Vanadium-induced color in calcium aluminates: grossite ($CaAl_4O_7$) and hibonite ($CaAl_{12}O_{19}$)

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SUPPLEMENTAL DATA

Table S1. Crystal data and structure refinement details for hibonite.

Temperature	297(2) K
Wavelength	0.71073 Å
Crystal system	hexagonal
Space group	$P6_3/mmc$
Unit cell dimensions	a = 5.5736(1) Å α = 90°
	b = 5.5736(1) Å β = 90°
	c = 21.9563(5) Å γ = 120°
Volume	590.70(3) Å^3
Z	2
Density (calculated)	3.80 kg·m^{-3}
Absorption coefficient	1.787 mm^{-1}
$F_{(000)}$	662.1
Crystal size	0.10 x 0.39 x 0.70 mm
θ-range for data collection	1.86 to 50.48°
Index ranges	$-12 \le h \le 10$, $-12 \le k \le 12$, $-47 \le l \le 47$
Reflections collected	24170
Independent reflections	1276 [$R_{(int)}$ = 0.0688]
Completeness to θ = 50.48°	99.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1276 / 0 / 49
Goodness-of-fit on F^2	1.133
Final R indices [I>2σ(I)]	R1 = 0.0293, wR2 = 0.0721
R indices (all data)	R1 = 0.0377, wR2 = 0.0791
Extinction coefficient	0.032(2)
Largest diff. peak and hole	0.589 and -1.554 e$^-$ Å^{-3}

Table S2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for hibonite U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Site	s.o.f.	*x*	*y*	*z*	U_{eq}
Ca	1Ca	2/3	1/3	1/4	0.0169(1)
*M*1	0.99(5)Al/0.01(5)Mg	0	0	0	0.0042(2)
*M*2	0.473(5)Al/0.027(4)V	0	0	0.74140(5)	0.0092(3)
*M*3	0.94(4)Al/0.06(4)Mg	1/3	2/3	0.02808(2)	0.0042(1)
*M*4	0.897(5)Al/0.103(5)V	2/3	1/3	-0.19096(2)	0.0045(1)
*M*5	0.990(4)Al/0.010(4)V	0.16862(3)	0.33724(5)	-0.10874(1)	0.0045(1)
O1	1 O	0	0	0.85128(4)	0.0054(1)
O2	1 O	1/3	2/3	-0.05453(4)	0.0058(1)
O3	1 O	-0.18053(9)	0.18053(9)	3/4	0.0077(1)
O4	1 O	0.15518(6)	0.31037(12)	0.05196(3)	0.0055(1)
O5	1 O	0.50363(6)	0.49637(6)	0.35107(3)	0.0060(1)

Table S3. Anisotropic displacement parameters (Å^2) for hibonite.

Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca	0.01687(14)	0.01687(14)	0.0168(2)	0.000	0.000	0.00844(7)
*M*1	0.0047(2)	0.0047(2)	0.0032(2)	0.000	0.000	0.00237(10)
*M*2	0.0052(2)	0.0052(2)	0.0171(8)	0.000	0.000	0.00260(12)
*M*3	0.00442(15)	0.00442(15)	0.00362(18)	0.000	0.000	0.00221(7)
*M*4	0.00518(13)	0.00518(13)	0.00312(15)	0.000	0.000	0.00259(6)
*M*5	0.00498(10)	0.00464(11)	0.00363(11)	0.00027(6)	0.00014(3)	0.00232(6)
O1	0.00521(19)	0.00521(19)	0.0058(3)	0.000	0.000	0.00261(9)
O2	0.00643(19)	0.00643(19)	0.0046(3)	0.000	0.000	0.00322(10)
O3	0.0103(2)	0.0103(2)	0.0053(2)	0.000	0.000	0.0070(3)
O4	0.00648(14)	0.00578(18)	0.00414(16)	-0.00012(13)	-0.00006(6)	0.00289(9)
O5	0.00587(14)	0.00587(14)	0.00530(17)	0.00096(7)	-0.00094(6)	0.00224(15)

Table S4. Bonds (Å) and geometrical parameters of hibonite.

*M*1-O4 ×6	1.8830(6)	*M*3-O4 ×3	1.7980(6)	*M*5-O1	1.8494(5)
<*M*1-O>	1.8830	*M*3-O2	1.8138(11)	*M*5-O2	1.9862(6)
V (Å^3)	8.87	<*M*3-O>	1.8019	*M*5-O4 ×2	2.0025(4)
OQE	1.0025	*V* (Å^3)	3.00	*M*5-O5 ×2	1.8116(4)
OAV (°^{2})	9.169	TQE	1.0018	<*M*5-O>	1.9106
		TAV (°^{2})	7.241	*V* (Å^3)	9.16
				OQE	1.0122
				OAV (°^{2})	35.87
*M*2-O3 ×3	1.7530(9)	*M*4-O3 ×3	1.9637(7)	Ca-O3 ×6	2.7900(1)
*M*2-O1	2.035(2)	*M*4-O5 ×3	1.8853(6)	Ca-O5 ×6	2.7205(6)
*M*2-O1	2.413(2)	<*M*4-O>	1.9245	<Ca-O>	2.7553
<*M*2-O>	1.9415	*V* (Å^3)	9.35	*V* (Å^3)	48.74
V (Å^3)	5.85	OQE	1.0115		
		OAV (°^{2})	39.128		

TQE = Tetrahedral Quadratic Elongation; TAV = Tetrahedral Angle Variance;
OQE = Octahedral Quadratic Elongation; OAV = Octahedral Angle Variance
(Robinson et al. 1971).

Table S5. Crystal data and structure refinement details for grossite.

Temperature	298(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	*C*2/*c*	
Unit cell dimensions	*a* = 12.8840(2) Å	α = 90°
	b = 8.88820(10) Å	β = 106.935(1)°
	c = 5.44130(10) Å	γ = 90°
Volume	596.093(16) Å^3	
Z	1	
Density (calculated)	2.895 kg·m^{-3}	
Absorption coefficient	1.632 mm^{-1}	
$F_{(000)}$	511	
Crystal size	0.29 x 0.35 x 0.45 mm	
θ-range for data collection	3.31 to 50.96°	
Index ranges	-28 ≤ *h* ≤ 28, -19 ≤ *k* ≤ 19, -8 ≤ *l* ≤ 11	
Reflections collected	13241	
Independent reflections	3212 [$R_{(int)}$ = 0.0370]	
Completeness to θ = 50.96°	98.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3212 / 0 / 59	
Goodness-of-fit on F^2	1.101	
Final R indices [I>2σ(I)]	R1 = 0.0253, wR2 = 0.0595	
R indices (all data)	R1 = 0.0279, wR2 = 0.0609	
Extinction coefficient	0.0397(15)	
Largest diff. peak and hole	0.912 and -0.828 e$^-$ Å^{-3}	

Table S6. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for grossite U_{eq} is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Site	s.o.f.	*x*	*y*	*z*	U_{eq}
Ca	1 Ca	0	0.80989(2)	¼	0.00783(3)
*T*1	0.997(2) Al	0.16411(2)	0.08659(2)	0.30304(3)	0.00522(4)
*T*2	1.000(2) Al	0.11954(2)	0.44068(2)	0.23950(3)	0.00604(4)
O1	1 O	0	0.53188(7)	¼	0.01022(8)
O2	1 O	0.11526(3)	0.05116(5)	0.56492(7)	0.00830(6)
O3	1 O	0.11871(3)	0.25492(5)	0.14853(7)	0.00834(6)
O4	1 O	0.19237(3)	0.44354(5)	0.57898(7)	0.00749(5)

Table S7. Anisotropic displacement parameters (Å^2) for grossite.

Site	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ca	0.00789(5)	0.00846(5)	0.00659(5)	0.000	0.00123(3)	0.000
*T*1	0.00568(6)	0.00489(6)	0.00489(6)	0.00019(4)	0.00120(4)	0.00045(4)
*T*2	0.00585(6)	0.00477(6)	0.00810(6)	-0.00047(4)	0.00298(4)	-0.00021(4)
O1	0.00709(16)	0.00692(17)	0.0180(2)	0.000	0.00581(15)	0.000
O2	0.00948(12)	0.00880(13)	0.00748(11)	0.00281(9)	0.00385(9)	0.00228(10)
O3	0.01125(13)	0.00491(11)	0.00738(10)	0.00045(9)	0.00039(9)	0.00113(10)
O4	0.00588(10)	0.00948(13)	0.00650(10)	-0.00105(9)	0.00100(8)	0.00143(10)

Table S8. Bonds (Å) and geometrical parameters of grossite.

*T*1-O4	1.7920(4)	*T*2-O4	1.8121(4)	Ca-O2 ×2	2.8736(5)
*T*1-O3	1.7323(4)	*T*2-O4	1.7833(4)	Ca-O2 ×2	2.3699(4)
*T*1-O2	1.7459(4)	*T*2-O3	1.7228(4)	Ca-O3 ×2	2.3327(4)
*T*1-O2	1.7603(4)	*T*2-O1	1.7560(3)	Ca-O1	2.4710(6)
<*T*1-O>	1.7577	<*T*2-O>	1.7685	<Ca-O>	2.5176
V (Å^3)	2.76	*V* (Å^3)	2.78	*V* (Å^3)	21.02
TQE	1.0077	TQE	1.0137		
TAV (°^{2})	30.435	TAV (°^{2})	54.712		

TQE = Tetrahedral Quadratic Elongation; TAV = Tetrahedral Angle Variance (Robinson et al. 1971).

References

Robinson, K., Gibbs, G.V., and Ribbe, P.H. (1971) Quadratic elongation: a quantitative measure of distortion in coordination polyhedra. Science, 172, 567–570.