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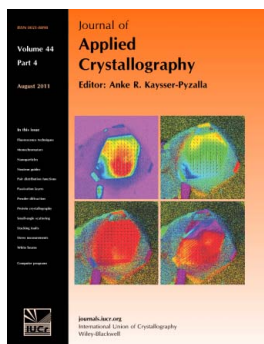
M. Allix, M. D. Alba, P. Florian, A. J. Fernandez-Carrion, M. R. Suchomel, A. Escudero, E. Suard and A. I. Becerro

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Structural elucidation of β-(Y,Sc)$_2$Si$_2$O$_7$: combined use of ^{89}Y MAS NMR and powder diffraction

M. Allix,[a,b] **M. D. Alba,**[c] **P. Florian,**[a,b] **A. J. Fernandez-Carrion,**[c] **M. R. Suchomel,**[d] **A. Escudero,**[c] **E. Suard**[e] **and A. I. Becerro**[c]*

[a]CNRS, UPR3079 CEMHTI, 1D Avenue de la Recherche Scientifique, 45071 Orléans Cedex 2, France, [b]Université d'Orléans, Avenue du Parc Floral, BP 6749, 45067 Orléans Cedex 2, France, [c]Instituto de Ciencia de Materiales de Sevilla (CSIC-Universidad de Sevilla), Calle Américo Vespucio 49, 41092 Sevilla, Spain, [d]Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA, and [e]Institut Laue–Langevin, F-38042 Grenoble 9, France. Correspondence e-mail: anieto@icmse.csic.es

Although the structures of pure Sc$_2$Si$_2$O$_7$ and β-Y$_2$Si$_2$O$_7$ have been described in the literature using the $C2/m$ space group, ^{29}Si magic angle spinning (MAS) NMR measurements of the intermediate members of the Sc$_2$Si$_2$O$_7$–β-Y$_2$Si$_2$O$_7$ system indicate a lowering of the symmetry to the $C2$ space group. Indeed, these compositions exhibit a unique Si crystallographic site and an Si—O—Si angle lower than 180°, incompatible with the $C2/m$ space group. $C2$ is the only possible alternative. Space group Cm can be discarded with regard to its two different Si sites per unit cell. Moreover, ^{89}Y MAS NMR data have revealed the existence of two different Y sites in the structure of the intermediate members of the Sc$_2$Si$_2$O$_7$–β-Y$_2$Si$_2$O$_7$ system, confirming the lowering of the symmetry to the $C2$ space group. The viability of the $C2$ model has therefore been tested and confirmed by refinement of synchrotron and neutron powder diffraction data for the different members of the system. The structural evolutions across the Sc$_2$Si$_2$O$_7$–β-Y$_2$Si$_2$O$_7$ system are discussed.

1. Introduction

Refractory rare earth (RE) oxides are used as sintering aids for the fabrication of silicon nitride structural ceramics. Upon annealing, (RE)$_2$Si$_2$O$_7$ crystallizes at the grain boundaries of Si$_3$N$_4$ and improves the high-temperature mechanical properties of the material (Tsuge *et al.*, 1975; Dinger *et al.*, 1988; Vomacka & Babushkin, 1995; Hong *et al.*, 2002). Knowledge of the crystalline structures adopted by the (RE)$_2$Si$_2$O$_7$ intergranular phase at different temperatures and RE contents is therefore of great value in understanding the behaviour of these materials. RE disilicates (RE$_2$Si$_2$O$_7$) exhibit different polymorphic forms depending on the RE ionic radius, temperature and pressure (Ito & Johnson, 1968; Felsche, 1973). Y$_2$Si$_2$O$_7$ shows, in particular, up to five polymorphs depending on temperature at room pressure (y, α, β, γ and δ, also called, respectively, y, B, C, D and E), while Sc$_2$Si$_2$O$_7$, or thortveitite, exhibits a unique polymorph (β, also called C) up to the melting point of the compound.

A remarkable feature of the Sc$_2$Si$_2$O$_7$ thortveitite structure is the unusual Si—O—Si angle, reported as 180° (Cruickshank *et al.*, 1962; Smolin *et al.*, 1973; Bianchi *et al.*, 1988). There has been a considerable amount of discussion about the correctness of this structural model, as the value of 180° is rather unusual for sorosilicates. Such angles are usually much smaller (130–140°; Liebau, 1986). The preference for a nonlinear structure with regard to the Si—O—Si bridge is supported by

quantum-mechanical calculations (Meagher *et al.*, 1979; Gibbs *et al.*, 1981): the energy of a bent Si—O—Si link is shown to be smaller than for the linear (180°) counterpart. This discussion also dealt with the question of whether the correct space group for thortveitite is $C2/m$ or $C2$; both of them are possible on the basis of the diffraction symmetry. However, it was concluded that the correct space group for Sc$_2$Si$_2$O$_7$ is the centrosymmetric $C2/m$, as it provides the most consistent bond lengths and angles, in spite of the Si—O—Si angle of 180° (Cruickshank *et al.*, 1962; Smolin *et al.*, 1973; Bianchi *et al.*, 1988).

The structure of β-Y$_2$Si$_2$O$_7$ was studied by Redhammer & Roth (2003), who initially refined it using the $C2$ space group with acceptable residual values. However, the thermal parameter values for two of the four O atoms were definitely nonpositive. Validation tests of the final $C2$ structural model clearly showed the presence of additional symmetry (mirror plane), suggesting that $C2/m$ was the correct space group. Thus, Redhammer & Roth (2003) concluded that $C2/m$ was in fact the correct assignment, based on a new structural resolution which revealed the known thortveitite structure type of β-Y$_2$Si$_2$O$_7$ and yielded better final residual values (with fewer refined parameters) and positive-definite displacement parameters for all atoms.

The Sc$_2$Si$_2$O$_7$–β-Y$_2$Si$_2$O$_7$ system has been studied previously as a function of temperature and composition

(Escudero *et al.*, 2007). The particular behaviour of this system annealed at 1573 K was analysed, showing a complete solid solubility of one member into the other, with the β-(Sc,Y)$_2$Si$_2$O$_7$ structure type. Structural refinements for every member of the system were performed using the $C2/m$ space group, as established in the literature for the end members. All unit-cell parameters were linear with composition, but the evolution of the c and β unit-cell parameters did show a slope change at the intermediate composition. Likewise, Si—O—Si angles were obtained for the intermediate compositions of the system from ^{29}Si magic angle spinning (MAS) NMR data (Escudero *et al.*, 2007). These angles varied with composition, showing a minimum of 170.8° at $x \simeq 1.0$. This result implied that $C2/m$ is not the space group of the intermediate members, as it forces the Si—O—Si angle to be equal to 180°.

Alternative possible space groups for the intermediate members are $C2$ and Cm. Both of them allow the Si—O—Si angles to differ from 180°, as suggested by the ^{29}Si MAS NMR data. However, Cm generates two different Si crystallographic sites, contrary to the single Si site observed on the ^{29}Si MAS NMR spectra of the intermediate members (Escudero *et al.*, 2007). On the other hand, the differences between the $C2/m$ and $C2$ structural models are very small. Both of them generate a unique Si crystallographic site. However, the $C2/m$ model has a unique RE (RE = Sc, Y) site, while in $C2$, two different RE sites exist, permitting a higher degree of distortion in the $C2$ structure for the SiO$_4$ tetrahedron. In addition, there is a supplementary oxygen site in the $C2$ model.

The aim of the present study is to analyse the structures across the Sc$_2$Si$_2$O$_7$–β-Y$_2$Si$_2$O$_7$ system using complementary techniques that allow the structure to be studied at long- and short-range ordering. ^{89}Y MAS NMR spectroscopy has been used to analyse the local environments of yttrium. The MAS NMR spectra inform on the number of Y crystallographic sites of the structures. In a second stage, and based on the NMR results, synchrotron and neutron powder diffraction refinements have been used to propose a structural model for the intermediate members of the system.

2. Experimental

2.1. Synthesis

The sol–gel route used for this study was derived from the synthesis of a well homogenized gel of Y$_2$Si$_2$O$_7$ (Díaz *et al.*, 2001). The starting materials were Y(NO$_3$)$_3$·6H$_2$O (99.9%, Sigma), Sc(NO$_3$)$_3$·3H$_2$O (99.999%, Sigma), Si(OC$_2$H$_5$)$_4$ (TEOS, 98% solution, Sigma) and 96% ethanol. A TEOS solution in ethanol (1:3 in volume) was added over appropriate amounts of Y(NO$_3$)$_3$·6H$_2$O and Sc(NO$_3$)$_3$·3H$_2$O previously dissolved in 5 ml of ethanol for the preparation of Sc$_{2-x}$Y$_x$Si$_2$O$_7$ members with x = 0, 0.50, 1.00, 1.50 and 2.00. The mixtures were stirred at 313 K until transparent gels were obtained. The gels were then dried at 333 K for 24 h in air. Nitrates were eliminated by calcination at 773 K for 1 h at a heating rate of 1 K min^{-1}. The white powder obtained was subsequently calcined at a heating rate of 5 K min^{-1} up to

1573 K for 24 h and then slowly cooled to room temperature. These conditions allowed isolation of the β-(Sc,Y)$_2$Si$_2$O$_7$ polymorph for all the solid solution compositions (Escudero *et al.*, 2007). (Y,Sc)$_2$SiO$_5$ and SiO$_2$ were obtained in some compositions as subproducts.

2.2. Characterization

2.2.1. ^{89}Y magic angle spinning nuclear magnetic spectroscopy.
The ^{89}Y MAS experiments were performed on a Bruker Avance WB 300 MHz (7.0 T) instrument operating at 14.7 MHz. Powdered samples were packed into 7 mm silicon nitride rotors and spun at 4 kHz in a double-resonance 'low-γ' Bruker probe specifically designed to work at low frequency. The ^{89}Y chemical shifts were referenced relative to a 1 M yttrium chloride solution. The spin-lattice relaxation time T_1 of Y$_2$Si$_2$O$_7$ was estimated to be 1300 s with a saturation-recovery experiment, and hence for this compound a Hahn-echo experiment was used for a $\pi/2$ pulse of 39 µs, a recycle delay of 1650 s (Ernst *et al.*, 1987) and 96 scans accumulated. We took advantage of the line broadening observed for Sc$_{2-x}$Y$_x$Si$_2$O$_7$, x = 1.5, 1.0, 0.5, and used a rotor-synchronized Carr–Purcell–Meiboom–Gill (CPMG; Carr & Purcell, 1954; Meiboom & Gill, 1958; Cheng & Ellis, 1989; Cowvans & Grutzner, 1993; Hung *et al.*, 2004) sequence where trains of whole spin echoes are recorded to obtain an increase in signal-to-noise ratio with respect to a regular Hahn-echo sequence. We used $\pi/2$ pulses of 39 µs, acquiring between 30 and 60 echoes separated by 28 rotor periods (7.0 ms) with a recycle delay of 700 s and summing between 100 and 400 transients. This adds up to one week of experiments for the lowest Y-containing samples. The echo trains were not directly Fourier transformed but rather the echoes were separated, convoluted with an adequate Gaussian line broadening, Fourier transformed and summed to obtain the final spectra.

2.2.2. Diffraction techniques.
High-intensity and high-resolution synchrotron powder X-ray diffraction data were recorded on the 11-BM diffractometer at the Advanced Photon Source (APS), Argonne National Laboratory. Data were collected over the 0.5–55° 2θ range with a 0.001° step size at room temperature using a wavelength of λ = 0.413581 Å. The sample was contained in a 0.5 mm capillary and was spun at 60 Hz during data collection.

Neutron powder diffraction patterns were recorded on the D2B high-resolution/high-flux powder diffractometer at the Institut Laue–Langevin in Grenoble, France. The sample was packed in a vanadium can. Data were acquired with a wavelength of λ = 1.594 Å at 2θ intervals of 0.05° over the 10 < 2θ < 160° angular range.

Diffraction patterns were analysed with the Rietveld method using the *GSAS* software (Larson & Von Dreele, 1994). Anisotropic displacement parameters were used only for the refinement of the neutron data. Structural refinements have been performed using both $C2$ and $C2/m$ space groups. In the $C2$ case, the starting parameters were those given by Smolin *et al.* (1971) for β-Yb$_2$Si$_2$O$_7$. The Y/Sc ratios have been refined on the two sites, using a composition constraint: the

occupancies Occ(Y1 + Y2) [and Occ(Sc1 + Sc2)] have been constrained to their nominal values in each sample. In the $C2/m$ case, the starting parameters for the refinements of the $Y_xSc_{2-x}Si_2O_7$ structures with $x \leq 1$ were taken from those reported for pure β-$Sc_2Si_2O_7$ (Smolin *et al.*, 1972), while the refinement of the $Y_xSc_{2-x}Si_2O_7$ structure with $x = 1.5$ was carried out from the parameters reported for pure β-$Y_2Si_2O_7$ (Redhammer & Roth, 2003). $(Y,Sc)_2SiO_5$ and SiO_2 have been added as secondary phases. The refined weight fraction of these impurity phases was never greater than 10% and no SiO_2 was detected for the $YScSi_2O_7$ composition.

3. Results

3.1. ^{89}Y nuclear magnetic resonance results

Fig. 1 shows the experimental ^{89}Y MAS NMR spectra of β-$Y_xSc_{2-x}Si_2O_7$ samples with $x = 0.5$, 1.0, 1.5 and 2.0, which have been registered using the CPMG technique to obtain a high signal-to-noise ratio. The spectrum of the Y-rich end member, β-$Y_2Si_2O_7$ (Fig. 1a), displays a narrow peak at 207.2 p.p.m. with FWHM = 2.3 Hz, in good agreement with the literature (Becerro *et al.*, 2004). The presence of a unique

Figure 1
Experimental (crosses), individual contributions (dashed lines) and fitted (solid lines) ^{89}Y CPMG NMR spectra of $Y_xSc_{2-x}Si_2O_7$ with $x = 2.0$ (a), 1.5 (b), 1.0 (c) and 0.5 (d).

Table 1
^{89}Y MAS NMR fit parameters for β-$Y_xSc_{2-x}Si_2O_7$.

x (β-$Y_xSc_{2-x}Si_2O_7$)	δ (p.p.m.)	$\Delta_{1/2}$ (p.p.m.)	Area under the curve (%)
0.5	199.9	64.0	34.6
	225.0	38.5	65.4
1.0	196.9	65.9	50.2
	220.9	34.7	49.8
1.5	207.8	35.3	51.6
	217.1	23.5	48.4
100	207.2	2.3	100

narrow ^{89}Y signal of β-$Y_2Si_2O_7$ indicates the existence of a unique Y crystallographic site in the structure, compatible with the $C2/m$ space group and an Si—O—Si angle of 180°, in agreement with previous structural studies on this compound (Redhammer & Roth, 2003).

The spectra of the rest of the compositions (Figs. 1b–1d) exhibit broad and asymmetric bands. As Sc^{3+} and Y^{3+} have very different ionic radii, a local distortion of the structure is expected when Y is replaced by Sc. The structure of β-$Y_2Si_2O_7$ is formed from planes consisting of YO_6 octahedra sharing edges. Thus Y sites form a two-dimensional hexagonal pattern with a maximum neighbouring of three Sc per Y. It could be thought that the broadening of the bands is just due to the existence of different Y chemical shifts depending on their Sc neighbouring. If this were the case, a unique symmetrical signal – Y(3Sc) – would be expected in the $C2/m$ space group for the $x = 1.0$ composition for a homogeneous distribution of Y and Sc in the lattice. On the other hand, for the same space group and composition and in the event of a random distribution of Y and Sc in the lattice, four different Y environments would be expected: Y(3Sc), Y(2Sc,1Y), Y(1Sc,2Y) and Y(3Y), with the respective proportions 1/3, 1, 1 and 1/3. The sum of these four signals would equally induce a symmetrical line in the ^{89}Y NMR spectrum. However, the experimental spectrum of the $x = 1.0$ composition shows a high asymmetry towards low frequencies that disagrees with either of the two possible assignations made above, based on the existence of a unique RE site ($C2/m$ space group). Conversely, the experimental spectrum does fit with two symmetrical lines that should be assigned to the two different Y crystallographic sites expected in the $C2$ unit cell. Similar results are obtained when examining the other compositions. This result implies the existence of more than one Y crystallographic site in the unit cell of the intermediate members and points to a $C2$ space group, which contains two different RE crystallographic sites in the unit cell. Two low intensity signals at 155.6 and 240.7 p.p.m. can be observed in the spectrum of β-$Y_{0.5}Sc_{1.5}Si_2O_7$, corresponding to Y in $X2$-$(Sc,Y)_2SiO_5$, which is a subproduct of the synthesis, as commented in the *Experimental* section. These signals are also present in the rest of the intermediate composition spectra, but are not clearly observed because of the high FWHM of the resonances.

The ^{89}Y MAS CPMG spectra have been simulated with the resonances corresponding to the expected Y sites in the structure (two sites for the intermediate compositions and a unique site for the end member). The results are displayed in
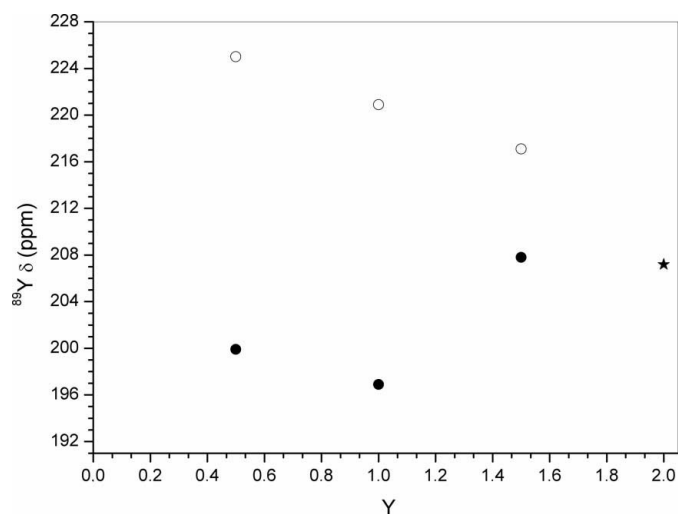
Table 1. The simulation included two additional resonances accounting for two Y sites in $X2$-$(Sc,Y)_2SiO_5$ (Becerro *et al.*, 2004). The [89]Y chemical shift of one of the Y sites of β-$(Y,Sc)_2Si_2O_7$ does vary linearly with composition (open circles in Fig. 2), and the chemical shift of the single Y site in pure β-$Y_2Si_2O_7$ is located in the extrapolation of that line. The second Y site does not show a linear dependence with composition (solid circles in Fig. 2). On the other hand, the area under the curve of each resonance indicates that $Sc_{2-x}Y_xSi_2O_7$ members with $x = 1.0$ and $x = 1.5$ show a homogeneous distribution of Y between both sites, while the $x = 0.5$ composition shows a preferential occupation of Y for one of the crystallographic sites, in good agreement with diffraction results, as will be shown below.

3.2. Diffraction results

Based on the [89]Y NMR data described above, which suggest the existence of two different RE crystallographic sites, as well as on the ^{29}Si MAS NMR data published by Escudero *et al.* (2007), which indicate the existence of a unique Si crystallographic site coupled to a nonlinear Si—O—Si angle, $C2$ appears to be the only alternative possible space group. In fact, Cm, giving the same reflection conditions, can be discarded because of its two different Si sites per unit cell. The viability of the $C2$ space group, compatible with these NMR data, will now be demonstrated by refinement of the structure under this space group from synchrotron and neutron powder diffraction patterns. Refinements using $C2/m$ have also been included for the purpose of comparison.

3.2.1. Study of the intermediate members of the system. *Synchrotron powder diffraction.* Structural refinements have been performed for $Y_xSc_{2-x}Si_2O_7$ compositions with $x = 0.5$, 1.0 and 1.5, using both $C2$ and $C2/m$ space-group models. Fig. 3 shows the experimental and fitted patterns for $Y_{0.5}Sc_{1.5}Si_2O_7$, using space groups $C2$ (Fig. 3*a*) and $C2/m$ (Fig. 3*b*). The fittings

Table 2
Refined atomic coordinates for $Y_{0.5}Sc_{1.5}Si_2O_7$ from synchrotron powder diffraction (11-BM APS) data collected at room temperature.

(*a*) Space group $C2$; $a = 6.62050$ (6), $b = 8.61152$ (7), $c = 4.67462$ (3) Å and $\beta = 102.366$ (1)°. An asterisk indicates the site occupation factors expected in the case of a homogeneous distribution of Sc and Y between both RE sites.

Atom	Site	x	y	z	U_{iso} ($\times$100)	Occupancy
Y1/Sc1	2*b*	0.5	0.8055	0	0.44 (6)	0.335 (4)/0.665 (4) (0.25/0.75)*
Y2/Sc2	2*b*	0.5	0.1935 (1)	0	0.66 (7)	0.165 (4)/0.835 (4) (0.25/0.75)*
Si	4*c*	0.7205 (1)	0.5034 (4)	0.4109 (1)	0.51 (2)	1
O1	2*a*	0.5	0.4778 (4)	0.5	1.23 (2)	1
O2	4*c*	0.8854 (2)	0.4992 (7)	0.7188 (2)	1.23 (2)	1
O3	4*c*	0.7297 (6)	0.6473 (4)	0.2276 (8)	1.23 (2)	1
O4	4*c*	0.7428 (6)	0.3392 (4)	0.2183 (8)	1.23 (2)	1

(*b*) Space group $C2/m$; $a = 6.62047$ (6), $b = 8.61153$ (7), $c = 4.67465$ (3) Å and $\beta = 102.366$ (1)°.

Atom	Site	x	y	z	U_{iso} ($\times$100)	Occupancy
Y/Sc	4*g*	0	0.30614 (4)	0	0.52 (1)	0.25/0.75
Si	4*i*	0.2212 (1)	0	0.4107 (1)	0.52 (2)	1
O1	2*c*	0	0	0.5	1.48 (2)	1
O2	4*i*	0.3847 (2)	0	0.7192 (2)	1.48 (2)	1
O3	8*j*	0.2367 (1)	0.1539 (1)	0.2233 (1)	1.48 (2)	1

Figure 3
Experimental (dots) and fitted (solid line) synchrotron patterns recorded on the 11-BM station (APS, USA) for $Y_{0.5}Sc_{1.5}Si_2O_7$, using (*a*) space group $C2$ and (*b*) space group $C2/m$. The difference curves are also included. Black indexing is the $RE_2Si_2O_7$ phase, red indexing is the RE_2SiO_5 phase and blue indexing is the SiO_2 phase.

Figure 2
[89]Y chemical shifts of the individual contributions of Fig. 1 *versus* nominal composition. Open and solid circles represent the two different Y sites in the intermediate members. The star corresponds to the chemical shift of the unique Y site in the Y-rich end member.
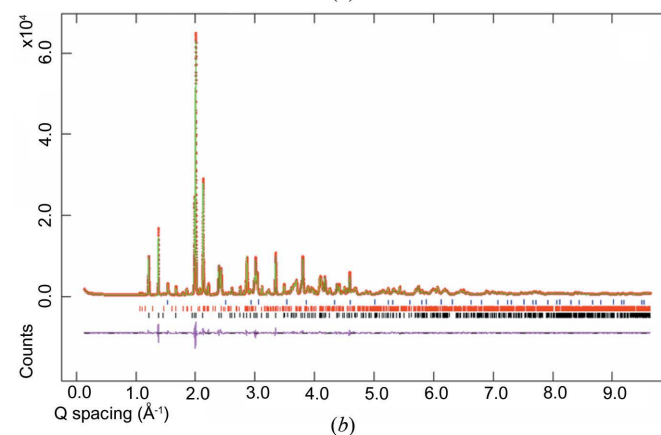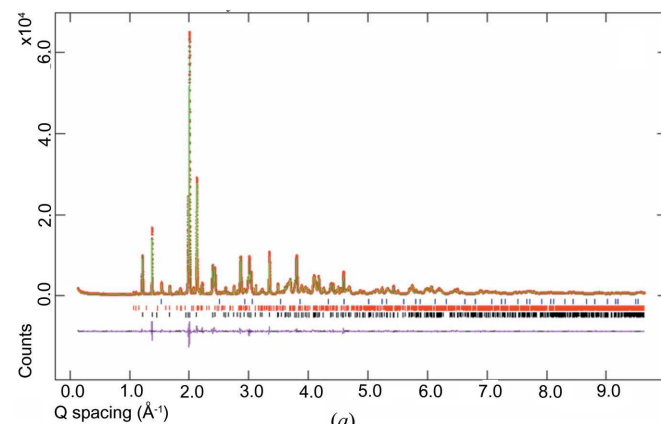
Table 3
Refined atomic coordinates for $YScSi_2O_7$ from synchrotron powder diffraction (11-BM APS) data collected at room temperature.

(a) Space group $C2$; $a = 6.71363$ (3), $b = 8.72253$ (5), $c = 4.67973$ (3) Å and $\beta = 102.084$ (1)°. An asterisk indicates the site occupation factors expected in the case of a homogeneous distribution of Sc and Y between both RE sites.

Atom	Site	x	y	z	U_{iso} ($\times 100$)	Occupancy
Y1/Sc1	2b	0.5	0.76960	0	0.66 (6)	0.50 (1)/0.50 (1) (0.50/0.50)*
Y2/Sc2	2b	0.5	0.15906 (5)	0	0.40 (6)	0.50 (1)/0.50 (1) (0.50/0.50)*
Si	4c	0.72062 (7)	0.4663 (4)	0.4131 (1)	0.64 (1)	1
O1	2a	0.5	0.4871 (3)	0.5	1.30 (2)	1
O2	4c	0.8809 (1)	0.4659 (7)	0.7163 (2)	1.30 (2)	1
O3	4c	0.7534 (3)	0.6204 (3)	0.2227 (6)	1.30 (2)	1
O4	4c	0.7161 (3)	0.3164 (3)	0.2213 (6)	1.30 (2)	1

(b) Space group $C2/m$; $a = 6.71352$ (3), $b = 8.72241$ (5), $c = 4.67975$ (3) Å and $\beta = 102.084$ (1)°.

Atom	Site	x	y	z	U_{iso} ($\times 100$)	Occupancy
Y/Sc	4g	0	0.30527 (2)	0	0.51 (1)	0.5/0.5
Si	4i	0.22097 (6)	0	0.41264 (9)	0.71 (1)	1
O1	2c	0	0	0.5	1.81 (2)	1
O2	4i	0.3817 (1)	0	0.7165 (2)	1.81 (2)	1
O3	8j	0.2345 (1)	0.1523 (1)	0.2225 (1)	1.81 (2)	1

Table 4
Refined atomic coordinates for $Y_{1.5}Sc_{0.5}Si_2O_7$ from synchrotron powder diffraction (11-BM APS) data collected at room temperature .

(a) Space group $C2$; $a = 6.80085$ (7), $b = 8.85057$ (9), $c = 4.70109$ (4) Å and $\beta = 101.854$ (1)°. An asterisk indicates the site occupation factors expected in the case of a homogeneous distribution of Sc and Y between both RE sites.

Atom	Site	x	y	z	U_{iso} ($\times 100$)	Occupancy
Y1/Sc1	2b	0.5	0.8244	0	0.68 (10)	0.71 (1)/0.29 (1) (0.75/0.25)*
Y2/Sc2	2b	0.5	0.2143 (1)	0	0.37 (9)	0.79 (1)/0.21 (1) (0.75/0.25)*
Si	4c	0.7204 (1)	0.5223 (10)	0.4144(2)	0.53 (3)	1
O1	2a	0.5	0.5005 (6)	0.5	1.21 (4)	1
O2	4c	0.8726 (2)	0.5185 (21)	0.7094(3)	1.21 (4)	1
O3	4c	0.7477 (8)	0.6717 (8)	0.2279(15)	1.21 (4)	1
O4	4c	0.7222 (8)	0.3714 (8)	0.2204(15)	1.21 (4)	1

(b) Space group $C2/m$; $a = 6.80082$ (7), $b = 8.85048$ (9), $c = 4.70108$ (4) Å and $\beta = 101.854$ (1)°.

Atom	Site	x	y	z	U_{iso} ($\times 100$)	Occupancy
Y/Sc	4g	0	0.30519 (4)	0	0.51 (1)	0.75/0.25
Si	4i	0.2203 (1)	0	0.4142 (2)	0.54 (2)	1
O1	2c	0	0	0.5	1.49 (3)	1
O2	4i	0.3735 (2)	0	0.7105 (3)	1.49 (3)	1
O3	8j	0.2358 (2)	0.1504 (1)	0.2252 (2)	1.49 (3)	1

of the two other compositions are very similar and are not shown. Tables 2, 3 and 4 show the atomic parameters obtained for the three compositions using space groups $C2$ and $C2/m$.[1] Refinements using the $C2$ space group indicate a preferential occupation of Y and Sc for one of the RE sites in $Sc_{2-x}Y_xSi_2O_7$ with $x = 0.5$ composition, while the two other samples show a homogeneous distribution of Sc and Y between both crystallographic sites, in good agreement with the NMR data (asterisks in Tables 2, 3 and 4 indicate the site occupation factors expected in the case of a homogeneous distribution of Sc and Y between both RE sites). This suggests that the Y/Sc distribution is not random and thus that the substitution mechanism is not linear. This is confirmed by the unusual behaviour of the cell parameters, especially along c, which does not follow Vegard's law. A more detailed study of the substitution mechanism will be the object of future work.

Figs. 4(a) and 4(b) are views of the structures obtained for $Y_{1.0}Sc_{1.0}Si_2O_7$ using space groups $C2$ and $C2/m$. The Si—O—Si angles obtained from the refinements in $C2$ were, respectively, 164.4 (3), 167.2 (3) and 166.4 (2)° for $Y_{0.5}Sc_{1.5}Si_2O_7$, $YScSi_2O_7$ and $Y_{1.5}Sc_{0.5}Si_2O_7$ compositions. The three values are lower than 180°, as calculated from ^{29}Si NMR data (Escudero et al., 2007). Fig. 4(c) is a Fourier map obtained by summing F_{obs} from 0.35 to 0.65 along the z axis of the $YScSi_2O_7$ pattern. The deviation of the Si—O—Si angle from 180° is clearly observed.

These results demonstrate that the refinements using the $C2$ space group are possible and stable for the intermediate
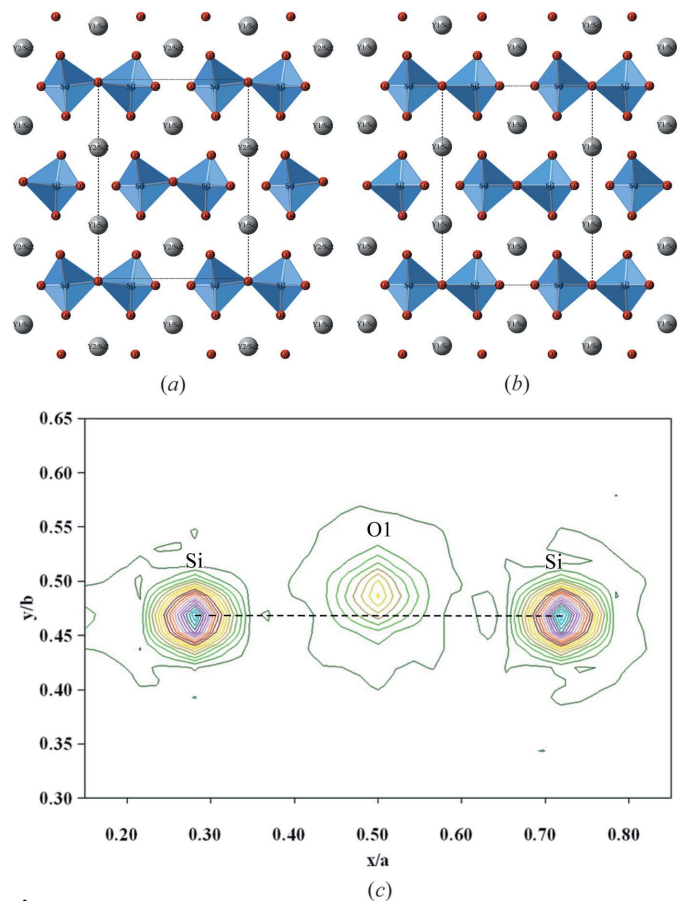

Figure 4
(a) and (b) Views of the structures of $YScSi_2O_7$ using, respectively, space groups $C2$ and $C2/m$. Data obtained from structure refinement of synchrotron data. (c) Fourier map of $YScSi_2O_7$ along the z axis; the deviation of the Si—O—Si angle from 180° is clearly observed.

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: HX5126). Services for accessing these data are described at the back of the journal.

Table 5
Reliability factors obtained from structural refinements of powder synchrotron and neutron diffraction patterns.

	Synchrotron diffraction (11-BM)				Neutron diffraction (D2B)			
	R_{wp} (%)	R_p (%)	R_F^2 (%)	χ^2	R_{wp} (%)	R_p (%)	R_F^2 (%)	χ^2
$Sc_2Si_2O_7$								
C2	8.22	6.42	2.32	7.57	Not recorded			
C2/m	8.27	6.46	2.53	7.66				
$Y_{0.5}Sc_{1.5}Si_2O_7$								
C2	7.20	5.32	2.65	6.49	Not recorded			
C2/m	7.34	5.46	2.85	6.75				
$YScSi_2O_7$								
C2	4.25	3.39	1.43	1.82	3.55	2.84	3.03	1.75
C2/m	4.41	3.55	1.65	1.97	3.59	2.85	3.09	1.80
$Y_{1.5}Sc_{0.5}Si_2O_7$								
C2	7.23	5.37	1.63	4.90	Not recorded			
C2/m	7.30	5.46	1.76	4.99				
$Y_2Si_2O_7$								
C2	6.60	5.16	1.61	4.01	3.64	2.97	2.43	1.94
C2/m	6.65	5.19	1.64	4.05	3.66	2.99	2.03	1.95

Table 6
Refined atomic coordinates for $YScSi_2O_7$ from neutron diffraction (ILL D2B) data collected at room temperature.

(a) Space group C2; a = 6.7396 (4), b = 8.7555 (5), c = 4.6981 (3) Å and β = 102.075 (3)°.

Atom	Site	x	y	z	U_{iso} ($\times 100$)	Occupancy
Y1/Sc1	2b	0.5	0.7702	0	0.57 (34)	0.46 (9)/0.54 (9)
Y2/Sc2	2b	0.5	0.1557 (4)	0	0.68 (37)	0.54 (9)/0.46 (9)
Si	4c	0.7211 (6)	0.4652 (27)	0.4126(9)	0.75 (9)	1
O1	2a	0.5	0.4828 (14)	0.5	2.34 (19)	1
O2	4c	0.8831 (4)	0.4683 (19)	0.7195(6)	0.95 (9)	1
O3	4c	0.7440 (14)	0.6186 (13)	0.2205(22)	0.76 (25)	1
O4	4c	0.7277 (14)	0.3125 (14)	0.2176(25)	1.15 (27)	1

(b) Space group C2/m; a = 6.7211 (4), b = 8.7314 (6), c = 4.6852 (3) Å and β = 102.077 (3)°.

Atom	Site	x	y	z	U_{iso} ($\times 100$)	Occupancy
Y/Sc	4g	0	0.3072 (2)	0	0.59 (5)	0.5/0.5
Si	4i	0.2217 (7)	0	0.4125 (9)	0.73 (10)	1
O1	2c	0	0	0.5	3.27 (15)	1
O2	4i	0.3827 (5)	0	0.7199 (6)	0.90 (9)	1
O3	8j	0.2361 (3)	0.1530 (2)	0.2186 (5)	0.91 (7)	1

compositions. Reliability factors are quite good in both space groups (Table 5), although, in terms of fit quality, there is no real difference between the two space-group refinements. Thus, synchrotron XRD data refinements indicate that the C2 model is possible for the intermediate members of the β-$(Sc,Y)_2Si_2O_7$ system, as suggested by the [89]Y MAS NMR data.

Neutron powder diffraction. Neutron diffraction data refinements performed on $Y_{1.0}Sc_{1.0}Si_2O_7$ composition were also possible in both C2 and C2/m space groups. Fig. 5 shows the experimental and fitted patterns for $YScSi_2O_7$, using space groups C2 (Fig. 5a) and C2/m (Fig. 5b). Reliability factors (Table 5) are quite good in both space groups, but, again, in terms of fit quality, there is no real difference between the two space-group refinements. Table 6 shows the atomic parameters obtained for this composition. The Si—O—Si angle obtained from the refinements in C2 was 169.2 (17)°, in good agreement with the synchrotron data.

3.2.2. Study of the end members of the system. Although the [89]Y MAS NMR and diffraction data on the intermediate members strongly suggest a C2 model, an extra argument to ensure that the non-180° values of the Si—O—Si angles of the intermediate compositions are real and probably linked to the C2 space group would be to obtain angle values close to 180° for the $Sc_2Si_2O_7$ and β-$Y_2Si_2O_7$ end members when refined in C2, even if it has been proved that this is not the proper symmetry for these compositions (Bianchi *et al.*, 1988; Redhammer & Roth, 2003).

Synchrotron powder diffraction patterns were recorded with this purpose on $Sc_2Si_2O_7$ and β-$Y_2Si_2O_7$ compositions and the structures were refined using the C2 space-group structural model. Refinements are possible in C2 for both compositions. In the $Sc_2Si_2O_7$ case, a refined Si—O—Si angle value very close [179.5 (1)°] to the linear 180° value required of the C2/m symmetry was obtained. Two conclusions can be

Figure 5
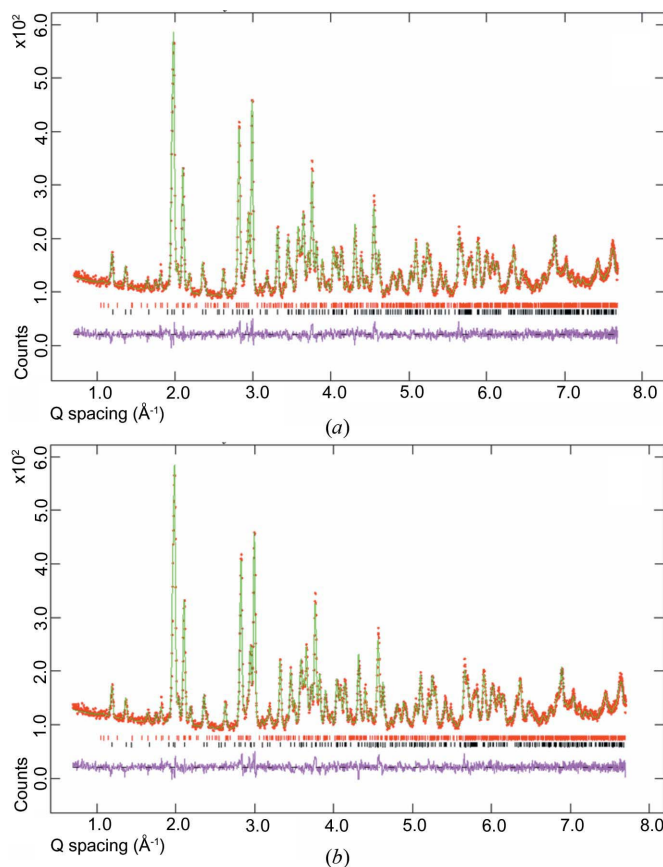Experimental (dots) and fitted (solid line) neutron patterns recorded at the D2B station (ILL, Grenoble, France) for $YScSi_2O_7$, using (a) space group C2 and (b) space group C2/m. The difference curves are also included. Black indexing is the $RE_2Si_2O_7$ phase and red indexing is the RE_2SiO_5 phase.

drawn from this result: (i) both $C2$ and $C2/m$ refinements converge to a similar physical description of the scandium end member crystal structure, and (ii) the Si—O—Si bond angles obtained in refinements using the $C2$ model are a good indication of the correct symmetry ($C2$ or $C2/m$ space group) for compositions in this system.

However, this was not exactly the case for β-$Y_2Si_2O_7$, where the Si—O—Si angle refined value was 177.2 (5)°. This result, though close to 180° and far from the values obtained for the intermediate compositions (164–167°), is not entirely conclusive. It could be linked to the fact that X-rays are not very sensitive to light elements like oxygen, especially when a heavy atom like yttrium is present in the structure. In order to overcome this disadvantage and obtain more accuracy on the Si—O—Si angle value, we have recorded neutron powder diffraction patterns of the β-$Y_2Si_2O_7$ composition. Indeed neutron scattering lengths of the different species (Y, Si and O) are much closer than the X-ray ones for which Y is far from predominant. Structure solution for β-$Y_2Si_2O_7$ using the neutron diffraction data has thus been performed in the $C2$ space group, leading to a 179.1 (16)° value for the Si—O—Si angle and so confirming our previous results.

4. Conclusions

[89]Y MAS NMR spectroscopy indicates the existence of a unique RE crystallographic site in the unit cell of the Y-rich end member of the $Sc_2Si_2O_7$–β-$Y_2Si_2O_7$ system, while the spectra of the intermediate members point to the presence of two different RE sites. Moreover, ^{29}Si MAS NMR measurements of the intermediate members show a unique Si crystallographic site and an Si—O—Si angle lower than 180°, incompatible with the $C2/m$ space group. These results suggest that, although $C2/m$ is the space group of the end members, the intermediate members crystallize in a lower-symmetry space group. The viability of $C2$, the only alternative space group matching the NMR results requirements, has been demonstrated by means of synchrotron and neutron powder diffraction data.

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