Ordering of nitrogen and oxygen in nitrogen-containing melilites $Y_2Si_3O_3N_4$ and $Nd_2Si_{2.5}Al_{0.5}O_{3.5}N_{3.5}$

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Ordering of N and O atoms in nitrogen-containing melilite $Y_2Si_3O_3N_4$ (Y-M) was investigated by Rietveld refinement in the space group $P\bar{4}2_1m$ using neutron powder diffraction data. The results show that, contrary to previous work using X-ray data, the occupancies by N and O atoms can be refined to show that about 1.7 N and 0.3 O atoms occupy 2c (in Wyckoff notation, space group no. 113) sites in the Y-M unit cell, while the remaining N atoms in the unit cell are disordered at 8f (in Wyckoff notation) sites. The similar ordering of N and O atoms in $Nd_2Si_{2.5}Al_{0.5}O_{3.5}N_{3.5}$ (Nd-M′) was also confirmed, by refinement from neutron data, which means that similar distributions of N and O atoms occurred at 2c sites in spite of the fact that the total numbers of N atoms per unit cell were eight and seven in Y-M and Nd-M′ respectively. The present results give a more detailed picture of O,N ordering in these structures than was provided by the previous work of Wang and Werner based on X-ray data alone.

Nitrogen-containing melilite and solid-solution phases, of general formula $R_2Si_{3-x}Al_xO_{3+x}N_{4-x}$ ($x \leqslant 1$, R = Y, Nd, Sm, Gd, Dy, *etc.*), frequently occur at grain boundaries when yttria and rare-earth oxides are used as sintering aids in the preparation of α-sialon and mixed α,β-sialon ceramics.[1,2] The suggested[3] structure of Y-M has space group $P\bar{4}2_1m$ and is derived from akermanite ($Ca_2MgSi_2O_7$) by substituting Y for Ca, Si for Mg and N for eight of the fourteen O in the unit cell ($Z = 2$) for N. Further structure refinements based on the Rietveld whole-pattern fitting technique for $Y_2Si_3O_3N_4$ (Y-M) and $Nd_2Si_{2.5}Al_{0.5}O_{3.5}N_{3.5}$(Nd-M′) confirmed the model, in which eight N atoms were located at 8f sites (eight-fold) of the unit cell[4] (Fig. 1). The O,N ordering in Y-M was studied[5] with MAS NMR by two of the authors and colleagues recently. Readers are referred to that paper for further details of the structure. It was found that N atoms probably occupy the 2c (bridging, two-fold) sites and O atoms occupy 4e (terminal, four-fold) sites in the $Si_2(O,N)_7$ units, while the remaining six N and two O atoms are distributed at 8f sites. This is in accordance with Pauling's rules for charge distribution that O atoms are located at the 4e sites as these are the only ones in the structure not coordinated to two silicon atoms and they have the lowest total positive valencies from surrounding cations (*ca.* 2). In order to determine the N,O ordering at the 2c and 8f sites of the Y-M unit, it is clearly more powerful if two techniques (Rietveld refinement and NMR) are used in combination. Since the scattering factors of N and O atoms for neutrons show a greater contrast than those for X-rays, neutron diffraction data were used to investigate the N,O ordering in Y-M to supplement the X-ray results. This paper describes the conclusions regarding N,O ordering from the refinement of the occupancies by N and O atoms together with other structural and profile parameters based on the distributions of N,O atoms of Y-M obtained by NMR.[5] The N,O ordering in the Nd-M′ unit cell was also derived and compared in this work.

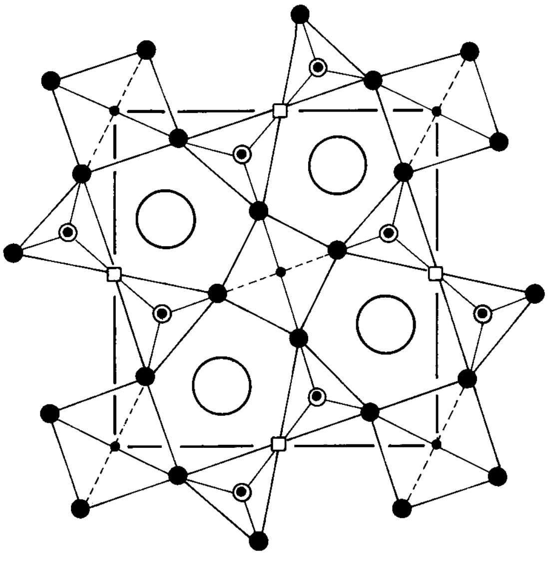

Fig. 1 N-Melilite crystal structure, (001) projection. Large circles represent Y/Nd cations and small filled circles, at tetrahedron centres, correspond to Si (and Al) in 4e and 2a sites. The remaining circles correspond to 8f (filled) and 4e (open) non-metal sites, while open squares indicate 2c sites.

Experimental

Samples of the Y-M and Nd-M′ phases were prepared by the hot-pressing technique. The starting powders used were silicon nitride (LC12, H.C. Starck, Berlin), aluminium oxide (Wu Song Chemical Works, China, 99.9%) and aluminium nitride (prepared at Shanghai Institute of Ceramics), while Y_2O_3 and Nd_2O_3 were the products of Yaolung Chemical Works, China. Powder mixtures were prepared with the overall nominal composition $R_2Si_{3-x}Al_xO_{3+x}N_{4-x}$ ($x = 0$ for R = Y and $x = 0.5$ for R = Nd), taking into account surface oxygen on the particles of both Si_3N_4 (1.8 mass%) and AlN (2.0 mass%). The powders were mixed in absolute alcohol and milled in an agate mortar for 1.5 h. The compacted samples were fired by the hot-pressing technique (20 MPa) in a flowing nitrogen atmosphere for 1 h at 1750 and 1675 °C for Y-M and Nd-M′ phases, respectively.[6] The synthesised samples were characterised by powder X-ray diffraction (XRD) and it was found that the major phase was melilite, with a very small amount of the J-phase $R_4Si_2O_7N_2$ (R = Y, Nd) also being present in both samples. The unit cells of the Y-M and Nd-M′ phases were refined, using Si powder as an internal standard, from X-ray Guinier-Hägg camera diffraction patterns (Cu-Kα_1 radiation, $\lambda = 1.540\,5981$ Å) evaluated with a computer-controlled film scanner and associated programs.[7,8] The neutron data collections ($\lambda = 1.470$ Å) of Y-M and and Nd-M′ were performed at 275 K at the Swedish Studsvik R2 reactor. Results were obtained in steps of 0.08° in the ranges for 2θ of 15–130 and 10–109.4° for Y-M and Nd-M′ respectively, with a measuring time of 3 min per step.

Results

Fig. 2 shows the observed and computer-fitted neutron diffraction pattern of Y-M. The unit-cell dimensions obtained after least-squares refinements are: $a = b = 7.6137(2)$, $c = 4.9147(2)$ Å for Y-M and $a = b = 7.7462(5)$, $c = 5.0390(4)$ Å for Nd-M′. The Rietveld refinements were performed with a version of the refinement program written by Wiles *et al.*[9] The background intensity Y_{bi} at the ith step was described by the polynomial

$$Y_{bi} = \Sigma B_m [2\theta_i / BKPOS - 1]^m$$

where B_m are parameters to be refined and $BKPOS$ is the origin of the polynomial for the background. The peak shape used was a Pearson VII function. The extent of a peak was taken to be 3.0 times the FWHM (full-width at half-maximum), H_k, on either side of the peak centre. H_k was given by

$$H_k^2 = U\tan^2\theta_k + V\tan\theta_k + W$$

where U, V, W are the width parameters and k is the reflection index. The atomic coordinates of Y-M and Nd-M′ obtained in our previous work[1] were used as the starting parameters. In the first trial for Y-M, two N atoms were located at 2c sites of the space group $P\bar{4}2_1m$, and the remaining six N atoms were taken to occupy 8f sites of the unit cell together with two O atoms. The convergent refinement involved twelve structural parameters and twelve profile parameters, *i.e.* one scale, ten atomic coordinates, and one isotropic temperature factor (so-called structural parameters), together with the zero-point position, three peak half-width parameters (U, V, W), the unit cell dimensions (a,c), one peak shape parameter and five background parameters (so-called profile parameters). No absorption correction was applied, and a common isotropic temperature factor was used for all the atoms. However, at the beginning of the refinement procedure, an attempt was made to refine thermal parameters together with occupancies (30 variables in total). Although the error parameters of the fitting were lowered by this procedure, some of the thermal parameters were found to be negative, which is unacceptable. For this reason, we prefer to quote results obtained by constraining all thermal parameters to be equal (see Table 3). The refinement was terminated when all shifts in the parameters were $<10\%$ of the corresponding standard deviations. At the final stage, the occupancies of N and O atoms for Y-M at 2c and 8f sites were refined together with 24 parameters, keeping the total number of N and O atoms constant. The final R values for 195 reflections, together with some essential data, are shown in Table 1. For comparison, the refinement results of Y-M from neutron and X-ray data,[4] in which two O and eight N atoms were located at 2c and 8f sites respectively, are also listed in Table 1.

Because of the higher scattering amplitudes of N,O atoms in the neutron case, the distributions of N,O atoms were much more sensitive indicators than in the X-ray case. It is shown in Table 1 that all reliability index R values were obviously reduced by fixing two N atoms at 2c sites, together with six N and two O atoms at 8f sites. The results were even better when the occupancies of N,O atoms at 2c and 8f sites were refined together. An unreasonable occupancy of N atoms at 2c sites was obtained for a similar refinement from X-ray data.

For refinements of Nd-M′ the models were more complicated, because there are three kinds of possible substitutions of Al for Si, *i.e.* one Al atom distributed in either 4e or 2a or in both of these sites, in addition to the different distributions of anions. Similar refinement procedures as used for Y-M were performed on Nd-M′ neutron data under the different distributions of Si, Al atoms. Table 2 gives the final R values for the different distributions of N,O,Si,Al in Nd-M′. The atomic coordinates, isotropic thermal and occupancy parameters for both Y-M and Nd-M′ structures are shown in Table 3. Some selected interatomic distances for Y-M and Nd-M′ are summarised in Table 4.

Similar refinement levels to those for Y-M were obtained for the Nd-M′ phase. The R values were much lower when N,O atoms were refined at (2c,8f) sites or were fixed at those sites (see Table 2). The results shown in Table 3 confirm that the N atoms occupy the two sites 2c and 8f in both Y-M and Nd-M′ cases. The occupancies of N, O atoms further indicate

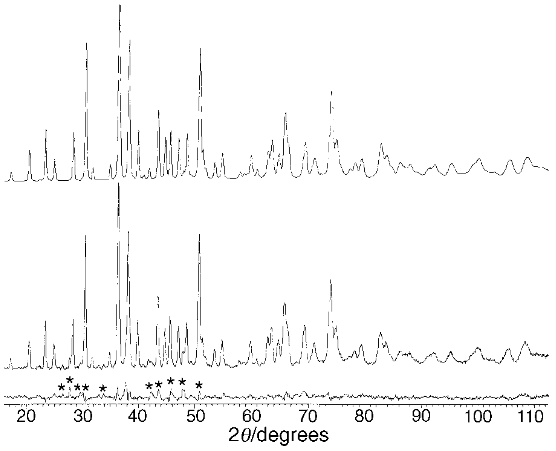

Fig. 2 The neutron diffraction pattern for Y-M. Top: profile calculated by least-squares Rietveld refinement. Middle: experimental pattern. Bottom: difference pattern. The asterisks indicate peaks assigned to $Y_4Si_2O_7N_2$, which is the principal impurity in Y-M.

Table 1 Final R values and refinement details for the different distributions of O,N in Y-M

	O(2c), N(8f)		N(2c) N,O(8f)	N,O refined at (2c,8f)
	X-ray[4]	neutron	neutron	neutron
R_F (%)[a]	5.25	6.37	4.00	3.94
R_B (%)	6.55	11.91	6.81	6.67
R_P (%)	6.76	6.88	4.97	4.89
R_{WP} (%)	8.45	9.06	6.77	6.69
U	0.047(0)	1.54(8)	1.41(6)	1.41(6)
V	−0.014(1)	−0.83(7)	−0.74(5)	−0.74(5)
W	0.024(1)	0.20(1)	0.18(1)	0.18(1)
no. of structural parameters	17	12	12	13
no. of profile parameters	11	12	12	12

[a] Reliability index R can be defined as R_F, R_B, R_P, R_{WP}. R_F: R value for structure amplitudes; R_B: R value for Bragg intensities; R_P: the pattern R factor; R_{WP}: the weighted pattern R factor.

Table 2 Final R values and refinement details for the different distributions of N,O,Si,Al in Nd-M′ ($x=0.5$) ($\lambda=1.470$ Å)

	1 Al and 3 Si at (4e) sites 2 Si at (2a) sites			4 Si at (4e) sites 1 A1 and 1 Si at (2a) sites			1 A1, 5 Si refined at (4e, 2a) sites		
	0(2c) N(8f)	N(2c) N,O(8f)	N,O refined	O(2c) N(8f)	N(2c) N,O(8f)	N,O refined	O(2c) N(8f)	N(2c) N,O(8f)	N,O refined
R_F (%)	6.52	3.46	3.52	6.59	3.50	3.52	6.54	3.44	3.49
R_B (%)	11.26	5.65	5.53	11.24	5.69	5.55	11.24	5.60	5.49
R_P (%)	7.24	5.16	5.06	7.25	5.20	5.11	7.24	5.16	5.06
R_{WP} (%)	9.27	6.81	6.71	9.28	6.84	6.74	9.26	6.81	6.70

Table 3 Final refinement results of atomic coordinates, isotropic thermal (B) and occupancy (N) parameters in Y-M and Nd-M′ ($x=0.5$) ($\lambda=1.470$ Å)

				Nd-M′ (N, O refined at (2c, 8f) sites)		
atom	Wyckoff notation	x,y,z, B, N	Y-M N, O refined at (2c, 8f) sites	1 Al, 3 Si at (4e) sites	1 Al, 1 Si at (2a) sites	1 Al, 5 Si refined at (4e, 2a) sites
Y/Nd	4e	x	0.3365(4)	0.3361(4)	0.3359(4)	0.3360(4)
		y	0.1635(4)	0.1639(4)	0.1641(4)	0.1640(4)
		z	0.5038(8)	0.5019(9)	0.5022(9)	0.5020(9)
		N	0.5	0.5	0.5	0.5
Si(1)/Al(1)	4e	x	0.1456(8)	0.1429(9)	0.1423(8)	0.1427(9)
		y	0.3544(8)	0.3571(9)	0.3577(8)	0.3573(9)
		z	0.9464(13)	0.9473(14)	0.9474(14)	0.9473(14)
Si(1)		N	0.5	0.375	0.5	0.407(26)
Al(1)		N		0.125		0.093(26)
Si(2)/Al(2)	2a	x	0.0	0.0	0.0	0.0
		y	0.0	0.0	0.0	0.0
		z	0.0	0.0	0.0	0.0
Si(2)		N	0.25	0.25	0.125	0.218(26)
Al(2)		N			0.125	0.032(26)
N(1)O(1)	2c	x	0.5	0.5	0.5	0.5
		y	0.0	0.0	0.0	0.0
		z	0.1882(12)	0.1785(11)	0.1783(11)	0.1784(11)
N(1)		N	0.213(6)	0.211(6)	0.212(6)	0.212(6)
O(1)		N	0.037(6)	0.039(6)	0.038(6)	0.038(6)
N(2)/O(2)	8f	x	0.0852(3)	0.0847(3)	0.0849(4)	0.0848(3)
		y	0.1600(4)	0.1641(4)	0.1641(4)	0.1641(4)
		z	0.7976(6)	0.8047(6)	0.8049(6)	0.8047(6)
N(2)		N	0.787(6)	0.664(6)	0.663(6)	0.663(6)
O(2)		N	0.213(6)	0.336(6)	0.337(6)	0.337(6)
O(3)	4e	x	0.1416(4)	0.1397(5)	0.1396(5)	0.1397(5)
		y	0.3584(4)	0.3603(5)	0.3604(5)	0.3603(5)
		z	0.2783(11)	0.2842(11)	0.2786(11)	0.2784(11)
		N	0.5	0.5	0.5	0.5
		B^a	0.83(4)	0.24(4)	0.24(4)	0.24(4)

[a] Isotropic thermal parameter, see text

Table 4 Some selected interatomic distances in Y-M and Nd-M′

	Y-M (N, O refined at 2c, 8f sites)	Nd-M′ (N, O, Al, Si refined)
M(Y/Nd)—[N(l) O(1)]	2.346(5)	2.426(5)
—O(3)	2.360(5)	2.428(6)
—[N(2), O(2)] (×2)	2.397(4)	2.472(5)
—O(3) (×2)	2.551(5)	2.607(5)
—[N(2), O(2)](×2)	2.754(4)	2.806(5)
average	2.514(5)	2.578(5)
(Si/Si,Al)—O(3)	1.661(8)	1.669(9)
—[N(1), O(1)]	1.702(7)	1.687(7)
—[N(2), O(2)] (×2)	1.714(7)	1.720(8)
average	1.698(7)	1.699(7)
(Si/Si,Al)—[N(2), O(2)] (×4)	1.701(3)	1.737(3)

that *ca.* 1.7 N and 0.3 O atoms occupy 2c sites in both Y-M and Nd-M′ units in spite of the fact that the total numbers of N atoms are eight and seven in Y-M and Nd-M′ respectively; the remaining N atoms in the unit cells are disordered to occupy 8f sites.

It was difficult to distinguish between Al and Si atoms in Nd-M′ because of the small difference in scattering factors, as stated in our previous work.[4] However, the atomic ratio of Al:Si at 4e sites (0.19:0.81) appears to be marginally higher than the one (0.13:0.87) at 2a sites.

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