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REDLEDGEITE, $Ba_x([Cr,Fe,V]^{3+}{}_{2x}Ti_{8-2x})O_{16}$, THE *I4/m* STRUCTURE AND ELUCIDATION OF THE SEQUENCE OF TUNNEL Ba CATIONS

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ABSTRACT

Redledgeite is a hollandite-group mineral, and its synthetic equivalent is important as a solid-state repository for toxic heavy-metal waste. Redledgeite has a Ti_8O_{16} framework of octahedra, with [0,0,*z*] and [½,½,*z*] tunnels; Ba occurs in the tunnels, allowing substitution of Cr^{3+}, Fe^{3+}, and V^{3+} for Ti^{4+}. The structure of redledgeite has been refined in space group *I4/m*, in contrast to an earlier study that used *I2/m* symmetry. The superior refinement ($R = 0.015$; $|\Delta\rho| \leq 0.42e^-/Å^3$) indicates that our crystal of redledgeite is tetragonal. The majority of the Ba atoms in redledgeite are located at the Ba1 site at 0,0,0 and ½,½,½. However, the short *c*-dimension (2.952 Å) prohibits occupancy of adjacent sites along [0,0,*z*] and [½,½,*z*], yielding the formula $Ba1_1[M^{3+}{}_2Ti^{4+}{}_6]O_{16}$. Ba occupancy greater than Ba_1 per unit cell is attained by partial occupancy of Ba2 sites at the special position 4*e* at 0,0,*z*; the Ba1 site and the pair of Ba2 sites 0.58 Å above and below Ba1 are termed a *set* of sites. A Markovian sequence of occupied sets of sites allows ⅔ of the sets to be occupied, yielding a hypothetical maximum occupancy of $Ba_{1.33}[M^{3+}{}_{2.67}Ti^{4+}{}_{5.33}]O_{16}$. The structural constraints on maximum occupancy have important implications for waste-loading in the synthetic phase.

Keywords: redledgeite, crystal structure, hollandite, heavy-metal waste.

SOMMAIRE

La redledgeïte fait partie du groupe de la hollandite; son équivalent synthétique est une phase importante dans l'enfouissement de déchets de métaux lourds toxiques à l'état solide. La redledgeïte possède une trame d'octaèdres de stoechiométrie Ti_8O_{16}, et des tunnels [0,0,*z*] et [½,½,*z*]; il est possible de loger des atomes de Ba dans ces tunnels, ce qui permet le remplacement du Ti^{4+} par Cr^{3+}, Fe^{3+}, et V^{3+}. Nous avons affiné la structure dans le groupe spatial *I4/m*, au lieu de la symétrie *I2/m*, proposée antérieurement. Le résultat supérieur de l'affinement ($R = 0.015$; $|\Delta\rho| \leq 0.42e^-/Å^3$) montre que notre cristal est bien tétragonal. La majorité des atomes de Ba occupe le site Ba1, de coordonnées 0,0,0 et ½,½,½ . Toutefois, la courte période *c* de la maille (2.952 Å) interdit l'occupation de sites adjacents le long des tunnels, ce qui mène à la formule $Ba1_1[M^{3+}{}_2Ti^{4+}{}_6]O_{16}$. Un taux d'occupation supérieur à Ba_1 par maille élémentaire résulte de l'occupation partielle de sites Ba2 à la position spéciale 4*e*, 0,0,*z*; le site Ba1 et la paire de sites Ba2 0.58 Å par dessus et par dessous Ba1 constituent un ensemble de sites. Une séquence markovienne d'ensembles de sites occupés permet une occupation de deux-tiers des sites, ce qui mène à un taux d'occupation maximal exprimé par la formule $Ba_{1.33}[M^{3+}{}_{2.67}Ti^{4+}{}_{5.33}]O_{16}$. Les limitations structurales de l'occupation maximale ont des implications importantes pour l'incorporation de déchets dans la phase synthétique.

(Traduit par la Rédaction)

Mots-clés: redledgeïte, structure cristalline, groupe de la hollandite, déchets de métaux lourds.

INTRODUCTION

Redledgeite is a rare mineral that belongs to the hollandite group. Although the mineral is not common, synthetic redledgeite is of particular interest because of its emerging use as an ecologically sustainable phase for the disposal of heavy-metal waste (White *et al.* 1995). In the patented *xtaltite* (pronounced crystal-tight) process, the synthetic phase is used to provide a stable nontoxic solid-state repository for toxic heavy metals such as chromium. Knowledge of the redledgeite structure is fundamental to its use as a toxic-waste repository.

The crystal structure of redledgeite was reported by Gatehouse *et al.* (1986). Redledgeite is dimensionally tetragonal, and other barium titanate hollandite-type

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phases have been reported in space group *I4/m* (Sinclair *et al.* 1980). Gatehouse *et al.*, however, suggested deviation from tetragonal symmetry, and reported the structure in the nonconventional monoclinic space-group *I2/m*. However, their reported atomic positions do not deviate greatly from tetragonal symmetry, all atoms being within 2σ of tetragonal equivalency [there is a typographical error in their Table II, with z_{M1} = 0.6664(1), not 0.664(1) as given]. The relatively high residuals (R = 0.063, R_w = 0.074) of the earlier study and the ambiguities regarding symmetry persuaded us to re-examine this mineral.

EXPERIMENTAL

A sample of redledgeite from the type locality was obtained and afforded excellent euhedral single crystals. A crystal was selected, trimmed to equant dimensions and mounted for examination by precession methods. The results of a precession study were compatible with tetragonal symmetry, and showed no superlattice reflections of the type noted by Gatehouse *et al.* (1986).

The crystal was mounted on an Enraf–Nonius CAD4 single-crystal diffractometer, and cell parameters were obtained by least-squares refinement of the setting angles of 25 independent diffraction-maxima, using graphite-monochromatized Mo$K\alpha$ radiation. Intensity data were collected on the same instrument; absorption effects were corrected by the ψ-scan method (relative transmission$_{max}$ = 99.86%, relative transmission$_{min}$ = 93.44%). Details of data collection and crystal-structure refinement are given in Table 1.

TABLE 1. CRYSTAL DATA AND RESULTS OF STRUCTURE REFINEMENTS FOR REDLEDGEITE

Dimensions	0.10 x 0.10 x 0.10 mm		
Unit cell (space group *I4/m*)			
a	10.1500(1) Å	*c*	2.9520(5) Å
θ limits	0 - 30°	Scan type	$\theta/2\theta$
Standards:		Scan time(s)	$\leq$60 s
Intensity,	3 per 4 h	R_{merge}	0.021
Orientation,	3 per 300 reflections	R	0.015
Data collected	1712 ($\pm h$, $\pm k$, $\pm l$)	R_w	0.019
Unique data	262	Goodness-of-fit	0.85
Data > $5\sigma_I$	221	Variables	27
Difference Peaks in Final Map:			
(+):	0.42e$^-$ Å^{-3}	(-):	0.29e$^-$ Å^{-3}

All crystal-structure calculations were done using the Enraf–Nonius SDP package of computer programs (Frenz 1985). Neutral-atom scattering factors, with corrections for anomalous dispersion, were used throughout the refinement. Refinement was initiated in the space group *I4/m*, with positional parameters calculated from the reported monoclinic structure. Refinement converged satisfactorily to R = 0.015, R_w = 0.019, and small electron-density residuals ($|\Delta\rho| \leq 0.42e^-/Å^3$) in *I4/m*. Table 2 reports the positional parameters and equivalent-isotropic *B* values, and Table 3 presents selected bond-distances. Table 4 gives anisotropic displacement parameters, and Table 5 reports observed and calculated structure-factors, and have been submitted to the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

TABLE 2. POSITIONAL PARAMETERS AND EQUIVALENT ISOTROPIC *B* VALUES IN REDLEDGEITE

Atom	*x*	*y*	*z*	*B* (Å^2)	*Site Occupancy*
Ba1	0	0	0	2.14(1)	0.525(2)
Ba2*	0	0	0.195(4)	0.5(1)	0.018(2)
Ti	0.15023(4)	0.66609(4)	0	0.620(7)	1.02(1)
O1	0.0401(2)	0.3334(2)	0	0.74(3)	1.00
O2	0.2960(2)	0.3446(2)	0	0.67(3)	1.00

The starred atom was refined isotropically. The Ti site is also occupied by M^{3+} cations, but modeled using scattering factors for Ti.

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) IN REDLEDGEITE

Ba1-O1 (x4)	3.409(2)	Ti-O1	1.932(2)
O2 (x8)	2.992(1)	O1' (x2)	1.960(1)
Mean	3.131	O2 (x2)	1.980(1)
		O2'	2.010(2)
Ba2-O1 (x4)	3.457(3)	Mean	1.970
O2 (x4)	2.753(4)		
O2 (x4)	3.315(8)		
Mean	3.175		

TABLE 6. CHEMICAL COMPOSITION OF REDLEDGEITE*

TiO_2 wt.%	60.42	Ti	6.13
Fe_2O_3	7.90	Fe^{3+}	0.80
Cr_2O_3	8.27	Cr^{3+}	0.88
V_2O_3	0.70	V^{3+}	0.08
BaO	20.92	Ba	1.10
Total	98.21		

Empirical formula:
$Ba_{1.10}[Cr_{0.88}Fe_{0.80}V_{0.08}Ti_{6.13}]_{\Sigma 7.89}O_{16}$

* Electron-microprobe data. The empirical formula is based on 16 atoms of oxygen.

Results of wavelength-dispersion electron-microprobe analysis of the crystal selected for structure analysis are given in Table 6. The low total (98.21 wt.%), as in the Gatehouse *et al.* (1986) study, is attributed to minor H_2O that occupies vacant Ba sites.

DESCRIPTION OF THE ATOMIC ARRANGEMENT

In the redledgeite structure, $[M^{3+},Ti^{4+}]O_6$ octahedra form a framework typical of hollandite-type phases (Fig. 1). Substitution of M^{3+} cations (in our crystal, M^{3+} stands for Fe^{3+}, Cr^{3+}, and V^{3+}) for Ti^{4+} requires insertion of charge-compensating cations (*i.e.*, Ba) into the tunnels (Fig. 1). For every two trivalent cations, one atom of Ba is incorporated in the [001] tunnels.

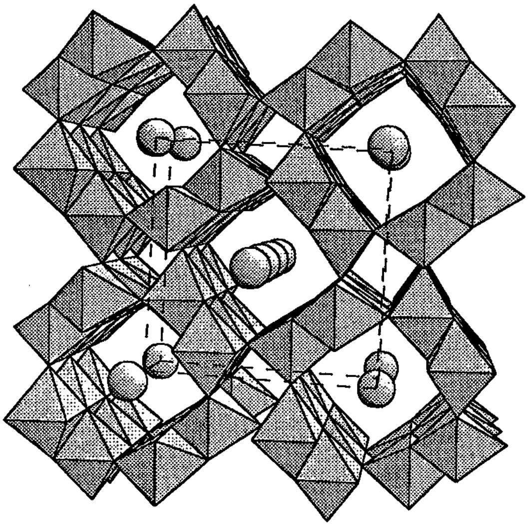

FIG. 1. The structure of redledgeite projected approximately down [001]. In columns of Ba1 sites at corners of the unit cell, every other Ba atom along *c* is absent, to denote half-occupancy of these sites. The Ba column at [½,½,*z*] is shown with full occupancy to illustrate the problem of close proximity of the Ba cations in fully occupied Ba1 sites. The Ba2 sites are not shown.

The Ba cations are principally incorporated at the 2*a* sites of space group *I*4/*m*, at 0,0,0 and ½,½,½ (termed Ba1 sites). In redledgeite, however, adjacent Ba1 sites along [001] are separated by the *c*-axis length, 2.95 Å. The short distance between sites prohibits occupancy >0.5 of the Ba sites. However, the Ba2 site is located at the 4*e* (0,0,*z*) position, with sites 0.58 Å above and below each Ba1 site (Fig. 2). Virtually all the Ba atoms occur at the Ba1 site, but the short Ba1 – Ba1 distance along *c* prohibits more than one Ba1 atom (site occupancy = 0.5) in the formula. Minor Ba occurs at the Ba2 site [refined site-occupancy = 0.018(2) Ba2 per site, or 0.07 Ba2 atoms per unit cell]. For purposes of discussion, we consider each Ba1 site and the pair of Ba2 sites 0.58 Å above and below that Ba1 atoms to constitute a *set* of Ba sites (Fig. 2), where the Ba2 site *below* the mirror is designated Ba2$_b$, and the Ba2 site *above* the mirror is designated the Ba2$_a$ site. Although adjacent Ba1 sites along *c* cannot be occupied, limiting maximum occupancy to ½ of the Ba1 sites, ⅔ of all *sets* of sites can be occupied because of the displacement of the Ba2 sites from the Ba1 sites.

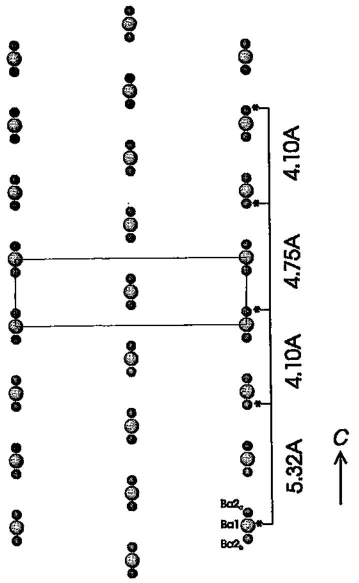

FIG. 2. The disposition of Ba sites in the [0,0,*z*] and [½,½,*z*] columns in redledgeite. The outline of the unit cell is depicted, and Ba1 is shown as the larger circle. A Ba1 site and adjacent Ba2$_a$ and Ba2$_b$ sites constitute a set of Ba sites. Occupancy of starred sites illustrates how two-thirds of all sets of sites can be occupied, with allowable Ba – Ba distances shown.

Figure 3 depicts possible sequences of occupancies or vacancies at *sets* of Ba sites. These sequences allow a Ba occupancy of up to $Ba_{1.33}[M^{3+}{}_{2.67}Ti^{4+}{}_{5.33}]O_{16}$. As shown, a vacancy at a given set of sites can be followed (along +*c*) by an occupied Ba2$_b$ site at the next set of sites, the set centered at 0,0,1. This can be followed by the third set of Ba sites along *c* (centered at 0,0,2), where the Ba2$_a$, site can be occupied, yielding a Ba–Ba distance of 4.10 Å. The next set of sites in the sequence along *c* must be vacant, however, as Ba occupancy in any of the three sites in the set would yield a Ba–Ba distance less or equal to 2.95 Å. This vacancy renews the sequence, allowing the next two sets of sites to be occupied as outlined above, and yielding a maximum occupancy of all sets of sites: $Ba_{1.33}[M^{3+}{}_{2.67}Ti^{4+}{}_{5.33}]O_{16}$.

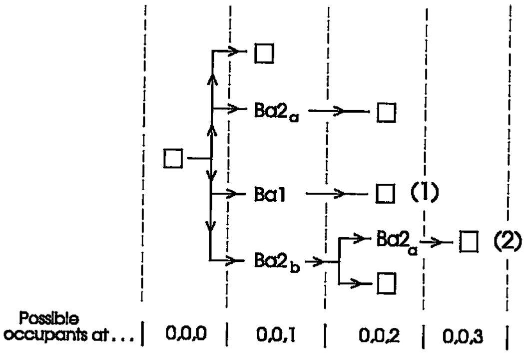

FIG. 3. Allowed sequences of occupied Ba1 sites along [0,0,*z*]. Starting from a vacancy in the set of Ba sites at 0,0,0, arrows lead through sequences of allowed occupants at the sets of sites at 0,0,1, 0,0,2 and 0,0,3. Sequence (1) yields $Ba_1[M^{3+}{}_2Ti_6]O_{16}$; sequence (2) yields the maximum occupancy, $Ba_{1.33}[M^{3+}{}_{2.67}Ti_{5.33}]O_{16}$. The sequences depicted are not mutually exclusive, as each vacancy renews the possibilities in sequence at the left of the diagram.

This occupancy yields a maximum of $Cr_{2.67}$ in the redledgeite formula (equivalent to 24.49 wt.% Cr_2O_3), providing a limit of waste-loading capacity for use of the phase as a heavy-metal repository. The occupancy of sites described here is thus a Markovian sequence, where the occupant of any set of sites is a function of the occupant of the immediately adjacent sets of sites.

The Ba occupancy of redledgeite is $Ba_{1.1}$ (Table 6). The occupancy in excess of $Ba_{1.0}$ results from domains of adjacent sets of sites that are occupied in the manner elucidated above. As *I4/m* symmetry is obeyed and no superstructures are observed, clearly these domains are disordered throughout the analyzed crystal, thus yielding average tetragonal symmetry. Although the crystal-chemical arguments presented above suggest that domains of Ba2-occupied sites can occur throughout the crystal, leading to a hypothetical maximum Ba occupancy of $Ba_{1.33}[M^{3+}{}_{2.67}Ti^{4+}{}_{5.33}]O_{16}$, both published compositions of redledgeite and studies on the synthetic phase (Kesson & White 1986), as well as lattice-energy calculations of hollandite *sensu stricto* (Post & Burnham 1986), all yield a maximum occupancy of $Ba_{1.1}$. This observation suggests that domains of Ba2-occupied sites may be less stable than domains with the majority of Ba located in the Ba1 site.

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