

# Single-crystal growth of $\text{La}_4\text{Si}_2\text{O}_7\text{N}_2$ by the floating zone method

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Single crystals of  $\text{La}_4\text{Si}_2\text{O}_7\text{N}_2$  were prepared successfully by the floating zone method using a radiation convergence type apparatus with a halogen lamp as the heat source. Crystals were grown under a nitrogen pressure of 11 atm and at a rate of  $2 \text{ mm h}^{-1}$ . The addition of 2.6 wt % ( $3\text{SiO}_2 + \text{Si}_3\text{N}_4$ ) to the stoichiometric raw mixture was used as the starting material in order to compensate for volatilization during growth. The crystals obtained were colourless, transparent and free from inclusions. Homogeneity was confirmed by means of EPMA and the chemical composition of  $\text{La}_4\text{Si}_2\text{O}_7\text{N}_2$  was assured by wet analysis and EPMA. The space group and cell constants were determined by the X-ray single-crystal diffraction method as  $P2_1/m$ ,  $a = 8.03 \text{ \AA}$ ,  $b = 10.96 \text{ \AA}$ ,  $c = 11.57 \text{ \AA}$  and  $\beta = 111.58^\circ$ , respectively.

## 1. Introduction

For densification of silicon nitride, various additives have been investigated including rare-earth oxides [1, 2]. The R-Si-O-N (R = rare-earth element) compounds are formed as the secondary phases between  $\text{Si}_3\text{N}_4$  grains when rare-earth oxides have been used as densification aids. It is known that their physical and chemical properties greatly influence the characteristics of the sintered materials. These facts led to investigations on the phases and their relationships in the R-Si-O-N systems, for example Y-Si-O-N [3], Ce-Si-O-N [4] and La-Si-O-N [5, 6]. The investigations were made, however, only by solid-state reactions. Uncertainty still remains on the structure and composition of each compound because of the inhomogeneous nature of the resulting samples and the presence of a large amount of glass phase in them. Weight loss during firing is also one of the confusing factors. To determine the physical properties, crystal structures and chemical compositions, it is desirable to obtain large single crystals of R-Si-O-N compounds which contain no inclusions. So far no report has been published on the single-crystal growth of R-Si-O-N compounds to the authors' knowledge.

The present study reports the application of the floating zone (FZ) method to the single-crystal growth of  $\text{La}_4\text{Si}_2\text{O}_7\text{N}_2$  using an apparatus with a halogen lamp as the heat source. Recently, the FZ method has been proved to be one of the most promising methods in preparing single crystals of high quality. The application of the method to the single-crystal growth of the incongruently melting YIG [7], solid solutions [8] and the silicates which formed a viscous molten zone [9], have been reported. This is why the FZ method was chosen for the crystal growth of the La-Si-O-N compound the melting nature of which was not known.

The La-Si-O-N system has been studied by several researchers [5, 6] and the existence of  $\text{La}_4\text{Si}_2\text{O}_7\text{N}_2$  phase was first reported by Wills *et al.* [5]. The phase was supposed to have cuspidine structure ( $\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$ , monoclinic,  $a = 10.93 \text{ \AA}$ ,  $b = 10.57 \text{ \AA}$ ,  $c = 7.57 \text{ \AA}$ ,  $\beta = 110.1^\circ$ , ASTM 13-410) from X-ray powder diffraction.

## 2. Experimental details

The starting materials used in the present work were powders of  $\text{Si}_3\text{N}_4$  (Advanced Materials Eng., high-purity grade, oxygen 1.2 wt %),  $\text{La}_2\text{O}_3$  (Shinetsu Chemical Co, Ltd, 99.99% pure) and  $\text{SiO}_2$  (Kojundo Chemical Co, Ltd, 99.99% pure). The

powders of  $\text{Si}_3\text{N}_4$ ,  $\text{SiO}_2$  and  $\text{La}_2\text{O}_3$  were mixed to the desired composition. The amount of oxide layer on  $\text{Si}_3\text{N}_4$  and ignition loss of each raw material were taken into consideration. After adjusting to the restricted value, they were mixed mechanically and pressed in the usual manner, giving a rod of the desired size [9]. The pressed rod was immediately sintered in a highly pure nitrogen (Nihon Sanso Co 99.9995% up,  $\text{O}_2$  0.5 ppm, dew point  $-70^\circ$ ) flow in a molybdenum-wound resistance furnace at atmospheric pressure. The sintering temperature was  $1530^\circ\text{C}$ . Average weight loss during firing was about 0.1 wt% for each batch used in this experiment.

The apparatus employed in this study was of the radiation convergence type (Nichiden Kikai Co, Ltd) with an ellipsoidal mirror. The radiation source was a 1.5 kW halogen lamp. Details of the apparatus are given elsewhere [10].

After the formation of the molten zone in the apparatus, the feed and the seed shafts were driven downwards at a rate of 1 to  $3\text{ mm h}^{-1}$ . The shafts were both counter-rotated at 30 to 45 rpm.

The same highly pure nitrogen gas as used during sintering was employed as the growth atmosphere at a flow rate of 0.5 to  $1.5\text{ litre min}^{-1}$ . In the present experiment, the applied pressure was 2 and 11 atm.

The boules obtained were cut and polished, and then characterized by microscopic examination mainly using a polarizing microscope. By means of the electron probe microanalyser (EPMA) the homogeneity of the grown crystals was examined and the chemical compositions of the phases were determined. For correction of the data obtained, the ZAF method recently refined by Love and Scott [11] was employed. Precession and Weissenberg cameras were used to determine the space group using single crystals.

Chemical analysis was also performed to confirm the composition. La was analysed using the chelatometry titration method and Si was determined gravimetrically as a form of  $\text{SiO}_2$ . Nitrogen content was measured by the modified Kjeldahl method with the use of hydrochloric acid as the medium for dissolving samples. The distillation and titration methods followed were after Bollman and Mortimore [12].

### 3. Results and discussion

When a feed rod which corresponded to  $\text{La}_4\text{Si}_2\text{O}_7\text{N}_2$  in the ratio which was used, an opaque boule

was grown at a rate of  $3\text{ mm h}^{-1}$  and under 2 atm. The  $\text{La}_4\text{Si}_2\text{O}_7\text{N}_2$  crystal obtained contained  $\text{La}_2\text{O}_3$  as inclusions, which was hydrolysed easily by atmospheric moisture and expanded to destroy the crystal by fragmentation. Line scanning by EPMA revealed that inclusions began to appear several millimeters away from the seed rod. This suggests the congruently melting nature of  $\text{La}_4\text{Si}_2\text{O}_7\text{N}_2$ . Furthermore, the variation of composition in the crystalline part was not found by means of EPMA. This fact also suggests the lack of solid solubility of the compound. A weight loss of 2.7 wt% was observed in this case. Chemical analysis of the obtained boule indicated that the weight loss was mainly due to the evaporation of Si, O and N.

In order to prevent the inconveniences from evaporation, two methods were tried; one method was to add the same amount and composition of the volatile component in advance to the feed rods, and the other was to raise the atmospheric pressure around the growth region to prevent volatilization.

#### 3.1. Evaporation during crystal growth

To compensate for the weight loss, ( $n\text{SiO}_2 + \text{Si}_3\text{N}_4$ ) mixture was previously added to the stoichiometric starting material. In this experiment, two series of ( $n\text{SiO}_2 + \text{Si}_3\text{N}_4$ ) mixtures, i.e.  $n = 1$  and 3, were chosen and tried. The reasons for this choice were as follows: the existence of  $\text{La}_2\text{O}_3$  as a secondary phase indicates that the composition of the molten zone moved along the  $\text{La}_4\text{Si}_2\text{O}_7\text{N}_2$  ( $2\text{La}_2\text{O}_3 + \text{Si}_2\text{N}_2\text{O}$ )– $\text{La}_2\text{O}_3$  line towards the  $\text{La}_2\text{O}_3$  corner of the system, so it seemed reasonable to assume that the total volatile composition was  $\text{Si}_2\text{ON}_2$  ( $n = 1$ ). On the other hand, the volatile species during firing have been assumed by several works to be  $3\text{SiO} + \text{N}_2$ , which corresponds to  $n = 3$  composition [13, 14].

The growth experiments were carried out under a pressure of 2 atm and at a growth rate of  $3\text{ mm h}^{-1}$ . The addition of up to 4.0 wt% of  $n = 1$  composition was tried, but the crystals obtained showed no improvement in their quality.

The addition of  $n = 3$  mixture improved the quality of the resulting crystals. It can be inferred from this that the evaporating species are near the  $3\text{SiO} + \text{N}_2$  composition in accordance with some published assumptions. But even 4.0 wt% addition could not wholly compensate for the weight loss and still left small amounts of  $\text{La}_2\text{O}_3$  inclusions in the crystal. The relationship between the amount of addition of  $n = 3$  composition and weight loss

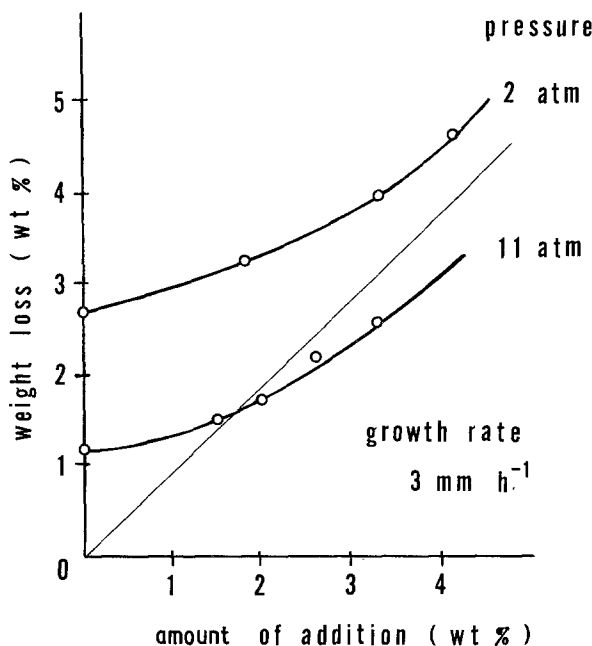


Figure 1 Weight loss after FZ procedure at 2 and 11 atm versus amount of addition of ( $3\text{SiO}_2 + \text{Si}_3\text{N}_4$ ) mixture.

is given in Fig. 1. In Fig. 1 the oblique straight line ("compensating line") is shown, on which the weight loss would be just compensated for by the addition.

### 3.2. Crystal growth under high nitrogen pressure

The evaporation may be reduced by applying a high nitrogen pressure around the growth region because nitrogen is one of the volatile species.

Using a stoichiometric mixture as a feed rod under 11 atm at a growth rate of  $3\text{ mm h}^{-1}$ , the weight loss was only 1.2 wt %, compared to 2.8 wt % at 2 atm. A series of addition experiments of  $n = 3$  composition was tried under 11 atm. The addition of 3.3 wt % yielded an almost transparent crystal with some cracks due to thermal stress and a small amount of Si-rich phase, whose composition was revealed to be near  $\text{LaSiO}_2\text{N}$ . This fact shows that the weight loss of 2.6 wt % is lower than the "compensating line". As seen from Fig. 1, the plotted line crosses the "compensating line" near 1.9 wt % addition. This is why the addition of 1.5 wt % and 2.0 wt % yielded the best crystals in experiments performed at a growth rate of  $3\text{ mm h}^{-1}$ .

### 3.3. The effect of growth rate

The growth rate can be set at 5 or  $6\text{ mm h}^{-1}$  if chemical composition of the molten zone and that of the obtained crystal are the same, but if the

compositions are different, as shown typically in the case of incongruently melting compounds such as YIG [7, 8], the growth rate should be lower, in order to prevent constitutional supercooling. The growth-rate employed in the present study,  $3\text{ mm h}^{-1}$ , was the same as that by which crystals of congruently melting silicates could be obtained free from inclusions [9]. As pointed out before, it is most likely that  $\text{La}_4\text{Si}_2\text{O}_7\text{N}_2$  melts congruently. There is, however, the possibility that a compositional gap between the liquid phase and crystal becomes large from time to time during growth due to evaporation from the molten zone. Even if the composition of the molten zone had not changed into the eutectic composition, inclusions can enter the grown crystals according to the mechanism of constitutional supercooling. From this standpoint, growth experiments at rates of 1 and  $2\text{ mm h}^{-1}$  were carried out.

When the starting powder mixture with 2.6 wt % of  $n = 3$  composition was used, the weight loss was measured as 2.4 wt % at  $2\text{ mm h}^{-1}$  and 2.6 wt % at  $1\text{ mm h}^{-1}$  under 11 atm as shown in Fig. 2. Unexpectedly, the weight loss did not increase inversely proportional to the growth rate. This suggests that evaporation occurred mainly soon after melting. The resulting crystals were transparent and of a higher quality than those grown at  $3\text{ mm h}^{-1}$ , but cracks still remained. Examination of the thin sections revealed the crystal to be free from inclusions for about a 2 cm length. In typical

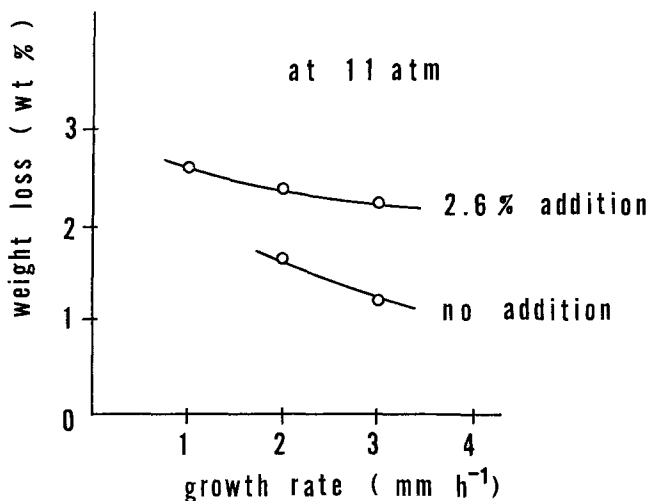


Figure 2 Weight loss under 11 atm at various growth rates.

experiments investigated, inclusions entered for about 1 cm from the seed rods. This is, because stable growth could not be attained during the early stages of growth. In a whole boule, there were still some  $\text{La}_2\text{O}_3$  inclusions but only in a negligible amount.

Thus the amount of  $\text{La}_2\text{O}_3$  inclusions could be reduced by lowering the growth rate and the inclusion-formation at a rate of  $3 \text{ mm h}^{-1}$  can, therefore, be partly ascribed to the constitutional supercooling phenomena.

Optimum growth conditions are summarized in Table I. An example of the as-grown boule is shown in Fig. 3. In Fig. 4 the thin section of the boule perpendicular to the growth direction is given, showing good transparency of the obtained crystal.

### 3.4. Characterization of the obtained crystals

The homogeneity of the crystals was confirmed by means of EPMA for each element. The results of

TABLE I Optimum growth conditions of  $\text{La}_4\text{Si}_2\text{O}_7\text{N}_2$  crystal

Starting material	2.6 wt % addition of ( $3\text{SiO}_2 + \text{Si}_3\text{N}_4$ ) to the stoichiometric mixture
Growth rate	$2.0 \text{ mm h}^{-1}$
Rotation	30–45 rpm (reverse)
Atmosphere	Highly pure nitrogen gas (99.9995% up) ( $0.5\text{--}1.5 \text{ litre min}^{-1}$ )
Pressure	11 atm
Zone width	5–6 mm
Diameter of boule	5–6 mm

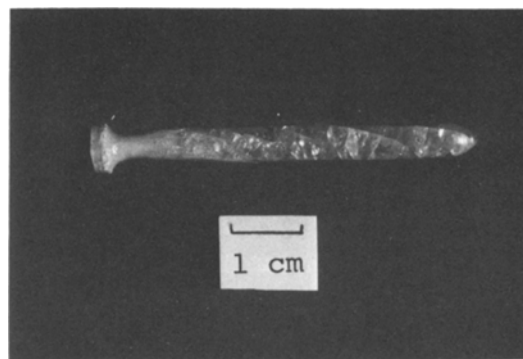


Figure 3 As-grown boule of  $\text{La}_4\text{Si}_2\text{O}_7\text{N}_2$  single crystal.

chemical analysis (wet analysis and electron probe microanalysis) of the inclusion-free crystals are given in Table II, showing that the chemical composition was well in accordance with the formula  $\text{La}_4\text{Si}_2\text{O}_7\text{N}_2$ , which was previously reported by Wills *et al.* [5].

Although large inclusion-free crystals could be obtained under the tabulated growth conditions (see Table I), the yielded crystals still had imperfections such as cracks and twins. As shown in the case of silicates [9], crack formation can be prevented by lowering the growth rate. In the present case, however, cracks entered the crystal during growth even at a rate of  $1 \text{ mm h}^{-1}$ . Seeded growth, which is also known to prevent the formation of cracks, was tried only to fail. The growth of a crack-free crystal is a still remaining problem.

Examination by polarized microscope on the thin sections taken from the obtained boules revealed the existence of twin lamellae of micron order. The width of lamellae varied from 1 to  $30 \mu\text{m}$ .

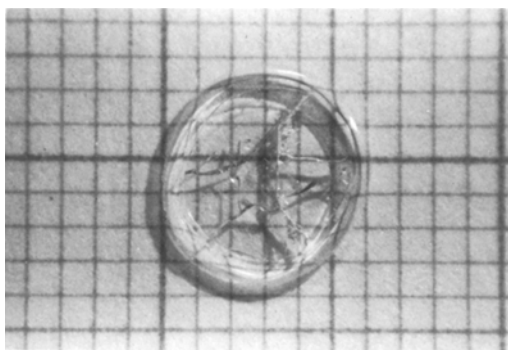


Figure 4 Thin section of  $\text{La}_4\text{Si}_2\text{O}_7\text{N}_2$  crystal perpendicular to the growth direction. 1 mm grid.

As there were some sections of the order of  $\text{mm}^2$  which were free from twins, the probable cause of twin formation is ascribed to thermal stress and not to phase transition.

An interesting feature was observed on the location of the inclusions. Examination of the thin sections showed that inclusions were located at the central region of the boules in every case.

The crystal symmetry was determined by X-ray single-crystal technique using Precession and Weissenberg cameras. The X-ray diffraction patterns revealed that the space group belonged to  $P2_1/m$  and the crystal lattice constants were:  $a = 8.03 \text{ \AA}$ ,  $b = 10.96 \text{ \AA}$ ,  $c = 11.57 \text{ \AA}$ ,  $\beta = 111.58^\circ$ . Thus the crystal data obtained are slightly different from those of  $a = 15.538 \text{ \AA}$ ,  $b = 10.437 \text{ \AA}$ ,  $c = 23.948 \text{ \AA}$ ,  $\beta = 113.53^\circ$  given by Wills *et al.* [5]. The refined crystal dimensions and further detailed crystallographic data on  $\text{La}_4\text{Si}_2\text{O}_7\text{N}_2$  will be discussed in another report.

Some properties of the obtained crystals were as follows. In contrast to the transparency of crystals obtained by the usual FZ procedure, quenched crystals were black, and became colourless and transparent after annealing. This is probably due to defects of N or O sites.

TABLE II Analytical results of the crystals obtained

	(wt%)				Total
	La	Si	O	N	
Method					
1	73.9	7.32	15.2*	3.54	—
2	74.0	7.60	15.0	3.6	100.3
Theoretical	73.91	7.47	14.90	3.73	100.0

Method 1 Wet chemical analysis.

Method 2 Electron probe microanalysis.

\*The remainder:  $100 - (\text{La} + \text{Si} + \text{N})$ .

The compound was sensitive to acid, such as HCl,  $\text{H}_3\text{PO}_3$  and  $\text{H}_2\text{SO}_4$ . It dissolved smoothly in 6N HCl at room temperature to give clear solution with a small amount of gelatinous matter. On the other hand, it was resistant to alkaline solution, for example boiling 40% NaOH aqueous solution. The compound oxidized to give opaque scales on its surface when subjected to heating in air at about  $1400^\circ \text{C}$ . The scales were determined to be mainly composed of La-Si-apatite which probably had a formula  $\text{La}_{4.67}(\text{SiO}_4)_3\text{O}$  by X-ray powder diffraction [15].

## Acknowledgements

The authors are much indebted to Mr Y. Yajima of National Institute for Researches in Inorganic Materials for chemical analysis of the samples, and to Dr F. Izumi of the same Institute for assistance in computer programing for ZAF correction. Acknowledgement also is due to Drs S. Kimura and I. Shindo of the same institute for helpful advice and encouragement.

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Received 30 August and accepted 13 November 1979.