

# Atomistic simulations on mullite $\text{Al}_2(\text{Al}_{2+2x}\text{Si}_{2-2x})\text{O}_{10-x}$ in a variable range of composition

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## Abstract

Two structural models representative of the average structure of mullite  $\text{Al}_2(\text{Al}_{2+2x}\text{Si}_{2-2x})\text{O}_{10-x}$  have been developed. The models have been used to perform a quantum mechanical (*ab initio*) calculation with the Castep program (Accelrys®) in order to evaluate the internal energy of mullite with a compositional range of  $x=0.25\text{--}0.492$ . In addition, the real sillimanite structure ( $x=0$ ) has been compared with the computational results. © 2007 Elsevier Ltd. All rights reserved.

**Keywords:** Mullite; Structural model

## 1. Introduction

Mullite is the name of a mineral which has been commonly described to exist in a solid solution series of composition  $\text{Al}_2(\text{Al}_{2+2x}\text{Si}_{2-2x})\text{O}_{10-x}$ .<sup>a</sup>

This aluminosilicate, to which is usually assigned space group *Pbam* (55), presents an incommensurate modulated structure which depends on the compositional variable  $x$ .

According to many authors<sup>1–5</sup> the incommensurate structure of mullite is described with models which comprise partial occupancies of mutually excluding positions with oxygen vacancies distributed among Oc and Oc\* sites. Of course not all the atomic sites can be simultaneously occupied because of steric and hindrance reasons. All the Oc and Oc\* almost overlapping sites are mutual excluding like the nearby T and T\* sites. The average atomic occupancy of aluminium, silicon and oxygen are given in the second column of Table 1 according to the distribution described by Angel and Prewitt.<sup>3</sup> Actually the distribution of Al and Si between the T and T\* sites in mullite is a tricky question.<sup>2</sup>

The aim of our study was to build simplified structural models to use in a computational simulation to evaluate the internal energy of mullite as a function of its average composition.

As a borderline composition of mullite we also considered the no vacancy case ( $x=0$ ) even if this composition actually does

not belong to mullite anymore but to sillimanite (whose structure is not incommensurate and well known).

## 2. The models

Despite the great versatility of the most common softwares designed for quantum mechanical simulations, it has not been possible so far to treat two mutually excluding atomic positions. The partial occupancy on the two positions alone is not satisfactory, because this does not exclude from the calculations the possibility of the simultaneous occupation of the two positions. Due to this limitation it is very difficult to simulate an incommensurate crystal structure like mullite. There are mainly two ways to face this problem. First, to consider a very large computational unit (supercell); second, to build a simplified supercell whose atomic sites have the same average statistical occupancy as the incommensurate structure. The former solution is very expensive from a computational point of view because, in case of quantum mechanical simulations, the calculation time is proportional to the cube of the number of atoms whereas the accuracy of the model increases with the number of atoms involved. For this reason we have been forced to follow the latter approach, even if potentially less accurate.

Energy optimization on 2:1 mullite with variable atomic positions and two crystallographic unit cells in the computational supercell (without symmetry constraints and s.g. P1) showed that the atoms tend to move in a structure which can be represented by one cell in the computational unit with atoms located and described here below according to two models.

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<sup>a</sup> □<sub>x</sub> is a symbol used to indicate O-vacancies.

Table 1  
Different site occupancies in mullite average structure, model 1 and model 2

Element on site	Average structure <sup>4</sup>	Model 1	Model 2
Al octahedral	1	1	1
Al on T	$\frac{1}{2}$	$\frac{(1+x)}{2}$	$\frac{(1+x)}{2}$
Si on T	$\frac{(1-x)}{2}$	$\frac{(1-x)}{2}$	$\frac{(1-x)}{2}$
Al on T*	$\frac{x}{2}$	$\frac{(1+x)}{2}$	0
Si on T*	0	$\frac{(1-x)}{2}$	0
O on Od	1	1	1
O on Oab	1	1	1
O on Oc	$1 - \frac{3}{2}x$	$1 - x$	$\frac{2-x}{2}$
O on Oc*	$\frac{1}{2}x$	1	0

In the first model, called *model 1* (Fig. 1), mutually excluding T–T\* and Oc–Oc\* positions receive full occupancy by lowering the symmetry from *Pbam* to *Pm* (6) space group. The lowering of the symmetry allows us to assign one Si/Al mixed position to one T\* position and three Si/Al mixed position to three T position/cell. As a consequence three oxygen atoms are placed in Oc (with incomplete occupancy) and one on Oc\* (full occupancy). Calculations with Oc\* site partially occupied yielded a higher

total energy content, therefore we placed vacancies only on Oc sites.

This model resembles somehow the second structure of all the series of possible unit cell contents (where the mullite structure is composed of different assemblages) according to the work of Freimann and Rahman.<sup>7</sup>

The second model, called *model 2* (Fig. 2), satisfies the symmetry requirements of the average mullite structure (*Pbam* space group). This choice shortens the computational time although it forces to neglect Oc\* and T\* sites whose occupancy decreases to zero as the software cannot treat mutually excluding positions. Therefore Si/Al atoms are all located on T positions and oxygen on Oc.

Both these models obey the general mullite composition  $Al_2(Al_{2+2x}Si_{2-2x})O_{10-x}\square_x$  and their site occupancies are shown in Table 1. In case of model 1, we concentrated all the oxygen vacancies on Oc.

### 3. Software used and computational method

Computational results have been obtained by using software programs from Accelrys<sup>®</sup>. *Ab initio* calculations have been performed with the Castep program<sup>8</sup> and graphical displays generated with Materials Studio<sup>®</sup>. Castep is a state of the art quantum mechanics based program which employs the density

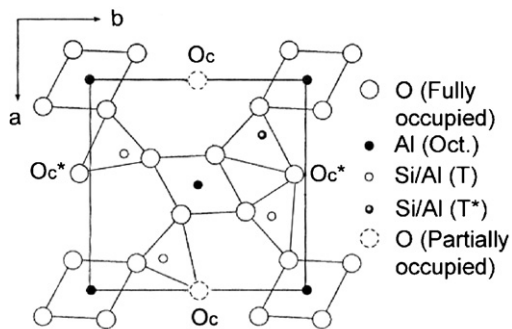


Fig. 1. Model 1: space group *Pm* (6).

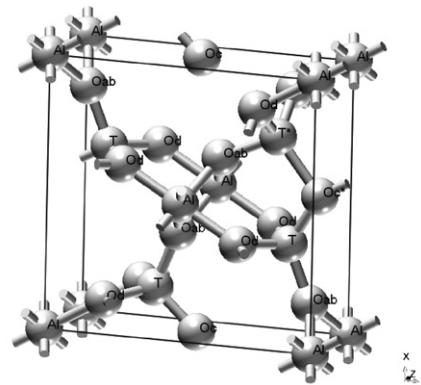


Fig. 2. Model 2: space group *Pbam* (55).

functional theory (DFT) plane-wave pseudopotential method to perform first-principles quantum mechanics calculations and explore the properties of crystals and surfaces in materials.

The Castep approach for dealing with disorder in first principles calculations is the so called *virtual crystal approximation* (VCA): technically this offers the simplest approach, allowing calculations on disordered systems to be carried out at the same cost as calculations on ordered structures. VCA ignores any possible short-range order and assumes that on each potentially disordered site there is a virtual atom which interpolates between the behaviour of the actual components. This approach neglects effects such as local distortions around atoms and cannot be expected to reproduce the finer details of the disordered structures very accurately.

The basic ideas of the workable VCA implementation for DFT methods, in particular for the pseudopotential-based techniques, were set out by Bellaiche and Vanderbilt.<sup>6</sup> The main statement for the implementation of VCA with ultrasoft potentials can be expressed as

$$V_{\text{ext}}(r, r') = \sum_I \sum_{\alpha} w^I V_{ps}^{\alpha}(r - R_{I\alpha}, r' - R_{I\alpha})$$

where Castep generate the total external potential as the sum of the nonlocal potentials of each atomic species,  $\alpha$ , taken with the weights,  $w$ , of the component atoms in the mixture atom. This means that all the key components of the ultrasoft potentials, i.e., the local part,  $V_{\text{loc}}$ , and the  $D$  and  $Q$  matrices, are all weighted according to the site occupancies.

Mixture atoms have been used to simulate the case when one atomic site (T or T\*) is randomly occupied by aluminium or silicon atoms. Atom occupancy has been used to simulate the oxygen vacancies randomly distributed through the Oc sites (we have concentrated all the oxygen vacancies in Oc).

#### 4. Computational work and results

The aim of the computational work was to evaluate the internal energy content of mullite as a function of its average composition. We considered a composition range from  $x = 0.25$  to 0.492 and we associated to every  $x$  the corresponding cell parameters obtained from Ban and Okada data collection.<sup>4</sup> For every mullite composition we built two different primitive cells according to our models and we imposed on them the experimental lattice parameters. Finally we run an energy optimization to evaluate the final cell energy and the residual pressures.

During the energy optimization, no geometry optimization was performed on cells and this means that Castep was not authorized to shift atom positions or to modify the cell parameters. Residual pressure on cells comes from residual forces that try to deform the lattice or change the atomic fractional coordinates in order to minimize energy even more. The residual pressures are very similar in both models; they vary with composition but have the same order of magnitude as the residual pressure on sillimanite (Fig. 3) and this is a hint that we may not be far from reality.

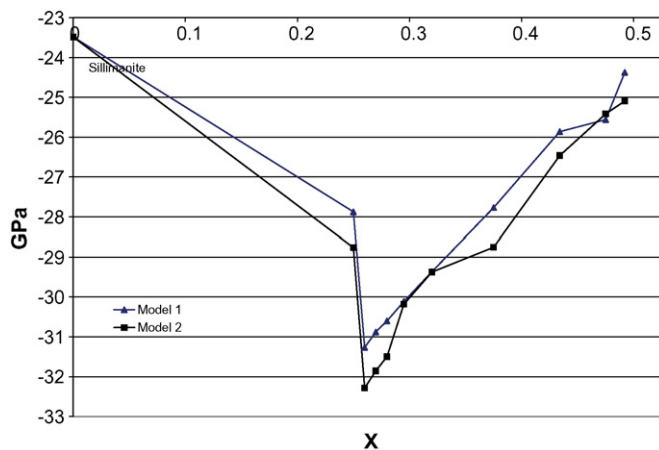


Fig. 3. Residual pressure on cells.<sup>b</sup>

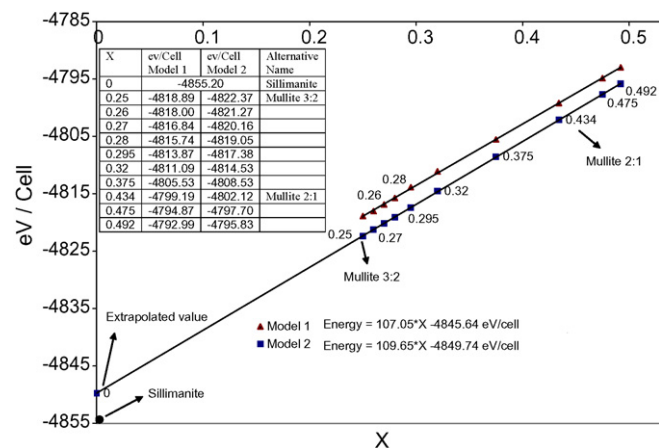


Fig. 4. Mullite internal energy/cell (see footnote b).

It is interesting to notice that if we perform a geometry optimization on one cell built with model 1, Castep enlarges the lattice parameters and shifts all the atomic sites until they occupy exactly the positions of model 2. This means that model 2 represents the model having the lowest energy according to our initial conditions.

In Fig. 4 we report the results of the computational evaluation of energy/cell in mullite as a function of  $x$ .

Despite the choice of the model, the energy values can be perfectly interpolated by a linear function of  $x$  with almost the same slope. The final energy, as expected, is generally lower in model 2 and increases with the number of oxygen vacancies  $x$ . Because of the arbitrariness of the realization of model 1 (as seen before in Section 2) it seems reasonable to infer that we could obtain always the same linear function, with the same slope, for any other model which obeys the initial request of using an ordered structure to simulate the incommensurate structure of mullite. Moreover, if we extrapolate the energy function until  $x = 0$ , we obtain an energy value which is

<sup>b</sup> Since sillimanite's cell is twice the mullite's one, its residual pressure (as its energy) has been divided by 2.

very close to the one obtained simulating the real structure of sillimanite.

## 5. Conclusions

We have developed two crystal models for mullite incommensurate structure, based on a primitive cell whose characteristics allow an atomistic quantum mechanical simulation and an evaluation of the internal energy of the structure along the compositional range  $\text{Al}_2(\text{Al}_{2+2x}\text{Si}_{2-2x})\text{O}_{10-x}\square_x$ . We have demonstrated that model 2, in which only T-positions are occupied has a lower internal energy with respect to model 1, in which T\* and Oc\* are present in the cell. Moreover, we have discovered that, despite the choice of the model, the internal energy of mullite is always a linear function of  $x$  with a slope close to 108 if we express the energy as eV/cell. Even the internal energy of sillimanite, considered as a borderline composition of mullite ( $x=0$ ) confirms the above trend.

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