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Formation of Nanocrystalline Yttrium Disilicate Powder by an Oxalate Gel Method

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Abstract

In the present work a new and simple method for the synthesis of α-$Y_2Si_2O_7$ nanoparticles is reported. The method consists of the reaction of $Y(NO_3)_3$ and TEOS in the adequate molar ratio to form a precursor complex gel composed by two cations, Si and Y, in the 1:1 ratio. From the precursor a crystalline nanosize ($\simeq$40 nm) powder of α-$Y_2Si_2O_7$ is obtained at 1060°C. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

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 to be used in high temperature structural applications as 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–reprecipitation 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 the 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 on 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 $Y_2Si_2O_7$ glassy phase refractoriness (m.p. = 1780°C) allows to increase the regime temperature of the material without reaching the softening point. Nevertheless, a knowledge of its stability at high temperature is needed in order to predict important processes such as devitrification or oxidation, which can produce either beneficial or undesirable results.[3]

Additionally the study of the high temperature mechanical properties of this particular $Y_2Si_2O_7$ compound will shed light on the high temperature performance of Si_3N_4-based materials.

Several groups[4–7] have synthesized and studied the crystallization process of glasses from the Y_2O_3–SiO_2–Al_2O_3 system, but a complete understanding of the system has not yet been reached. $Y_2Si_2O_7$ has been synthesized by solid-state reaction of the mixed oxides SiO_2 and Y_2O_3 at 1300°C. However, below this temperature the oxides do not react within a reasonable time of heating.[8] Ito and Johnson have synthesized $Y_2Si_2O_7$ from pure silicic acid solutions and YCl_3, but this route requires an exhaustive 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.[9]

In the present communication a new and simple preparation method for the synthesis of $Y_2Si_2O_7$ is reported. The method consists of the reaction of $Y(NO_3)_3$ and TEOS in the adequate molar ratio to form a complex gel composed by the two cations, Si and Y, which yields the stoichiometric $Y_2Si_2O_7$ after calcining.

2 Experimental Procedure

The following reactants have been used as starting materials: $Y(NO_3)_3$·4H2O (Prolabo, France), $Si(OC_2H_5)_4$ 98% purity TEOS (Merck, Germany), $C_2H_2O_4$·2H2O 99.5% purity (Merck, Germany) and 2-Propanol (Panreac, Spain).

The synthesis method of $Y_2Si_2O_7$ precursor is summarized in the flow chart of Fig. 1.

The precursor was analysed by DTA and TGA until 1200°C in static air atmosphere at a heating

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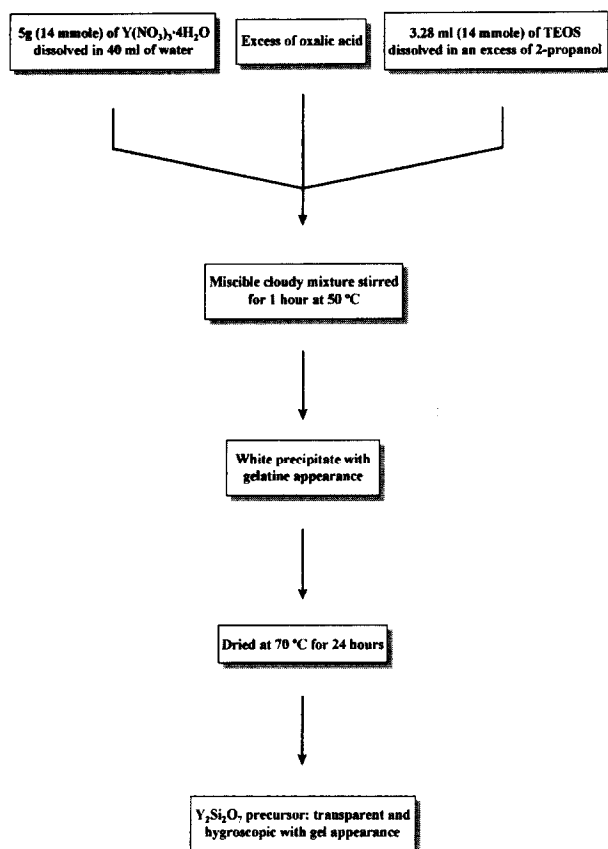†On leave from: IPEN-CNEN/SP-CP11049, ZIP: 05422-970, São Paulo (Brazil).

Fig. 1. Flow-chart of the preparation method for the synthesis of $Y_2Si_2O_7$.

rate of 10°C/min using alumina as reference material. The measurements were made using a Seiko SSC/5200 instrument. One part of the sample was pre-heated at 900°C for 5 min with a heating rate of 20°C/min and was subsequently studied by XRD and DTA-TGA until 1200°C with a heating rate of 10°C/min.

The residue obtained after DTA-TGA test was studied by XRD and TEM (Jeol instrument, JEM 2000 FXII model, at 200 kV).

3 Results and Discussion

The reaction sequence presented in the flow-chart of Fig. 1 yielded a transparent gel-like precursor, which after calcining at 1250°C was converted into a white powder.

The DTA and TGA curves corresponding to the precursor and the pre-heated precursor at 900°C are shown in Fig. 2. As can be seen in Fig. 2(a), after a fast initial loss of water at $\simeq$150°C ($\simeq$11% of the weight) a weight loss of $\simeq$42% takes place in successive steps between 287 and 518°C due to decomposition[10] of NO_3^- and $C_2O_4^{2-}$. Following a weight loss of approximately 6%, which occurs between 720 and $\simeq$1040°C, caused probably by the combustion of residual free carbon (broad exothermic peak centred at 900°C), a sharp

exothermic peak at 1065°C typically due to crystallization of a compound, accompanied by a weight loss of $\simeq$1% [Fig. 2(b)] is observed. This weight loss can be associated with a final combustion of
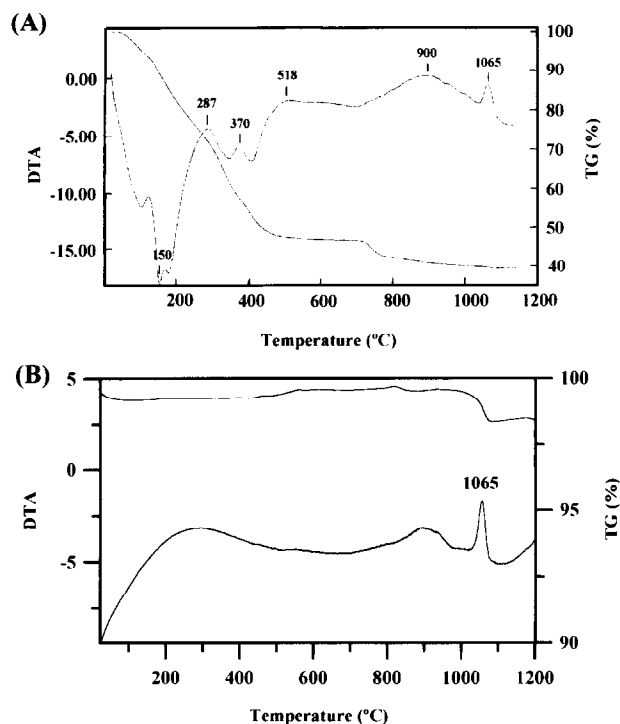

Fig. 2. (a) DTA and TGA of the $Y_2Si_2O_7$ precursor showing the exothermic peak corresponding to crystallization of α-$Y_2Si_2O_7$. (b) DTA-TGA of the pre-heated precursor at 900°C in air atmosphere.
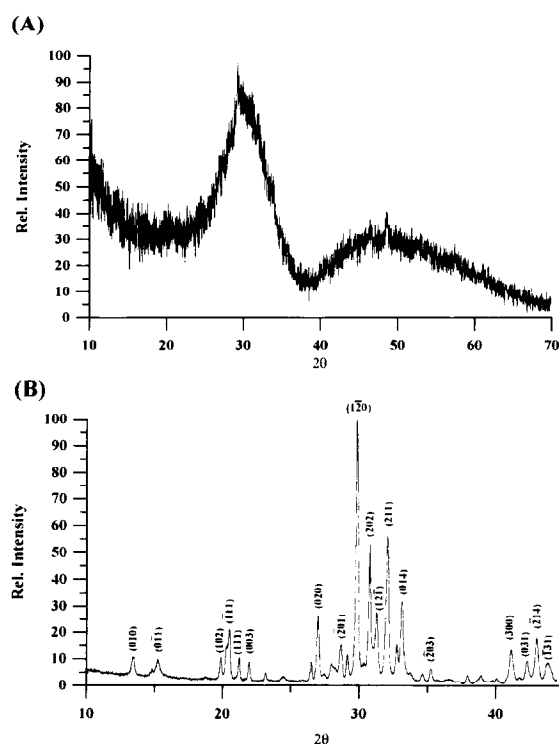

Fig. 3. (a) XRD pattern of calcined precursor at 900°C for 5 min in air atmosphere showing its amorphous character. (b) Indexed XRD pattern of the residue obtained from DTA-TGA test of the pre-calcined precursor at 900°C in air atmosphere.
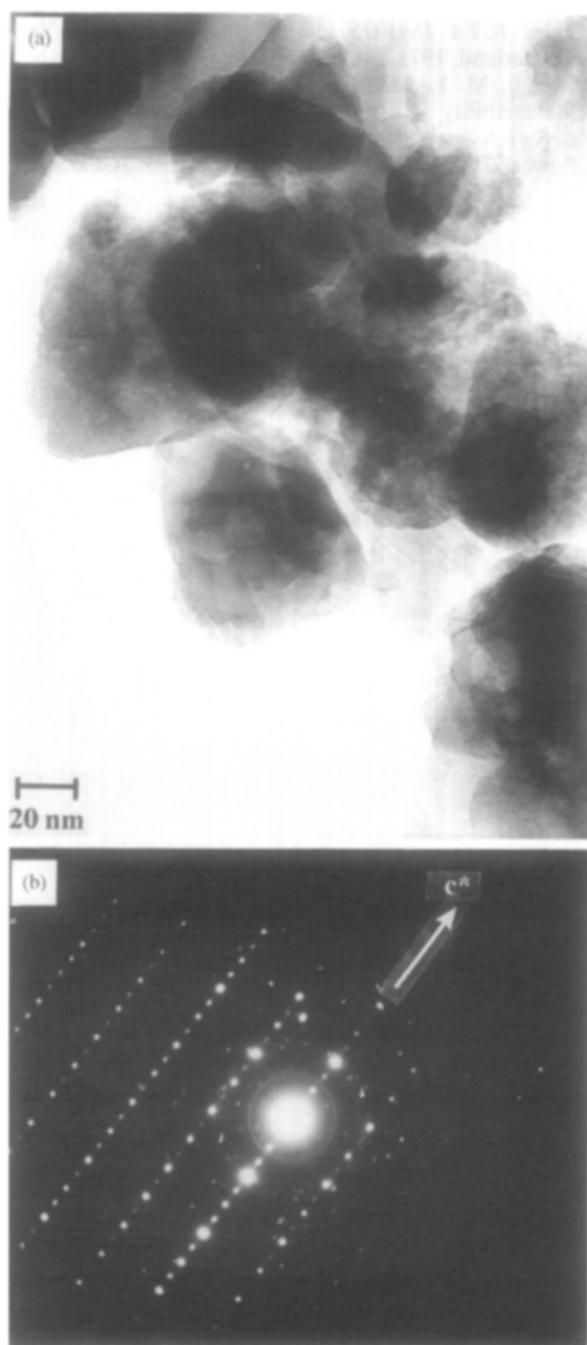
Fig. 4. TEM micrograph and the corresponding SAD pattern of the nanosize α-$Y_2Si_2O_7$ particles showing the c* axe.

residual carbon using gaseous oxygen at the surface and probably lattice oxygen at the bulk. A similar phenomenom has been observed during the crystallization of t-ZrO_2 by thermal decomposition of zirconyl acetate.[11]

The XRD patterns corresponding to the pre-heated precursor at 900°C and to the residue obtained from the DTA-TGA test are shown in Fig. 3. The pre-heated precursor pattern [Fig. 3(a)] is that of an amorphous material, indicating that no crystallization process takes place below 900°C. Therefore the weight loss, which accompanies the exothermic effect observed at this particular temperature in the DTA-TGA analysis [Fig. 2(a)],

must be caused by combustion of free carbon, as has been mentioned above.

The indexed XRD pattern [Fig. 3(b)] corresponding to the residue of the DTA-TGA test just after the exothermic peak at 1065°C corresponds to a single phase[12] of α-$Y_2Si_2O_7$.

As observed under TEM (Fig. 4) this powder is constituted by non-agglomerate particles of $\simeq$40 nm average size. The corresponding SAD pattern of this powder shows the crystalline character of the α-$Y_2Si_2O_7$ nanoparticles.

The fact that the amorphous XRD pattern of the pre-heated precursor [Fig. 3(a)] shows a band with a maximum located in a similar position to the peak with the higher intensity ($2\theta \simeq 30°$) of the α-$Y_2Si_2O_7$ [Fig. 3(b)], indicates that the short range order of this precursor is similar to the α-$Y_2Si_2O_7$ crystals.

4 Conclusions

A gel-like precursor of α-$Y_2Si_2O_7$ has been obtained starting from yttrium nitrate and TEOS solutions. From this precursor a crystalline nano-size ($\simeq$40 nm) powder of α-$Y_2Si_2O_7$ is obtained at $\simeq$1060°C.

Acknowledgement

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