2006

Low-temperature synthesis and sintering of Y-Y2Si2O7

Ziqi Sun
*University of Wollongong, ziqi@uow.edu.au*

Yanchun Zhou
*Chinese Academy of Sciences*

Meishuan Li
*Chinese Academy of Sciences*

http://ro.uow.edu.au/engpapers/5371

**Publication Details**


Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au
Low-temperature synthesis and sintering of $\gamma$-$Y_2Si_2O_7$

Ziqi Sun

High Performance Ceramic Division, Shenyang National Laboratory for Materials Science,
Institute of Metal Research, Chinese Academy of Sciences, Shenyang, 110016, China;
and Graduate School of Chinese Academy of Sciences, Beijing, 100039, China

Yanchun Zhou$^{a}$ and Meishuan Li

High Performance Ceramic Division, Shenyang National Laboratory for Materials Science,
Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

(Received 2 December 2005; accepted 1 March 2006)

In this article, a novel pressureless solid-liquid reaction method is presented for preparation of yttrium disilicate ($\gamma$-$Y_2Si_2O_7$). Single-phase $\gamma$-$Y_2Si_2O_7$ powder was synthesized by calcination of $SiO_2$ and $Y_2O_3$ powders with the addition of $LiYO_2$ at 1400 °C for 4 h. The addition of $LiYO_2$ significantly decreased the synthesis temperature, shortened the calcination time, and enhanced the stability of $\gamma$-$Y_2Si_2O_7$. The sintering of these powders in air and $O_2$ was studied by means of thermal mechanical analyzer. It is shown that the $\gamma$-$Y_2Si_2O_7$ sintered in oxygen had a faster densification rate and a higher density than that sintered in air. Furthermore, single-phase $\gamma$-$Y_2Si_2O_7$ powder with a density of 4.0 g/cm$^3$ (99% of the theoretical density) was obtained by pressureless sintering at 1400 °C for 2 h in oxygen. Microstructures of the sintered samples are studied by scanning electron microscope.

I. INTRODUCTION

Yttrium disilicate ($Y_2Si_2O_7$), one of the most refractory silicates having a melting point of 1775 °C,$^1$ has the potential for high-temperature application. Dense $\gamma$-$Y_2Si_2O_7$ can be used in some harsh environments with corrosive atmospheres or fast cooling/heating because of its low thermal expansion coefficient and good erosion resistance.$^2$ It is also an interesting material for luminescent applications as plasma displays, laser materials, and high-energy phosphors when it is doped with rare earth elements.$^4$ Moreover, $Y_2Si_2O_7$ plays an important role in sintering of silicon nitride ($Si_3N_4$). $Y_2Si_2O_7$ is one of the most encountered intergranular phases of $Si_3N_4$ when the $Y_2O_3$ or $Y_2O_3 + SiO_2$ are used as the sintering aids. It provides the $Si_3N_4$ with good high-temperature properties.$^7$ Thus, a comprehensive understanding of $Y_2Si_2O_7$ is essential to the application of $Si_3N_4$.

$Y_2Si_2O_7$ has up to six polymorphs: $\alpha$, $\beta$, $\gamma$, $\delta$, and $\zeta$.$^1$ Transformation temperatures between the different $Y_2Si_2O_7$ polymorphs, as determined by different researchers, exhibit a wide variation. The results obtained by Ito et al.$^{15}$ are widely cited in the literature.

However, the low temperature $\gamma$-polymorph was not included in Ref. 15. Later, Beccero et al.$^{16}$ reported a phase-transformation temperature from the $\gamma$ to $\beta$–$Y_2Si_2O_7$ of 1050 °C. These polymorphs have different densities: 4.30 g/cm$^3$, 4.03 g/cm$^3$, 4.04 g/cm$^3$, and 4.11 g/cm$^3$ for $\alpha$, $\beta$, $\gamma$, and $\delta$, respectively. Therefore, the polymorphic transformations are accompanied by volume changes, which may induce serious internal stress that can lead to fracture of the material. A single-phase material without phase transformations is important for high-temperature applications.

Previous studies have shown that the synthesis of a stoichiometric single-phase $Y_2Si_4O_9$ is particularly difficult, and most of them concentrated on synthesis via a sol-gel route using yttrium nitrate and tetraethyl orthosilicate as precursors.$^3,17,18$ Despite the precursors having been mixed on a nanoscale, only $\alpha$-$Y_2Si_2O_7$ was formed. High-temperature phases were still not produced by calcining the silica/yttria powders, even at elevated temperatures between 1200 °C and 1600 °C.$^{19}$ The hydrothermal method was also used to synthesize $\gamma$-$Y_2Si_2O_7$.$^{16,20}$ However, this method requires extended processing duration, for instance, 100 days at 300 °C or 10 days at 650 °C, to obtain single-phase $\gamma$-$Y_2Si_2O_7$ from
Y(NO₃)₃ solution and saponite or some other silica-contained ores in a high-pressure tank. Recently, Diaz et al. successfully synthesized crystalline γ-Y₂Si₂O₇ by means of hydrothermal method without the addition of stabilizing cations.

From the practical point of view, long synthesis time, expensive precursors, and special apparatus are undesirable. A more convenient and economical method is needed to synthesize bulk Y₂Si₂O₇. It is known that the reaction of mixed powders is the most commonly used method for ceramic preparation. Unfortunately, a high temperature (up to 2100 °C for 5–15 h) or a long calcining time (between 500 and 1800 °C) was needed if Y₂O₃ and amorphous SiO₂ powders were directly used as starting materials for synthesizing Y₂Si₂O₇; in addition, high-purity, single-phase Y₂Si₂O₇ was still not available. Even if the pure high-temperature phase was synthesized at high temperature ranges, the low-temperature polymorphs easily developed during cooling. Kumar et al. have drawn hypothetical time-temperature-transformation curves for the eutectic melts. They showed that the synthesis of the high-temperature phases, such as the α or γ polymorphs, require a very fast quenching rate, e.g., 520 °C/min. The quenching rate has a decisive influence on maintaining homogeneity of the high-temperature polymorphs. Otherwise, some low-temperature polymorphs, such as α and β, would appear as the second phases.

An effective way to obtain high-purity, single-phase γ-Y₂Si₂O₇ at lower temperatures is to introduce a new additive. To our knowledge, no work has been reported on the effects of additives on the synthesis of γ-Y₂Si₂O₇. LiYO₂ has been used in the sintering of Si₃N₄ as a new type of effective, single-component additive. It significantly lowered the sintering temperature. In the present work, LiYO₂ was used as an additive that could transform the reaction between yttria and silica. As will be demonstrated, the addition of LiYO₂ dramatically lowered the synthesis temperature, greatly shortened the isothermal holding time, and eliminated the undesirable phases, even at low cooling rates. In addition, we show the effect of LiYO₂ on the synthesis and sintering of γ-Y₂Si₂O₇, and report on the sintering behavior of γ-Y₂Si₂O₇ compacts in different atmospheres.

II. EXPERIMENTAL PROCEDURE
A. Synthesis of Y₂Si₂O₇ powders using LiYO₂ as additive

The starting powders were yttria (Y₂O₃, 99.99% purity; Yuelong Reagent Co., Shanghai, China), amorphous silica (SiO₂, 99.99% purity; Yangxian Reagent Co., Shanghai, China), and lithium carbonate (Li₂CO₃, 99.99% purity; Hengxin Reagent Co., Shanghai, China).

LiYO₂ was synthesized at first by calcining the as-received Y₂O₃ and Li₂CO₃ powders mixture at 1400 °C for 4 h. The final product was single-phase LiYO₂ confirmed by x-ray diffraction (XRD) analysis.

Y₂O₃ and amorphous SiO₂ powders were mixed in a near-stoichiometric ratio and the amount of the LiYO₂ additive varied from 0, 2, 3, to 5 mol%. The powder mixture was milled for 4 h in isopropanol by attrition milling with agate media. The slurry was separated from the milling media and was dried at 80 °C for 24 h in an oven. Afterward, some of the powders were calcined at 1400 °C for 4 or 6 h in air, and some were calcined at 1500 °C for 8 h to evaporate the residual Li, and then ball-milled again for 24 h to break up agglomerates. They were subsequently sieved to obtain particles with a maximum size of 100 μm.

B. Sintering of the synthesized powder

The calcined powders were uniaxially pressed into pellets at 40 MPa and then isostatically cold pressed at 285 MPa. The green body was 7 mm in diameter and 6 mm in height and had a relative density of about 60%. Some samples were heated up to 1500 °C at a constant rate of 5 °C/min in air and O₂ separately. Some samples were heated up to 1200 °C in air, or up to 1400 °C in oxygen at the same rate and then held isothermally for 2 h. After sintering, the samples were cooled at a rate of 5 °C/min. Densification curves were obtained using a thermal mechanical analyzer (Netzsch 24; Netzsch Instruments, Caluire, France). The sintering runs were again conducted in an air or oxygen atmosphere. Based on the initial density and shrinkage, the density of the samples during sintering was evaluated and the final density was checked by the Archimedes method.

C. Characterization of Y₂Si₂O₇ powders and the sintered samples

The synthesized LiYO₂ additive and γ-Y₂Si₂O₇ powders were characterized by XRD (D/max-2400; Rigaku Instruments, Tokyo, Japan) using Cu Kα radiation and a scanning rate of 2 °/min. A theoretical XRD pattern of γ-Y₂Si₂O₇ was simulated using the diffraction package in the Cerius² 4.2 program for materials research (Molecular Simulation Inc., Waltham, MA). This pattern was used to compare with the experimental results.

The microstructures of the sintered samples were observed by scanning electron microscope (SEM; Cambridge S360 equipped with an Oxford energy dispersive x-ray spectroscopy; EDS, Cambridge, UK), after chemical etching.

III. RESULTS
A. Synthesis of γ-Y₂Si₂O₇ powder

XRD patterns of the synthesized powders with different amounts of LiYO₂ additives are demonstrated in
Fig. 1. The samples have been calcined at 1400 °C for 4 h. Without LiYO₂ additive, the calcined powder composed of γ-Y₂Si₂O₇, Y₂SiO₅, and Y₄Si₇(SiO₄)₃, as shown in Fig. 1(a). When the amount of LiYO₂ additive increases from 2 to 5 mol%, as shown in Figs. 1(b)–1(d), respectively, Y₂SiO₅ disappeared and the Y₄Si₇(SiO₄)₃ content decreased. Furthermore, when the calcination time was prolonged up to 6 h, only γ-Y₂Si₂O₇ was identified by XRD when the amount of additive was equal or higher than 3 mol%. The powders were also heated to 1500 °C for 8 h to modify the residual Li content. The XRD pattern of powders calcined in this condition (Fig. 2) matched perfectly with the simulated one shown in Fig. 1(e). The amount of LiYO₂ additive in the starting powders synthesized for all sintering cases was chosen as 3 mol%.

B. Sintering behavior of γ-Y₂Si₂O₇ powders

Specimen shrinkage during heating to and holding at the sintering temperature was obtained by thermal mechanical analyzer (TMA). Based on the extent of shrinkage and the density of the compact before sintering (ρ₀), the instantaneous density (ρ) was calculated by the following equation

\[
ρ = \frac{ρ₀}{(1 - \Delta L/L₀)^3}
\]

where \( \Delta L = L₀ - L \), and \( L₀ \) and \( L \) are the initial and the instantaneous specimen lengths, respectively, with an assumption of isotropic shrinkage. The relative density was determined as the instantaneous density normalized by the theoretical density (ρ₀) of 4.04 g/cm³.

Figure 3 illustrates the densification curves of the γ-Y₂Si₂O₇ compacts sintered up to 1500 °C at a constant heating rate in the two atmospheres mentioned above. The relative densities, ρ/ρ₀ [Fig. 3(a)], and the densification rates, (1/ρ)dρ/dt [Fig. 3(b)], are plotted as a function of sintering temperature. Figure 3(a) shows that the sample sintered in oxygen achieved a higher relative density of 97.5%, while the sample sintered in air reached a lower relative density of 93%. According to Fig. 3(b), a slight shrinkage occurred at 778 °C for all these samples, which may be the result of the formation of a liquid phase containing residual Li₂O. It was supposed being deduced from a complex compound, such as Li-Y-Si-O, that melted at 778 °C. Densification of the samples began obviously at about 870 °C in each atmosphere. Furthermore, the maximum densification rate occurred at a temperature of ~960 °C for all cases. In addition to the shrinkage peaks centered on 778 °C and ~960 °C, two other small peaks appeared at around 925 °C and 1012 °C. The two small peaks may be associated with phase transformations during the sintering process. However, no second phases were detected by XRD or SEM backscattered electron image analysis in the sintered samples. Therefore, these peaks may come from a
transition phase that only existed in the temperature range of 925 °C–1012 °C. To clarify the presence of transition phases, XRD measurements were performed on a sample quenched from 940 °C to room temperature. The result is shown in Fig. 4. It shows that γ phase is the dominant phase, with a minor amount of β-Y$_2$Si$_2$O$_7$ (JCPDS card number 38-0400).

The sintering kinetics are different in the two different atmospheres. When the sintering was carried out in air, the largest densification rate achieved at 958 °C, and afterward, the densification rate decreased continuously until the temperature reached 1365 °C. At this temperature, the densification of sample was ceased at a relative density of 93%. When the temperature increased to higher than 1365 °C, the relative density decreased slightly because the residual Li$_2$O evaporated. While in oxygen atmosphere, the sample shrunk continually until the maximum relative density of 97.5% was reached at 1470 °C; beyond that temperature, no dilation was detected.

The isothermal sintering behavior of Y$_2$Si$_2$O$_7$ compact was also studied in air and oxygen, and the results are summarized in Table I. The relative density of the samples and the temperature as functions of the sintering time are shown in Fig. 5 for sintering at 1200 °C in air and 1400 °C in oxygen. As can be seen, the sintering curves below 1200 °C were very similar to those shown in Fig. 3(a), which was a good evidence that the sintering were reproducible. The highest relative density was achieved at 94% after holding at 1200 °C in air for ~80 min. A higher density was not obtained even at a higher temperature (1300 °C) or a longer holding time (Table I). The sample sintered in oxygen was well densified after holding at 1400 °C for 2 h, reaching a relative density of 99% (a density of 4.0 g/cm$^3$). XRD analysis revealed that all samples sintered in different atmospheres were composed of single-phase γ-Y$_2$Si$_2$O$_7$. For example, Fig. 6 presents the XRD pattern of a sample sintered in oxygen at 1400 °C for 2 h, showing that only γ-Y$_2$Si$_2$O$_7$ was detected.

**TABLE I.** The relative density of γ-Y$_2$Si$_2$O$_7$ isothermally sintered at different temperatures for 2 h in air and in oxygen.

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Air</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>1100</td>
<td>1200</td>
</tr>
<tr>
<td>Relative density (%)</td>
<td>92</td>
<td>94</td>
</tr>
</tbody>
</table>
IV. DISCUSSION

A. Solid-liquid reaction synthesis of $Y_2Si_2O_7$ powders

Figure 1 shows that the addition of LiYO$_2$ greatly promoted the reaction between $Y_2$O$_3$ and SiO$_2$. According to the studied component range, the greater amount of LiYO$_2$, the higher the purity of $Y_2$Si$_2$O$_7$. It is suggested that a liquid phase, which formed at a certain temperature because of the addition of LiYO$_2$, efficiently benefited the reaction between yttria and silica. As previously reported, LiYO$_2$ and SiO$_2$ formed a mixed liquid phase at 1225 °C.$^{25}$ The liquid state of LiYO$_2$–SiO$_2$ would act as a “molten pool” that allows rapid transportation of various substances through the liquid. This process would facilitate a complete synthesis reaction between $Y_2$O$_3$ and SiO$_2$ at a lower temperature range and in a shorter amount of time. According to the XRD results, possible reactions occurred in the powder mixtures are proposed as follows:

\[ Y_2O_3 + SiO_2 \rightarrow Y_2SiO_5 \quad , \quad (2) \]
\[ Y_2SiO_5 + SiO_2 \rightarrow Y_2Si_2O_7 \quad , \quad (3) \]
\[ Y_2O_3 + 2SiO_2 \rightarrow Y_2Si_3O_7 \quad , \quad (4) \]
\[ 2.335Y_2O_3 + 3SiO_2 \rightarrow Y_{4.67}(SiO_4)O \quad \]  \[ , \quad (5) \]

Paramentier et al.$^{28}$ have reported that O-apatite, $Y_{5.67}(SiO_4)O_3$, was a metastable phase in air, and it decomposed into $Y_2SiO_5$ and $Y_2Si_3O_7$ at 1600 °C after prolonged holding time. The decomposition was greatly accelerated by the LiYO$_2$ additive and it would succeed at a lower temperature. Afterward, $Y_2SiO_5$ interacted with SiO$_2$ to form $Y_2Si_3O_7$. Eventually, only single-phase $Y_2Si_3O_7$ was presented.

During the synthesis process, LiYO$_2$ can decompose into Li$_2$O, and $Y_2O_3$, as well.$^{25}$ Most of the Li$_2$O would be evaporated when the temperature was higher than 1300 °C because of its high vapor pressure,$^{29}$ but a small amount of Li$_2$O would remain in the powders.

As discussed above, residual Li$^+$ can form a complex Li–Y–Si–O liquid phase at low temperatures during the sintering process and hence promote the densification. However, too much retained Li$^+$ might also degrade the high-temperature properties of the sintered material. To avoid negative effects of LiYO$_2$, the optimized synthesis process for $Y_2Si_2O_7$ is taken as follows: the LiYO$_2$ additive content is chosen as 3 mol%, and the synthesis condition is calcination at 1500 °C for 8 h. As illustrated in Fig. 1, the optimized additive can induce a pure $Y_2Si_2O_7$. If adding less amount of LiYO$_2$, a longer holding time is needed to form a pure product. When Matovic et al.$^{25}$ investigated the effect of the calcination time on the remains of Li$_2$O in sintering of Si$_3$N$_4$, they...
found that only 0.08 wt% Li$_2$O was detected after 8 h heating the Si$_3$N$_4$ samples with 15% wt. LiYO$_2$ additive at 1500 °C. Thus, we concluded that the amount of residual Li$_2$O in γ-Y$_2$Si$_2$O$_7$ was very small after high-temperature treatments and it would be nondeleterious to the high-temperature properties of γ-Y$_2$Si$_2$O$_7$ ceramic. The XRD pattern of the synthesized powders in the optimum conditions is shown in Fig. 2.

B. Sintering behavior of Y$_2$Si$_2$O$_7$ in different atmospheres

Figure 3 indicates that the atmosphere has an obvious influence on the sintering behavior of γ-Y$_2$Si$_2$O$_7$. When the sintering was conducted in oxygen at a constant rate of heating up to 1500 °C, the densification was accelerated and the final relative density was 97.5%. However, the densification was hindered when the sample was heated in air, keeping other conditions unchanged, and the maximum relative density was 93% at 1365 °C.

A possible explanation is provided to better understand these differences. The solubility of gas in the pores of samples could affect pore elimination during the sintering process. Compared with oxygen, the solubility and outward diffusibility of nitrogen (the major component of air) atoms in oxide ceramics are essentially negligible. First, the oxygen vacancies benefit the diffusion of oxygen atoms. Second, the smaller atomic radius of oxygen (0.65 Å for O and 0.75 Å for N) ensures a fast transport of oxygen in the pores. Therefore, the pores in the specimens would be easily eliminated during the sintering process in oxygen and the resulting samples would have comparatively higher densities than those sintered in air.

The SEM images of the sintered samples (Fig. 7) show that the sintering atmospheres are important for the development of microstructures. The reason for these differences has not been identified at present. In the sintering of Si$_3$N$_4$ with Y$_2$O$_3$/Y$_2$O$_3$ + SiO$_2$ as additives, one of the major factors for micrographic differences was the viscosity of the liquid phase formed during sintering. A liquid phase with higher viscosity would lead to elongated grains with a higher aspect ratio. Nitrogen would diffuse into the intergranular glassy phase and increase
the viscosity of liquid phase,\textsuperscript{31} which reasonably explains the appearance of elongated grains for samples sintered in air. In contrast, samples sintered in oxygen exhibited equiaxed platelet-like grains because a liquid phase with lower viscosity was formed. Furthermore, the oxygen atmosphere served as an activated sintering atmosphere, accelerated the growth velocity of grains, and favored the formation of large equiaxed grains.\textsuperscript{32} Therefore, samples sintered in oxygen had higher densification speed, and large equiaxed platelet grains were identified in Fig. 7(f).

V. CONCLUSIONS
Stoichiometric single-phase $\gamma$-Y$_2$Si$_2$O$_7$ powders were synthesized at 1400 °C by a novel solid-liquid reaction process using LiYO$_2$ as an additive. The addition of 3 mol\% LiYO$_2$ would decrease the synthesis temperature to 1400 °C, shorten the calcination time to 4 h, and efficiently enhance the stability of $\gamma$-Y$_2$Si$_2$O$_7$. The residual Li$^+$ would also form a complex liquid phase and facilitate the densification during the sintering process.

The sintering behavior of synthesized $\gamma$-Y$_2$Si$_2$O$_7$ was investigated in atmospheres of air and oxygen. The oxygen atmosphere obviously improved the sintering process. A density of 99\% of the theoretical was obtained after sintering in oxygen for 2 h at 1400 °C. All sintered materials were single-phase $\gamma$-Y$_2$Si$_2$O$_7$ without any other low-temperature phases.

The microstructures were observed on chemically etched surfaces using SEM. The samples sintered in air had elongated grains, whereas equiaxed grains appeared when sintering was conducted in oxygen.

ACKNOWLEDGMENTS
This work was supported by the National Outstanding Young Scientist Foundation for Y.C. Zhou under Grant No. 59925208 and by the Natural Sciences Foundation of China under Grant Nos. 50232040, 50302011, 90403027, and ‘863’ project. The authors are grateful to Dr. P.Y. Hou for useful discussions.

REFERENCES
27. J.C. Bressiani, V. Izhevskiy, and H.A. Bressiani: Development of