DFT of incommensurate, disordered structures: ordering phenomena in mullite

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The crystal structure of mullite $Al_{4+2x}Si_{2-2x}O_{10-x}$ was tackled many times with different approaches since the 1970s. Diffuse scattering and satellite reflections with a modulation wave vector **q** that depends on the vacancy concentration *x* require a comprehensive model. Recently, the superspace approach was used to reveal the underlying pattern of the vacancy distribution, presenting either a highly disordered vacancy distribution [1] or a fully ordered vacancy distribution [2]. However, a clear Al/Si ordering pattern could not be established experimentally. The objective of this study is to compare ordered and disordered structures of mullite and to define the Al/Si ordering pattern by means of synchrotron single crystal X-ray diffraction and density functional theory (DFT). DFT calculations on modulated structures are rare and this study suggests, that superspace and DFT are a powerful combination for the investigation of ordered and disordered structures with incommensurate modulations.

Synchrotron single crystal X-ray diffraction measurements with a commercial mullite sample ($x \approx 0.4$) showed 1st order satellite reflections and weak 2nd order satellites. The refinement in superspace group *Pbam*(α0½)0*ss* results in a model with a harmonic occupational modulation and displacive modulation. The amplitude of the modulation function varies for different samples, which was interpreted in terms of different degrees of ordering [3]. The distribution of Si on tetrahedral sites could not be refined.

A commensurate approximation of the refined model is not suitable for DFT calculations as fully occupied atom sites are required. However, an ordered model can be developed in superspace by replacing the harmonic modulation functions of the refined model by block wave functions. The vacancy distribution is then described by an alternating pattern of vacancy blocks and vacancy-free blocks. Different Si distribution patterns were combined with the model for DFT calculations of a commensurate approximation. The relaxed model with the lowest energy is considered to define the ideal Al/Si ordering pattern (Fig. 1), which was used to correct the initial superspace model with block wave functions (Fig. 2).

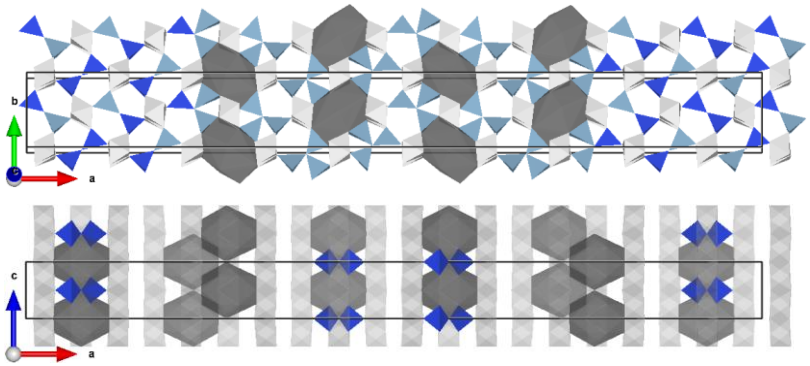

Figure 1. Ordered model (10 × 1 × 2 supercell) of mullite with vacancy and Al/Si ordering. Vacancies plotted as dark polyhedra. Bottom view along **b** omits tetrahedra network except Si-Si diclusters.

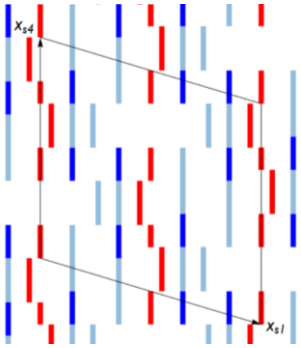

Figure 2. Projection of superspace model. Atoms of octahedra omitted.

The constraints that determine the vacancy distribution depend on **q** and the vacancy concentration *x*, which allows to establish a unified superspace model where the modulation functions also depend on the chemical composition. The Al/Si ordering was determined by relaxing the structures with DFT

calculations for several compositions, and all resulted in almost the same superspace models. Two unified models are necessary to describe the solid solution range with $x \leq 1/2$. For $1/3 \leq x \leq 1/2$ the model of Figure 2 is valid with a varying length of the vacancy blocks and vacancy-free blocks. For $x < 1/3$ the vacancy ordering pattern at the block borders changes, which causes a rotation of certain Al-Si diclusters. Independent of that, Si-Si diclusters (Si_2O_7 units) are sandwiched between two vacancies as shown in Figure 1 for the whole solid solution range. Currently, mullite is classified as a nesosilicate mineral, but this study suggests that mullite should be classified as sorosilicate.

Structure factor calculations of this fully ordered model indicate, that 5^{th} order satellite reflections must be present in reciprocal space, but with a few exceptions [4] usually only low order satellites are observed and mullite is disordered. The displacive modulation in the refined model with harmonic modulation functions leads to a modulation of the volumes of the tetrahedra, which must be consistent with the modulation of the Al/Si occupancy. Harmonic occupational modulation functions of Al and Si were calculated using the DFT model as source of reference volumes of pure SiO_4 and AlO_4 tetrahedra. If triclusters are preferably of the type Al-Al-Al and the Löwenstein rule holds, then the Al/Si ordering can be expressed as the probability that Al-Si diclusters, Si-Si diclusters, Al-Al-Al triclusters and Si-Al-Al triclusters are present.

The ordered model (DFT) describes precisely where Al, Si and vacancies are present, whereas the refined model is based on probabilities. However, these probabilities are highest at physical space sections where the respective atomic domain (cf. Figure 2) is at or close to the center of the block wave function (Tab. 1). Small differences are probably related to the disorder in the structure. Nevertheless, the comparison of the DFT model and disordered model results in a remarkable agreement, i.e. in superspace the compared models are very similar and show the same ordering patterns, but to different extents.

Table 1. Comparison of refined model and DFT model. Values correspond to the physical space section *t* with the highest probability and the center of the block wave function, respectively.

cluster type	vacancy	Si-Si	Si-Al	Al-Si	Al-Al-Al*	Al*-Al-Al	Si-Al-Al	Al-Al-Si
t of highest probability (refined model)	0.25	0.75	0.13	0.37	0.60	0.90	0.63	0.87
t of center of block wave function (DFT model)	0.25	0.75	0.075	0.425	0.575	0.925	0.685	0.825

In the case of mullite, the disordered model represents a less ordered structure of the ordered model. The ordered, commensurate structure can therefore be used for DFT calculations to study the disordered, incommensurate structure of mullite. The Al/Si ordering and its relationship with the distribution of vacancies could be determined and extended to a broad range of compositions. This approach allows to investigate the modulation functions of other complex materials on a fundamental level by means of DFT.

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