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THE CRYSTAL STRUCTURE OF DISSAKISITE-(Ce), THE Mg ANALOGUE OF ALLANITE-(Ce)[1]

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ABSTRACT

The crystal structure of dissakisite-(Ce) [*a* 8.905(1), *b* 5.684(1), *c* 10.113(1) Å, β 114.62(2)°, space group $P2_1/m$, $Z = 2$], a member of the epidote group having the analyzed composition $Ca_{1.05}(Ce_{0.57}La_{0.33}Nd_{0.07}Pr_{0.03})_{\Sigma 1.00}Mg_{0.93}Fe_{0.14}Ti_{0.06}Al_{1.91}Si_{2.94}O_{12}[(OH)_{0.94}F_{0.06}]$, has been refined to an unweighted *R*-factor of 2.4% for 1102 observed reflections. The Ca and lanthanide atoms were found to be completely ordered in sites *A*1 and *A*2, respectively. Consistent with local balance of charges for *REE* substitutions, Mg and minor Fe^{2+} occupy *M*3. Minor Ti (and possibly Fe^{3+}) substitute in *M*1, whereas *M*2 is occupied only by Al. Local balance of charges is maintained by the formation of a hydrogen bond O10–H...O4.

Keywords: dissakisite, crystal structure, rare-earth aluminosilicate, epidote group.

SOMMAIRE

Nous avons résolu la structure cristalline de la dissakisite-(Ce) [*a* 8.905(1), *b* 5.684(1), *c* 10.113(1) Å, β 114.62(2)°, groupe spatial $P2_1/m$, $Z = 2$], membre du groupe de l'épidote ayant la composition $Ca_{1.05}(Ce_{0.57}La_{0.33}Nd_{0.07}Pr_{0.03})_{\Sigma 1.00}Mg_{0.93}Fe_{0.14}Ti_{0.06}Al_{1.91}Si_{2.94}O_{12}[(OH)_{0.94}F_{0.06}]$, jusqu'à un résidu *R* non pondéré de 2.4% (1102 réflexions observées). Les atomes de Ca et des terres rares sont complètement ordonnés dans les sites *A*1 et *A*2, respectivement. Comme le requiert la satisfaction locale des charges à la suite des substitutions impliquant les terres rares, Mg et une faible quantité de Fe^{2+} occupent *M*3. Une faible quantité de Ti (et peut être aussi de Fe^{3+}) se trouve dans le site *M*1, tandis que *M*2 ne contient que de l'aluminium. La formation de liaisons hydrogène O10–H...O4 assure la neutralité électrostatique locale.

(Traduit par la Rédaction)

Mots-clés: dissakisite, structure cristalline, aluminosilicate de terres rares, groupe de l'épidote.

INTRODUCTION

Dissakisite-(Ce), a new member of the epidote group having the idealized formula $Ca(Ce,La)MgAl_2Si_3O_{12}(OH)$, was recently described by Grew *et al.* (1991) from Balchen Mountain, East Antarctica, where it occurs in marble closely associated with calcite, dolomite, forsterite, phlogopite, chlorite, and geikielite. Dissakisite is a secondary mineral, having been formed at about 600°C and pressures ≤7 kbar during the amphibolite-facies metamorphism of a regional granulite-facies terrane. Additional occurrences, including those of compositional varieties (ferroan, chromian), have been reported from Sweden, southern Yakutia in Russia, Finland, China, and France. Except for the French locality, dissakisite occurs in metamorphic rocks that are highly enriched in Mg relative to Fe, undersaturated in silica, and relatively rich in Ca. In addition to the reported occurrences in marbles, skarns, and garnet–corundum rock, Grew *et al.* suggested that pegmatites having high bulk Mg/Fe ratios and no quartz may be potential hosts for dissakisite.

With respect to crystal-chemical properties, Grew *et al.* determined, in part by analogy with other members of the epidote group, that the new mineral has space group $P2_1/m$, with cell parameters *a* 8.916(20), *b* 5.700(8), *c* 10.140(25) Å, and β 114.72(14)°, as refined from powder-diffraction data. The composition [normalized to 12 O + (OH,F)] of type material from Balchen Mountain was reported to be $Ca_{1.05}(Ce_{0.57}La_{0.33}Nd_{0.07}Pr_{0.03})_{\Sigma 1.00}Mg_{0.93}Fe_{0.14}Ti_{0.06}Al_{1.91}Si_{2.94}O_{12}(OH)_{0.94}F_{0.06}$, for which $Z = 2$. The numbers of each of the major cations in the formula approximate their ideal end-member values, and these values correspond to equipoint

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ranks (2 and 4) for sites in which corresponding cations have been found to be ordered in other members of the epidote group (*e.g.*, Dollase 1968, 1969, 1971, Peacor & Dunn 1988, Sokolova *et al.* 1991). Of the three octahedrally coordinated sites (*M*1, *M*2 and *M*3), *M*2 has been found to be exclusively occupied by Al in members of the epidote group. However, Dollase (1971) found that in allanite, which ideally has Fe^{2+} in place of the Mg of dissakisite-(Ce), there was ambiguity regarding substitution of Fe^{2+} (and some Fe^{3+}) in the *M*1 and *M*3 sites. Because dissakisite-(Ce) has a composition for which order–disorder relationships are more easily determined, we have refined the structure to determine those relationships, and to compare them with those of other members of the epidote group in order to better define the factors controlling substitutions on specific sites.

REFINEMENT OF THE STRUCTURE

Intensity data were measured with an Enraf-Nonius CAD4 diffractometer, and the structure was solved and refined using the Enraf-Nonius crystallographic software package MolEN. Conditions of data measurement, relevant parameters, and data-correction procedures are summarized in Table 1. The intensities of 2124 reflections in two asymmetric units were measured, and these were then averaged to yield 1175 unique reflections, of which 73 were judged to be "unobserved" using the criterion $I_{obs} > 3\sigma(I)$. The cell parameters *a* 8.905(1), *b* 5.684(1), *c* 10.113(1) Å, and β 114.62(2)°, were refined by least squares from the diffractometer setting angles of 25 reflections from the crystal used for intensity measurement.

TABLE 1. EXPERIMENTAL DETAILS

Crystal size	0.08 X 0.09 X 0.05 mm
Radiation	Monochromatized MoKα (λ = 0.7107Å)
Maximum 2θ	54.90°
Reflection scans	
Scan type	ω-2θ
Scan rates	Between 0° and 7°/min in ω
Scan widths	0.70 + 0.350tanθ
Data corrections	For Lorentz-polarization and absorption effects (by the psi-scan method)
Refinement	
Type	Full-matrix least-squares
Function minimized	$\Sigma w(\lvert F_{obs}\rvert - \lvert F_{cal}\rvert)^2$
Weights	$4F^2_{obs}/\sigma^2(F^2_{obs})$
Anomalous dispersion	For all atoms except H
Observations	1102 reflections with $I_{obs} > 3\sigma(I_{obs})$
Variables	118 parameters
R (obs. data)	0.024
R_w (obs. data)	0.057
R (all data)	0.028
Goodness-of-fit	2.19
Largest shift/error	0.00 (in final cycle)
Largest Δρ(x,y,z)	1.2 e/Å^3 (on final difference map)
Diffractometer	Enraf-Nonius CAD4
Computer hardware	MicroVAX 3100
Computer software	MolEN system

Refinement was initiated using the atomic coordinates of dollaseite-(Ce), except that H was omitted. The form factor of Ce was used as an approximation for all lanthanides because that form factor approximates the weighted average for La and the other lanthanides present. The Ca and lanthanide atoms are ordered in the *A*1 and *A*2 sites, respectively, of dollaseite-(Ce) (Peacor & Dunn 1988) and allanite (Dollase 1971). To determine the presence of any disorder involving the Ca and lanthanides in the *A*1 and *A*2 sites of dissakisite, form factors for Ca and Ce were applied to both sites, and the occupancies of Ca in *A*1 and Ce in *A*2 were refined together with coordinates and isotropic temperature-factors. The resulting values were found to be consistent with Ca and lanthanides fully ordered in *A*1 and *A*2, respectively, and those occupancies were therefore held constant at their ideal values for the remainder of the refinement.

Because normalization of the chemical data to 3 Si per formula unit yielded a satisfactory formula, and because the tetrahedral sites in epidote have generally been found to be occupied only by Si, the refinement was carried out with only Si assigned to the tetrahedral sites. Form factors for *M*1, *M*2, and *M*3 were modeled with (Al + Ti), Al, and (Mg + Fe), respectively, based on considerations of charge balance (see below), the results for other members of the epidote group, and the known interatomic distances in dissakisite. Al has been found to have a strong preference for *M*2 in epidote-type structures, whereas any ambiguity in the distribution of other cations is in part accommodated by the similarity in the form factors of Al and Mg, and Ti and Fe. A refinement of the site-occupancy factors of the octahedral cation sites yielded the site contents 1.66(2) Al + 0.34 Ti in *M*1 and 1.71(1) Mg + 0.29 Fe in *M*3. An attempt to place the lighter of the two substituents (Ti) on *M*2 yielded a value of 2.03(2) Al on that site, confirming the assumption of full occupancy by Al. These results may be tested by comparing the expected mean bond-lengths for the *M* sites, calculated using the proportions of Al, Ti, Mg, and Fe from the refinement and the grand mean values for Al–O, Ti–O, Mg–O and Fe^{2+}–O from the survey of Baur (1981), with the observed mean bond-lengths (Table 5, see below). The resulting values (in Å) are 1.92 (calc.) and 1.94 (obs.) for *M*1, 1.91 (calc.) and 1.89 (obs.) for *M*2, and 2.09 (calc.) and 2.11 (obs.) for *M*3. As the differences are no more than ± 0.02 Å, the agreement between predicted and observed means is considered satisfactory.

Refinement with isotropic temperature-factors and the refined values of the occupancy factors (but with H excluded) progressed satisfactorily until convergence was reached at an *R* factor of 3.3%, at which time a difference electron-density synthesis verified the essential correctness of the structure. A peak of height 0.99 e/Å^3, which was found to be very near the position of the

TABLE 2. ATOMIC COORDINATES AND EQUIVALENT ISOTROPIC TEMPERATURE-FACTORS (Å^2)

Atom	x	y	z	B_{eq}
A1	0.2380(2)	1/4	0.8480(1)	0.60(3)
A2	0.40515(5)	1/4	0.57282(4)	0.735(8)
M1	0	0	0	0.53(3)
M2	0	0	1/2	0.23(3)
M3	0.2980(2)	1/4	0.2128(2)	0.45(4)
Si1	0.6624(2)	1/4	0.9609(2)	0.27(3)
Si2	0.6859(2)	1/4	0.2807(2)	0.25(3)
Si3	0.8144(2)	1/4	0.6791(2)	0.23(3)
O1	0.7647(4)	0.0088(7)	0.9657(4)	0.45(6)
O2	0.6919(4)	0.0255(7)	0.6400(3)	0.43(6)
O3	0.7945(4)	0.0138(7)	0.3405(3)	0.34(6)
O4	0.0508(6)	1/4	0.1293(5)	0.43(9)
O5	0.9540(6)	1/4	0.8503(5)	0.39(9)
O6	0.9340(6)	1/4	0.5911(5)	0.29(9)
O7	0.4886(6)	1/4	0.8235(5)	0.54(9)
O8	0.5374(6)	1/4	0.3293(5)	0.8(1)
O9	0.6190(6)	1/4	0.1031(5)	0.7(1)
O10	0.0821(5)	1/4	0.4266(5)	0.5(1)
H	0.077	1/4	0.349	2.0

Site contents are 2Ca for A1, $(Ce_{0.57}La_{0.33}Nd_{0.07}Pr_{0.03})$ for A2, $(Al_{1.66}Ti_{0.34})$ for M1, 2Al for M2, and $(Mg_{1.71}Fe_{0.29})$ for M3. Esds of the parameters are in parentheses. The coordinates of H were fixed at those indicated by the difference synthesis; its isotropic B was fixed at 2.0 Å^2.

TABLE 6. EMPIRICAL BOND-VALENCES (v.u.)

	A1	A2	M1	M2	M3	Si1	Si2	Si3	Σv_a
O1	0.31 0.31		0.45 0.45		0.25 0.25	0.97 0.97			1.98
O2		0.25,0.39 0.25,0.39			0.31 0.31			1.02 1.02	1.97
O3	0.36 0.36	0.21 0.21		0.55 0.55			1.02 1.02		2.14
O4			0.63(X2)		0.44				1.70
O5	0.21		0.43(X2)					0.91	1.98
O6	0.09			0.49(X2)				0.94	2.01
O7	0.36	0.63				1.09			2.08
O8		0.11(X2),0.07			0.50		1.09		1.88
O9						0.97	0.96		1.93
O10		0.28		0.53(X2)					1.34
Σv_c	2.00	2.90	3.02	3.14	2.06	4.00	4.09	3.89	

Bond valences are weighted averages of (Ce,La,Nd,Pr) for A2, (Al,Ti) for M1, and (Mg,Fe) for M3 calculated using the atomic proportions from the chemical analysis (for A2) and from the structure refinement (for M1 and M3). The bond-valence constants used in the calculations are those of Brese and O'Keeffe (1991).

H atom in dollaseite-(Ce), was assigned to H. Refinement of its coordinates resulted in a shift into near-coincidence with its associated O10 atom. The coordinates of the H atom were therefore fixed at those determined from the difference synthesis, and its temperature factor was fixed at an arbitrary value of 2.0 Å^2. Refinement was completed with variation of anisotropic temperature-factors for all non-H atoms. The final unweighted and weighted *R* factors for the 1102 observed reflections are 2.4% and 5.7%, respectively. For all reflections, the final unweighted *R* factor is 2.8%. Final coordinates and equivalent isotropic temperature-factors are listed in Table 2, structure factors in Table 3, anisotropic temperature-factors in Table 4, selected interatomic distances in Table 5, and empirical bond-valences in Table 6. Copies of Tables 3 and 4 may be obtained from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å)

A1-O7	2.346(6)	A2-O7	2.326(5)
O3	2.347(4) X2	O2	2.506(4) X2
O1	2.399(4) X2	O10	2.630(5)
O5	2.539(6)	O2′	2.676(4) X2
O6	2.867(6)	O3	2.734(4) X2
Mean	2.463	O8	2.983(2)* X2
		O8′	3.142(5)*
		Mean	2.599
M1-O4	1.855(3) X2	Si1-O7	1.592(5)
O1	1.976(4) X2	O1	1.636(4) X2
O5	1.991(4) X2	O9	1.637(6)
Mean	1.941	Mean	1.625
M2-O3	1.870(3) X2	Si2-O8	1.591(6)
O10	1.886(3) X2	O3	1.617(4) X2
O6	1.914(3) X2	O9	1.640(6)
Mean	1.890	Mean	1.616
M3-O8	1.959(6)	Si3-O2	1.617(4) X2
O4	2.003(6)	O6	1.649(5)
O2	2.136(4) X2	O5	1.658(6)
O1	2.213(4) X2	Mean	1.635
Mean	2.110		
H-O10	0.768	O4-O10	2.902(7)
O4	2.134	O4-H-O10	177°

Esds are in parentheses. The A2-O8 distances marked with asterisks are not included in the calculation of the mean value.

DISCUSSION

The average M–O distances for *M*1, *M*2, and *M*3 are consistent with the refined occupancies of $(Al_{1.66}Ti_{0.34})$ and $(Mg_{1.71}Fe_{0.29})$ for *M*1 and *M*3, respectively, and with the full occupancy of *M*2 by Al. The chemical composition reported for the type material by Grew *et al.* (1991) yields the formula $Ca_{1.08}(REE)_{1.02}Ti_{0.06}Al_{1.95}Mg_{0.95}Fe_{0.14}Si_3O_{12.25}(OH)_{0.69}F_{0.06}$ with $Z = 2$. Here the normalization is to 3 Si, rather than to [12 O + (OH,F)], and *REE* represents the rare-earth elements (lanthanides). The formula derived using the refined site-occupancies and assuming only OH on the O(10) site, is $Ca(REE)(Al_{0.83}Ti_{0.17})(Al)(Mg_{0.85}Fe_{0.15})Si_3O_{12}(OH)$ with $Z = 2$, in reasonable agreement with the formula derived from results of the chemical analysis.

Refinement of occupancies for the *A*1 and *A*2 sites clearly indicated a lack of Ca in *A*2 and lanthanides in *A*1, consistent with the nearly complete order found in dollaseite-(Ce). Such order is in accord with the longer distances inherent in the *A*2 site compared with those for *A*1, as noted by Dollase (1971). However, the observed order is also consistent with local charge-balance, as pointed out by Peacor & Dunn (1988). In zoisite, *A*2 and *M*3 are occupied by Ca^{2+} and Al^{3+}, respectively, with O2 and O8 being coordinated to atoms on both sites; substitution of a divalent cation in *M*3, such as the dominant Mg in that site in dissakisite, is coupled directly with substitution of REE^{3+} in *A*2 in order to maintain charge balance for O2 and O8. As shown by the bond valences for O2 and O8 in Table 6, such coupled solid-solution is essential for local-charge balance. Thus, in the allanite structure refined by Dollase (1971), some Ca in *A*2 is balanced by some Al and Fe^{3+} in *M*3. Likewise, Sokolova *et al.* (1991) showed that substitution of lanthanides in *A*2 is coupled with Mn^{2+} in *M*3. The average *M*3–O distance (2.110 Å) of dissakisite is consistent with the refined occupancy ($Mg_{1.71}Fe_{0.29}$) for *M*3, based on the assumption that Fe^{2+} substitutes there (rather than in *M*1 or *M*2).

Assuming that O4 is occupied by O^{2-} as implied by results of the chemical analysis, charge balance for O atoms coordinated to *M*1 and *M*2 is achieved by occupancy of the latter sites by trivalent cations, as confirmed by the bond-valence sums for O5 and O6 (Table 6). The refined occupancy of *M*2 is consistent with occupancy only by Al, but that of *M*1 ($Al_{1.66}Ti_{0.34}$) clearly indicates the presence of a second cation of atomic number greater than that of Al. Although the refined occupancy of 0.34 Ti is somewhat greater than the value calculated from the analytical data, it may include a small amount of Fe^{3+}, and is reasonable considering errors of analysis and possible slight differences in composition among specimens. Grew *et al.* (1991) stated that their analytical results suggest small variations in Mg, Al, and Ti from one grain to another, but that the differences are within the precision of the measurements at the 2σ level. The average *M*–O bond lengths for *M*1 and *M*2 in clinozoisite, in which both sites are occupied only by Al, are 1.906 and 1.878 Å, respectively; the difference is quite small but nevertheless consistent with a possible preference by larger cations such as Fe^{3+} and Ti for *M*1. This is, in fact, the situation in dissakisite, as evidenced by the refinement of the occupancies of the octahedral sites.

Dollase (1968) pointed out the possible existence of an O10–H...O4 hydrogen bond in clinozoisite and zoisite, and Peacor & Dunn (1988) noted that bond lengths are compatible with an equivalent O10–H...F bond in dollaseite-(Ce), in which the O4 site is occupied by F. An analogous situation occurs in dissakisite, where the empirical bond-valence sums for O4 and O10 are 1.70 and 1.34 v.u., respectively, indicating that O10 is a hydroxyl O atom (but see below) and O4 is in need of an additional valence contribution by way of an H bond. The O10–H, O4–H, and O4–O10 distances of 0.77, 2.13, and 2.902 Å, respectively, are in accord with this interpretation, except that the O10–H distance is too short by 0.2 Å owing to a large error in the position of the H atom. This is normally the case when H atom positions are determined by X-ray diffraction, since the latter locates the centroid of the electron density rather than the position of the nucleus. The observed O4–H distance will also necessarily be erroneously large, but the important point is that it is well below the 2.4 Å separation given by Baur (1972) as the maximum allowable for O...H to be considered an H bond, 2.4 Å being the sum of the van der Waals radii of O and H.

Some additional comments about the bond-valence sum to O10 are also in order. A sum of 1.34 v.u. is rather high for a hydroxyl oxygen and might be taken to indicate partial occupancy of this site by O^{2-}. This is in accord with the previously cited chemical formula derived from the electron-microprobe data and normalized to 3 Si. The anion component of that formula is $O_{12.25}(OH)_{0.69}F_{0.06}$, which can be rewritten as $O_{12.00}(OH,O,F)_{1.00}$. The latter agrees nicely with the idealized formula, but, given the fact that H_2O was not experimentally determined by Grew *et al.* (1991), this agreement may be fortuitous. Since a refinement of the site-occupancy factor for H is obviously impractical, the exact contents of the O10 site cannot be specified, except to say that hydroxyl is by far the dominant species.

Although the errors in bond parameters involving H are large, a few observations about the nature of the H...O4 bond may still be made based upon the more accurately determined O10–O4 distance of 2.902(7) Å. Applying the criterion cited by Cotton & Wilkinson (1988), the separation of 2.902 Å indicates an H bond of moderately weak strength. In terms of empirical bond-valences, that strength may be estimated at 0.15 v.u. from the graph in Figure 2 of Brown & Altermatt (1985), which gives H...O bond valence as a function of the O(donor)–O(acceptor) distance. Adding 0.15 v.u. to the valence sum for O4 in Table 6 improves the sum to 1.85 v.u.

Finally, it is of interest to note that the distances O2–H and O2–O10 are 2.55 and 2.844(6) Å, respectively. The latter falls within the range of donor–acceptor O distances in "medium strength" H bonds (Cotton & Wilkinson 1988), whereas the former is near the 2.4 Å limit for H...O bond distances cited by Baur (1972). This raises the possibility of a bifurcated hydrogen bond to O4 and O2 in dissakisite, a possibility that can be dismissed for several reasons: (1) H would be equidistant from two equivalent O2 acceptors; (2) the angles O10–H–O2 are improbably small (105°) for an H bond; and (3) atom O2 would become overbonded, as its valence sum is already 1.97 v.u.

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