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Revisiting $Y_2Si_2O_7$ and Y_2SiO_5 polymorphic structures by ^{89}Y MAS-NMR spectroscopy

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Abstract

This paper describes the ^{89}Y MAS-NMR spectra for all the established polymorphs of $Y_2Si_2O_7$ (y, α, β, γ and δ) and Y_2SiO_5 ($X1$ and $X2$). The combination of our spectroscopic data with the structural information published up to now from diffraction data permits the revision and correction of mistakes which appear in the literature. Finally, the influence of different structural factors, such as yttrium coordination number and Y–O distances on the ^{89}Y NMR isotropic chemical shift is analyzed.

Keywords: Crystal structure; ^{89}Y MAS-NMR spectroscopy; Polymorphism; Silicates; Yttrium

1. Introduction

Although yttrium does not belong to the rare earth (RE) elements, it shows similarities to this group because of the equivalent electronic configuration of Y and La, and also because the radius of Y^{3+} lies within the range of the trivalent radii of the second half of the lanthanides [1]. Phase relationships in RE and yttrium silicates have been extensively studied for both applied and academic interests. They were originally studied because of an interest in laser materials and in high-energy phosphors based on RE-doped yttrium silicate [2]. Recently, interest in these systems has been renewed because yttrium and other RE oxides are used as additives for advanced ceramic materials, mainly Si_3N_4 and SiC. After firing, a glassy yttrium or RE disilicate phase is formed at the grain boundaries, which, upon crystallisation, improves the high temperature mechanical properties of the material [3]. From an academic point of view, yttrium silicate compounds show an extensive polymorphism and they constitute clear examples of reconstructive phase transitions. Yttrium orthosilicate (Y_2SiO_5) exhibits two different polymorphs with temperature (namely, $X1$ and $X2$), while yttrium disilicate ($Y_2Si_2O_7$) shows up to six polymorphs (y, α, β, γ, and δ, and, possibly, z) [4].

The need for reliable crystallographic information on the different polymorphs led Liddell and Thompson, in 1986, to summarize reliable X-ray diffraction data for all these phases [5]. Since then, new diffraction data have been compiled for both compounds Y_2SiO_5 and $Y_2Si_2O_7$, and they show some controversy about the space groups assigned to some of the $Y_2Si_2O_7$ polymorphs and the number of crystallographic sites of Y atoms varies from one description to the other.

Spectroscopic techniques, such as nuclear magnetic resonance (NMR), have proven to be extremely useful for structure elucidation in solid materials. In fact, well-resolved ^{29}Si MAS-NMR spectra have been published for five out of six $Y_2Si_2O_7$ polymorphs [6,7] and for both Y_2SiO_5 polymorphs [8,9] which agree well with the existing crystallographic data. Additional data are, nevertheless, needed to definitively determine the structural arrangement of the different polymorphs. ^{89}Y MAS-NMR spectroscopy provides an additional

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source of data which has the potential to clearly differentiate chemically distinct Y environments in each structure. However, although ^{89}Y has the favorable NMR characteristics of 1/2 spin and 100% natural abundance, the extremely long relaxation time and poor sensitivity, due to its low γ, make it difficult to obtain a spectrum with high signal/noise ratio within a reasonable time frame. Obtaining ^{89}Y MAS-NMR data is further hindered by the fact that probe ringing (seen as a rolling baseline) is not negligible with this low frequency nucleus [10]. In addition, if the crystallinity of the sample is not high enough, the spectral lines do not resolve and the different contributions to the ^{89}Y resonance cannot be separated. Dupree and Smith [11] have reported the isotropic ^{89}Y NMR chemical shifts for the α, β, γ, and δ-$Y_2Si_2O_7$ polymorphs as well as for $X2$-Y_2SiO_5. However, the linewidths reported for some of them are extremely broad and, the different resonances cannot be separated.

The aims of the present study are the following: (i) to describe, for the first time, the ^{89}Y MAS-NMR spectra of y-$Y_2Si_2O_7$ and $X1$-Y_2SiO_5; (ii) to show improved spectra for the other polymorphs, with narrower lines, which enables the establishment of the exact number of different crystallographic Y sites in each structure; (iii) the combination of this spectroscopic information with the structures published from diffraction data allows revising and correcting possible errors which appear in the literature and; finally, (iv) the influence of different structural factors, such as yttrium coordination number (CN) and Y–O distances, on the ^{89}Y NMR isotropic chemical shift is analyzed.

2. Experimental

2.1. Synthesis of the yttrium silicate compounds

All $Y_2Si_2O_7$ polymorphs, except the y-phase, were synthesised following the ceramic method. SiO_2 (Silica fumed 99.8%, Sigma) and $Y(NO_3)_3 \cdot 6H_2O$ (Aldrich) in molar ratio 1:1 were mixed in excess ethanol with magnetic stirring for 2 h. The solution was dried in the oven at 60°C for 24 h and the nitrate were then removed by heating up to 500°C for 1 h at 1°C/min. The powder was divided into four portions and pressed into pellets, which were sintered at different temperatures in air.

The low temperature y-$Y_2Si_2O_7$ polymorph (y-phase) could not be obtained following the ceramic method because at low temperatures the reaction between SiO_2 and $Y(NO_3)_3$ is too slow and if the reaction temperature is enhanced, the high temperature polymorphs appear. A hydrothermal method, recently described by us [7], was followed, which involves the use of layered clay as silicon source. The clay, saponite, is submitted to hydrothermal treatment in a 0.1 M $Y(NO_3)_3$ aqueous solution at 365°C and the reaction yields y-$Y_2Si_2O_7$ in the bulk without high temperature polymorphs.

Regarding the synthesis of Y_2SiO_5 polymorphs, the low temperature one, $X1$-Y_2SiO_5, was obtained following the ceramic method, in a similar way to that for the $Y_2Si_2O_7$ polymorphs. In this case, the molar ratio was $1SiO_2{:}2Y(NO_3)_3 \cdot 6H_2O$ and the powder was annealed, after removal of nitrates, at 1050°C for 5 days in air, at a heating rate of 5°C/min. Synthesis of $X2$-Y_2SiO_5 was not necessary as it always appeared as a secondary product in the $Y_2Si_2O_7$ synthesis. The ^{89}Y MAS-NMR study of this phase has been carried out from the signal observed in the spectrum of the γ-$Y_2Si_2O_7$, which showed the best signal to noise ratio for the Y resonance due to $X2$-Y_2SiO_5.

2.2. ^{89}Y MAS-NMR spectra

The ^{89}Y MAS-NMR spectra were obtained with a Bruker MSL-300 spectrometer operating at 14.7 MHz for ^{89}Y. The powder samples were packed into 7 mm zirconia rotors and spun at 4 kHz at the magic angle. Single pulse spectra were recorded by using 10° pulses with an optimized delay time of 6 s. Spectral smoothing of up to 5 Hz was employed to improve the signal/noise ratio. Chemical shifts are reported to be relative to a 1 M solution of YCl_3. The spectra were simulated using a modified version of the Bruker Winfit program to handle the finite spinning speed in MAS experiments [12]. A Gaussian–Lorentzian model was used for all the peaks and fitted parameters were amplitude, position, linewidth and the Gaussian/Lorentzian ratio.

2.3. X-ray diffraction diagrams

The X-ray diffraction patterns were taken in a Siemens D-501 diffractometer, using Ni-filtered Cu $K\alpha$ radiation, with steps of 0.05° and a counting time of 5 s.

3. Results and discussion

Fig. 1 displays the experimental and simulated ^{89}Y MAS-NMR spectra of the y, α, β, γ and δ-$Y_2Si_2O_7$ and $X1$ and $X2$-Y_2SiO_5 polymorphs. The isotropic chemical shifts were easily retrieved from these spectra because of the very small ^{89}Y chemical shift anisotropy and because the spinning speed was high enough as to avoid any spinning side bands. The results of all simulations (isotropic chemical shifts and full-width at half-maximum (fwhm)) are given in Table 1.

The spectrum of y-$Y_2Si_2O_7$ (Fig. 1a) shows a single Y resonance at 118.14 ppm with a fwhm of 60.0 Hz, suggesting the presence of a unique Y site in the structure. Fig. 2 shows the agreement between the X-ray diffraction pattern of our sample and the pattern calculated from the y-$Y_2Si_2O_7$ standard data [13]. However, the ^{89}Y NMR result is in disagreement with the crystallographic description obtained from the structural data given by Batalieva and Pyatenko [13] (see Table 1) which indicate the presence of two crystallographically different Y sites, equally populated, in the unit cell. Were the y-$Y_2Si_2O_7$ unit cell to contain two different Y sites, they would give two well-separated resonances in the ^{89}Y MAS-NMR spectrum, even when the CN of both Y sites was the same (=6). This is the case, for example, of c-Y_2O_3, which shows two well resolved Y resonances in the MAS-NMR spectrum (separated by 41.5 ppm one from the other) [14] corresponding to two crystallographically different Y sites in the unit cell, both with CN 6 and Y–O mean distances as close as 2.283 and 2.284 Å [15].

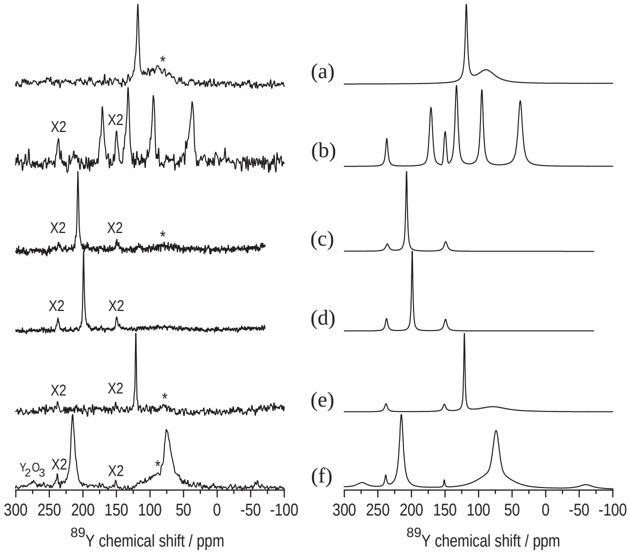

Fig. 1. Experimental (left) and simulated (right) ^{89}Y MAS-NMR spectra of the y- (a), α- (b), β- (c), γ- (d), δ-$Y_2Si_2O_7$ (e) and $X1$-Y_2SiO_5 (f) polymorphs. ^{89}Y resonances for $X2$-Y_2SiO_5 are marked in spectra b, c, d and e. The asterisk corresponds to Y from the NMR rotor (Y-stabilised zirconia).

The spectrum of α-$Y_2Si_2O_7$ (Fig. 1b) shows four Y resonances clearly resolved, spread over a range of ~130 ppm, which are due to the four different crystallographic Y sites expected in the α-$Y_2Si_2O_7$ polymorph. No structural study (in terms of atomic positions) has been reported for α-$Y_2Si_2O_7$; the structural arrangement of the α-type polymorph has only been established, to our knowledge, for α-$Ho_2Si_2O_7$ [16] and α-$Dy_2Si_2O_7$ [17] and in both of them, the RE element presents four different crystallographic sites. Our spectrum considerably improves the resolution of Dupree and Smith's data for α-$Y_2Si_2O_7$ [11] which shows a unique signal, at 114 ppm and 110 Hz fwhm. In addition to the four resonances corresponding to α-$Y_2Si_2O_7$, two peaks can be observed in Fig. 1b corresponding to $X2$-Y_2SiO_5, which appear as a secondary product in the ceramic synthesis of all the disilicates (see Section 2).

The β-$Y_2Si_2O_7$ spectrum (Fig. 1c) displays, in addition to the resonances of $X2$-Y_2SiO_5, a unique Y resonance at 207.31 ppm with fwhm of 40.5 Hz, which indicates a single Y site in the structure, in good agreement with the data of Dupree and Smith [11], who report a unique but broader signal (fwhm of 55 Hz) at 208 ppm. Like the case of α-$Y_2Si_2O_7$, only the unit cell dimensions are known for β-$Y_2Si_2O_7$ [5], but no structural data have been published. The structural

Table 1
Crystallographic data for $Y_2Si_2O_7$ and Y_2SiO_5 polymorphs and ^{89}Y MAS-NMR parameters obtained from the simulation of the spectra

Compound	Crystallography from diffraction data				^{89}Y MAS-NMR parameters from this study (digital resolution = 7.6 Hz/point)	
	No. of crystallographic Y sites	Y Coord. number	Mean Y–O distance (Å)	Ref.	^{89}Y Chemical shift (ppm)	Line-width (Hz)
y-$Y_2Si_2O_7$	2	6	2.355	[13]	118.1	60.0
			2.290			
α-$Y_2Si_2O_7$	4	8	2.418	[4]	170.8	84.2
			2.422		132.9	78.8
			2.461		95.1	74.7
			2.471		37.7	114.1
β-$Y_2Si_2O_7$	1	6	2.269[a]	—	207.3	40.5
γ-$Y_2Si_2O_7$	1	6	2.281	[21]	198.9	35.4
δ-$Y_2Si_2O_7$	1	7	2.34	[22]	121.1	33.9
	2	7	2.307	[19]		
			2.397			
$X1$-Y_2SiO_5	2	7	2.390	[23]	215.1	7.1
		9	2.456		73.9	10.6
$X2$-Y_2SiO_5	2	6	2.268	[24]	237.1	52.8
		7	2.349		149.5	56.7

[a] See text for calculation.

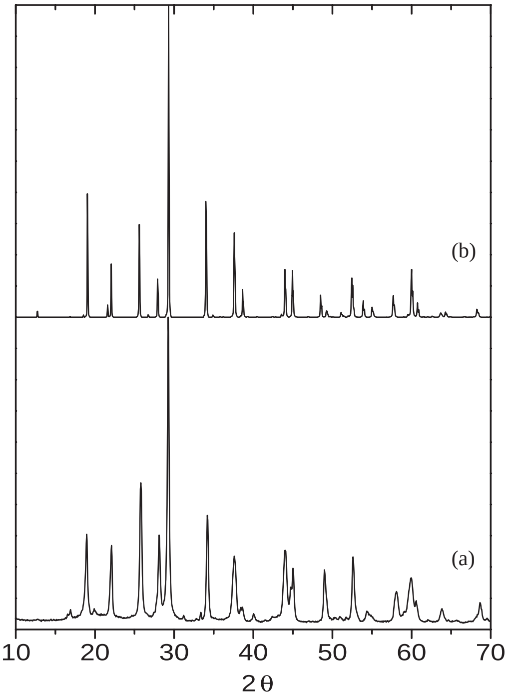

Fig. 2. X-ray diffraction patterns of γ-$Y_2Si_2O_7$: (a) as-synthesized by hydrothermal method (this study) and (b) calculated from the structural data given by Batalieva and Pyatenko [13] (the linewidth in (b) is arbitrary).

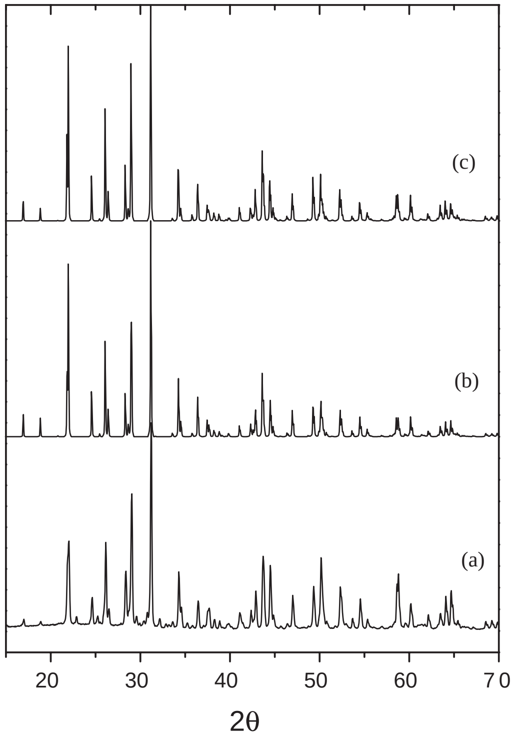

Fig. 3. X-ray diffraction patterns of δ-$Y_2Si_2O_7$: (a) as-synthesized by ceramic method (this study), (b) calculated pattern from data in Dias et al. [22] and (c) calculated pattern from data in Christensen [19] (the linewidths in (b) and (c) are arbitrary).

arrangement of the β-polymorph has been established for $Lu_2Si_2O_7$ [18], $Yb_2Si_2O_7$ [19], $Er_2Si_2O_7$ [19] and $Sc_2Si_2O_7$ [20]; all of them consist of a single RE element site. The ^{89}Y NMR spectrum, shown in Fig. 1c, is in agreement with this description.

A similar spectrum is observed for the γ-$Y_2Si_2O_7$ polymorph (Fig. 1d), with the single Y resonance at slightly lower fields (198.89 ppm) and fwhm of 35.4 Hz. The spectrum recorded by Dupree and Smith [11] for this polymorph also shows a single Y resonance at 198 ppm but double fwhm. The low fwhm of our γ-$Y_2Si_2O_7$ spectrum reconfirms the single nature of the Y site in the unit cell of this polymorph, as inferred from diffraction data [21].

The spectrum of δ-$Y_2Si_2O_7$ (Fig. 1e) exhibits a single Y resonance at higher fields, 121.14 ppm. Regarding crystal structure analyses, two different studies have been published. The first one, by Dias et al. [22], describes the unit cell in terms of the orthorhombic space group *Pnam* and assigns a unique site to Y, with CN = 7. The second one, by Christensen [19], uses the orthorhombic space group *Pna*2_1 and assigns two different crystallographic sites to Y, both with CN = 7. Fig. 3 shows that both crystallographic descriptions produce indistinguishable theoretical X-ray diffraction patterns. Therefore, only a technique such as ^{89}Y NMR spectroscopy, which informs directly about the short-range order of Y, is able to clarify the real structure of the polymorph. The spectrum shown in Fig. 1e is in contradiction with the powder diffraction data analysis of Christensen [19], which gives two different Y sites for the unit cell of δ-$Y_2Si_2O_7$, and reinforces the single crystal X-ray diffraction study by Dias et al. [22], which assigns a unique crystallographic site to Y. The assertion that there is a unique Y crystallographic site in the unit cell of the δ polymorph is now possible from the low fwhm (33.9 Hz), compared to that of 130 Hz reported by Dupree and Smith [11].

Fig. 1f displays the ^{89}Y MAS-NMR spectrum of *X*1-Y_2SiO_5. It shows two well-resolved Y resonances at 215.2 and 75.2 ppm, in agreement with the recent crystallographic description of this polymorph [23]. The spectrum shows, in addition, several resonances corresponding to *c*-Y_2O_3 and *X*2-Y_2SiO_5, which have been marked in the figure.

The ^{89}Y magnetic resonance in *X*2-Y_2SiO_5 has been analyzed from the spectrum of Fig. 1d, where the signals corresponding to this compound are clearly visible. The *X*2-Y_2SiO_5 structure has two crystallographically distinct Y sites [24], which produce two well-separated resonances in the ^{89}Y MAS-NMR spectra at 237.09 and 149.45 ppm.

Table 1 displays the spectroscopic data from this study as well as the structural parameters for each

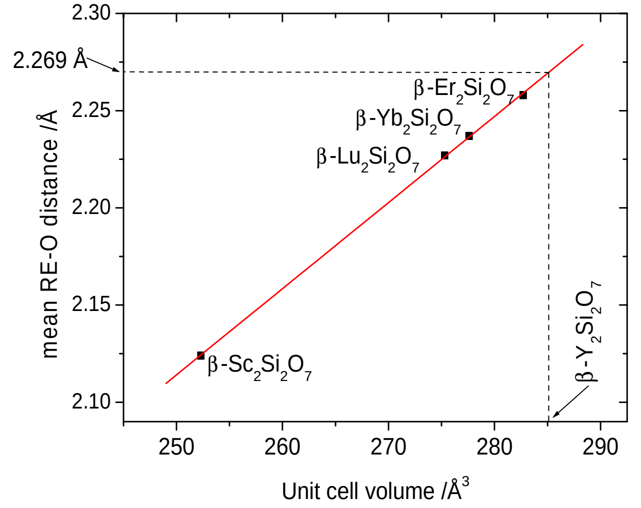

Fig. 4. Determination of the mean Y–O distance in β-$Y_2Si_2O_7$ (regression line: $y = 1.006(4) + 0.0044x$; regression coefficient = 0.9999).

polymorph obtained from the diffraction data in the literature. In the case of α- and β-$Y_2Si_2O_7$, due to the lack of a crystallographic study, the Y–O distances data have been obtained as follows:

(i) *α-polymorph*: The α-$Y_2Si_2O_7$ structural data are expected to be very close to those of α-$Ho_2Si_2O_7$ given the similar ionic radius of Y(III) and Ho(III) (0.900 and 0.901 Å, respectively, in 8-fold coordination) [25]. An illustrative example is the comparison between the structural data of δ-$Y_2Si_2O_7$ [19], and δ-$Ho_2Si_2O_7$ [19]: the mean RE–O distances are exactly the same for both compounds. Thus, Y–O distances of α-$Y_2Si_2O_7$ are taken, for the present study, as those in α-$Ho_2Si_2O_7$.

(ii) *β-polymorph*: To determine the mean Y–O distance in β-$Y_2Si_2O_7$, we have taken the mean RE–O distance of the unique RE site in those disilicates that show the β modification ($Lu_2Si_2O_7$ [18], $Yb_2Si_2O_7$ [19], $Er_2Si_2O_7$ [19], and $Sc_2Si_2O_7$ [20]) and plotted it versus their unit cell volume (Fig. 4). The data exactly fit into a line (regression coefficient = 0.9999) and a mean Y–O distance of 2.269 Å is obtained by extrapolation of the line to the β-$Y_2Si_2O_7$ unit cell volume value (taken from Ref. [5]).

Fig. 5 displays the relation of the ^{89}Y chemical shift with two structural parameters: Y CN (Fig. 5a) and mean Y–O distance (Fig. 5b). In general, an increase in the cation CN corresponds to a lower Pauling electrostatic bond strength, i.e. to a more ionic character of the bond between the cation and the oxygen [1] and hence the isotropic Y signal shifts to lower frequency [26]. Based on this hypothesis, we have assigned the lower ^{89}Y chemical shift values to the higher Y CN in those compounds with different Y CNs (namely, $X1$-Y_2SiO_5 and $X2$-Y_2SiO_5). Fig. 5a shows an overall tendency to decrease the isotropic chemical shift upon increasing Y CN. However, it also shows a strong overlap between various Y CN; for example, the signal corresponding to CN = 9 (one of the Y sites in $X1$-Y_2SiO_5) is inside the range found for CN = 8. Similar behavior is observed in the system Y_2O_3–Al_2O_3 and the authors attribute this result to the 74% ionic character of the Y–O bond, that leads to nondirectional bonding schemes and therefore to a loss of definition of CN and/or to the influence of higher coordination spheres [27]. The data point for y-$Y_2Si_2O_7$ has not been included inside the bar due to the disagreement between the crystallographic structure

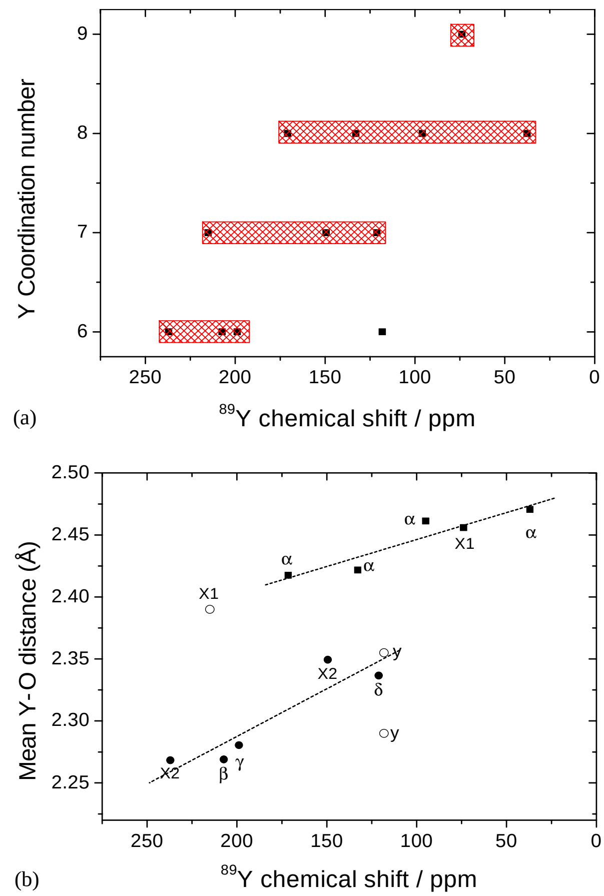

Fig. 5. (a) CN of Y in the different $Y_2Si_2O_7$ and Y_2SiO_5 polymorphs (taken from the diffraction data and described in Table 1) plotted versus the corresponding ^{89}Y isotropic chemical shift. The data point for y-$Y_2Si_2O_7$ has not been included inside the bar due to the disagreement between the crystallographic structure obtained from diffraction data and the spectroscopic data in this work. (b) Mean Y–O distance of all the Y sites in the $Y_2Si_2O_7$ and Y_2SiO_5 polymorphs (taken from the diffraction data) plotted versus the corresponding ^{89}Y isotropic chemical shift. Two regression lines have been calculated for both high (upper line, squares) and low (lower line, filled circles) CN Y sites. The data of y-$Y_2Si_2O_7$ and of the low CN Y site in $X1$-Y_2SiO_5 (open circles) have not been taken into account for the regression line for the reasons explained in the text.

obtained from diffraction data and the spectroscopic data in this work. However, its position seems to indicate an Y CN > 6 for the unique Y site in y-$Y_2Si_2O_7$.

Fig. 5b shows a trend where the isotropic chemical shift decreases with increasing Y–O mean distance for the polymorphs with a unique Y site (β, γ and δ). The same trend has been assumed for the assignment of the chemical shifts to the Y–O distances in the rest of polymorphs, which is also in agreement with the trend of decreasing chemical shift with increasing Y CN observed above. Two regression lines can be drawn for low (YO_6 and YO_7) and high (YO_8 and YO_9) CNs, which indicate a close to linear dependence of the isotropic chemical shift with mean Y–O distance. Several remarks are appropriate at this point:

- the data points corresponding to y-$Y_2Si_2O_7$ have not been included for the linear regression of the low CN curve due to the disagreement between the current crystallographic description of the y-$Y_2Si_2O_7$ structure [13] and the ^{89}Y MAS-NMR data reported here. The regression line, however, indicates that the suggested unique Y site in the y-$Y_2Si_2O_7$ unit cell should be very similar to that with the higher mean Y–O distance described in Ref. [13].
- The data point corresponding to the low CN Y site in $X1$-Y_2SiO_5 is extremely far from the curve corresponding to the low CN data points of the rest of polymorphs. This fact indicates a possible error in the structural determination of the Y–O coordination sphere in Ref. [23], and the data point has not been included for the regression line calculation in Fig. 5b. To support this hypothesis we have calculated the mean RE–O distance for the low CN RE site in other $X1$-RE_2SiO_5 compounds, namely Lu_2SiO_5 [28], Er_2SiO_5 [28] and Tm_2SiO_5 [28] (no structural data have been found for the rest of $X1$-RE_2SiO_5). The mean RE–O distance has been plotted against both the ionic radius of the RE (III) cation in CN = 7 [25] and the unit cell volume (Fig. 6). The RE–O mean distance increases linearly with increasing both ionic radius and unit cell volume (regression coefficients = 0.9937 and 0.9988, respectively) for all three RE cations. An Y–O distance of 2.35 Å is obtained, which deviates strongly from the mean Y–O distance (2.39 Å) calculated from Ref. [23]. However, the extrapolated distance is still a long way from the low CN correlation in Fig. 5b. A further crystallographic study on $X1$-Y_2SiO_5 is demanded.

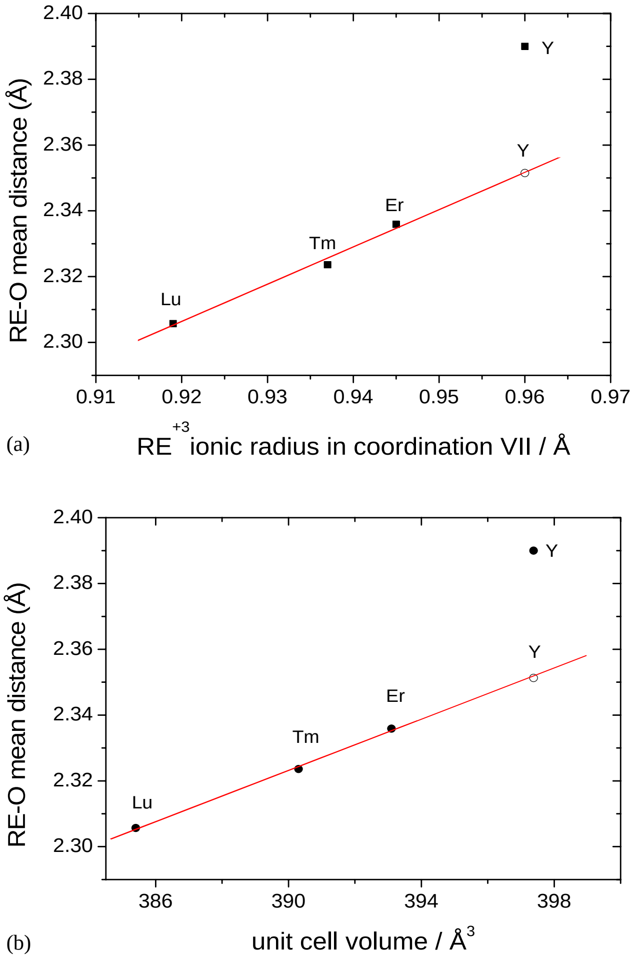

Fig. 6. Solid circles: Mean RE–O distance for the low CN RE site in $X1$-Lu_2SiO_5, $X1$-Er_2SiO_5, $X1$-Tm_2SiO_5 and $X1$-Y_2SiO_5 plotted versus (a) the ionic radius of the RE (III) cation in CN = 7 and (b) the unit cell volume. The data point for $X1$-Y_2SiO_5 has not been taken for the linear fits. White circles: Y–O distance obtained by extrapolation of the line towards the Y ionic radius (in (a)) and the $X1$-Y_2SiO_5 unit cell volume (in (b)).

4. Conclusions

The new ^{89}Y MAS-NMR data for the y-$Y_2Si_2O_7$, α-$Y_2Si_2O_7$, and $X1$-Y_2SiO_5 polymorphs presented in this paper as well as the narrower lines obtained for the other polymorphs, in comparison with the data already published, permit the clarification of some structural aspects of these compounds and the establishment of several correlations between the ^{89}Y chemical shift and structural parameters. The y-$Y_2Si_2O_7$ unit cell does not seem to contain two crystallographically different Y sites, but only one, as suggested by the unique Y resonance in the spectrum of this compound. A revised diffraction experiment is necessary to reconfirm or not this suggestion. The four Y sites in the α-$Y_2Si_2O_7$ structure can be clearly resolved in the ^{89}Y MAS-NMR spectrum when a well-crystallized sample is used. The narrow unique Y resonance obtained for δ-$Y_2Si_2O_7$ enables the establishment of the correct crystallographic description of this polymorph between the two existing in the literature, so that the one accounting for a single crystallographic Y site in the unit cell seems to be the correct one.

A quasi-linear correlation between the mean Y–O distance and the ^{89}Y chemical shift is observed for most of the yttrium silicate compounds, except for one of the two Y sites in $X1$-Y_2SiO_5. This exception could correspond to an error in the crystallographic description of this compound. Finally, a general trend to decrease the isotropic chemical shift with increasing Y CN is also observed, although a strong overlap from the next nearest neighbors effects occurs so that detailed structural assignments based on chemical shift alone need to be approached cautiously.

Acknowledgments

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