Phase Transitions in Lu-Doped $Y_2Si_2O_7$ at High Temperatures

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Phase transitions in $Lu_xY_{2-x}Si_2O_7$ with $x = 1.0$ are studied as a function of temperature because they are important in the field of Si_3N_4 and SiC structural ceramics sintered with rare-earth oxides. Several complementary techniques of long- and short-range order study have been selected for a detailed ex-situ characterization of the samples. At low temperatures (≤1100 °C), *y*- and α-$RE_2Si_2O_7$ polymorphs form, with Y and Lu sharing the RE crystallographic site. At 1200 °C the structure transforms to β-$RE_2Si_2O_7$ (RE = Y and Lu), and this polymorph remains as the stable phase up to, at least, 1650 °C. The comparative study of these results with pure $Lu_2Si_2O_7$ and $Y_2Si_2O_7$ constitutes the first step for the construction of the phase diagram $Lu_2Si_2O_7$−$Y_2Si_2O_7$.

Introduction

The structure of rare-earth silicates has been intensively studied for a few decades due to both basic and applied interests. They play an important role in the sintering of silicon nitride (Si_3N_4), which has become an important class of materials for structural applications at high temperature. Si_3N_4 has high-temperature strength, resistance to oxidation, creep resistance, a low coefficient of thermal expansion, and good thermal shock and chemical attack.[1−5] However, it is difficult to sinter because of the low diffusivity of this covalent material.[6] Densification was initially achieved by liquid-phase sintering using MgO as the sintering additive,[7] but it caused high-temperature strength loss which is attributed to the formation of a vitreous silicate intergranular phase.[8,9] The silicate, formed from the surface silica on the Si_3N_4 powders and the MgO, melts at 1500−1600 °C and acts as the densifying flux in liquid-phase sintering. The silicate concentrates alkali impurities, which reduces the softening temperature causing the premature strength loss. Much effort has been made to improve the high-temperature mechanical properties of silicon nitride including the use of other oxides and crystallization of the intergranular glassy phase by a postsintering heat treatment. It has been shown that when RE oxides (RE = lanthanides and yttrium), single or mixed, are added to the powder of pure Si_3N_4 as sintering aids, a glassy disilicate phase ($RE_2Si_2O_7$) forms in the intergranular regions which, upon crystallization, improves the high-temperature mechanical properties of the material.[10−15]

Knowledge of the crystalline structures adopted by the $RE_2Si_2O_7$ intergranular phase at different temperatures and RE contents is therefore of great value in understanding the behavior of these materials. Several studies have shown that the high-temperature strength and oxidation resistance of Si_3N_4 are correlated with the cationic radius of the RE cation in the oxide additives, such that the smaller the RE cationic radius the better the properties of the silicon nitride.[15,16] The three RE oxides that show the highest flexural strength values are Y_2O_3, Lu_2O_3, and Sc_2O_3. We selected the first two cations to examine the phase transitions with temperature and composition in the $Lu_2Si_2O_7$−$Y_2Si_2O_7$ system. This paper is part of a basic solid-state inorganic chemistry study which aims to analyze the structure and properties of the different members along $Ln_2Si_2O_7$−$Y_2Si_2O_7$ (Ln = lanthanide) with increasing temperature.

The academic interest of the present study resides in the fact that $Lu_2Si_2O_7$ forms a unique polymorph in the whole temperature range, called β-$Lu_2Si_2O_7$, while $Y_2Si_2O_7$ shows up to five polymorphs with increasing temperature (*y*, α, β, γ, and δ).[17] Transition temperatures between the different $Y_2Si_2O_7$ polymorphs as well as temperature stability ranges

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vary considerably from one author to the other.[12,18−23] In addition, the results are limited in the lower temperature range by the slow reaction rate of the starting materials. Ito and Johnson[24] established the following sequence

$$\alpha \xrightarrow{1225\ °C} \beta \xrightarrow{1445\ °C} \gamma \xrightarrow{1535\ °C} \delta$$

but did not include the other low-temperature polymorph (*y*). Direct transitions from y-$Y_2Si_2O_7$ to β-$Y_2Si_2O_7$ have also been reported.[25,26]

We selected the $Lu_xY_{2-x}Si_2O_7$ member with $x = 1.0$ and examined its phase transitions as a function of temperature. Long- and short-range order study techniques have been used to examine whether Y and Lu share the same crystallographic site in the different polymorphs formed with increasing temperature or whether phase segregation occurs in which Lu forms exclusively β-$Lu_2Si_2O_7$ while Y forms the different polymorphs characteristic of $Y_2Si_2O_7$.

Experimental Section

Synthesis. The sol−gel route used for this study was derived from the synthesis of a well-homogenized gel of $Y_2Si_2O_7$.[27] The starting materials were $Y(NO_3)_3 \cdot 6H_2O$ (99.9% Sigma), $Lu(NO_3)_3 \cdot 6H_2O$ (99.9% Sigma), $Si(OC_2H_5)_4$ (TEOS, 98% solution Sigma), HCl 35% aqueous solution, and 96% ethanol. A TEOS solution in ethanol (1:3 in volume) was added over appropriate amounts of $Y(NO_3)_3 \cdot 6H_2O$, $Lu(NO_3)_3 \cdot 6H_2O$, and HCl in molar ratio 0.5:0.5: 0.05, and the mixture was stirred at 40 °C for 72 h. The transparent gel obtained was dried at 60 °C for 24 h in air, and a yellow powder was obtained. The nitrates were eliminated by calcination at 500 °C for 1 h at a heating rate of 1 $°C \cdot min^{-1}$. The white powder obtained was subsequently divided into several portions, and each portion was calcined at 1000−1600 °C in steps of 100 °C and at 1650 °C. The heating rate was 5 $°C \cdot min^{-1}$ up to the selected temperature; the samples were kept at this temperature for 24 h and slowly cooled to room temperature. β-$Y_2Si_2O_7$ and β-$Lu_2Si_2O_7$ were synthesized following the same method and calcined at 1300 °C.[17]

Characterization. The global composition of the sample was examined by X-ray fluorescence (X Siemens SRS-3000) in the gel calcined at 1000 °C; Y/Lu and Y/Si molar ratios were 0.95(5) and 0.55(5), respectively, indicating $YLuSi_2O_7$ stoichiometry. Several complementary techniques were selected which allowed a detailed ex-situ characterization of the gel calcined at different temperatures. X-ray diffraction (XRD) studies were carried out using a Siemens D-501 diffractometer with Ni-filtered Cu Kα radiation, steps of 0.05°, and a counting time of 5 s. Selected XRD patterns (recorded with 0.02° steps and 10 s counting time) were analyzed using the Rietveld method with the GSAS software (Larson and Von Dreele).[28] Refined parameters were background coefficients, phase fractions, lattice constants, line widths, asymmetry parameters, site occupation fractions for the RE site, and isotropic temperature factors. Powder elemental silicon mixed with the sample was used as internal standard. ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy was carried out in a Bruker DRX400 (9.39 T) spectrometer equipped with a multinuclear probe, using 4 mm zirconia rotors spinning at 12 kHz. A single-pulse sequence was used with an observation frequency for ^{29}Si of 79.49 MHz, a pulse width of 2.5 μs ($\pi/2$ pulse length $= 7.5\ \mu s$), and delay time optimized to 60 s. The chemical shifts are reported in ppm from tetramethylsilane (TMS). The spectra were simulated using a modified version of the Bruker Winfit program to handle the finite spinning speed in MAS experiments.[29] Transmission electron micrographs (TEM, Philips 200 CM) were used to examine the morphology of the samples, while the chemical homogeneity was studied by energy dispersive X-ray analysis in a Philips DX4 attached to the microscope. The samples were dispersed in ethanol by sonication and dropped on a conventional carbon-coated copper grid.

Results and Discussion

X-ray Diffraction. Representative portions of the XRD patterns of the samples calcined at 500, 1000, 1100, 1200, and 1600 °C are shown in Figure 1 (left). The removal of nitrate at 500 °C produces an amorphous material, which crystallizes as a mixture of $RE_2Si_2O_7$ (RE = Y and Lu) polymorphs after calcination at 1000 °C for 24 h. The main reflections observed at 1000 °C closely match the JCPDS card 32-1448[30] (y-$Y_2Si_2O_7$), with several reflections of JCPDS 38-0223[31] (α-$Y_2Si_2O_7$) and JCPDS 38-0440[31] or 35-326[32] (β-$Y_2Si_2O_7$ and β-$Lu_2Si_2O_7$, respectively), although the peak positions and intensities do not coincide exactly with the standard patterns. Lu is smaller than Y and has a different X-ray scattering factor; the different position and intensity of the XRD lines in comparison with the standard patterns could indicate, therefore, that *y*-, α-, and β-$RE_2Si_2O_7$ have formed at 1000 °C, where Y and Lu share the RE crystallographic site. This observation is interesting because pure $Lu_2Si_2O_7$ presents a unique polymorph (β) in the whole temperature range.

At 1100 °C the reflections corresponding to y-$RE_2Si_2O_7$ have decreased considerably while those of α-$RE_2Si_2O_7$ and β-$RE_2Si_2O_7$ have increased, the highest intensity corresponding to α-$RE_2Si_2O_7$. Again, the peak positions and intensities do not coincide exactly with the standard patterns for pure $Y_2Si_2O_7$, indicating the miscibility of Y and Lu in the RE site. The number of phases in these patterns is too high as to arrive at a reliable fitting to extract atomic content and

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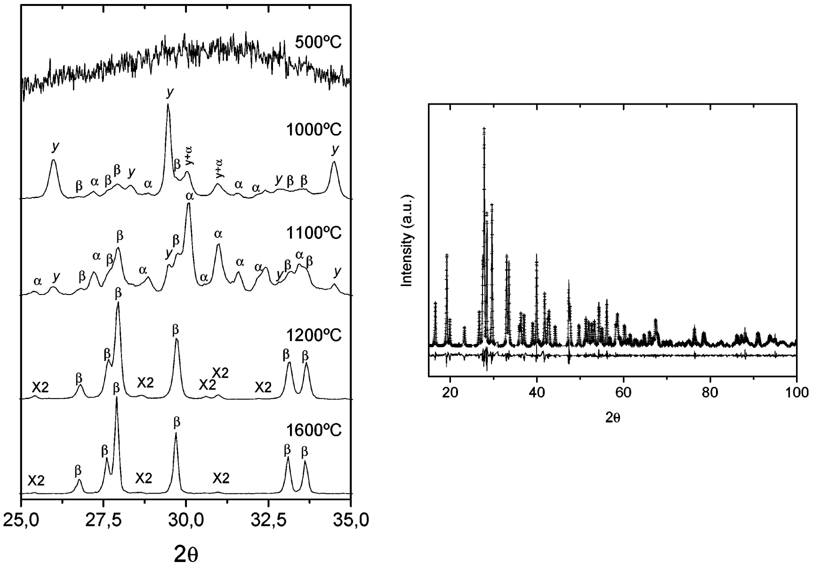

Figure 1. (Left) XRD patterns of the samples calcined at 500, 1000, 1100, 1200, and 1600 °C for 24 h. $y = y$-$RE_2Si_2O_7$; α = α-$RE_2Si_2O_7$; $\beta = \beta$-$RE_2Si_2O_7$; X2 = X2-RE_2SiO_5. (Right) XRD pattern of the sample calcined at 1200 °C (crosses) and the corresponding GSAS calculated pattern (continuous line). The difference plot is also shown.

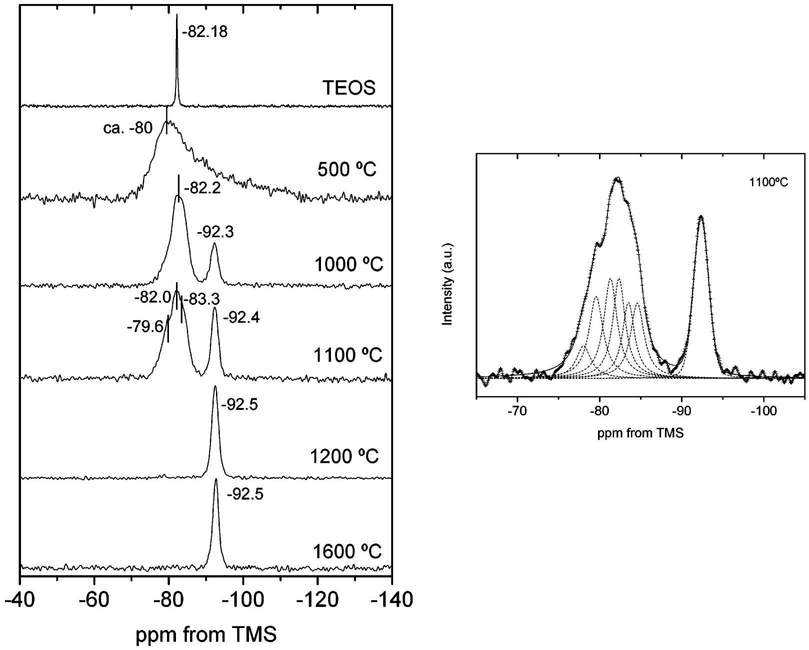

Figure 2. (Left) ^{29}Si MAS NMR spectra of the samples calcined at 500, 1000, 1100, 1200, and 1600 °C for 24 h. (Right) Experimental (crosses), simulated (solid line), and contributions (dashed lines) to the ^{29}Si MAS NMR spectrum of the sample calcined at 1100 °C.

Table 1. Unit Cell Parameters of Pure β-$Lu_2Si_2O_7$[34] and β-$Y_2Si_2O_7$[33] and the Average Values Obtained from Rietveld Refinement of $LuYSi_2O_7$ Samples Calcined at 1200, 1400, and 1600 °C

composition	*a* (Å)	*b* (Å)	*c* (Å)	angle (deg)	vol. (Å^3)
β-$Lu_2Si_2O_7$[34]	6.762(2)	8.835(3)	4.711(2)	101.99(4)	275.3(1)
β-$LuYSi_2O_7$	6.8153(2)	8.8954(2)	4.7142(1)	101.86(1)	279.7(1)
β-$Y_2Si_2O_7$[33]	6.8691(16)	8.960(2)	4.7168(11)	101.73(2)	284.3(1)

parameters of the unit cells. The XRD patterns of the samples calcined at 1200−1650 °C are all very similar and contain, almost exclusively, reflections corresponding to β-$RE_2Si_2O_7$, also with shifted peaks and different relative intensities compared to the standard patterns of β-$Y_2Si_2O_7$ and β-$Lu_2Si_2O_7$. The line widths get narrower with increasing synthesis temperature as a consequence of the higher degree of crystallization. Some low-intensity reflections corresponding to X2-RE_2SiO_5 [Yttrium oxyorthosilicate (Y_2SiO_5) shows two polymorphs with temperature: X1, stable at temperatures <1100 °C, and X2, stable at higher temperatures. Lutetium oxyorthosilicate (Lu_2SiO_5) only shows the X2 form in the whole temperature range.[17] Given the behavior of the $RE_2Si_2O_7$ polymorphs, it is very likely that the X2-RE_2SiO_5 phase observed here contains both Y and Lu in the RE crystallographic site. In addition, it is reasonable that some X1-RE_2SiO_5 (RE = Lu and Y) is present in the samples calcined at temperatures <1100 °C.] can be observed in the XRD pattern of the sample calcined at 1200 °C, which decrease with increasing heating temperature.

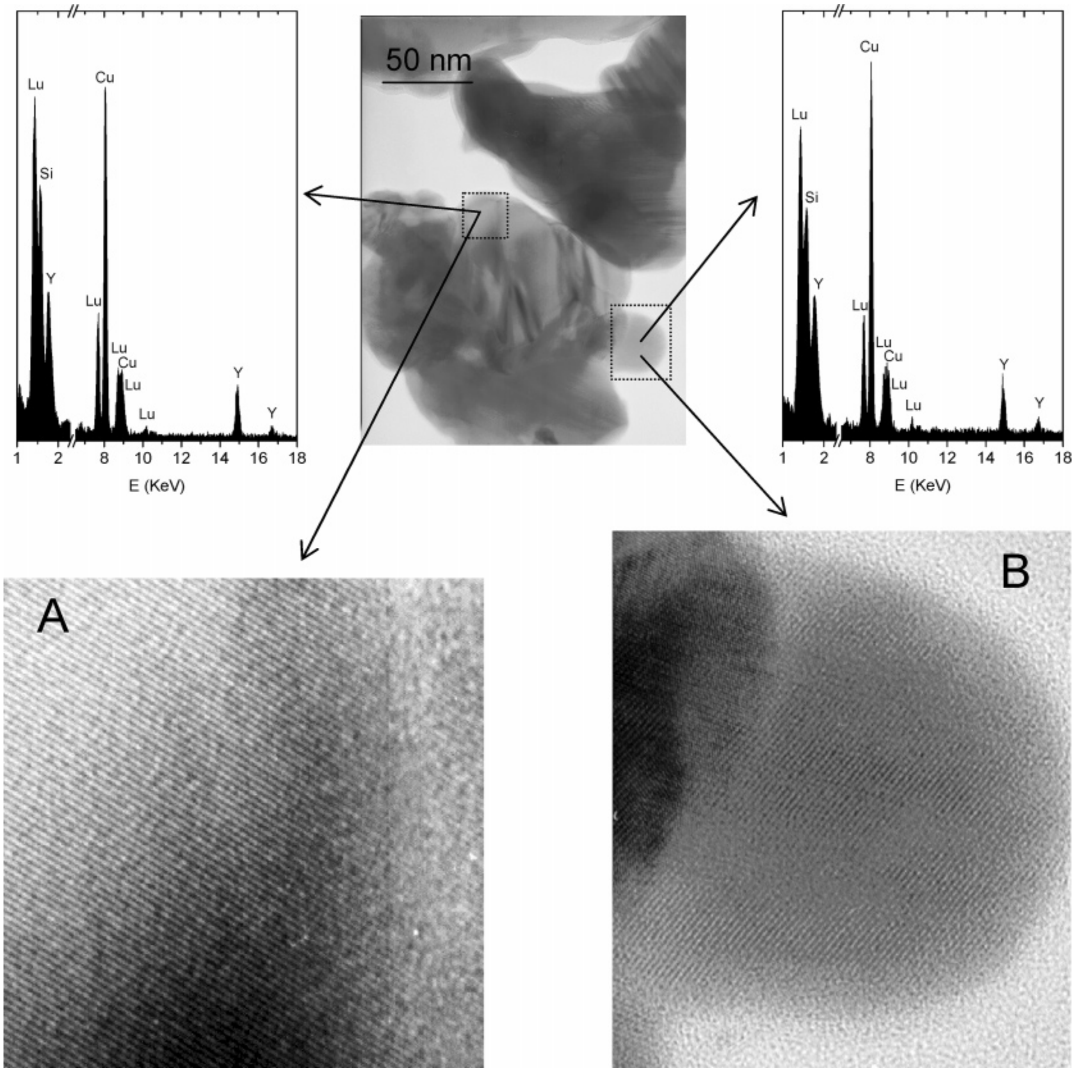

Figure 3. (Top) TEM micrograph of the sample calcined at 1000 °C, and EDX spectra of two different grains. A break region from 2.5 to 6.5 keV has been used in the EDX spectra for better observation of the peaks. (Bottom) HREM images of the grains.

Table 2. ^{29}Si Chemical Shifts (ppm) of Pure $Y_2Si_2O_7$, $Lu_2Si_2O_7$, Y_2SiO_5, and Lu_2SiO_5 Polymorphs[a]

polymorph	^{29}Si chemical shifts (ppm)	ref
β-$Y_2Si_2O_7$	−93.7(1)	this work
β-$Lu_2Si_2O_7$	−91.5(1)	this work
y-$Y_2Si_2O_7$	−83.2, −85.2	36
α-$Y_2Si_2O_7$	−81.0, −82.4, −83.4, −84.9	18
X1-Y_2SiO_5	−82.3	37
X2-Y_2SiO_5	−79.4	23
X2-Lu_2SiO_5	−77.1	38

[a] The numbers in parentheses are the estimated standard deviations in units of the last digit.

Table 3. ^{29}Si MAS NMR Parameters Obtained after Simulating the Spectra of the Sample Calcined at 1100 °C

peak	^{29}Si chemical shift value (ppm)	fwhm (Hz)	area under the curve (%)	polymorph
1	−92.4(1)	159(2)	22(1)	β-$RE_2Si_2O_7$
2	−84.7(2)	151(25)	13(3)	*y*-$RE_2Si_2O_7$
3	−83.6(2)	135(25)	12(3)	α-$RE_2Si_2O_7$
4	−82.5(2)	140(30)	14(3)	*y*- + α-$RE_2Si_2O_7$
5	−81.5(2)	159(20)	17(2)	α-$RE_2Si_2O_7$
6	−79.4(2)	175(10)	15(2)	α-$RE_2Si_2O_7$
7	−78.0(2)	167(21)	6(2)	X2-RE_2SiO_5

[a] The numbers in parentheses are the estimated standard deviations in units of the last digit.

To calculate the dimensions and atomic content of the unit cell of the β-$RE_2Si_2O_7$ polymorph, the XRD patterns of the gels calcined at 1200, 1400, and 1600 °C have been analyzed with the Rietveld method using the GSAS software.[28] The low-intensity reflections from X2-RE_2SiO_5 have been deleted. The starting parameters have been taken from Redhammer and Roth[33] for pure β-$Y_2Si_2O_7$, but the occupation factor for the RE site has initially been set to 0.5 for Lu and 0.5 for Y, according to the nominal composition of the sample. Figure 1 (right) exhibits the observed pattern, the GSAS fitted curve, and the difference curve obtained from the Rietveld refinement of the structure of the sample calcined at 1200 °C (the samples calcined at 1400 and 1600 °C show very similar fits to this one). It can be observed that all the reflections could be fitted on the basis of a monoclinic unit cell with space group *C*2/*m*, corresponding to the crystal structure of the β-polymorph. The dimensions of the unit cell do not change appreciably with synthesis temperature. The average values are given in Table 1 together with the unit cell dimensions for pure β-$Lu_2Si_2O_7$[34] and β-$Y_2Si_2O_7$.[33] Both *a* and *b* lattice parameters increase linearly at ap-

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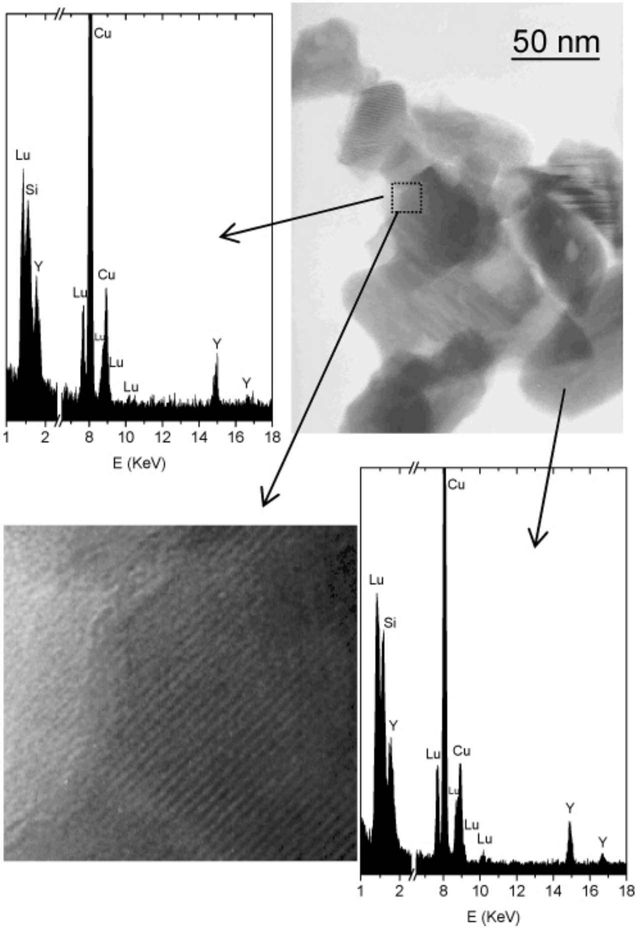

Figure 4. (Top) TEM micrograph of the sample calcined at 1100 °C, and EDX spectra of two different grains. A break region from 2.5 to 6.5 keV has been used in the EDX spectra for better observation of the peaks. (Bottom) HREM image of one of the grains.

proximately the same rate with increasing Y content, while the *c* parameter does not change appreciably with composition. The unit cell volume also increases in a linear manner with increasing Y content; this is in agreement with the behavior of the unit cell volume versus the ionic radius of the RE^{3+} in different β-$RE_2Si_2O_7$ compounds (RE = Lu, Yb, Tm, Er, and Ho).[35] Finally, the β angle of the unit cell decreases with increasing Y content. In conclusion, the linear behavior of the unit cell parameters with composition is an indication that both β-$Lu_2Si_2O_7$ and β-$Y_2Si_2O_7$ form a solid solution at the composition studied in this investigation ($YLuSi_2O_7$) and at temperatures ≤1650 °C.

^{29}Si MAS NMR. The ^{29}Si chemical shifts of pure *y*-$Y_2Si_2O_7$, α-$Y_2Si_2O_7$, β-$Y_2Si_2O_7$, β-$Lu_2Si_2O_7$, X1- and X2-Y_2SiO_5, and X2-Lu_2SiO_5 are given in Table 2 for the purpose of comparison with the composition studied.

Figure 2 (left) shows the ^{29}Si MAS NMR spectra of the gels calcined at 500, 1000, 1100, 1200, and 1600 °C. The ^{29}Si MAS NMR spectrum of the Si source (TEOS) has been included as well with the purpose of analyzing the transformations of the Si environment with temperature. TEOS produces an NMR signal at −82.2 ppm, typical of the unique type of Si environments consisting of Q^0 units (i.e., isolated Si tetrahedra). The hydrolysis and polycondensation occurred during the gelification process plus the removal of nitrate at 500 °C transform the unique Si environment in a set of different Si environments as inferred from the ^{29}Si MAS NMR spectrum of the sample, which shows a very broad band.

The ^{29}Si MAS NMR spectrum of the sample calcined at 1000 °C exhibits two peaks, a single one at −92.3 ppm with fwhm ∼159 Hz and a wider band centered at ∼−82.2 ppm. The band at −82.2 ppm contains a range of chemical shift values that are compatible with the Si environments in *y*- and α-$RE_2Si_2O_7$, in agreement with the XRD data. The band must be composed a total of six resonances (two intense ones from the *y* polymorph and four small peaks from the α polymorph, as seen in Table 2) and possibly an additional small resonance due to X1-RE_2SiO_5, which does not allow achieving convergence in the simulation of the spectrum. We cannot conclude, therefore, whether the band is produced by pure *y*-$Y_2Si_2O_7$ and α-$Y_2Si_2O_7$ phases or if lutetium is incorporated into the crystalline structure of these two polymorphs. The second ^{29}Si resonance, at −92.3 ppm, corresponds neither to β-$Y_2Si_2O_7$ nor to β-$Lu_2Si_2O_7$ (see Table 2) but it is at halfway between them. This fact is an indication that the β-$RE_2Si_2O_7$ polymorph formed at 1000 °C contains both Y and Lu in the rare-earth crystallographic site.

Calcination at 1100 °C increases the intensity of the resonance at high fields, with a chemical shift value of −92.4 ppm, while the band at low fields broadens and shows some slightly resolved components (Figure 2, left). The higher proportion of α polymorph at this temperature, with four ^{29}Si resonances, is responsible for the broadening of the signal. The spectrum has been simulated with the resonances corresponding to *y*-, α-, and β-$RE_2Si_2O_7$ and X2-RE_2SiO_5. Starting chemical shifts were those corresponding to pure $Y_2Si_2O_7$ and Y_2SiO_5. Two resonances corresponding to the *y* and α polymorphs show very close chemical shifts, and it was necessary to make them a unique contribution in order to achieve convergence in the simulation. Figure 2, right, shows the results of the fitting. The assignation of the peaks to the different polymorphs is not straightforward due to the close chemical shifts of the resonances corresponding to the *y* and α polymorphs. The most reasonable one is given in Table 3, and it indicates that all chemical shift values have decreased an average of 1 ppm when compared to pure $Y_2Si_2O_7$ and Y_2SiO_5. This is again an indication that both Lu and Y are occupying the same crystallographic site in the crystalline structures of all the polymorphs.

When the sample is calcined at 1200−1650 °C, a very similar spectrum is obtained for all the calcination temperatures, consisting in a unique symmetric resonance at ∼−92.5 ppm, corresponding to the β polymorph, in agreement with the XRD patterns of the samples. A small ^{29}Si resonance due to X2-RE_2SiO_5 at ∼−78 ppm is also present but is not observed in the plots due to the scale used.

TEM-EDX. The global composition of the sample was examined by X-ray fluorescence in the gel calcined at 1000

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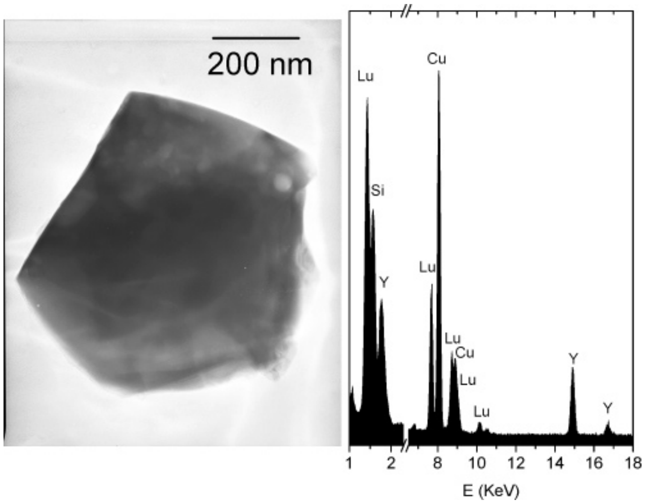

Figure 5. Micrograph and EDX spectrum of particles observed in the sample calcined at 1600 °C. A break region from 2.5 to 6.5 keV has been used in the EDX spectra for better observation of the peaks.

°C giving $YLuSi_2O_7$ stoichiometry. The composition of each individual grain was analyzed by EDX in the TEM; the vast majority of grains analyzed show the same chemical composition (Lu, Y, and Si) with very few particles showing some chemical inhomogeneity. The powders calcined at 1000 and 1100 °C are all formed by rounded particles with variable particle size (micrographs in Figures 3 and 4). Isolated grains from each sample were selected to record EDX spectra; all of them are very similar to each other and show the characteristic X-ray emissions lines of Si, Lu, and Y. The samples calcined at these temperatures show, therefore, a high degree of chemical homogeneity, although very few particles containing only Si and Lu or Si and Y could also be observed after very careful examination. The EDX spectra of two grains of the sample calcined at 1000 °C are shown in Figure 3 together with the HREM images of the grains. Grain A shows an *hkl* spacing of 3.2(1) Å, compatible with a single crystal of any of the *y*-, α-, or β-$RE_2Si_2O_7$ polymorphs; its EDX spectrum (Figure 5, left) shows that the RE site is occupied by both Lu and Y atoms. Grain B shows a higher *hkl* spacing of 5.8(1) Å and could correspond to the 0−11 and 101 planes in α-$RE_2Si_2O_7$. The composition of grain B (Figure 4, right) indicates that lutetium shares with yttrium the RE sites in the α-$RE_2Si_2O_7$ polymorph, although polymorph α does not show a stability field in pure $Lu_2Si_2O_7$. These results confirm the indications of the XRD data presented above.

The EDX spectra corresponding to two different grains in the sample calcined at 1100 °C are shown in Figure 4. The HREM image of one of the grains showed an interplanar spacing of 5.8(1) Å, which could correspond to an α-$RE_2Si_2O_7$ single crystal with Y and Lu in the RE crystallographic site. These results confirm the indications of the XRD and ^{29}Si MAS NMR data presented above.

The morphology of the samples calcined at 1200−1400 °C is similar to that observed for the lower temperature samples, with particle size increasing with increasing temperature and more pronounced edges. At $T > 1500$ °C the particle edges become sharper and higher particle sizes are observed, in agreement with the higher calcination temperature (see micrograph and chemical composition in Figure 5) and the narrower lines observed in the corresponding XRD patterns.

Conclusions

Combination of the results presented above allows concluding that although $Lu_2Si_2O_7$ has a unique polymorph in the whole temperature range, namely, β- $Lu_2Si_2O_7$, when 50% Lu is added to $Y_2Si_2O_7$, Lu atoms are able to replace Y while maintaining the structures of the *y*- and α-polymorphs at low temperatures. At 1200 °C the structure transforms to β-$RE_2Si_2O_7$ with Y and Lu sharing the RE crystallographic site, and this polymorph is the stable phase up to, at least, 1650 °C.

Exact transition temperatures cannot be given here because we might not be in thermodynamic equilibrium. However, we can observe that β-$LuYSi_2O_7$ does not transform into γ-$RE_2Si_2O_7$ in the temperature range studied here. This is to be compared with the results obtained by Ito and Johnson[24] for pure β-$Y_2Si_2O_7$, which transforms into γ-$Y_2Si_2O_7$ at 1445 °C and to δ at 1535 °C. The presence of Lu, therefore, stabilizes the β polymorph up to, at least, 1650 °C, and it is very likely that the structure stays as β up to the melting point.

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