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Supporting information for article:

Ordered vacancy distribution in 2/1 mullite: a superspace model

Paul Benjamin Klar, Noelia de la Pinta, Gabriel Alejandro Lopez, Iñigo Etxebarria, Tomasz Breczewski and Gotzon Madariaga

Supporting information

S1. Constraints for the refinement of the superspace model

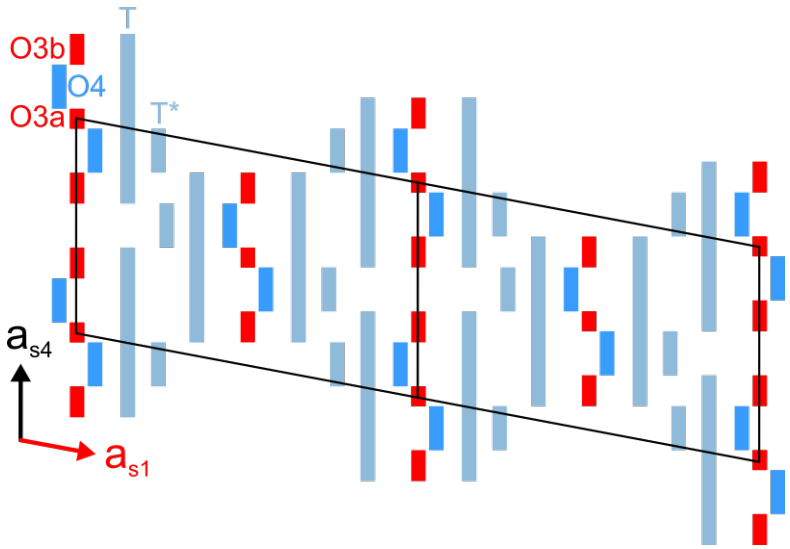


Figure S1 $a_{s1}a_{s4}$ projection of two adjacent unit cells in superspace. Only atomic domains that are shorter than unity (Δ < 1) are shown. The displacive modulation of the *T* site is neglected. Note that the thickness of the atomic domains has no physical meaning.

Several atomic domains must be in phase in order to avoid dangling bonds or missing atoms in the polyhedra, which becomes visible by inspection of the projection of adjacent superspace unit cells (Fig. S1). The set of necessary constraints is presented in Table S1 and in the following is derived for the *T* site from the requirement that x_{s4} of adjacent *T* sites must be located at the same *t* section. The two sites are related by the following symmetry operation:

$$\left\{2_{001}, -1 \mid 0,0,0, -\frac{1}{2}\right\} : \boldsymbol{x} \Rightarrow \boldsymbol{x}'$$

$$\begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 1 & -1 \end{pmatrix} \begin{pmatrix} x_{s1} \\ x_{s2} \\ x_{s3} \\ x_{s4} \end{pmatrix} - \begin{pmatrix} 0 \\ 0 \\ 0 \\ \frac{1}{2} \end{pmatrix} = \begin{pmatrix} -x_{s1} \\ -x_{s2} \\ x_{s3} \\ x_{s3} - x_{s4} - \frac{1}{2} \end{pmatrix}$$

Equalizing their position in *t* space, the following constraint results:

$$t = t'$$

$$x_{s4} - \boldsymbol{q} \cdot \begin{pmatrix} x_{s1} \\ x_{s2} \\ \frac{1}{2} \end{pmatrix} = \left(x_{s3} - x_{s4} - \frac{1}{2}\right) - \boldsymbol{q} \cdot \begin{pmatrix} -x_{s1} \\ -x_{s2} \\ \frac{1}{2} \end{pmatrix}$$

$$x_{s4} = \alpha x_{s1}$$

Table S1 Constraints for the Crenel parameters and site occupation factor (SOF) used for the refinement of the superspace model

Site label	Constraint on Δ	Constraint on x_{s4}	Constraint on SOF
Al2	$1-\Delta^{Al3}$	αx_{s1}^{Al2}	$1/(4\Delta^{Al2})$
Si2	$1-\Delta^{Al3}$	αx_{s1}^{Al2}	$0.5-1/(4\Delta^{Al2})$
Al3	-	$\alpha x_{s1}^{Al3}+\frac{1}{2}$	0.5
O3a	$\alpha-\Delta^{O4}$	0	0.25
O3b	$(1-3\Delta^{O4}-\Delta^{O3a})/2$	$(1-\Delta^{O3b}+\Delta^{O4})/2$	0.5
O4	Δ^{Al3}	$\alpha x_{s1}^{O4}+\frac{1}{2}$	0.5

In fact the same constraints can be derived from the symmetry relationships between the *T** or O4 sites adjacent to a vacancy. The *T* and *T** of the asymmetric unit are never occupied together and therefore the atomic domains exhibit a relative phase shift of ½ in *t* space. The other Crenel parameters are then derived from the requirement that *T** and the bonded O4 site must be occupied in phase. The *T* sites must be either bonded to O3 or O4, and from that the parameters for the atomic domains of O3a and O3b can be derived (*cf.* Fig. S1).

S2. Commensurate approximation of 2/1 mullite

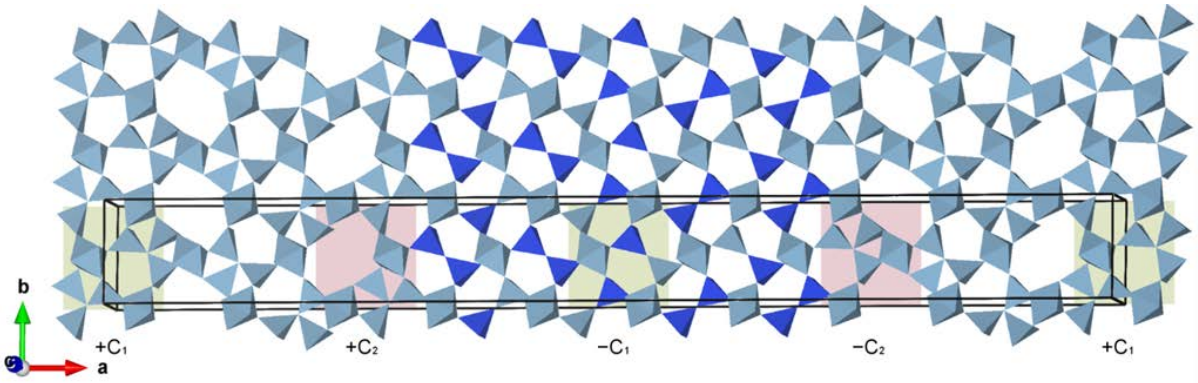


Figure S2 Idealized model for 2/1 mullite in space group $Bb2_1m$ with Al/Si and vacancy ordering derived from the superspace model. Al polyhedra in light blue, Si tetrahedra in dark blue. Only tetrahedra of cations with z = 0 are shown with the interconnecting octahedra. The supercell was generated with *Jana2006* at t = 0.275 with a from 0.75 to 10.75, b from 0 to 1 and c from 0.5 to 2.5, which corresponds to an origin shift of (¾, 0, ½). The colored squares indicate the position of the component structures (*cf.* §S3) of $+C_{1o}$, $+C_{2o}$, $-C_{1o}$ and $-C_{2o}$ with different origin shifts of (0.25, 0, 0), (2.75, 0, 0), (5.25, 0, 0) and (7.75, 0, 0), respectively.

The commensurate approximation in a 10 × 1 × 2 supercell is described in space group $Bb2_1m$. For this structure the constraints scheme described in §S1 is applied but the parameter Δ^{Al3} is set to 0.2 instead of being refined. The Al/Si ordering scheme from §3.3 is also included. The resulting structure is considered to represent the idealized, completely ordered crystal structure of 2/1 mullite (Fig. S2).

S3. Transformation of modulation components by the superspace group

Table S2 Character table showing how the displacement amplitudes of first order harmonics transform under the operations of the superspace group *Pbam*(α0½)0*ss*.

R-irep label				{1,1|0}	$\{2_{001},-1\|0,0,0,½\}$	$\{2_{010},-1\|½,½,0,½\}$	$\{2_{100},1\|½,½,0,0\}$	{−1,−1|0}	$\{m_{001},1\|0,0,0,½\}$	$\{m_{010},1\|½,½,0,½\}$	$\{m_{100},-1\|½,½,0,0\}$
McConnell & Heine, 1984	*Bilbao Cryst. Server*	Displacement component	Affected sites								
X_8	Z_4^-	$u_{x,\,cos}$ (z = 1/2)	*T*, *T**, O1/4	1	−1	1	−1	−1	1	−1	1
X_7	Z_2^+	$u_{x,\,sin}$ (z = 1/2)	*T*, *T**, O1/3/4	1	1	−1	−1	1	1	−1	−1
X_2	Z_3^-	$u_{y,\,cos}$ (z = 1/2)	*T*, *T**, O1/4	1	−1	−1	1	−1	1	1	−1
X_1	Z_1^+	$u_{y,\,sin}$ (z = 1/2)	*T*, *T**, O1/3/4	1	1	1	1	1	1	1	1
X_8	Z_4^-	$u_{z,\,cos}$ (z = 0)	O2	1	−1	1	−1	−1	1	−1	1
X_7	Z_2^+	$u_{z,\,sin}$ (z = 0)	Al1, O2	1	1	−1	−1	1	1	−1	−1

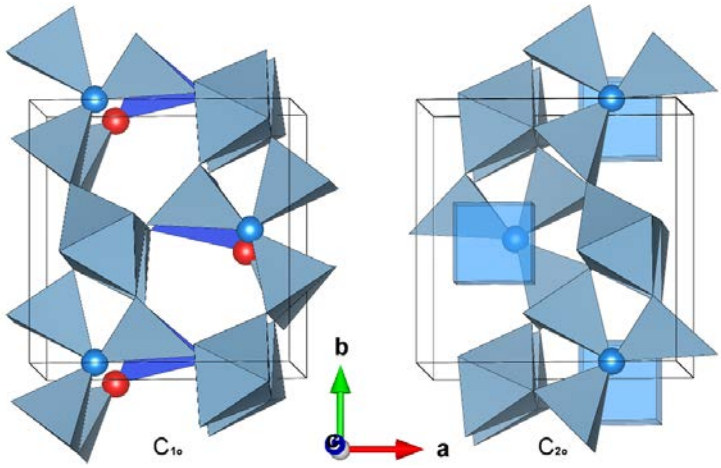
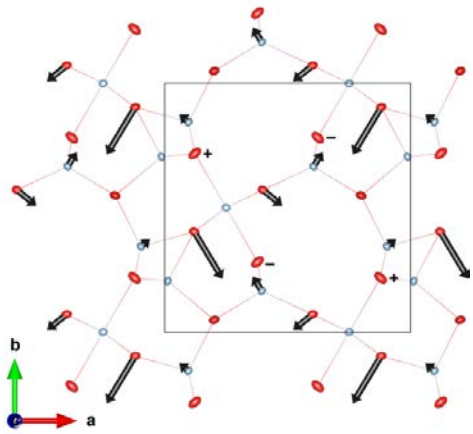
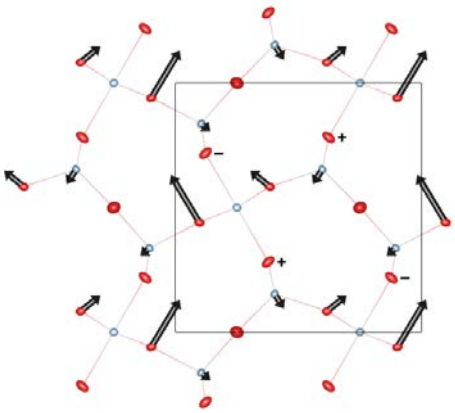
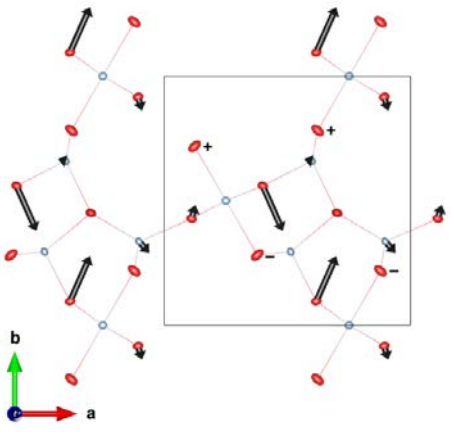
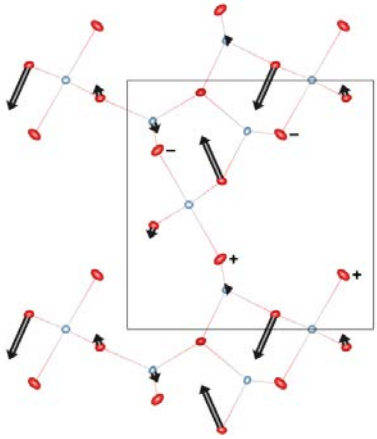


Figure S3 Component structures C_{1o} and C_{2o} (t = 0.275) as present in Fig. S2. Only O3 (red) and O4 (blue) atoms shown. Al/Si ordering included. Vacancies are represented by transparent boxes.

For the comparison with the model developed by Angel *et al.* (1987, 1991) it was analyzed how the superspace group *Pbam*(α0½)0*ss* transforms the displacement amplitudes, which is summarized in Table S2 with the labels of the irreducible representations (*R*-irep) used by McConnell & Heine

(1984) and the *Bilbao Crystallographic Server*. Figure S3 and Table S3 show the component structures derived from the ordered superspace model (SSM), which can be compared with Fig. 9 in the work of Angel & Prewitt (1987). The position of C_{1o} and C_{2o} is also indicated in the commensurate approximation in Figure S2.

Table S3 Relevant information on the orthorhombic component structures derived from the ordered SSM. The *R*-ireps are given relative to an average cell setting as chosen by McConnell & Heine (1984) with an additional origin shift of (¼, 0, 0). Two layers are plotted for each component structure where atoms are represented by their anisotropic displacement ellipsoid (50% probability level). Displacements within the *xy* plane are indicated by black arrows with a length that is proportional to the displacement amplitude. Displacement directions of O2 are indicated with + (out of plane) and − (into the plane).

	$0.2 < z \leq 0.5$	$0.7 < z \leq 1$
C_{1o} $Pb2_1m$ $t = 0.275$ X_1, X_8 (Z^{1+}, Z^{4-})		
C_{2o} $Pn2_1m$ $t = 0.025$ X_2, X_7 (Z^{2+}, Z^{3-})		

S4. Comparison with ADPs and occupancy parameters of Birkenstock *et al.* (2015)

The following set of graphics (Fig. S4) shows that the maximum occupancy of the disordered SSM coincides with the center of the atomic domain of the ordered SSM. Moreover, the ADP modulation and the occupancy modulation of the disordered SSM are strongly correlated with a phase shift of about ½. In the case of O3 the occupancy minimum coincides with the center of the vacancy at t = ¼.

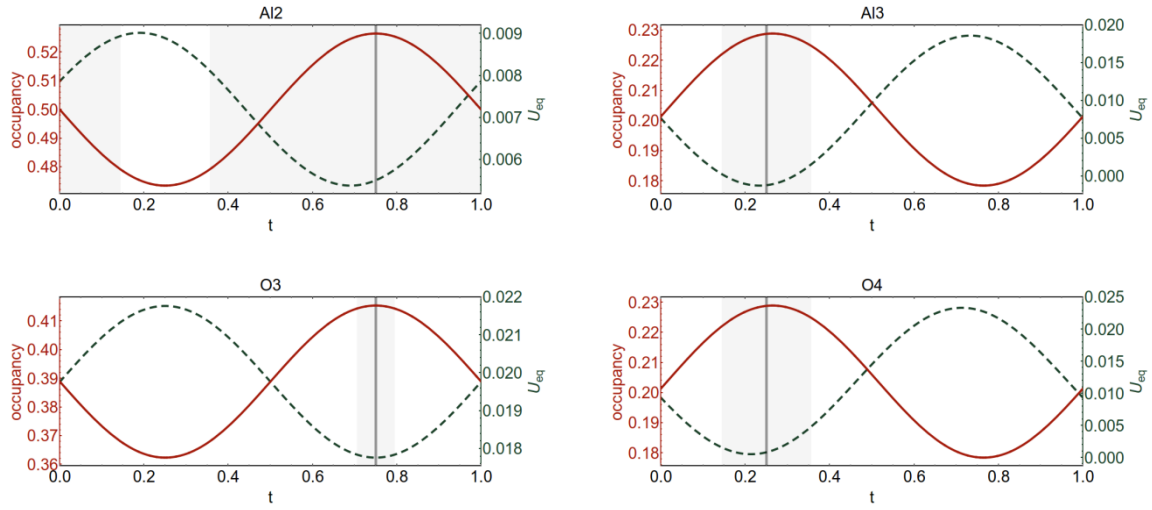


Figure S4 t plots for Al2, Al3, O3 and O4 that show the phase relationship between the occupancy modulation (solid curve) and the ADP modulation represented by the equivalent isotropic displacement parameter Ueq (dashed durve) that is calculated from the ADP and ADP modulation parameters based on the model by Birkenstock et al. (2015). The t value of the center of each atomic domain of the ordered SSM (§3.3) is indicated as vertical line and the t range where the site is occupied is shaded in gray. Only the Crenel parameters of O3a were used for the plot of O3. Different scales for Ueq were used in order to emphasize the phase relationships.