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Determination and refinement of the crystal structure of M_2SiAlO_5N "B-phase" (M = Y, Er, Yb)

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Abstract

The crystal structure of the compound M_2SiAlO_5N "B-phase" (with M = Y, Yb, Er) is determined by Rietveld analysis of X-ray powder diffraction patterns. The pseudo α-wollastonite derived structure, often proposed in the literature [D.P. Thompson, The crystal chemistry of nitrogen ceramics, Materials Science Forum 47 (1989) 21–42], is used as a model for simulation of an X-ray diffraction pattern. The simulated pattern obtained with this model exhibits several peaks that are not observed on the experimental pattern. Moreover, when refining this model by Rietveld analysis, the final atom co-ordinates are strongly shifted with respect to their initial values and lead to aberrant bond lengths. A new model of the structure of B-phase is proposed: after refinement, the final reliability factors show that this new model is in very good agreement with experiments. According to this new model, the alternative layers of yttrium cations and $(Si,Al)(O,N)_4$ tetrahedra proposed in the pseudo α-wollastonite model is confirmed but the tetrahedra do not form rings as was initially suggested, but instead are randomly linked to each other. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Crystal structure; Refinement; M_2SiAlO_5N "B-phase"

1. Introduction

In the past 20 years, researches carried out on the devitrification of glass compositions in the systems M-Si-Al-O-N (with M = Y, Ln) led to the discovery of several new phases. Few of these are potential glass ceramic formers. One of the most interesting phases discovered is termed the B-phase. It was first obtained in the system Y-Si-Al-O-N. This compound has a range of compositions extending along the line $YSiO_2N$-$YAlO_3$ from 40 to 70 m% $YAlO_3$ [2,3] and is usually referred by its mid-point composition Y_2SiAlO_5N. The B-phase occurs when appropriate glass compositions are heat treated in the temperature range 950–1150°C [4]. Since the phase composition does not fall into the glass-forming region, B-phase is always obtained with residual glass or other crystalline products. Samples containing B-phase as a single crystalline phase are obtained from the composition Y35 Si45 Al20 O83 N17 (equivalent%) following a two stage devitrification heat treatment [5]. More recently it has been shown that B phase can also be obtained by replacing Y with Er or Yb in the same initial glass compositions.

In the literature [1] B-phase is often proposed to be a 2-layer pseudo α-wollastonite modification consisting of alternate layers of yttrium cations and rings of three $(Si,Al)(O,N)_4$ tetrahedra sharing corners (Fig. 1). This model is based on an orthorhombic unit-cell with:

$$a = 1.1487\,\text{nm} \qquad b = 0.6635\,\text{nm} \qquad c = 0.9811\,\text{nm}$$

This model was used as a starting point for the present study.

2. Experimental procedure

2.1. X-ray patterns

The determination and the refinement of the crystal structure were carried out using X-ray powder diffraction and Rietveld analysis. The diffractometer used is a Siemens D5000 with a θ–θ goniometer and the Cu $K_{\alpha1,2}$ radiation. The K_β lines are filtered by diffraction on a mosaic graphite crystal diffracted-beam monochromator.

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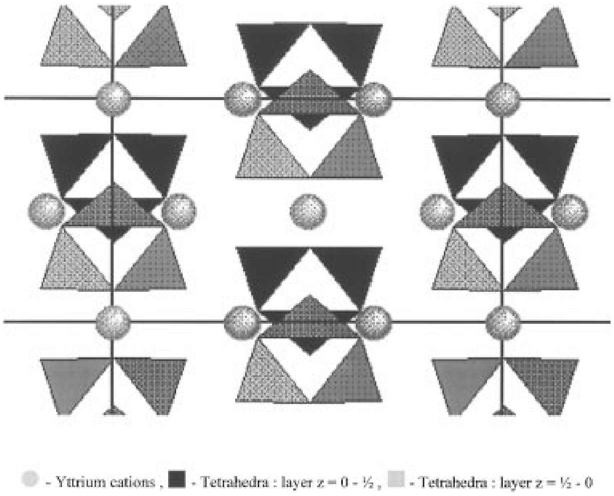

Fig. 1. Initial ring model [1]- model 1 [projection down (001)].

Two X-ray patterns were collected on powder samples of Y_2SiAlO_5N B-phase. One pattern was obtained on the B-phase with addition of α-Al_2O_3 used as a reference for the peak positions. The purpose of this pattern was the determination of accurate unit-cell dimensions. The second pattern was obtained with the B-phase powder alone and was used for the refinement of the crystal structure.

For both patterns, the diffractometer was running with the step scan mode, a step size of 0.02° and the counting time of 40 seconds per step. The scanned angles were 17–100°.

2.2. Rietveld analysis

The Rietveld analysis was carried out using the software "Win–Rietveld" supplied by Siemens. This software allows the simulation of a theoretical X-ray diffraction pattern from an hypothetical model of the structure. It is also possible to refine each parameter introduced in the model. The refinement process uses the Newton–Raphson algorithm to minimise the quantity R:

$$R = \int_i w_i \cdot |y_i - y_{ci}|^2 \qquad w_i = \frac{1}{\sigma_i^2} = \frac{1}{y_{ci}} \approx \frac{1}{y_i} \tag{1}$$

where y_i is the intensity measured on the experimental diffraction pattern at step i and y_{ci} is the theoretical intensity at step i calculated from the model. The weight w_i, assigned to the individual intensities is the reciprocal of the variance σ_i^2 at the ith step and is based on counting statistics.

The quantities used to estimate the agreement between the experimental pattern and the model during the course of refinement are:

$$\text{The profile residual:}\quad R_p = \frac{\int_i |y_i - y_{ci}|}{\int_i |y_i|} \tag{2}$$

$$\text{The weighted profile residual:}\quad R_{wp} = \sqrt{\frac{\int_i w_i \cdot |y_i - y_{ci}|^2}{\int_i w_i \cdot |y_i|^2}} \tag{3}$$

The numerator of R_{wp} is the quantity to be minimised by the Newton–Raphson algorithm. Therefore this factor is statistically more significant than R_p even if the value is higher. The expectation value R_{exp} is the minimum that R_{wp} can obtain during a refinement if only statistical errors are present and all systematic errors have been corrected:

$$R_{exp} = \sqrt{\frac{N - (P - C)}{\int_i w_i \cdot |y_i|^2}} \tag{4}$$

where N is the total number of data points, P is the number of refined parameters and C is the total number of constraints between parameters.

The ratio $S = R_{wp}/R_{exp}$ gives the goodness of fit and should reach 1 when the refinement is complete. R_{exp} being theoretical, in certain cases S can become slightly lower than 1.

3. Structure of $YSiAlO_5N$ "B-phase"

3.1. The wollastonite model (model 1)

According to the data found in the literature (Table 1) an X-ray pattern has been simulated on the basis of the wollastonite model. Before the simulation the lattice parameters were refined and we obtain:

$a = 1.1508$ nm $\qquad b = 0.6644$ nm $\qquad c = 0.9753$ nm

Fig. 2 compares the experimental and calculated X-ray patterns obtained with this model. The simulated pattern exhibits several strong peaks that are not observed on the experimental pattern. To check that the additional peaks observed are not due to inaccurate atom coordinates, these coordinates were refined. During a first step the bond lengths in the tetrahedra were kept to acceptable values. In that condition, it is

Table 1
Initial model of the structure of B-phase [1] [space group: Cmcm (63)]

Site	Site multiplicity	*x*	*y*	*z*
Y(1)	4	0	0	0
Y(2)	8	0.3314	0	0
(Si, Al)(1)	8	0.1454	0.2055	0.25
(Si, Al)(2)	4	0	0.5649	0.25
(O, N) (1)	16	0.1858	0.1577	0.0871
(O, N) (1)	4	0	0.1524	0.25
(O, N) (1)	8	0.1330	0.4445	0.25
(O, N) (1)	8	0	0.6359	0.0871

Table 2
Atom site for model 2 before refinement

Atoms	Co-ordinates			Multiplicity *k*
	x	*y*	*z*	
Y	0	0	0	2
(Si, Al)	1/3	1/3	1/4	2
(O, N)(1)	1/3	2/3	z	4
(O, N)(2)	0	0	1/4	2

Table 3
Atom site for model 2 after refinement (model 2a)

Atom	Co-ordinates			Multiplicity *k*	β
	x	*y*	*z*		
Y	0	0	0	2	2.72
(Si, Al)	1/3	1/3	1/4	2	10.20
(O, N)(1)	1/3	2/3	0.104	4	8.45
(O, N)()	0	0	1/4	2	23.79

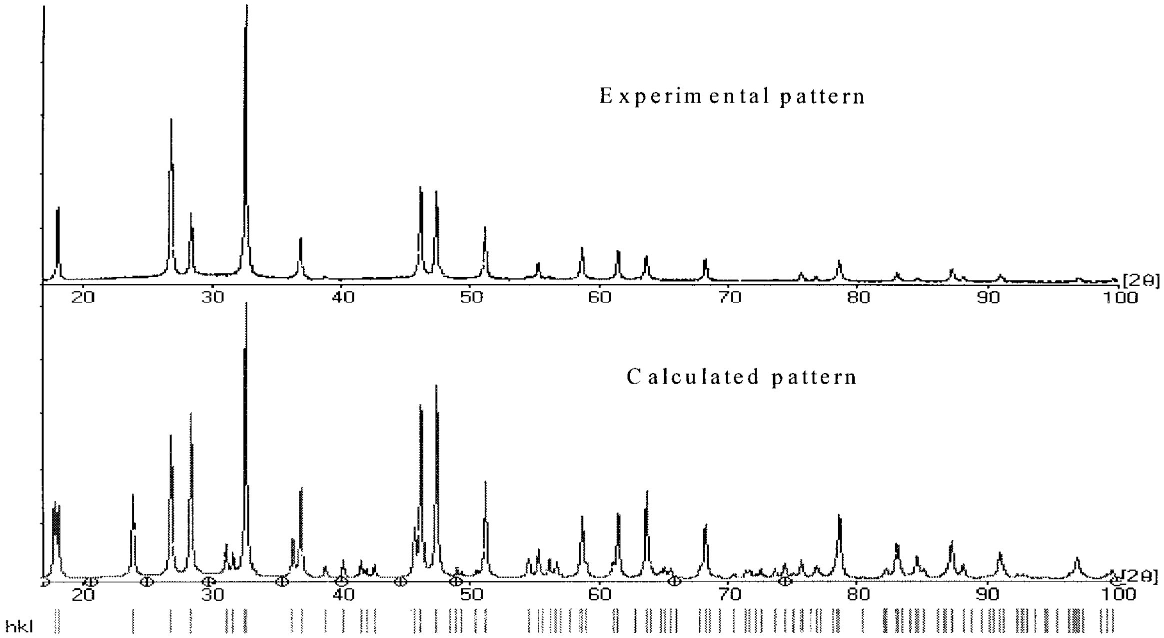

Fig. 2. Comparison of the experimental X-ray pattern of B-phase with the theoretical pattern (model 1).

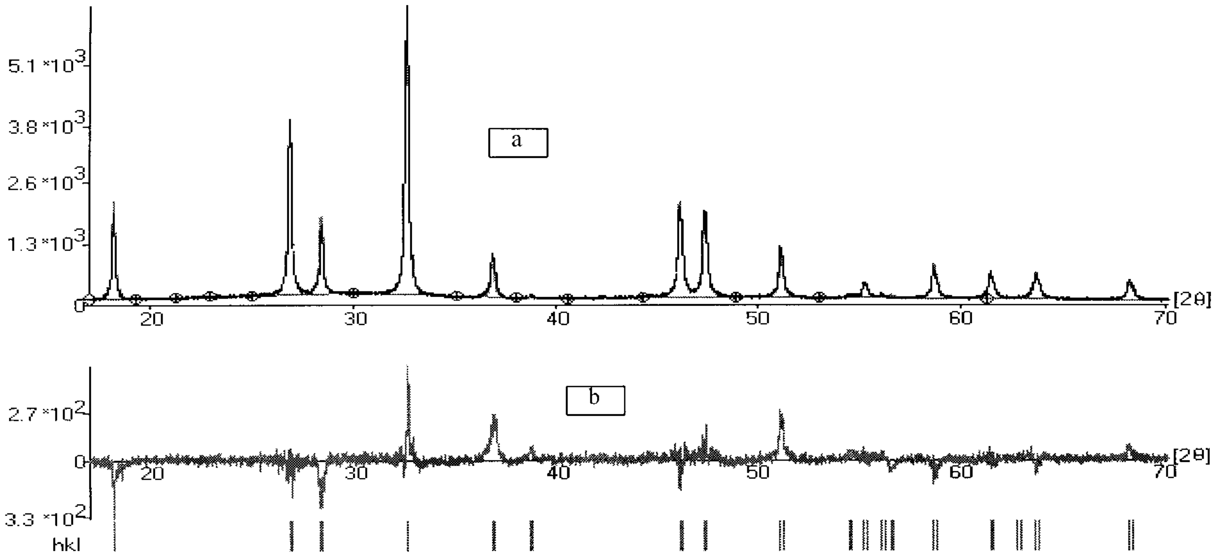

Fig. 3. (a) Comparison of the experimental X-ray pattern of B-phase (dark line) with the theoretical pattern (light line) (model 2a). Difference between the two patterns (b).

impossible to make the additional peaks disappear. Subsequently, the atom site co-ordinates were allowed to move without constraint. Even in this case some additional peaks remain. Moreover, the final co-ordinates are strongly shifted by comparison to the initial values. The tetrahedra do not form rings any longer and are highly distorted leading to aberrant values for the bond lengths and angles.

3.2. Determination of a new model

When indexing the experimental X-ray pattern, we only can find peaks corresponding to an hexagonal unit-cell six times smaller than the previous orthorhombic cell ($a = 0.38359$ nm and $c = 0.97539$ nm). Considering this hexagonal cell we observe systematic absences for plans: $hh\text{-}2hl$ with $l = 2n+1$. Only three space groups answer to that condition: P 6_3 m c (176); P-6 2 c (190) and P 6_3/m m c (194). According to the dimensions of the unit-cell (124.29 A^3) and the density of the compound (approx. 4.2 g/cm^3) the number of atoms in the cell must be: 2Y; 1Si; 1Al; 5O and 1N. From these informations, the only model possible (model 2) requires the atom sites given in Table 2. This model assumes that the Si and Al atoms are sharing the same sites and the O and N atoms are also sharing the same sites. After refinement of the z co-ordinate for site (O,N)(1) and the Debye–Waller coefficients for each sites we obtain model 2a. The refined parameters are given in Table 3. The reliability factors for model 2a are:

$$R_p = 6.94\% \qquad R_{wp} = 9.31\% \qquad S = 1.18$$

The simulated X-ray pattern based on this model and the experimental pattern are compared in Fig. 3. The agreement between the two patterns is correct but this requires quite high values for the Debye–Waller coefficient for

Table 4
Atom size for model 2b

Atoms	Co-ordinates x	y	z	Multiplicity k	Occupancy ratio	β
Y	0	0	0	2	1	2.94
(Si, Al)	0.406	0.812	1/4	6	1/3	3.34
(O, N)(1)	1/3	2/3	0.100	4	1	5.97
(O, N)(2)	0.216	0.108	1/4	6	1/3	5.04

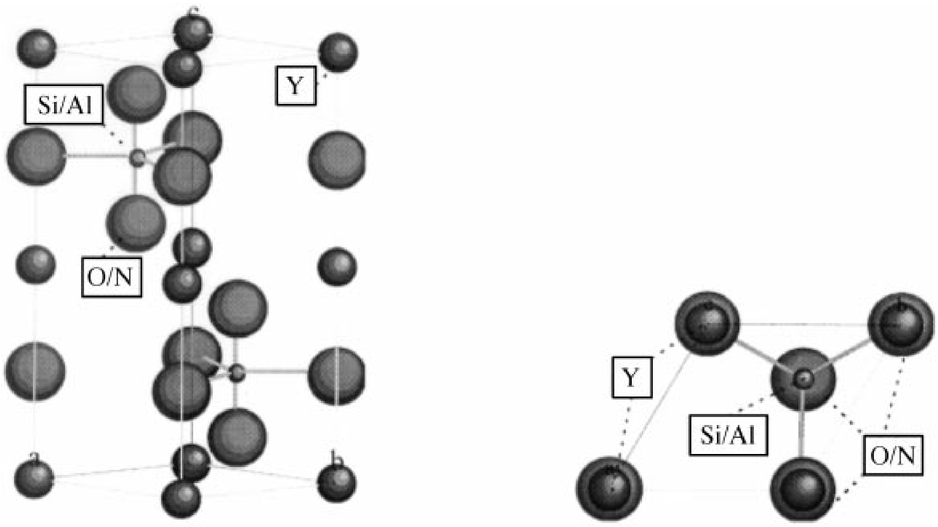

Fig. 4. Atom positions according to model 2a. (Si, Al) site in a 5 fold co-ordination.

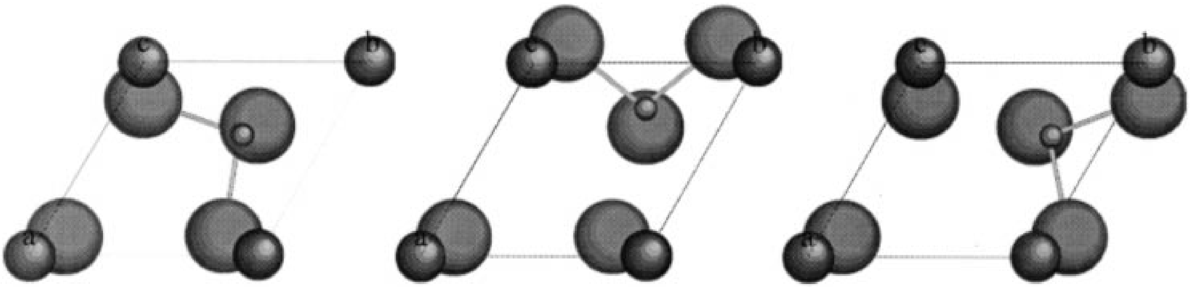

Fig. 5. Atom positions according to model 2b. (Si, Al) site in a 4 fold co-ordination.

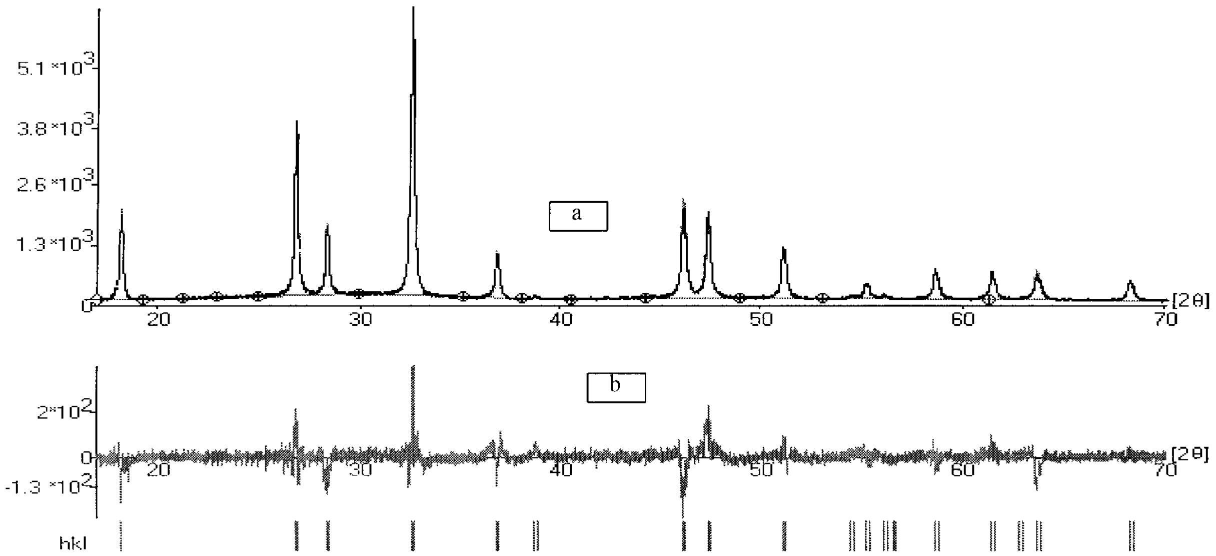

Fig. 6. (a) Comparison of the experimental X-ray pattern of B-phase (dark line) with the theoretical pattern (light line) (model 2b). Difference between the two patterns (b).

Table 5
Experimental and calculated data (model 2b)

h	k	l	2θ	d (mm)	I Calc (cps)	I Calc (%)	I Obs (cps)	I Obs (%)	F Calc	F Obs
0	0	2	18.18	0.4876	31634	27	32266	27	9326	9418
0	1	0	26.82	0.3322	64330	55	65085	54	11254	113200
0	1	1	28.36	0.3144	29281	25	25362	21	5670	5277
0	1	2	32.59	0.2745	116642	100	120173	100	12943	13137
0	0	4	36.83	0.2438	22550	19	20795	17	15667	15045
0	1	3	38.72	0.2323	416	< 1	1029	1	911	1432
0	1	4	46.14	0.1966	51825	44	47484	40	11956	11444
1	1	0	47.36	0.1918	4131	36	45096	38	15607	16147
1	1	2	51.14	0.1785	26830	23	28027	23	9429	9637
0	1	5	54.51	0.1682	1060	1	1470	1	1980	2333
0	2	0	55.26	0.1661	8270	7	9537	8	7916	8501
0	2	1	56.13	0.1637	2799	2	2289	2	3300	2984
0	0	6	56.57	0.1625	429	< 1	324	< 1	3185	2767
0	2	2	58.67	0.1572	21149	18	18902	16	9411	8897
1	1	4	61.46	0.1507	16760	14	17576	15	8699	8908
0	2	3	62.77	0.1479	69	< 1	93	< 1	569	659
0	1	6	63.68	0.1460	19025	16	18902	16	9531	9500
0	2	4	68.27	0.1373	11800	10	14507	12	7909	8770
0	1	7	73.67	0.1285	1015	1	1599	1	2445	3070
0	2	5	75.05	0.1265	383	< 1	549	< 1	1521	1820
1	2	0	75.69	0.1256	5095	4	6028	5	5576	6065
1	2	1	76.42	0.1245	3	< 1	3	< 1	100	100
1	1	6	76.80	0.1240	3917	3	3306	3	4934	4533
0	0	8	78.37	0.1219	2657	2	2368	2	10076	9512
1	2	2	78.62	0.1216	16627	14	15091	13	7290	6945
1	2	3	82.24	0.1171	322	< 1	406	< 1	1041	1168
0	2	6	83.07	0.1162	6881	6	6833	6	6838	6814
0	1	8	84.60	0.1144	4397	4	3502	3	5518	4924
1	2	4	87.27	0.1116	8105	7	10083	8	5374	5994
0	3	0	88.16	0.1107	2424	2	3365	3	5904	6957
0	3	1	88.87	0.1100	4	< 1	7	< 1	171	222
0	3	2	91.02	0.1080	5002	4	5897	5	6074	6596
0	2	7	92.37	0.1067	349	< 1	510	< 1	1613	1950
1	2	5	93.71	0.1056	26	< 1	32	< 1	313	347
0	3	3	94.60	0.1048	3	< 1	8	< 1	158	252
0	1	9	96.78	0.1030	3	< 1	93	< 1	791	843
1	1	8	96.95	0.1029	4573	4	5100	4	5923	6255
0	3	4	99.64	0.1008	1797	2	2983	2	3735	4813

atom sites (Si,Al) and (O,N)(2). This seems to compensate for error in the exact co-ordinates. Moreover, according to this model, the (Si,Al) ions would be in a 5 fold co-ordination what is quite unusual (Fig. 4). What we can consider is that the silicon atoms do not occupy exactly the site 1/3 2/3 1/4 but occupy a range of positions slightly shifted around this site. We may assume also that the site (O,N)(2) is slightly shifted around the co-ordinates 0 0 1/4. Then the (Si,Al) site becomes four-coordinated (Fig. 5). However, in that case the (Si,Al) site has for general co-ordinates x, $2x$, 1/4 and its multiplicity becomes 6 instead of 2 with the co-ordinates 1/3 2/3 1/4. This imposes an occupation ratio equal to 1/3. The situation is exactly the same for the site (O,N)(1) in $2x'$, x', 1/4 with an occupancy ratio of 1/3. Introducing these modifications to the refinement we obtain model 2b. The final reliability factors become:

$$R_\mathrm{p} = 6.0\% \qquad R_\mathrm{wp} = 7.6\% \qquad S = 0.96$$

The refined parameters are given in Table 4. The experimental and simulated patterns are now very close (Fig. 6). Table 5 gives the angles, the d spacings, the observed and calculated values for the diffracted the intensity and the structure factor for each Bragg reflection.

3.3. Order in the occupied/unoccupied sites

The next step was to determine if there is, or is not, order in the occupied and unoccupied equivalent positions for sites (Si,Al) and (O,N)(2). It was found that the only possibility to have order on a large scale corresponds to initial orthorhombic ring structure Fig. 7(a). As this symmetry leads in any case to peaks which are not present on the experimental X-ray pattern, and that only the peaks corresponding to the hexagonal unit cell are

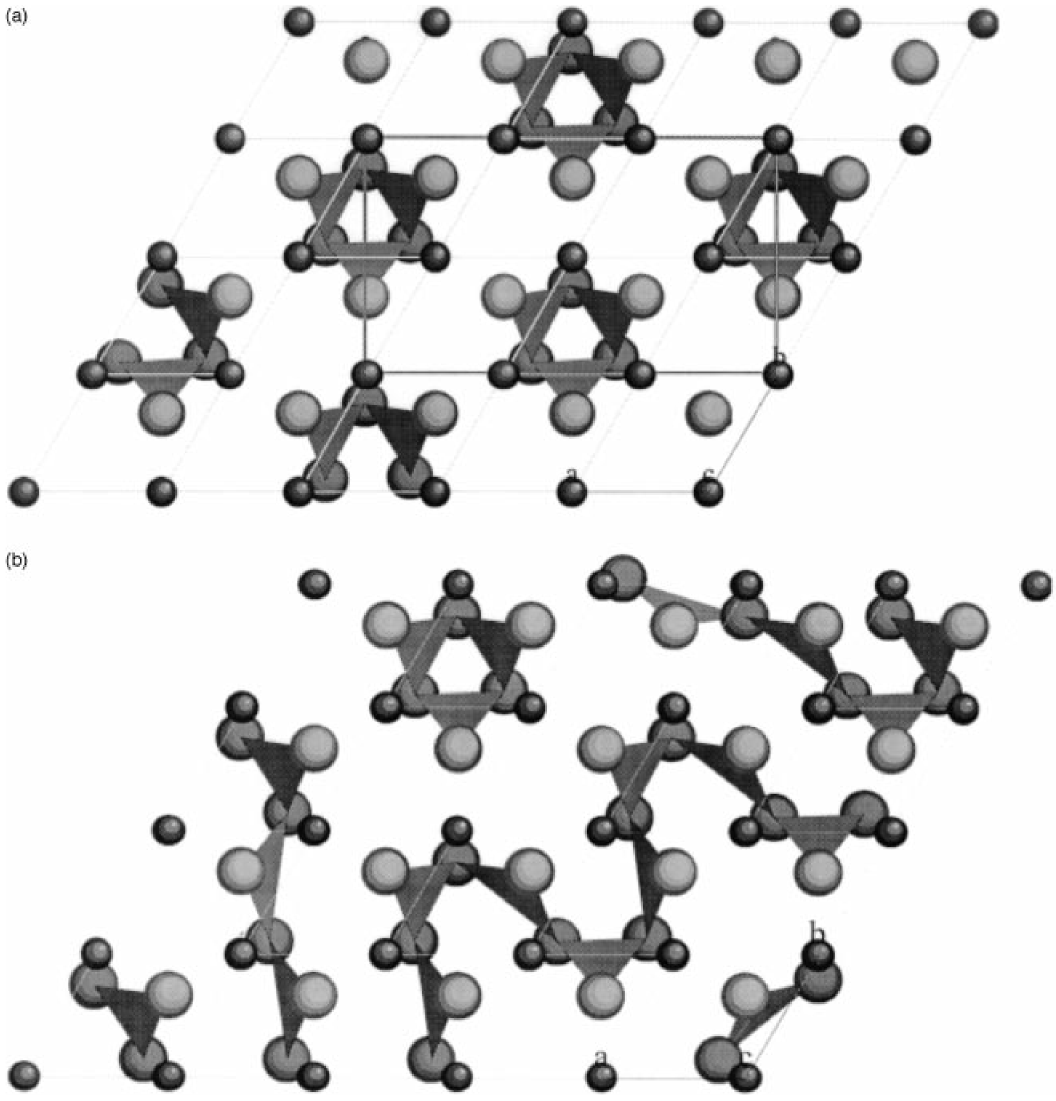

Fig. 7. (a) Periodic ordering of the occupied/non-occupied positions in model 3. Projection of layer $z = 0$ to 1/2 down (001). (b) Random occupied/non-occupied positions in model 3. Projection of layer $z = 0$ to 1/2 down (001).

Table 6
Bond lengths in model 2b

Atom	Co-ordination	Bond type	Experimental value (nm)	Theoretical value (mm) [6]
Y	6	6x Y-(O, N)(1)	0.240	0.237 to 0.243
Si/Al	4	2x (Si, Al)-(O, N)(2)	0.163 to 0.192	0.155 to 0.186
		2x (Si, Al)-O(1)	0.159	0.155 to 0.186

observed, it is reasonable to assume that there is no ordering in the occupancy of the (Si,Al) and (O,N)(2) equivalent positions at a large scale. The equivalent positions are randomly occupied with the same overall occupation ratio for each of them. A picture of this structure is given by Fig. 7(b). The tetrahedra are randomly linked to each other between two layers of yttrium cations. Considering that the usual co-ordination for nitrogen and oxygen are, respectively, 3 and 2, it is reasonable to assume that the nitrogen would preferentially occupy the site (O,N)(2) bridging two tetrahedra, whereas the non-bridging site (O,N)(1) would only be occupied by oxygen atoms [the site will now be called O(1)]. Due to the difference of bond length between Si-O; Al-O; Si-N and Al-N, the position of sites O(1) and (O, N)(2) may slightly vary with the nature of the atom occupying the site (Si, Al). That is certainly why the thermal coefficient β remains high for these sites.

3.4. Bond lengths

Bond lengths have been calculated (Table 6). The value obtained for the Y–(O,N) bonds, 0.240 nm, is in a very good agreement with the theoretical values (0.237–0.243 nm). The bonds (Si,Al)–O(1), 0.159 nm, are correct for Si–O bonds (0.155–0.167 nm) but are a bit short for Al–O bonds (0.171–0.186 nm). The bonds (Si,Al)-(0,N)(2) may vary from 0.163 to 0.192 nm according to the position occupied. These values are in the same range as those of the theoretical values (0.155–0.186 nm).

4. Conclusion

According to the present study, the model usually proposed for the crystal structure of the B-phase, that is to say, a 2-layer α-wollastonite modification consisting of alternate layers of yttrium cations and rings of three $(Si,Al)(O,N)_4$ tetrahedra sharing corners, does not fit accurately with the experimental results. Several strong peaks, not present on the experimental X-ray pattern, are observed on the simulated pattern based on this model.

The indexation of the experimental pattern shows only peak corresponding to an hexagonal cell six times smaller that the orthorhombic cell based on a pseudo α-wollastonite model.

A model based on this hexagonal cell has been elaborated. After refinement of this model we obtained a very good agreement between the experimental and simulated patterns. The proposed structure is a bi-dimensional network of tetrahedra $(Si,Al)(O,N)_4$ randomly linked to each other between two layers of yttrium cations. The various positions for the atoms, according to their nature, leads to a range of bond lengths that takes into account the type of the bond (Si–0, Al–O, Si–N or Al–N).

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