

Polymorphism in the $\text{Lu}_{2-x}\text{Y}_x\text{Si}_2\text{O}_7$ system at high temperatures

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Abstract

Samples in the system $\text{Lu}_{2-x}\text{Y}_x\text{Si}_2\text{O}_7$ ($1.25 \leq x \leq 2$) have been synthesised following a sol–gel method and calcined to high temperatures ($\geq 1400^\circ\text{C}$). X-ray diffraction (XRD) has shown that all compositions crystallize as $\beta\text{-Lu}_{2-x}\text{Y}_x\text{Si}_2\text{O}_7$ at the low temperatures, while increasing calcination temperature produces the formation of the γ - and δ -polymorphs, the temperatures of formation of each polymorph depending on the Y/Lu ratio. Unit cell parameters of the samples crystallizing as $\gamma\text{-Lu}_{2-x}\text{Y}_x\text{Si}_2\text{O}_7$ have been calculated and plotted as a function of composition. They show a linear change with increasing Y content, indicating a degree of solid solubility of $\text{Lu}_2\text{Si}_2\text{O}_7$ in $\gamma\text{-Y}_2\text{Si}_2\text{O}_7$. Based on these data and on those reported in our previous studies [Becerro, A.I. and Escudero, A., XRD and ^{29}Si MAS NMR spectroscopy across the $\beta\text{-Lu}_2\text{Si}_2\text{O}_7\text{-}\beta\text{-Y}_2\text{Si}_2\text{O}_7$ solid solution. *J. Solid State Chem.*, 2005, **178**; Becerro, A.I. and Escudero, A., Phase transitions in Lu-doped $\text{Y}_2\text{Si}_2\text{O}_7$ at high temperatures. *Chem. Mater.*, 2005, **17**, 112] a temperature–composition diagram of the $\text{Lu}_2\text{Si}_2\text{O}_7\text{-Y}_2\text{Si}_2\text{O}_7$ system is given. Finally, the influence of Lu on the reversibility of the $\gamma\text{-Y}_2\text{Si}_2\text{O}_7 \rightarrow \beta\text{-Y}_2\text{Si}_2\text{O}_7$ transition is studied by means of XRD and ^{29}Si MAS NMR spectroscopy. © 2005 Elsevier Ltd. All rights reserved.

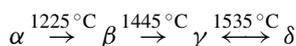
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1. Introduction

Silicon nitride (Si_3N_4) has become an important class of materials for structural applications at high temperature.^{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 however, it caused high temperature strength loss attributed to the formation of a vitreous silicate intergranular phase.^{8,9} Much effort has been made to improve the high temperature mechanical properties of Si_3N_4 including the use of other oxides and subsequent crystallization of the intergranular glassy phase by a post-sintering heat treatment. It has been shown that when RE oxides (RE = lanthanides and yttrium) are added to the powder of pure Si_3N_4 , a glassy disilicate phase ($\text{RE}_2\text{Si}_2\text{O}_7$) 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 $\text{RE}_2\text{Si}_2\text{O}_7$ intergranular

phase at different temperatures and RE contents is, therefore, of great value in understanding the behaviour 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 cation the better the properties of the Si_3N_4 .^{15,16} Y_2O_3 , Lu_2O_3 and Sc_2O_3 are the three RE oxides showing the highest flexural strength values. We have selected the first two cations to examine the phase transitions with temperature and composition in the $\text{Lu}_2\text{Si}_2\text{O}_7\text{-Y}_2\text{Si}_2\text{O}_7$ system.

The academic interest of this study resides in the fact that $\text{Lu}_2\text{Si}_2\text{O}_7$ forms a unique polymorph in the whole temperature range, called $\beta\text{-Lu}_2\text{Si}_2\text{O}_7$, while $\text{Y}_2\text{Si}_2\text{O}_7$ shows up to five polymorphs with increasing temperature (γ , α , β , γ and δ).^{17,18} Transition temperatures between the different $\text{Y}_2\text{Si}_2\text{O}_7$ polymorphs as well as temperature stability ranges vary considerably from one author to the other.^{12,19–24} Ito and Johnson²⁵ established the following sequence:



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but direct transitions from γ - $Y_2Si_2O_7$ to β - $Y_2Si_2O_7$ have also been reported.^{14,26}

The study of phase transformations with temperature in the $Lu_{2-x}Y_xSi_2O_7$ member with $x = 1$ was recently reported by us;²⁷ the results show that at 1200 °C β - $RE_2Si_2O_7$ is formed, with Y and Lu sharing the RE crystallographic site and this polymorph is the stable phase up to, at least, 1650 °C. A second study on the $Lu_{2-x}Y_xSi_2O_7$ system describing the structures at 1300 °C shows that a complete solid solution exists between β - $Lu_2Si_2O_7$ and β - $Y_2Si_2O_7$ at that temperature.²⁸

The present study analyses the phase transitions of $Lu_{2-x}Y_xSi_2O_7$ samples with high Y contents ($1.25 \leq x \leq 2$) at high temperatures ($1400 \text{ °C} \leq T \leq 1700 \text{ °C}$). Transition temperatures and evolution of lattice parameters with temperature and composition as well as reversibility of phase transitions have been studied with ex situ X-ray diffraction and ²⁹Si MAS NMR spectroscopy. Finally, a temperature–composition diagram of the $Lu_2Si_2O_7$ – $Y_2Si_2O_7$ system is given, based on data presented in this article and in our previous studies.^{27,28}

2. Experimental section

2.1. Synthesis of the xerogels

The sol–gel route used for this study was derived from the synthesis of a well-homogenized gel of $Y_2Si_2O_7$.²⁹ The starting materials were $Y(NO_3)_3 \cdot 6H_2O$ (99.9% Sigma), $Lu(NO_3)_3 \cdot 5H_2O$ (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 $Y(NO_3)_3 \cdot 6 H_2O$, $Lu(NO_3)_3 \cdot 6 H_2O$ and HCl for the preparation of $Lu_{2-x}Y_xSi_2O_7$ members with nominal $x = 1.25, 1.50, 1.66, 1.80$ and 2.00. The mixtures were stirred at 40 °C for 72 h and the transparent gels obtained were dried at 60 °C for 24 h in air. Nitrate was eliminated by calcination at 500 °C for 1 h at a heating rate of 1 °C/min.

2.2. Calcination experiments

The xerogel of each composition was divided into four portions and they were calcined at 1400, 1500, 1600 and 1650 °C for 12 h at a heating rate of 5 °C/min. Samples were slowly cooled down to room temperature. After characterization, each sample was subsequently calcined at the same temperature for another 24 h and slowly cooled down to room temperature.

2.3. Reversibility studies

To study the reversibility of the $\gamma \rightarrow \beta$ transition, the γ -polymorph of each composition was annealed for 240 h at 1300 °C, a temperature at which the β -polymorph is the stable phase for all five compositions.²⁷ Asterisks in Table 2 indicate samples submitted to the reversibility study.

Table 1

Nominal and real Y/(Y + Lu) and Si/(Y + Lu) ratios of the $Lu_{2-x}Y_xSi_2O_7$ samples

x	Y/(Y + Lu)		Si/(Y + Lu)	
	Nominal	Real	Nominal	Real
1.25	0.625	0.63	1.00	0.87
1.50	0.75	0.76	1.00	0.89
1.66	0.83	0.82	1.00	0.88
1.80	0.90	0.90	1.00	0.87
2.00	1.00	1.00	1.00	0.92

Data obtained from XRF analyses.

2.4. Characterization

The global composition of the samples was examined by X-ray fluorescence (X Siemens SRS-3000) in the gel calcined at 500 °C (xerogels); Table 1 shows the nominal and real compositions obtained; real Y/(Y + Lu) ratios show always a good agreement with the nominal compositions, while the Si/(Y + Lu) ratios indicate a Si content lower than that expected for the $Lu_{2-x}Y_xSi_2O_7$ stoichiometry. On the other hand, the chemical homogeneity of each sample was studied by TEM (TEM, Philips 200 CM); a number of single crystals were selected and EDX spectra (Philips DX4 equipment attached to the microscope) were recorded on each one, showing the spectra of the same sample very similar Y, Lu and Si contents. Several complementary techniques were selected which allowed a detailed ex situ characterization of the xerogels calcined at different temperatures. X-ray diffraction (XRD) studies were carried out using a Siemens D-501 diffractometer, with Ni-filtered Cu K α radiation, steps of 0.05° and counting time of 5 s. Selected XRD patterns (recorded with 0.02° steps and 10 s counting time) were analyzed using the Le Bail method with the GSAS software (Larson and Von Dreele).³⁰ Refined parameters were: background coefficients, phase fractions, lattice constants, line widths and asymmetry parameters. Powder elemental silicon mixed with the sample was used as internal standard. ²⁹Si Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) spectroscopy was carried out in a Bruker DRX400 AVANCE (9.39 T) spectrometer equipped with a multinuclear probe, using 4 mm zirconia rotors spinning at 11.5 kHz. A single pulse sequence was used, with an observation frequency for ²⁹Si of 79.49 MHz, a pulse width of 2.5 μ s ($\pi/2$ pulse length = 7.5 μ s) and a delay of 600 s.²⁷ Chemical shifts are reported in ppm from tetramethylsilane (TMS).

3. Results and discussion

3.1. Phase transitions in $Lu_{2-x}Y_xSi_2O_7$ ($1.25 \leq x \leq 2$) as a function of temperature and composition

Fig. 1 shows representative portions of the XRD patterns of the $Lu_{2-x}Y_xSi_2O_7$ sample with $x = 2$ at different temperatures and calcination times. After annealing the xerogel at

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