Acta Cryst. (1993). C**49**, 205–207

Structure of Wadalite $Ca_6Al_5Si_2O_{16}Cl_3$

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(*Received* 22 *November* 1990; *accepted* 15 *May* 1992)

Abstract. Calcium chloride framework aluminosilicate, $(Ca_{5.88}Mg_{0.23})(Al_{4.26}Fe_{0.46})Si_{2.00}O_{15.68}Cl_{2.64}$, $Al_5Ca_6Si_2Cl_3O_{16}$ (ideal), $M_r = 793.9$ (ideal), cubic, $I\bar{4}3d$, $a = 12.001$ (2) Å, $V = 1729$ (1) Å^3, $Z = 4$, $D_m = 3.01$, $D_x = 3.056$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha_1) = 0.70930$ Å, $\mu = 2.95$ mm^{-1}, $F(000) = 1565$, $T = 301$ K, $R = 0.062$ for 243 reflections with $F \geq 3\sigma(F)$. Wadalite is a new mineral found in a skarn xenolith in two-pyroxene andesite at a quarry in Fukushima, Japan. The structure consists of a framework of $(Al,Si)O_4$ tetrahedra. A large cavity in the framework accommodates Ca—Cl—Ca linearly coordinated atoms.

Introduction. Wadalite is a new mineral found in a skarn xenolith in two-pyroxene andesite at a quarry in Tadano, Koriyama City, Fukushima, Japan (Bunno, Aoki & Tsukimura, 1992). Recently, a second occurrence of wadalite was reported from skarns of La Negra mine, Queretaro, Mexico (Kanazawa, Aoki & Takeda, 1992). The cell dimensions, diffraction intensities and chemical composition of both are similar to those of grossular garnet $Ca_6Al_4Si_6O_{24}$, but the crystal form is a trigonal tristetrahedron (no inversion symmetry) indicating that the space group is different from that of grossular ($Ia3d$). The chemistry of wadalite is characterized by the existence of Cl atoms and a high Al:Si ratio.

Experimental. D_m by Berman balance. Crystal dimensions: 0.07 × 0.06 × 0.05 mm. Rigaku AFC-5 four-circle diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Rapid intensity measurement with the diffractometer in a full sphere of reciprocal space showed Laue group $m3m$; systematic absences hkl with $h + k + l = 2n$ and hhl with $2h + l = 4n$ lead to one possible space group $I\bar{4}3d$. 402 reflections collected up to $2\theta = 69.3°$ ($\sin\theta/\lambda = 0.8$ Å^{-1}); $h \geq k \geq l \geq 0$, ω–2θ scan mode. Two standard reflections (420, 042) every 55 reflections, variations less than 1.2% about mean. Lorentz and polarization corrections but no absorption or extinction corrections. Lattice parameters from 8 reflections (888) at 48.34° in 2θ with Mo $K\alpha_1$. Chemical composition obtained from measured density and chemical analysis by electron-probe microanalysis is $(Ca_{5.88}Mg_{0.23})(Al_{4.26}Fe_{0.46})Si_{2.00}O_{15.68}Cl_{2.64}$. The ideal chemical formula is $Ca_6Al_5Si_2O_{16}Cl_3$.

Initial crystal structure used in the refinement was derived from the structure of grossular garnet $Ca_6Al_4(SiO_4)_6$ (Abrahams & Geller, 1958), because the Patterson maps of wadalite and grossular have the same peak positions, indicating that most atomic positions in wadalite are the same as those in grossular. However, the crystal structure of grossular cannot be used as the initial parameters of the refinement because wadalite is non-centrosymmetric and grossular is centrosymmetric; the space group of wadalite ($I\bar{4}3d$) is a subgroup of that of grossular ($Ia3d$). We have therefore modified the crystal structure of grossular to be non-centrosymmetric. The structural formula of grossular expressed in $I\bar{4}3d$ becomes $Ca_6Al_4(SiO_4)_3(SiO_4)_3$, in which $(SiO_4)_6$ tetrahedra are split into two symmetrically distinct sets of tetrahedra (Table 1). As the chemical formula of wadalite is $Ca_6Al_4\{(Si,Al)O_4\}_3Cl_3O_4$, three SiO_4 tetrahedra of grossular garnet are missing in

Table 1. *Relation of atomic positions between the grossular garnet and wadalite structures*

Grossular garnet						Wadalite			
$Ia3d$			$I\bar{4}3d$			$I\bar{4}3d$*		$I\bar{4}3d$†	
Ca	24(c)	($\frac{1}{8}$, 0, $\frac{1}{4}$)	Ca	24(d)	(x, 0, $\frac{1}{4}$)	Ca	24(d)	Ca	24(d)
Al	16(a)	(0, 0, 0)	Al	16(c)	(x, x, x)	T(1)	16(c)	T(1)	16(c)
Si	24(d)	($\frac{3}{8}$, 0, $\frac{1}{4}$)	Si(1)	12(a)	($\frac{3}{8}$, 0, $\frac{1}{4}$)	T(2)	12(a)	T(2)	12(a)
			Si(2)	12(b)	($\frac{7}{8}$, 0, $\frac{1}{4}$)			Cl	12(b)
O	96(h)	(x, y, z)	O(2)	48(e)	(x, y, z)	O(2)	48(e)	O(2)	48(e)
			O(1)	48(e)	($-x$, $-y$, $-z$)				
								O(1)	16(c)

* Initial atomic positions of wadalite analogized from the grossular garnet structure.

† Final atomic positions of wadalite.

wadalite. Thus we have deleted half the tetrahedra of the grossular garnet structure and the formula becomes $Ca_6Al_4\{(Al,Si)O_4\}_3$. As this crystal structure is non-centrosymmetric, we have started the crystal structure refinement using it as the initial structure. The remaining O and Cl atoms were found by successive Fourier syntheses using the program *RSSFR*5 (Sakurai, 1967).

The structure was refined on F with unit weights using the program *RADY* (Sasaki, 1987) and scattering factors (neutral) and anomalous-dispersion factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The disordered distribution of Al and Si in the $T(1)$ and $T(2)$ sites was assumed because R is similar even when the Al/Si distribution is changed. Fe was assumed to occupy the $T(1)$ site because the concentration of Fe in the $T(1)$ sites has an R value lower than the random distribution. The occupancy of the Cl site calculated from the chemical composition is 88%, which implies the existence of a vacancy in the Cl site. In the final stage, we have refined the positional parameters, anisotropic temperature factors and occupancy of the Cl site, assuming the chemical compositions of the Ca, $T(1)$ and $T(2)$ sites as $Ca_{0.96}Mg_{0.04}$, $Al_{0.60}Si_{0.28}Fe_{0.12}$ and $Al_{0.68}Si_{0.32}$, respectively. The occupancy of the Cl site was refined to 92 (3)%. Final $R = 0.062$, $wR = 0.066$ and $S = 3.13$ for 243 reflections with $F > 3\sigma(F)$. $(\Delta/\sigma)_{max} = 0.004$, $(\Delta\rho)_{max} = 1.3$ and $(\Delta\rho)_{min} = -1.2$ e Å^{-3}.

Table 2. *Positional parameters and equivalent isotropic temperature factors* (Å$^2 \times 10^4$) *with e.s.d.'s in parentheses for wadalite* $Ca_6Al_5Si_2O_{16}Cl_3$

$$U_{eq} = (1/3)\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

		x	y	z	U_{eq}
Ca	24(*d*)	0.1043 (2)	0.0	0.25	86 (13)
T(1) (Al,Si)	16(*c*)	−0.0169 (2)	−0.0169	−0.0169	65 (3)
T(2) (Al,Si)	12(*a*)	0.375	0.0	0.25	66 (13)
O(1)	16(*c*)	0.0628 (9)	0.0628	0.0628	178 (11)
O(2)	48(*e*)	0.0308 (6)	0.0500 (7)	0.6488 (7)	120 (35)
Cl	12(*b*)	0.125	0.5	0.25	189 (16)

Discussion. Table 2* shows the positional parameters and equivalent isotropic temperature factors for the title mineral. Fig. 1 shows part of the crystal structure. Table 3 shows the bond distances and angles.

The framework of wadalite ($D = 1.73$) is open compared with those of common framework silicates such as quartz, feldspar ($D = 2.6$–2.7) and zeolites ($D = 2.0$–2.2). This is related to the large internal cavity in wadalite. The framework consists of two symmetrically distinct tetrahedra, $T(1)O_4$ and $T(2)O_4$. These two tetrahedra link alternately to produce the framework. The $T(1)$ site is bonded to one O(1) and three O(2) atoms while the $T(2)$ site is bonded to four O(2) atoms. O(1) is a non-bridging atom while O(2) is bridging. The existence of non-bridging O(1) atoms is responsible for the open framework. The Ca

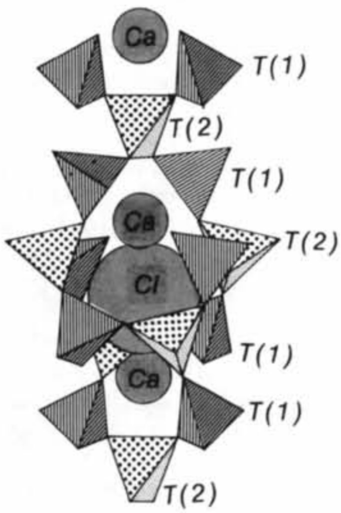

Fig. 1. Part of the crystal structure of wadalite $Ca_6Al_4Si_6O_{24}Cl_3$.

Table 3. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses for wadalite* $Ca_6Al_5Si_2O_{16}Cl_3$

Ca decahedron		O—*M*—O(Cl)			O—*M*—O(Cl)
Ca—O(1)	2.422 (9)		O(2)—O(2^{i})	2.643 (15)	64.6 (4)
—O(2)	2.429 (8)		—O(2^{ii})	4.215 (8)	117.0 (2)
—O(2^{i})	2.515 (8)		O(2^{i})—O(2^{ii})	2.710 (18)	65.2 (4)
—Cl	2.752 (3)		O(1)—Cl	3.270 (3)	78.1 (2)
O(1)—O(2)	3.700 (9)	99.4 (4)	O(2)—Cl	3.643 (9)	89.1 (2)
—O(2^{ii})	3.126 (18)	78.6 (4)			
—O(2^{iii})	3.126 (18)	80.2 (4)			
T(1) tetrahedron			*T*(2) tetrahedron		
T(1)—O(1)	1.657 (18)		*T*(2)—O(2)	1.765 (8)	
—O(2)	1.729 (9)		O(2^{i})—O(2^{ii})	2.710 (18)	100.3 (5)
O(1)—O(2)	2.902 (18)	118.0 (3)	O(2^{i})—O(2^{iv})	2.965 (14)	114.3 (3)
O(2)—O(2)	2.643 (15)	99.7 (4)			

Symmetry code: (i) $0.5-z, -x, 0.5+y$; (ii) $0.5-z, x, -y$; (iii) $x, -y, 0.5-z$; (iv) $0.25+z$ $0.25+y, 0.25+x$.

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* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55487 (4 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

atom forms a decahedron with two O(1), four O(2) and one Cl atoms. The Cl atoms is linearly bonded with two Ca atoms. The structure type of wadalite is completely different from that of grossular; wadalite is classified as a framework aluminosilicate, whereas grossular garnet is classified as a monosilicate (or nesosilicate). However, the atomic positions of grossular and wadalite are closely related to each other (Table 1). Thus, wadalite and grossular have similar cell dimensions and diffraction intensities. Since the powder diffraction pattern of wadalite cannot be distinguished from that of grossular, some wadalites may have been wrongly identified as grossular.

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Acta Cryst. (1993). C49, 207–209

A New Layered $ZnIn_2S_4$-(III*a*) Polytype: Structure of $FeCr_{0.8}Ga_{1.2}Se_4$

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(*Received* 16 *March* 1992; *accepted* 18 *June* 1992)

Abstract. Chromium gallium iron selenide, $FeCr_{0.8}Ga_{1.2}Se_4$, $M_r = 496.95$, rhombohedral, $R\bar{3}m$, $a = 3.8284\ (6)$, $c = 37.914\ (5)$ Å, $V = 481.2$ Å^3, $Z = 3$, $D_x = 5.14$ g cm^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0.7093$ Å, $\mu = 308.70$ cm^{-1}, $F(000) = 655$, $T = 293$ K, $R = 0.049$ for 265 reflections. The structure is a novel centrosymmetric $ZnIn_2S_4$-(III*a*) polytype with an unusual $(cM^thM^ohM^tc)_3$ stacking, which results from the random distribution of the tetrahedrally coordinated metal atoms.

Introduction. X-ray powder diffraction analyses of the system $FeCr_{2x}Ga_{2-2x}Se_4$ (Siwert & Lutz, 1987) have revealed a large range of solid solutions ($0.65 < x < 0.8$). Because of the composition of the solid solutions and the site preference of the metals involved, the structure of these novel compounds was suggested to be that of $ZnIn_2S_4$-(III*a*) type. The end-member phase $FeCr_2Se_4$ possesses a defect NiAs structure with all metal ions in an octahedral environment contrary to $FeGa_2Se_4$, the other end-member phase, where all metal ions are tetrahedrally coordinated (defect zinc-blende type). Therefore, samples of composition $FeCrGaSe_4$ should exhibit a tetrahedral coordination of Fe and Ga and an octahedral coordination of Cr. This cation distribution should be proved by an X-ray single-crystal measurement.

Experimental. Single crystals of $FeCr_{0.8}Ga_{1.2}Se_4$ were grown by recrystallization of powdery material at 1073 K for two weeks using $AlCl_3$ as mineralization agent (Stingl, 1991). The composition of the crystal obtained differs from that of the starting material. A plate-like crystal 0.2 × 0.2 × 0.02 mm was transferred to an Enraf–Nonius CAD-4 diffractometer. Graphite-monochromated Mo *Kα* radiation was used. Unit-cell parameters were obtained from least-squares treatment of 25 reflections ($16.9 \leq 2\theta \leq 34.9°$). The intensity data of 1433 reflections ($2\theta \leq 70°$; ω–2θ scan; $0 \leq h \leq 6$, $0 \leq k \leq 6$, $0 \leq l \leq 60$) were corrected for Lorentz and polarization effects with the Enraf–Nonius *SDP* (B. A. Frenz & Associates, Inc., 1982). Of the 330 unique reflections ($R_{\text{int}} = 0.036$), 65 with $I \leq 3\sigma_I$ (σ_I from counting statistics) were considered unobserved. Empirical absorption corrections were applied using nine reflections in the 2θ range $24.8 \leq 2\theta \leq 58.8°$. The minimum and maximum transmission values were 20.0 and 99.5%. 030, 220, $\bar{3}00$ were chosen as standard reflections in order to control intensity variations. The variations in intensity throughout the data collection were less than 1%. The structure was refined by full-maxtrix least-squares techniques including the positional and anisotropic thermal parameters, the extinction coefficient, and the scale factor ($Np = 13$), using scattering factors for neutral atoms (*International Tables for X-ray Crystallography*, 1974, Vol. IV) including the terms for anomalous dispersion. Initial parameters for the atomic positions were taken from a Patterson map based on a $ZnIn_2S_4$-(III*a*) structure type (Razzetti, Lottici & Zanotti, 1984). The final

0108-2701/93/020207-03$06.00