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Synthesis of nanocrystalline yttrium disilicate powder by a sol–gel method

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Abstract

In the present work a new route for the synthesis of α - $Y_2Si_2O_7$ is reported. The method consists in the gelation of an acid solution composed by $Y(NO_3)_3$ and tetraethylorthosilicate (TEOS) in the adequate molar ratio to form a precursor complex gel containing the Y^{3+} and Si^{4+} cations in the 1:1 ratio, which yields the stoichiometric α - $Y_2Si_2O_7$ after calcining. The nanosize powder of $Y_2Si_2O_7$ obtained at 1060°C was characterised by XRD and TEM. The conditions and main parameters such as temperature, pH or time for the hydrolysis of the $Y(NO_3)_3$ /TEOS solution in HCl medium was investigated and optimised to obtain the precursor gel which was analysed by DTA and TGA. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The main objective of this work is the fabrication of a single phase $Y_2Si_2O_7$ nanoparticulate powder to be used as Si_3N_4 sintering aid.

Due to its excellent high temperature properties including a low linear coefficient of thermal expansion and a very good thermal shock resistance, Si_3N_4 is an adequate material for use in high-temperature structural applications as a component for gas turbine engines. Because of its low bulk and boundary diffusion coefficients, Si_3N_4 is generally sintered with the use of densification aids to obtain high-density bodies. These sintering aids react with the ever-present oxide layer on the

surface of Si_3N_4 particles to form a eutectic liquid phase in which solution-precipitation of the Si_3N_4 particles occurs. The resulting ceramic has a glassy phase at grain boundaries which is responsible for the loss of strength at high temperature due to a grain boundary sliding mechanism which becomes active when the softening point of the glass is reached. However, the sintered Si_3N_4 ceramic prepared using Y_2O_3 as sintering additive with a 2:1 molar ratio of $SiO_2:Y_2O_3$, placing the composition directly on the Si_3N_4 – $Y_2Si_2O_7$ tie line, has shown a significant improvement in the high-temperature mechanical properties [1]. During the sintering process a $Y_2Si_2O_7$ glassy phase at grain boundaries is formed by oxidation of the Y–Si–O–N glass present in such regions of the material [2]. The high melting point of the $Y_2Si_2O_7$ glassy phase (m.p. = 1780°C) allows an increase of the application temperature of the material without reaching the softening point. Indeed, the ability to

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crystallise the $Y_2Si_2O_7$ glassy phase at the grain boundary will improve the high temperature properties of Si_3N_4 -based composites.

Several groups [3–6] have synthesised and studied the crystallisation process of glasses from the Y_2O_3 – SiO_2 – Al_2O_3 system, but a complete understanding of the system has not been reached yet. $Y_2Si_2O_7$ has been synthesised by solid-state reaction of the mixed oxides SiO_2 and Y_2O_3 at $1300^\circ C$. However, below this temperature the oxides do not react within a reasonable heating time [7]. In the same way, the hydrothermal synthesis requires long processing times, of the order of 100 days at $300^\circ C$, which can only be reduced by increasing the hydrothermal processing temperature in an autoclave. On the other hand, Ito and Johnson [8] have synthesised $Y_2Si_2O_7$ from pure silicic acid solutions and YCl_3 , but this route requires the removal of the Na^+ cation from the starting Na_2SiO_3 solutions in order to carry out an accurate determination of the phase transition temperatures. Trusty et al. [9] have obtained $Y_2Si_2O_7$ after calcination of amorphous precursors synthesised from yttrium acetate and TEOS using hydrothermal processing. However, this route is relatively complex requiring several synthesis steps and specific facilities for hydrothermal treatments.

Moya et al. [10] have developed a simple sol–gel method to obtain $Y_2Si_2O_7$ nanometric powders. In the present communication a modification of this route is reported. The method consists in the reaction of $Y(NO_3)_3$ and TEOS in the adequate molar ratio in an acidic aqueous media to obtain a gel containing Y^{3+} and Si^{4+} which yields the stoichiometric compound $Y_2Si_2O_7$ after calcining. This route shows less sensitivity to experimental conditions.

2. Experimental procedure

The following reactants have been used as starting materials: $Y(NO_3)_3 \cdot 4H_2O$, $Si(OC_2H_5)_4$ 98% solution TEOS, HCl 35% aqueous solution and 96% ethanol.

The $Y_2Si_2O_7$ precursor was obtained by gelation of acidic aqueous $Y(NO_3)_3$ solutions, containing different concentrations of HCl.

Appropriate $Y(NO_3)_3 \cdot 4H_2O$ and HCl were used in order to prepare two aqueous solutions with final $Y(NO_3)_3:H_2O:HCl$ molar ratios of 1:4:0.05 and 1:4:1 (routes 1 and 2, respectively). A TEOS solution in ethanol (molar ratio 1:3) was added over both $Y(NO_3)_3$ solutions and the mixtures were stirred at $40^\circ C$ for 72 h. Gels obtained were dried at 60° for 24 h and subsequently calcined using the following heat treatment, divided in two steps: (i) 30 – $800^\circ C$ and (ii) 800 – $1100^\circ C$, with a heating rates of 3 and $5^\circ C/min$, respectively.

The precursors obtained from both experimental conditions were analysed by DTA and TGA until $1200^\circ C$ in static air atmosphere at a heating rate of $10^\circ C/min$ using alumina as reference material. One part of the sample was pre-heated at $900^\circ C$ for 5 min with a heating rate of $20^\circ C/min$ and subsequently it was studied by DTA–TGA until $1200^\circ C$ with a heating rate of $10^\circ C/min$.

The residue obtained after DTA–TGA test was studied by XRD and TEM.

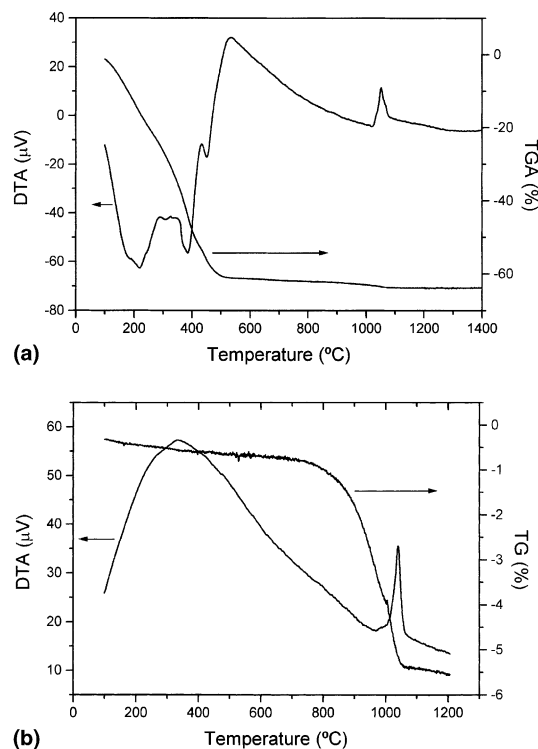


Fig. 1. DTA and TGA curves corresponding to precursor (a) and to preheated precursor at $900^\circ C$ (b).

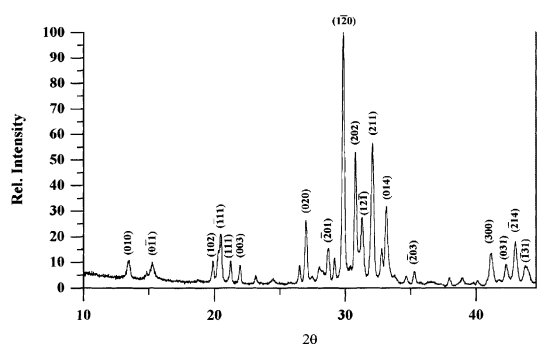


Fig. 2. Indexed XRD pattern corresponding to the residue of the DTA–TGA test just after the exothermic peak at 1052°C.

3. Results

The reaction sequence yielded a transparent gel precursor which after calcining at 1100°C was converted into a white powder. The DTA and

TGA curves corresponding to precursor and to pre-heated precursor at 900°C are shown in Fig. 1. For both experimental conditions the same behaviour was found. As can be seen in Fig. 1(a) after a fast initial loss of water at $\approx 150^\circ\text{C}$ ($\sim 11\%$ of the weight) a weight loss of $\sim 42\%$ takes place in successive steps between 290°C and 500°C because of decomposition of NO_3^- and $\text{C}_2\text{H}_6\text{O}$. Close to 1000°C a weight loss of approximately 2% can be distinguished. In order to carry out a better analysis of this effect the sample preheated at 900°C was studied. Fig. 1(b) shows that this is a complex effect including two steps. The first, located at 960°C, that can be assigned to the combustion of residual carbon [10] and the second at 1030°C related to the $\text{Y}_2\text{Si}_2\text{O}_7$ crystallisation and probably due to the dehydration of silanol groups and subsequent crystalline network formation.

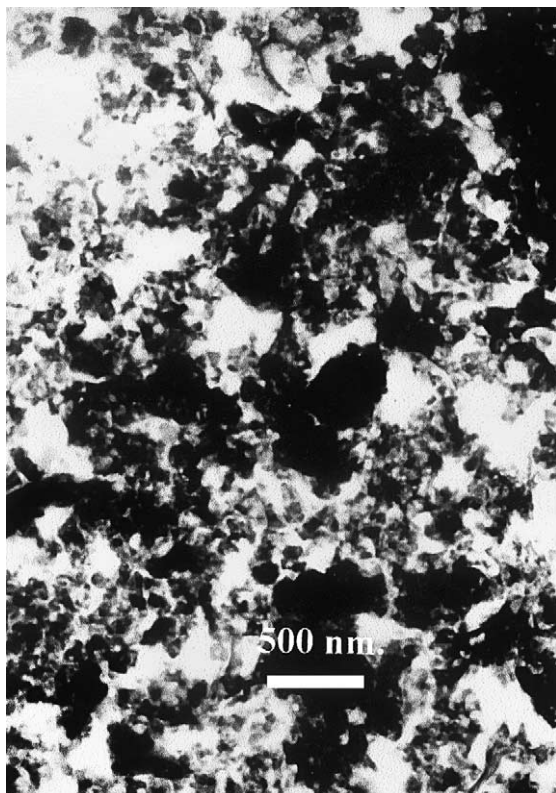


Fig. 3. TEM of the powder obtained by route 1 (molar ratio 1:4:0.05) after calcining at 1200°C.

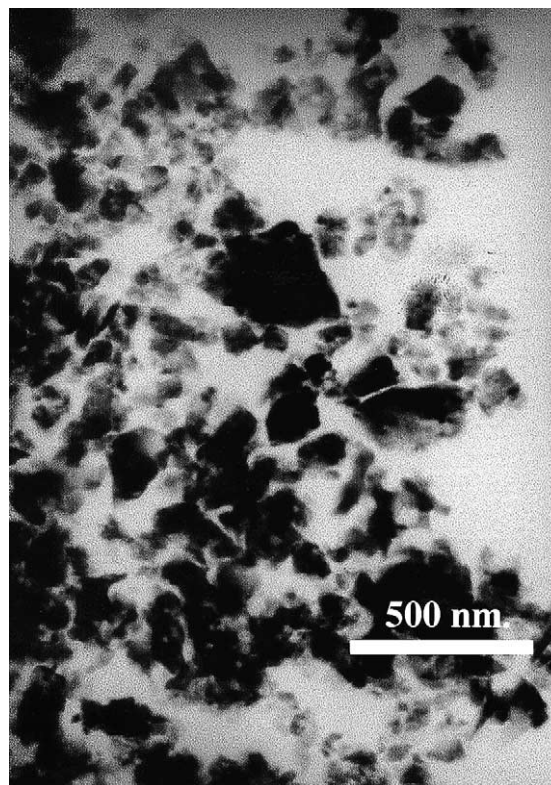


Fig. 4. TEM of the powder obtained by route 2 (molar ratio 1:4:1) after calcining at 1200°C.

The indexed XRD pattern (Fig. 2) corresponding to the residue of the DTA–TGA test just after the exothermic peak at 1052°C corresponds to a single phase [11] of α - $\text{Y}_2\text{Si}_2\text{O}_7$.

As observed under TEM (Figs. 3 and 4) this powder is made up of non-agglomerated particles with size lower than 200 nm. There are no significant differences in size or morphology between both the synthesis routes.

4. Conclusions

A gel-like precursor of α - $\text{Y}_2\text{Si}_2\text{O}_7$ has been obtained starting from yttrium nitrate and TEOS solutions in two different HCl molar ratios. From this precursor a crystalline nanosize (<200 nm) powder of α - $\text{Y}_2\text{Si}_2\text{O}_7$ is obtained at \sim 1052°C.

As can be deduced from the results, the fabrication of α - $\text{Y}_2\text{Si}_2\text{O}_7$ by the proposed method is almost insensitive to HCl starting concentration. This fact is an important positive factor regarding a future mass production of this precursor.

Acknowledgements

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