Supplementary Material

The incommensurate structure of $Ca_2Al_2O_5$ at high temperatures – structure investigations and Raman spectroscopy

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A high-temperature X-ray diffraction study revealed that brownmillerite-type $Ca_2Al_2O_5$ transforms to an incommensurately modulated structure at elevated temperatures. Single crystals of $Ca_2Al_2O_5$ were synthesised in an end-loaded piston cylinder press at 2.5 GPa and 1273K. The diffraction pattern observed at 1090(10) K by *in situ* single crystal diffraction experiments can be indexed by an *I*-centred orthorhombic cell: a = 5.2699(5), b = 14.698(1), c = 5.4196(5) Å with a modulation wave vector of $\mathbf{q} = 0.595(1)\mathbf{c}^*$. A (3+1)-dimensional model in superspace group *Imma(00γ)s00* was used to refine the modulated structure. The structure is assembled from two building units: (1) layers of corner-sharing $[AlO_6]$-octahedra, stacked along b alternate with (2) layers of *zweier* single chains of $[AlO_4]$-tetrahedra running along *a.* The modulated structure arises from an aperiodic sequence of two different configurations of the chains within the tetrahedral layers. The modulated high-temperature phase of $Ca_2Al_2O_5$ is isotypic to the modulated high-temperature modification of $Ca_2Fe_2O_5$. A large hysteresis was found in the phase transition temperature. On heating, the transition occurs at about 1075(10) K, on cooling satellite reflections can be observed down to 975(10) K. The characterisation of $Ca_2Al_2O_5$ is completed by Raman spectroscopy, including a partly interpretation of the spectra.

Table 1 Atomic coordinates and equivalent isotropic displacement factors (Å^2)

Atom	*x*	*y*	*z*	*U(eq)*
Al1	0	0	0.5	0.0267(4)
Al2	0.9527(3)	0.25	0.5744(3)	0.0224(4)
Ca1	0	0.10837(5)	0.02219(13)	0.0276(2)
O1	0.75	0.00922(14)	0.75	0.0224(6)
O2	0	0.14308(17)	0.4457(6)	0.0325(8)
O3	0.3830(6)	0.25	0.6372(8)	0.0274(11)

Table 2 Anisotropic displacement parameters (Å^2).

Atoms	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Al1	0.0159(6)	0.0471(9)	0.0173(7)	0	0	-0.0008(5)
Al2	0.0278(7)	0.0191(7)	0.0204(7)	0	0.0015(5)	0
Ca1	0.0325(4)	0.0230(4)	0.0273(4)	0	0	0.0010(2)
O1	0.0185(9)	0.0286(10)	0.0201(11)	0	0.0031(7)	0
O2	0.0379(14)	0.0262(13)	0.0333(14)	0	0	-0.0081(10)
O3	0.0252(16)	0.0299(19)	0.0271(21)	0	-0.0045(13)	0

Table 3 Selected bonding angles, including averages (ave) and extrema caused by the modulation

Atoms	ave [°]	min [°]	max [°]	symmetry codes
Al1-O1				-1+x,y,z
O1-Al1-O1	179.61(10)	179.41(11)	180	1-x,-y,1-z
O1-Al1-O1	88.11(13)	88.11(15)	88.11(11)	1-x,y,z
O1-Al1-O1	91.90(14)	91.77(14)	92.01(14)	-1+x,-y,1-z
O1-Al1-O2	91.69(13)	90.34(11)	92.91(11)	x,y,z,
O1-Al1-O2	88.44(13)	87.45(14)	89.30(14)	-x,-y,1-z
Al1-O1				1-x,-y,1-z
O1-Al1-O1	91.88(13)	91.77(13)	92.01(14)	1-x,y,z
O1-Al1-O1	88.11(12)	88.11(15)	88.11(10)	-1+x,-y,1-z
O1-Al1-O2	88.36(13)	87.44(15)	89.30(15)	x,y,z,
O1-Al1-O2	91.51(13)	90.33(11)	92.92(11)	-x,-y,1-z
Al1-O1				1-x,y,z
O1-Al1-O1	179.60(9)	179.41(13)	180	-1+x,-y,1-z
O1-Al1-O2	91.55(13)	90.34(11)	92.91(11)	x,y,z,
O1-Al1-O2	88.31(13)	87.45(15)	89.30(15)	-x,-y,1-z
Al1-O1				-1+x,-y,1-z
O1-Al1-O2	88.39(13)	87.44(15)	89.30(14)	x,y,z,
O1-Al1-O2	91.74(13)	90.33(11)	92.92(11)	-x,-y,1-z
Al1-O2				x,y,z,
O2-Al1-O2	178.60(16)	177.93(18)	180	-x,-y,1-z
Al2-O2				1+x,y,z
O2-Al2-O2	128.72(17)	128.10(16)	129.25(16)	1+x,1/2-y,z
O2-Al2-O3	105.70(12)	105.21(12)	106.13(12)	3/2-x,1/2-y,3/2-z
O2-Al2-O3	103.69(14)	102.93(15)	104.54(15)	1-x,y,z
Al2-O2				1+x,1/2-y,z
O2-Al2-O3	105.70(12)	105.21(12)	106.13(12)	3/2-x,1/2-y,3/2-z
O2-Al2-O3	103.69(14)	102.93(15)	104.56(15)	1-x,y,z
Al2-O3				3/2-x,1/2-y,3/2-z
O3-Al2-O3	108.11(19)	108.11(19)	108.11(19)	1-x,y,z