystal was analyzed by electron microprobe. A Cameca SX–50 instrument was operated in wavelength-dispersion mode at 15 or 20 kV and 20 nA using the following standards: albite (Na), diopside (Ca, Si), titanite (Ti), fayalite (Fe), YAG (Y), UO_2 (U), ThO_2 (Th), forsterite (Mg), riebeckite (F), spessartine (Mn), Sc metal (Sc), $SrTiO_3$ (Sr), kyanite (Al), zircon

TABLE 2. ATOMIC POSITIONS AND DISPLACEMENT FACTORS* FOR TADZHIKITE

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Si(1)	0.1025(2)	0.4847(8)	0.6480(3)	19(1)	28(2)	13(1)	0(1)	6(1)	0(1)	20(1)
Si(2)	0.3870(2)	0.4963(8)	0.8365(3)	19(2)	27(2)	12(1)	0(1)	6(1)	1(1)	20(1)
Ti	0	0	0	19(1)	30(2)	14(1)	–3(1)	2(1)	1(1)	22(1)
B(1)	0.1724(6)	0.5238(28)	0.4515(9)	15(4)	27(6)	9(4)	1(4)	4(3)	2(5)	17(3)
B(2)	0.2465(6)	0.4582(25)	0.8650(10)	17(5)	22(5)	8(4)	4(4)	5(3)	1(4)	15(3)
Ca(1)	0.2521(1)	0.0011(5)	0.3402(2)	22(1)	29(1)	11(1)	1(1)	7(1)	0(1)	21(1)
Ca(2)	0.3443(1)	0.9615(4)	0.0703(1)	17(1)	30(1)	13(1)	–1(1)	7(1)	0(1)	20(1)
RE(1)	0.0385(9)	0.0147(16)	0.3593(5)	–	–	–	–	–	–	11(1)
RE(2)	–0.0475(7)	0.0809(45)	0.6369(10)	–	–	–	–	–	–	11(1)
RE(3)	0.0371(8)	0.1225(52)	0.3585(12)	–	–	–	–	–	–	11(1)
RE(4)	0.0474(11)	0.0230(16)	0.3628(5)	–	–	–	–	–	–	11(1)
O(1)	0.4567(5)	0.2525(9)	0.4341(8)	30(4)	32(4)	16(3)	2(3)	9(3)	5(4)	26(3)
O(2)	0.3226(5)	0.3155(19)	0.2430(8)	24(4)	34(5)	20(4)	2(3)	6(3)	0(4)	27(3)
O(3)	0.0719(4)	0.7002(19)	0.7329(8)	29(4)	36(5)	20(4)	–1(3)	5(3)	10(4)	30(3)
O(4)	0.1329(5)	0.6660(18)	0.5416(8)	29(4)	32(4)	21(4)	2(3)	13(3)	–1(4)	26(3)
O(5)	0.4619(5)	0.1964(20)	0.1308(8)	32(4)	43(5)	19(4)	3(4)	11(3)	7(4)	31(3)
O(6)	0.2537(5)	0.7545(19)	0.1398(8)	29(4)	36(5)	19(4)	2(3)	11(3)	2(4)	27(3)
O(7)	0.1673(5)	0.2288(19)	0.4473(8)	22(4)	37(5)	17(3)	0(3)	6(3)	–4(4)	26(3)
O(8)	0.1330(5)	0.6713(20)	0.3096(8)	36(5)	35(5)	14(3)	2(3)	4(3)	2(4)	30(3)
O(9)	0.3125(5)	0.3286(20)	0.8392(8)	25(4)	37(5)	28(4)	–5(4)	13(3)	–4(4)	29(3)
O(10)	0.0864(4)	0.7294(20)	0.0431(8)	22(4)	38(5)	20(4)	3(3)	7(3)	2(4)	27(3)
O(11)	0.0538(5)	0.2578(20)	0.1584(8)	28(4)	38(5)	18(3)	–1(3)	8(3)	–10(4)	28(3)
O(12)	1/4	0.3315(27)	0	37(7)	38(7)	10(4)	0	8(4)	0	29(4)
O(13)	1/4	0.6494(26)	1/2	25(6)	32(6)	24(5)	0	10(4)	0	27(4)

* *U* is multiplied by 10^3

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) IN TADZHIKITE

Si(1)–O(1)a		1.581(9)	*B*(1)–O(4)	1.547(16)
Si(1)–O(2)a		1.666(8)	*B*(1)–O(7)	1.398(16)
Si(1)–O(3)		1.587(10)	*B*(1)–O(8)	1.547(12)
Si(1)–O(4)		1.656(10)	*B*(1)–O(13)	1.501(12)
<*Si*(1)–O>		1.623	<*B*(1)–O>	1.498
Si(2)–O(8)a		1.639(9)	*B*(2)–O(2)	1.536(12)
Si(2)–O(9)		1.636(10)	*B*(2)–O(6)	1.402(15)
Si(2)–O(10)a		1.599(9)	*B*(2)–O(9)	1.508(16)
Si(2)–O(11)a		1.582(10)	*B*(2)–O(12)	1.496(12)
<*Si*(2)–O>		1.614	<*B*(2)–O>	1.486
Ca(1)–O(2)		2.450(10)	*Ca*(2)–O(2)e	2.586(9)
Ca(1)–O(4)b		2.618(8)	*Ca*(2)–O(3)a	2.416(8)
Ca(1)–O(6)c		2.384(9)	*Ca*(2)–O(5)e	2.372(9)
Ca(1)–O(7)		2.509(10)	*Ca*(2)–O(6)	2.314(10)
Ca(1)–O(7)a		2.423(7)	*Ca*(2)–O(6)f	2.489(7)
Ca(1)–O(8)c		2.677(10)	*Ca*(2)–O(9)g	2.831(9)
Ca(1)–O(9)a		2.384(8)	*Ca*(2)–O(10)f	2.333(10)
Ca(1)–O(13)d		2.353(8)	*Ca*(2)–O(12)f	2.422(9)
<*Ca*(1)–O>		2.475	<*Ca*(2)–O>	2.470
Ti–O(5)f	x2	1.982(10)	*RE*(1)–*RE*(2)h	0.48(2)
Ti–O(10)c	x2	2.004(9)	*RE*(1)–*RE*(3)	0.51(2)
Ti–O(11)	x2	1.997(8)	*RE*(1)–*RE*(4)	0.16(2)
<*Ti*–O>		1.994	*RE*(2)–*RE*(3)h	0.98(3)
			RE(2)–*RE*(4)h	0.49(2)
			RE(3)–*RE*(4)	0.51(3)
RE(1)–O(1)a		2.384(11)	*RE*(2)–O(1)a	2.260(18)
RE(1)–O(1)i		2.345(18)	*RE*(2)–O(1)i	2.646(18)
RE(1)–O(3)j		2.386(17)	*RE*(2)–O(3)c	2.785(19)
RE(1)–O(4)c		2.650(12)	*RE*(2)–O(4)j	2.300(16)
RE(1)–O(5)i		2.485(10)	*RE*(2)–O(5)a	2.419(13)
RE(1)–O(7)		2.499(18)	*RE*(2)–O(7)k	2.582(18)
RE(1)–O(8)c		2.609(18)	*RE*(2)–O(8)j	2.233(19)
RE(1)–O(11)		2.478(13)	*RE*(2)–O(11)i	2.688(18)
<*RE*(1)–O>		2.480	<*RE*(2)–O>	2.489
RE(3)–O(1)a		2.189(17)	*RE*(4)–O(1)a	2.388(13)
RE(3)–O(1)i		2.640(22)	*RE*(4)–O(1)i	2.480(20)
RE(3)–O(3)j		2.116(18)	*RE*(4)–O(3)j	2.494(18)
RE(3)–O(4)c		3.008(21)	*RE*(4)–O(4)c	2.592(12)
RE(3)–O(5)i		2.719(18)	*RE*(4)–O(5)i	2.572(11)
RE(3)–O(7)		2.365(17)	*RE*(4)–O(7)	2.340(19)
RE(3)–O(8)c		2.970(23)	*RE*(4)–O(8)c	2.525(19)
RE(3)–O(11)		2.292(18)	*RE*(4)–O(11)	2.425(13)
<*RE*(3)–O>		2.537	<*RE*(4)–O>	2.477

a: ½–x, y, 1–z; b: ½–x, y–1, 1–z; c: x, y–1, z; d: x, 1–y, z; e: x, 1+y, z; f: ½–x, y, –z; g: x, 1+y, z–1; h: –x, –y, 1–z; i: ½+x, –y, z; j: –x, 1–y, 1–z.

TABLE 4. REFINED SITE-SCATTERING VALUES (*epfu*) AND ASSIGNED SITE-POPULATIONS (*apfu*)* IN TADZHIKITE

	site scattering	site population	effective scattering
Ti	20.4(3)	0.56 Ti + 0.30 Fe + 0.07 Al + 0.04 Mn	21.9
RE(1)	41.7(8.6)	0.70 R^{3+}	41.7
RE(2)	7.0(4)	0.12 R^{3+}	7.0
RE(3)	5.8(4)	0.10 R^{3+}	5.8
RE(4)	38.0(8.6)	0.63 R^{3+}	38.0
Ca(1)	41.7(5)	1.96 Ca + 0.04 R^{3+}	41.6
Ca(2)	56.7(6)	0.90 Ca + 0.89 Y + 0.18 Na + 0.03 R^{3+}	56.5

* R^{3+} = rare-earth species (mean *Z* ~ 60 for tadzhikite)

TABLE 5. CHEMICAL COMPOSITION* AND UNIT FORMULA FOR TADZHIKITE

SiO_2	22.04	Si	4.000
TiO_2	4.13		
Al_2O_3	0.33	Ti^{4+}	0.564
Fe_2O_3	2.17	Fe^{3+}	0.296
Mn_2O_3	0.28	Al	0.071
CaO	14.68	Mn^{3+}	0.038
Na_2O	0.96	Σ	0.969
Ce_2O_3	10.22		
Y_2O_3	9.26	Ca	2.855
Sm_2O_3	1.21	Na	0.338
Pr_2O_3	1.42	Y	0.894
Nd_2O_3	5.20	Ce	0.679
La_2O_3	2.64	Nd	0.337
Gd_2O_3	1.42	La	0.177
Dy_2O_3	1.96	Dy	0.115
Er_2O_3	0.84	Pr	0.094
Yb_2O_3	0.28	Gd	0.085
Ho_2O_3	0.32	Sm	0.076
UO_2	0.68	Er	0.048
ThO_2	0.06	Ho	0.018
(B_2O_3)	12.77	Yb	0.015
Total	93.87	U	0.027
		Th	0.002
		Σ	5.760
		B	4

* Zr, Sc, Eu, Tm, Tb, Lu, Pb, Sr, Mg, F not detected

(Zr), PbTe (Pb), CeO_2 (Ce), *REE* glass 1 (Eu, Gd, Tm, Tb), *REE* glass 2 (Sm, Nd, Yb, Lu), *REE* glass 3 (Pr, La), and *REE* glass 4 (Dy, Er, Ho).

The chemical composition of tadzhikite is given in Table 5. It was normalized to Si = 8.0 *apfu* (atoms per formula unit), as the results of crystal-structure refinement indicate that the two *Si*-sites are occupied only by Si.

DISCUSSION

The results of the current work indicate that tadzhikite does have a hellandite-type structure, as suggested by Efimov *et al.* (1970) and Mellini & Merlino (1977) and as shown by Chernitsova *et al.* (1983). However, the current results do show very significant differences from the results of Chernitsova *et al.* (1983), particularly with regard to the distribution of *REE* in the structure. Chernitsova *et al.* (1983) showed a single *REE*-site in their refinement, whereas our refinement shows that the *REE*-site is positionally disordered into four distinct sites from 0.16 to 0.98 Å apart. However, prior to any detailed considerations of this disorder and its resulting chemical implications, it is necessary to assign site populations.

TABLE 6. BOND-VALENCE SUMS AT ANIONS COORDINATING A VACANCY AT THE *Ca*(1), *Ca*(2) AND *RE* SITES, RESPECTIVELY

	Ca(1)	*Ca*(2)	*RE*
O(1)	–	–	1.50(1.12)*
O(2)	1.73	1.79	–
O(3)	–	1.45	1.40
O(4)	1.76	–	1.71
O(5)	–	0.79	0.92
O(6)	1.57	–	–
O(7)	1.57	–	1.45
O(8)	1.83	–	1.74
O(9)	1.76	1.96	–
O(10)	–	1.61	–
O(11)	–	–	1.67
O(12)	–	1.73	–
O(13)	1.74	–	–

* value for locally associated pair of vacancies

Site populations

The <*B*–O> and <*Si*–O> distances indicate a well-ordered chain of tetrahedra with complete occupancy of the *B*- and *Si*-sites by B and Si, respectively. However, the other cation sites show evidence of disorder, and the refined site-scattering values (in *epfu*: electrons per formula unit) are given in Table 4. The <*Ti*–O> distance, 1.994 Å (Table 3), indicates that this site is occupied by small high-valence cations, and the sum of Ti^{4+} + Fe^{3+} + Al + Mn^{3+} is close to the ideal sum for this site (Table 5). The effective site scattering for this assignment matches the refined site-scattering (Table 4), and these cations were thus assigned.

There are three remaining cation sites if we temporarily ignore the positional disorder at the *RE* sites, *Ca*(1), *Ca*(2) and *RE*, and these constitute six sites in the structural formula. As there are only 5.76 cations to occupy these sites (Table 5), it is not possible to assign the site populations unambiguously owing to the presence of vacancies. Moreover, the mean bond-lengths at these three sites are all ~2.48 Å, and hence give no information as to relative occupancy. However, we may look at the bond-valence requirements of the anions coordinating the *Ca*(1), *Ca*(2) and *RE* sites to examine whether it is possible to locally compensate for a vacancy at that cation site. Table 6 shows the bond-valence sums at the coordinating anions for vacancies at *Ca*(1), *Ca*(2) and *RE*, respectively. For vacancies to occur at *Ca*(1) or *Ca*(2), there need to be symmetrical H-bonds, as none of the bond-valence sums in Table 6 under the *Ca*(1) or *Ca*(2) columns are less than 1.5 *vu* (valence units). Symmetrical H-bonds are very uncommon and considered to be energetically unfavorable. Hence, it seems more probable that the vacancies occur at the *RE* site.

The *Ca*(1) site-scattering (Table 5) indicates that it is almost completely occupied by Ca. The *Ca*(2) site-scattering indicates that *Ca*(2) must be occupied by Ca and a species of higher aggregate X-ray scattering power than Ca. If all the remaining Ca in the formula unit (2.86–1.96 = 0.90 *apfu*) is assigned to *Ca*(2), then the remaining occupancy must be dominated by Y ($Z = 39$) rather than by the *REE* ($Z \approx 60$) in order to

TABLE 7. BOND-VALENCE TABLE FOR TADZHIKITE

	Si(1)	*Si*(2)	*B*(1)	*B*(2)	*Ti*	*Ca*(1)	*Ca*(2)	Σ	*RE*(1)	*RE*(2)	*RE*(3)	*RE*(4)	Σ
O(1)	1.12							1.12	0.18 0.19	0.04 0.02	0.04 0.01	0.15 0.12	1.87
O(2)	0.89			0.64		0.26	0.20	1.99					1.99
O(3)	1.10						0.30	1.40	0.17	0.01	0.05	0.12	1.75
O(4)	0.91		0.62			0.18		1.71	0.09	0.04	0.01	0.09	1.94
O(5)					$0.59^{\times2}{\downarrow}$		0.33	0.92	0.13	0.03	0.01	0.09	1.12
O(6)				0.93		0.30	0.39 0.25	1.87					1.97
O(7)			0.94			0.23 0.28		1.45	0.13	0.02	0.03	0.17	1.80
O(8)		0.96	0.62			0.16		1.74	0.09	0.04	0.01	0.11	1.99
O(9)		0.96		0.69		0.30	0.11	2.06					2.06
O(10)		1.06			$0.55^{\times2}{\downarrow}$		0.37	1.98					1.98
O(11)		1.11			$0.56^{\times2}{\downarrow}$			1.67	0.13	0.01	0.03	0.14	1.98
O(12)				$0.72^{\times2}{\rightarrow}$			$0.29^{\times2}{\rightarrow}$	2.02					2.02
O(13)			$0.71^{\times2}{\rightarrow}$			$0.32^{\times2}{\rightarrow}$		2.06					2.06
Σ	4.02	4.09	2.89	2.98	3.40	2.03	2.24		1.11	0.21	0.19	0.99	
Σ*	(4)	(4)	(3)	(3)	(3.58)		(2.36)		(1.05)	(0.18)	(0.15)	(0.95)	

* aggregate charge at each cation site calculated from the assigned site-populations

TABLE 8. PROPOSED H-ATOMS AND H-BONDS LOCALLY ASSOCIATED WITH □ AT THE *RE*-SITES IN TADZHIKITE

	Σ*	*H*(1)	*H*(3)	*H*(7)	Σ
O(1)	1.12	0.80			1.92
O(3)	1.40		0.65		2.05
O(4)	1.71	0.20			1.91
O(7)	1.45			0.65	2.10
O(8)	1.74			0.35	2.09
O(11)	1.67		0.35		2.02

* sum from neighboring cations

achieve the refined value of the site scattering (Table 4). If all Y is assigned to *Ca*(2), then a small amount of Na and *REE* at this site completes the occupancy (Table 5). This leaves the *REE* (plus minor Na and U) to be assigned over the four *RE*-sites. The mean atomic number of the *REE* in tadzhikite is ~60, and the site populations of the four *RE*-sites was assigned directly from their refined site-scattering values using 60 as the effective site-scattering of the occupying *REE* species. Complete site-populations are given in Table 4.

Bond-valence summation

The bond-valence table, calculated from the parameters of Brown (1981), is shown as Table 7. For the *RE*-sites, the sums were calculated for the mean *REE* composition of the unit formula (Table 4) weighted according to the site populations of Table 4. The sums of the bond valence around the *RE*-sites are in good accord with the aggregate charge at these sites (see bottom line of Table 7).

Inspection of Table 7 immediately shows that O(5) is an OH-anion, and hence tadzhikite does contain essential H in contrast to the analytical results of Efimov *et al.* (1970). Table 7 is a long-range representation of the bond-valence arrangement in the crystal; it is the average of all the short-range bond-valence arrangements in the crystal. If we require that all the short-range bond-valence arrangements obey the valence-sum rule of Brown (1981), then we may derive information on the patterns of short-range order in the crystal (Hawthorne 1996, 1997). This approach is of particular relevance to tadzhikite as the *RE*-sites are not completely occupied (*i.e.*, Σ*REE* = 1.55 *apfu* ≠ 2.0 *apfu*, the number of *RE*-sites available. Thus some local configurations in tadzhikite must involve □ (vacancies) at the *RE*-site(s), and hence this local arrangement could also involve a different type of anion (*e.g.*, OH) than the local arrangement where *RE* is occupied by a *REE* cation. In Table 7, the first of the columns labeled Σ denotes the incident bond-valence around each anion without any contribution from cations at the *RE*-sites. Hence this column denotes the bond-valence sums around the anions when the *RE*-sites are all locally occupied by □ (*i.e.*, 0.45/2.00 = 22.5% of the site, or 0.45 □ *pfu*). The sum at the O(1)-site is 1.12 *vu* (Table 7), and hence O(1) is an OH group when locally associated with a □ at the adjacent *RE*-sites. The H of this OH-group, designated as H(1), can form a H-bond with O(4), [O(1)–O(4) = 3.00 Å], thus also satisfying the bond-valence requirement at the O(4)-site. Table 8 shows the proposed arrangement of H-atoms and H-bonds.

Positional disorder of the REE cations

The *REE* cations occupy four sites in tadzhikite: *RE*(1), *RE*(2), *RE*(3) and *RE*(4). The separations between these sites lie between 0.16 and 0.98 Å (Table 3), whereas in heated tadzhikite (Chernitsova *et al.* 1983), there is one corresponding *RE*-site, and the constituent cations at this site have a normal displacement parameter (1.02 Å^2). Tadzhikite contains detectable U (Table 5), and the broad reflections (Chernitsova *et al.* 1983, this study) of unheated crystals suggest that tadzhikite shows significant radiation damage. This being the case, it seems reasonable to assign the positional disorder of the *RE*-sites to radiation damage.

The chemical composition of tadzhikite

If we simplify the formula of tadzhikite slightly by disregarding the small (0.04 *apfu*) amount of *REE* at the *Ca*(1)-site, the formula unit may be written as

$$Ca_2(Ca_{0.86}Y_{0.89}Na_{0.25})(Ti_{0.56}Fe^{3+}{}_{0.30}Al_{0.07}Mn^{3+}{}_{0.04})(R^{3+}{}_{1.55}\square_{0.45})$$
$$[B_4Si_4O_{16}(O_{0.78}\{OH\}_{0.22})_6](OH)_2.$$

This formula is not quite neutral (having an excess 0.08$^+$ charge), but this deviation is acceptable considering the chemical and structural complexity of the material. Mellini & Merlino (1977) suggested two alternative structural hypotheses for tadzhikite: (1) tadzhikite contains essential (OH); (2) tadzhikite is anhydrous and contains Ti^{4+} in square-pyramidal coordination. It is apparent from the current study that hypothesis (1) of Mellini & Merlino (1977) is correct. Furthermore, the formula of tadzhikite can be simplified and generalized to:

$$Ca_2(Ca,Y)_2(Ti^{4+},Fe^{3+})(R^{3+},\square)[B_4Si_4O_{16}(O,OH)_6](OH)_2.$$

Nomenclature

Tadzhikite was originally described by Efimov *et al.* (1970), and the structure was solved by Chemitzova *et al.* (1983); these authors used the name *tadzhikite.* However, the mineral appears as "tadzhikite-(Ce)" in Fleischer & Mandarino (1995). Furthermore, Pekov (1998) described the minerals from this locality as "tadzhikite-(Ce)" and "tadzhikite-(Y)", based on the date of Efimov *et al.* (1970). "Tadzhikite-(Y)" is said to be much more abundant at Dara-Pioz than "tadzhikite-(Ce)".

First, neither "tadzhikite-(Ce)" nor "tadzhikite-(Y)" are valid, as they have not been approved by the CNMMN of the IMA (J.D. Grice, pers. commun., 1998). Second, Efimov *et al.* (1970) described two varieties of tadzhikite: I and II. "Tadzhikite-I" is enriched in Y relative to "tadzhikite-II". The crystal refined here is enriched in Y and corresponds closely to "tadzhikite-I", informally named "tadzhikite-(Y)" by Pekov (1998). In the structure of tadzhikite (Table 5), Y occurs at the Ca(2) site, whereas the *REE* cations occur predominantly at the *RE* sites. The dominant *REE* at the *RE* site is Ce (Table 4), and hence the suggestion that this variety of tadzhikite be named "tadzhikite-(Y)" is not correct; Y has a role different from that of the *REE*s in tadzhikite. Tadzhikite could be formally renamed "tadzhikite-(Ce)".

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