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Solid solubility of $Yb_2Si_2O_7$ in β-, γ- and δ-$Y_2Si_2O_7$

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ABSTRACT

This paper examines the structural changes with temperature and composition in the $Yb_2Si_2O_7$–$Y_2Si_2O_7$ system; members of this system are expected to form in the intergranular region of Si_3N_4 and SiC structural ceramics when sintered with the aid of Yb_2O_3 and Y_2O_3 mixtures. A set of different compositions have been synthesised using the sol–gel method to obtain a xerogel, which has been calcined at temperatures between 1300 and 1650 °C during different times. Isotherms at 1300 and 1600 °C have been analysed in detail to evaluate the solid solubility of $Yb_2Si_2O_7$ in β-$Y_2Si_2O_7$ and γ-$Y_2Si_2O_7$. Although $Yb_2Si_2O_7$ shows a unique stable polymorph (β), Yb^{3+} is able to replace Y^{3+} in γ-$Y_2Si_2O_7$ and δ-$Y_2Si_2O_7$ at high temperatures and low Yb contents. IR results confirm the total solid solubility in the system and suggest a constant SiOSi angle of 180° in the Si_2O_7 unit across the system. The temperature–composition diagram of the system, obtained from powder XRD data, is dominated by the β-$RE_2Si_2O_7$ polymorph, with γ-$RE_2Si_2O_7$ and δ-$RE_2Si_2O_7$ showing reduced stability fields. The diagram is in accordance with Felsche's diagram if average ionic radii are assumed for the members of the solid solution at any temperature, as long as the β–γ phase boundary is slightly shifted towards higher radii.

1. Introduction

Rare Earth disilicates ($RE_2Si_2O_7$) exhibit different polymorphic forms depending on the *RE* ionic radius, temperature and pressure [1,2]. $Y_2Si_2O_7$ shows, in particular, up to five polymorphs with increasing temperature at room pressure (y, α, β, γ and δ, also called, respectively, y, B, C, D and E); while $Yb_2Si_2O_7$ exhibits a unique polymorph (β, also called C) up to the melting point of the compound. These silicates are important materials in the sinterization of the structural advanced ceramic Si_3N_4. 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 crystallisation, improves the high-temperature mechanical properties of the material [3,4]. 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 behaviour of these materials.

The aim of this research is to analyse the solid solubility of $Yb_2Si_2O_7$ in β-, γ- and δ-$Y_2Si_2O_7$ and to describe a temperature–composition diagram showing the polymorphism of the system. Study of the solid solubility of $Yb_2Si_2O_7$ in *y*- and α-$Y_2Si_2O_7$ is not reported due to the slow kinetics at the stability temperatures of these phases (<1200 °C) [5].

2. Experimental section

2.1. Synthesis of the xerogel

The following reactants have been used as starting materials: $Yb(NO_3)_3\cdot 5H_2O$ (99.99% Aldrich Chemical Co.), $Y(NO_3)_3\cdot 4H_2O$ (99.99% Aldrich Chemical Co.), $Si(OC_2H_5)_4$ (TEOS, 99% Aldrich Chemical Co.) and absolute ethanol (AnalaR Normapur). To verify the amount of water per formula unit present in the nitrates, thermogravimetric analyses (TGA) were carried out using a SDT Q600 (TA instruments). $Yb_{2-x}Y_xSi_2O_7$ members with nominal x=0.00, 0.40, 0.80, 1.00, 1.20, 1.40, 1.60, 1.80 and 2.00 were synthesised. A TEOS solution in ethanol (1:3 in volume) was added over the appropriate amounts of $Yb(NO_3)_3\cdot 5H_2O$ and $Y(NO_3)_3\cdot 4H_2O$ previously dissolved in 5 ml of absolute ethanol. The mixture was stirred at 40 °C for 5–7 h and the transparent gels obtained were dried at 60 °C for 24 h in air. Nitrates were eliminated by calcination at 500 °C for 2 h at a heating rate of 1 °C min^{-1}. Importantly, only a slight excess of TEOS in the initial mixture yielded satisfactorily the $Yb_{2-x}Y_xSi_2O_7$ phase, otherwise oxiorthosilicate phase was obtained in a large proportion.

2.2. Calcination experiments

The xerogel of each composition was ground in an agate mortar and subsequently divided into different portions, which

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were calcined in air at different temperatures between 1300 °C and 1650 °C and different periods of time (Table 1), using a heating rate of 5 °C min^{-1} and a platinum crucible. Finally, the samples were slowly cooled down to room temperature.

2.3. Characterisation

The global composition of the samples was examined by X-Ray fluorescence (Panalytical, AXIOS model). Table 2 shows the agreement between the nominal and real compositions.

An analytical transmission electron microscope (ATEM, Philips CM20FEG) operating at 200 kV and equipped with an energy-dispersive X-ray spectrometer (EDX, NORAN Ge detector) was used to observe the morphology of the samples as well as to examine chemical composition. The EDA software was used to index the electron diffraction patterns [6]. EDX analyses on $Yb_{2-x}Y_xSi_2O_7$ single crystals were carried out to determine yttrium and ytterbium contents. The quantification included an absorption correction and the calibration of Cliff–Lorimer factors for ytterbium and yttrium with respect to silicon, determined from pure $Yb_2Si_2O_7$ and $Y_2Si_2O_7$, respectively. At least 10 rare earth disilicate single crystals were analysed in each sample to calculate the mean compositions (results are displayed in third column of Table 2). A counting time from 100 to 300 s has been used in order to accumulate enough X-ray counts. The samples were dispersed in ethanol by sonication and dropped on a conventional carbon-coated copper grid.

X-Ray diffraction patterns (PANalytical XPert Pro Diffractometer, Cu$K\alpha$ and X-Celerator detector) were recorded over the angular range $10^\circ < 2\theta < 120^\circ$ 2θ with step width of 0.02° and 10 s counting time. The patterns were analysed using the Rietveld method with the TOPAS software (TOPAS version 4.2, Bruker AXS 2009). Refined parameters were background coefficients, zero correction, scale, unit cell parameters, site occupation factors for the rare earth sites, isotropic atomic displacement parameters, atomic positions and microstructure parameters.

Finally, Infrared Fourier Transform spectra (Nicolet 510 FTIR instrument equipped with DTGS detectors) were recorded over the 1500–400 cm^{-1} range with a resolution of 2 cm^{-1}. The measurements were made using dried KBr pellets, which were prepared by mixing and pressing 1.5 mg of sample with 100 mg KBr.

Table 1
Polymorphs obtained after calcination of the $Yb_{(2-x)}Y_xSi_2O_7$ compositions at different temperatures and times.

T (°C)	t (h)	0.00	0.40	0.80	1.00	1.20	1.40	1.60	1.80	1.94	2.00
1300	24	β	β	β	β	β		β			β
1400	12										β
	36										γ+β
	72						β	β+γ	β+γ		
1500	24							β+γ	β+γ		γ+(β)
1550	24						β+γ	β+γ			
	48						γ	γ			
1600	24		β	β	β	β	β+γ				
	36										γ
	48							γ+β			
	63.2							γ			
1650	12					β	γ+β	γ	γ	γ+δ	γ+δ
	24					β+γ	γ	γ	γ		γ+δ

Table 2
Compositional data obtained with different techniques for $Yb_{2-x}Y_xSi_2O_7$ samples.

× Nominal	× FRX	× Rietveld		× EDX/TEM
		β	γ	
0.00	0.00	0.00 (0.00)	–	0.00
0.40	0.35	0.36 (0.01)	–	0.40
0.80	0.81	0.80 (0.01)	–	0.85
1.00	1.00	1.00 (0.01)	–	0.96
1.20	1.21	1.26 (0.01)	–	Non-recorded
1.40	Non-recorded	–	1.40 (0.01)	Non-recorded
1.60	1.59	1.64 (0.01)	1.58 (0.03)	1.61
1.80	Non-recorded	–	1.81 (0.01)	Non-recorded
2.00	2.00	2.00 (0.00)		2.00

3. Results and discussions

3.1. Solid solubility of $Yb_2Si_2O_7$ in β-$Y_2Si_2O_7$: Study of the 1300 °C isotherm

3.1.1. X-ray diffraction study

Representative portions of the XRD patterns of different $Yb_{2-x}Y_xSi_2O_7$ members calcined at 1300 °C for 24 h are shown in Fig. 1. The diagram of the $x=0.0$ sample matches the standard pattern of pure β-$Yb_2Si_2O_7$ (PDF 00-025-1345), as expected. Increasing Y content produces very similar patterns, with slight variations in peak positions and intensity; see, for example, the shift of the peaks under the dashed lines, the intensity decrease in the

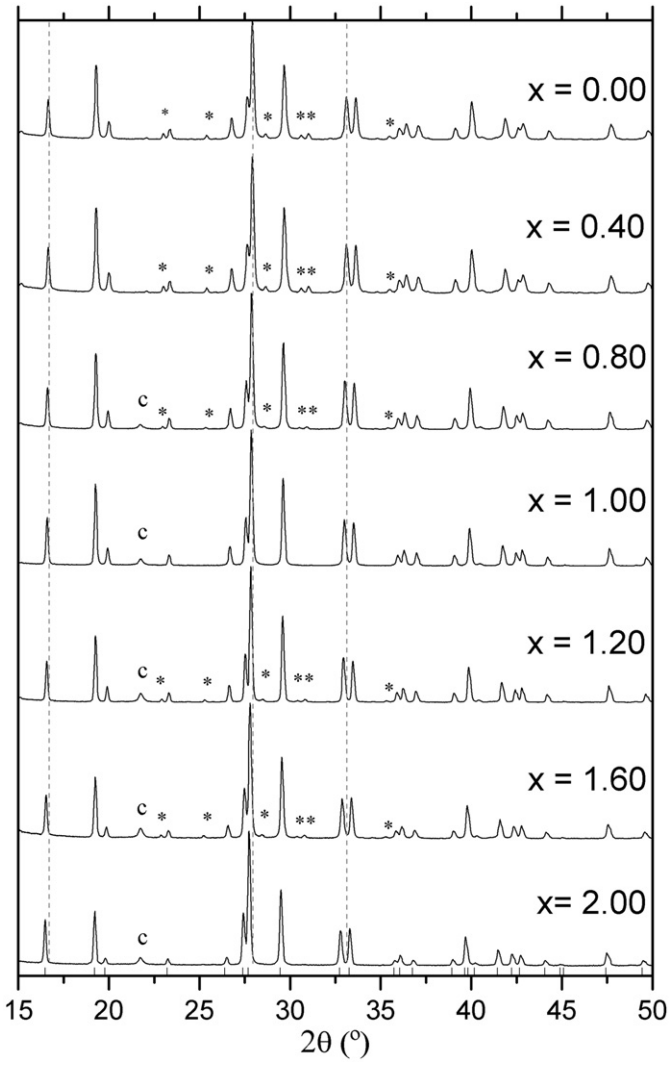

Fig. 1. Selected portions of the XRD patterns of $Yb_{2-x}Y_xSi_2O_7$ samples annealed at 1300 °C for 24 h. Asterisks: X2-RE_2SiO_5; c: cristobalite. Dashed lines are guides to the eye to show shift of reflections with composition.