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Solubility of Si in YAG

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Solubility of Si in YAG was determined by using EDX for qualitative analysis and electron microprobe technique for quantitative analysis. The results obtained proved that Al can be substituted by Si to some extent only in the presence of N presumably with the simultaneous substitution of N for O. The limit of solubility of Si in YAG was determined by both solid state reaction and crystallizing from a Y/Al-rich silicate glassy matrix. The same results obtained by both methods proved that the limit of solid solution is near to $3Y_2O_3 \cdot 4.65Al_2O_3 \cdot 0.35Si_2N_2O$.

1. Introduction

Previous research on sintering of Si_3N_4 had demonstrated the important role played by the combined additives Y_2O_3 and Al_2O_3. Many researchers (*1–4*) studied the phase relationships in the system Si, Al, Y/N, O. They indicated the possibility of obtaining β-Sialon ceramics with YAG as the crystalline second phase present at the grain boundaries. In practice (*5, 6*), however, it is difficult to get a complete crystallization of the YAG phase and thus the high temperature mechanical properties of the material have not yet reached an ideal level. In order to get more information on this matter with an aim to promote the processing of silicon nitride ceramics with better high temperature properties, it seems necessary to understand the composition of YAG in Si_3N_4 ceramics. Lewis *et al.* (*7*), using energy dispersive X-ray spectrometer (EDX), quantitatively analyzed the grain boundary phases in β-Sialon ceramics containing YAG. They found that a Si-substituted YAG (Al : Y : Si = 1.21 : 1.0 : 0.45) was crystallized from the Y/Al-rich silicate glassy matrix after heat treatment. The result showed that Al can be substituted by Si in YAG. Because of the difficulty of analyzing nitrogen *in situ* of the phases concerned, it is hard to make an unambiguous explanation of the type of substitution occurred. The absence of nitrogen in the lattice would require that the substituted YAG contains Al vacancies (1 for every 3 substituted Si atoms). An unlikely alternative is oxygen interstitial formation. However, the most likely possibility is the simultaneous substitution of N for O and Si for Al, by defining a general composition $Y_6Al_{10-x}Si_xO_{24-x}N_x$ for the garnet structure without vacancies. This kind of substitution solid solution should exist on the line between $3Y_2O_3 : 5Al_2O_3$ and $3Y_2O_3 : 5Si_2N_2O$ in the system $Y_2O_3–Si_2N_2O–Al_2O_3$, which is shown in Fig. 1. While the substitution solid solution without N and with Al vacancies should lie on the line between $3Y_2O_3 : 5Al_2O_3$ and $3Y_2O_3 : 7.5SiO_2$ in the system $Y_2O_3–SiO_2–Al_2O_3$, which is also shown in Fig. 1. This paper describes the

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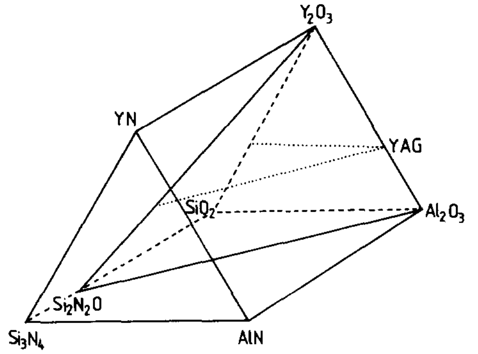


FIG. 1. The system Si, Al, Y/N, O in prismatic representation. The compositions YAS-1 to YAS-3 are shown to lie on the dotted line between YAG and $3Y_2O_3:5Si_2N_2O$, while the composition YAS-4 is shown on dotted line between YAG and $3Y_2O_3:7.5SiO_2$.

qualitative and quantitative analyses of Si in YAG phase synthesized in both systems Y_2O_3–Si_2N_2O–Al_2O_3 and Y_2O_3–SiO_2–Al_2O_3 by using EDX and electron microprobe techniques.

2. Experimental

The starting powders used for all compositions except YAS-3′ were yttrium oxide (Y_2O_3: 99.9%), aluminum oxide (Al_2O_3: 99.99%, decomposed ammonium alum), silicon oxide (SiO_2: high quality gelatinoid silica), and silicon nitride (Si_3N_4: AME, England, combined oxygen 1.3%). The composition YAS-3′ was synthesized with yttrium oxide, aluminum oxide, and silicon oxynitride (Si_2N_2O: 26.7% N, synthesized in the laboratory with SiO_2, C, and N_2 as starting materials). The oxygen content of the nitride powders was taken into account when computing the compositions. Starting powders were weighed and mixed in agate mortar under absolute alcohol for 2 h. The mixes were dried and isostatically pressed (400 MPa) to form small cylindrical pellets or immediately hot-pressed in BN-coated graphite dies. All compositions except YAS-4 were fired or hot-pressed in a graphite resistance furnace under mildly flowing nitrogen. Samples of composition YAS-4 were fired in a platinum resistance furnace in air. The specimens containing N were both weighed before and after firing to check the weight loss. The fired or hot-pressed specimens were further heat-treated under nitrogen or air atmosphere (only for YAS-4 samples) at 1370°C for 20 h and were used for determination of the phases present by focusing X-ray diffraction method. Samples of YAS-3′ and YAS-4 were chosen to be analyzed by EDX and electron microprobe techniques, besides, two other samples, YAS-3 and YAS-5 were also analyzed by electron microprobe. Energy dispersive spectrometer EDX-Link in conjunction with transmission electron microscope H-700 (Hitachi) was used for qualitative analysis of crystalline grains of small size in the specimens. JCXA-733 electron probe X-ray microanalyzer (JEOL) was used for quantitative analysis on crystalline grains with exaggerated growth. The specimens (except YAS-5) for electron probe analysis were etched in boiling NaOH for about 15 sec. Besides, electron diffraction patterns taken under the TEM were also used in identifying the yttro-garnet phase present.

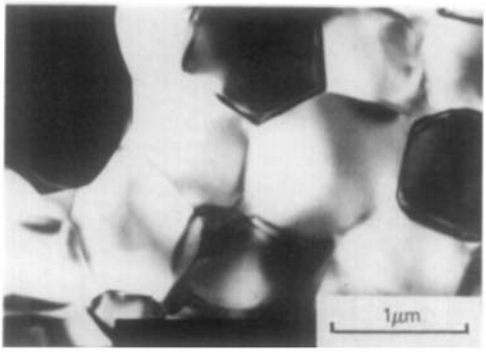


FIG. 2. Transmission electron micrograph of garnet microstructure in YAS-3′.

TABLE I

COMPOSITIONS AND PHASE ANALYSIS

Specimen	Composition	Firing condition	Weight loss (%)	Phases present[a]
YAS-1	$3Y_2O_3 : 3.5Al_2O_3 : 0.75SiO_2 : 0.75Si_3N_4$	1500°C, 1 hr	1.2	YAGvs, Hm, Y2Sw, α-SNw, β-SNvw, α-Al_2O_3 tr.
YAS-2	$3Y_2O_3 : 4Al_2O_3 : 0.5SiO_2 : 0.5Si_3N_4$	H.P. 1500°C, 1 hr	—	YAGvs, Hw, α-Al_2O_3vw, Y2Str., α-SNtr.
YAS-3	$3Y_2O_3 : 4.5Al_2O_3 : 0.25SiO_2 : 0.25Si_3N_4$	1600°C, 1 hr	1.1	YAGvs, α-Al_2O_3 tr.
YAS-3′	$3Y_2O_3 : 4.5Al_2O_3 : 0.5Si_2N_2O$	H.P. 1650°C, 0.5 hr	—	YAGvs, α-Al_2O_3 tr.
YAS-4	$3Y_2O_3 : 4.5Al_2O_3 : 0.75SiO_2$	1550°C, 1 hr	—	YAGvs, α-Al_2O_3 vw, Y2Str.
YAS-5	$3Y_2O_3 : 2.5Al_2O_3 : 1.8SiO_2 : 1.8Si_3N_4$	H.P., 1550°C, 0.5 hr	—	YAGw, Hvw

[a] H, H phase $5Y_2O_3 \cdot 4SiO_2 \cdot Si_2N_2O$; Y2S, $Y_2O_3 \cdot 2SiO_2$; α-SN, α-Si_3N_4; β-SN, β-Si_3N_4.

3. Result and Discussion

The compositions studied, firing conditions used, and the phases present are shown in Table I. As the results show, for compositions lying on the line between YAG and $3Y_2O_3 : 5Si_2N_2O$, the samples consisted of YAG, H Phase ($Y_{10}Si_6O_{24}N_2$), $Y_2O_3 \cdot 2SiO_2$, and other phases such as α-Si_3N_4, β-Si_3N_4, α-Al_2O_3 in very minor quantities. For the composition near to $3Y_2O_3 \cdot 5Al_2O_3$(YAS-3), YAG became the sole phase present with only traces of α-Al_2O_3 in coexistence. As the compositions moved toward the $3Y_2O_3 : 5Si_2N_2O$ end, H phase, $Y_2O_3 \cdot 2SiO_2$, and Si_3N_4 began to appear and gradually increased in amount. The presence of these phases was in accord with the known phase relationships (*1*), as the line is exactly located in the compatibility tetrahedra Si_3N_4–$3Y_2O_3 \cdot 5Al_2O_3$–H–$Y_2O_3 \cdot 2SiO_2$. The appearance of very small amounts of α-Al_2O_3 may be accounted for by incomplete reaction. The existence of α-Al_2O_3 and $Y_2O_3 \cdot 2SiO_2$ in specimen YAS-4 could also be expected from the known phase relationship, for the composition YAS-4 is located in the compatibility triangle YAG–Al_2O_3–$Y_2O_3 \cdot 2SiO_2$. The same results obtained in YAS-3 and YAS-3′ samples proved that Si_2N_2O can be replaced by Si_3N_4 and SiO_2 in forming the composition. The results of EDX analysis demonstrated that the cubic garnet phase in specimen YAS-3′ which was also identified by electron diffraction patterns, as shown in Fig. 3, contained silicon, as is evident from Fig. 4. While in specimen YAS-4, the garnet phase was also identified by TEM (Fig. 5) and electron diffraction patterns, it contained only traces of silicon, as can be seen in Figs. 6 and 7. Because of the fact that the detection of small amounts of Si in YAG was complicated by the overlapping of the Al*Kα*, Si*Kα*, and Y*Lα* lines, the Y*Lα* line was intentionally stripped off from these overlapped peaks, in

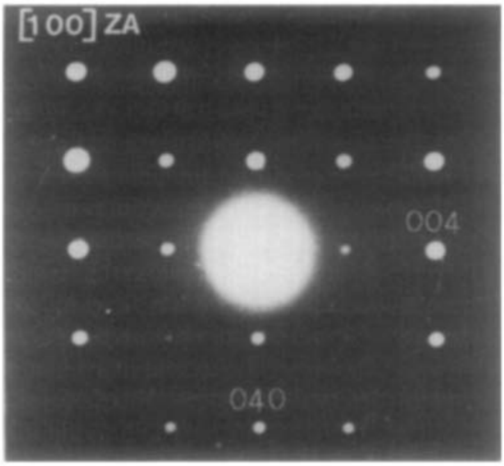


FIG. 3. Electron diffraction pattern of garnet phase in YAS-3′.

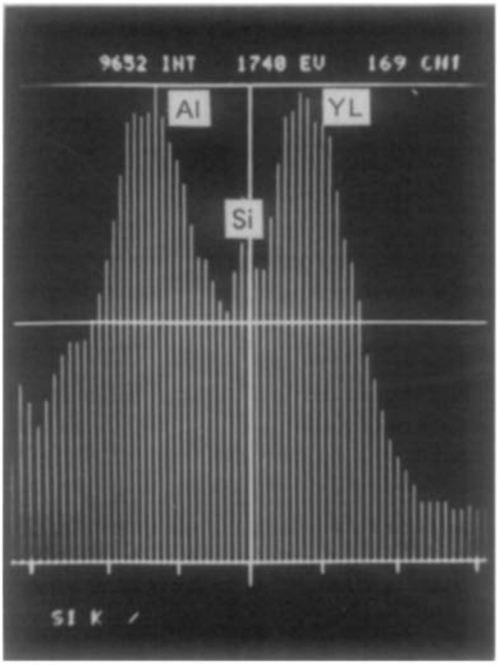
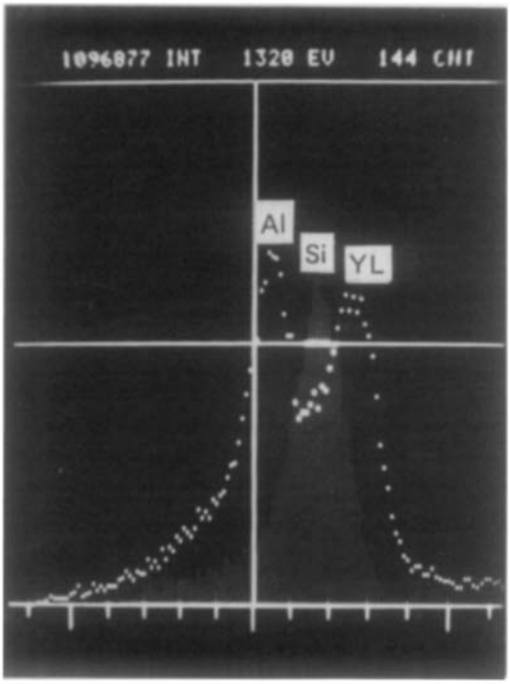


FIG. 4. Spectrum of garnet phase in YAS-3′.



order to show out the weak peak of Si$K\alpha$, if it existed. From the stripped spectrum, as shown in Fig. 7, it is evident that Al in YAG is hard to be replaced by Si alone. If there were any, the content must be very low indeed. The results of electron microprobe analysis indicated that in specimen YAS-3′

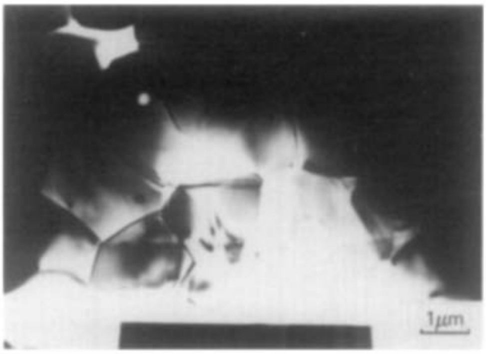


FIG. 5. Transmission electron micrograph showing garnet microstructure in YAS-4.

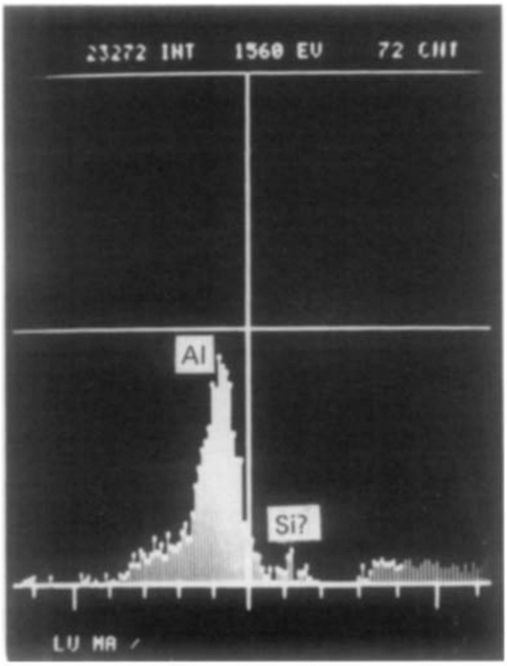


FIG. 7. Spectrum of garnet phase in YAS-4, stripped off *YL*, showing traces of Si.

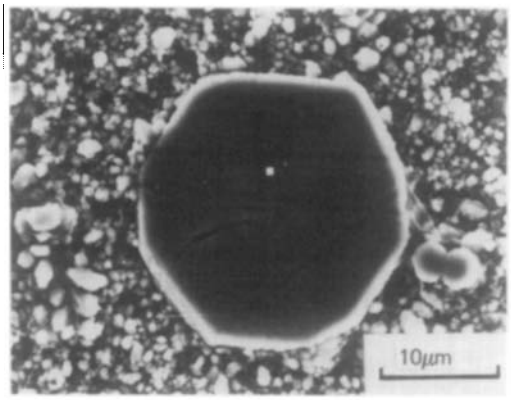


FIG. 8. Scanning electron micrograph of YAS-3′ (secondary electron image), showing occasionally found large crystalline grains, which were chosen to be detected by electron microprobe.

(or YAS-3), the elemental ratios of Y : Al : Si were 1.00 : 1.57 : 0.10, respectively (corresponding to $3Y_2O_3:4.7Al_2O_3:0.3Si_2N_2O$), and in specimen YAS-4, the ratios were 1.00 : 1.64 : 0.02. In determining the elemental ratios, the small amount of nitrogen content in YAG phase concerned was neglected and stoichiometric compositions of Y_2O_3, SiO_2, and Al_2O_3 were assumed. The calculation was made by use of the Quantitative Analysis Program of Bence and Albee. In order to avoid the possible interference of grain boundaries and porosity, the determination was made on large crystalline grains that were exaggeratedly grown, as shown in Fig. 8, which were obviously exposed by etching. In specimens of YAS-4 where no such exaggerated grain growth occurred, microprobe analyses were made on small grain aggregates, as shown in Fig. 9. From these results combined with those by EDX analyses, it is evident that the substitution of Si can only take place to any appreciable amount in the presence of N. Therefore in YAG, Al and O can be simultaneously substituted by Si and N to some extent. In comparison with the result obtained by Lewis *et al.* (*7*), the quantity of Si in YAS-3′ (or YAS-3) is small. This may be the result due to the difference in processing. By crystallizing from a Y/Al-rich silicate glassy matrix, the content of Si in the YAG phase may be higher; but by solid state reaction, it may be difficult for Si to enter into the lattice to any appreciable extent. In order to learn if the solubility of Si could really be increased by crystallizing from a Y/Al-rich silicate glassy matrix, electron microprobe analyses were also made on some large crystalline grains in sample YAS-5. Specimen YAS-5, after it was hot-pressed at 1550°C, was partly melted and stuck to the graphite dies. The fragments were taken out for analyses. Without annealing or annealing at 1370°C for 24 h, only a small amount of small YAG crystalline grains was found (except H phase in minor quantities). After annealing at 1470°C for 24 h, crystalline grains obviously grew up, but most of them were imperfect, which always contained more Al and Si in contrast with the ratio Y : Al = 1.00 : 1.67 in YAG composition and varied with each other (Y : Al + Si varying from 1.00 : 1.95 with 0.31 Si to 1.00 : 1.72 with 0.1 Si). After annealing at 1470°C for 48 h,

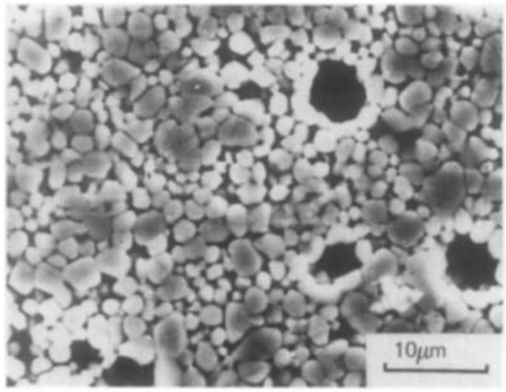


FIG. 9. Scanning electron micrograph of YAS-4 (secondary electron image), showing fine and uniform grain growth with no excessively large grains. Microprobe analysis was made on grain aggregates.

TABLE II
THE RESULTS OF QUALITATIVE AND QUANTITATIVE ANALYSES

Specimen	Qualitative analysis	Quantitative analysis (corresponding composition)
YAS-3	—	$Y:Al:Si = 1.00:1.57:0.10$ $(3Y_2O_3 \cdot 4.7Al_2O_3 \cdot 0.3Si_2N_2O)$[b]
YAS-3′	Y,Al,Si[a]	$Y:Al:Si = 1.00:1.57:0.10$ $(3Y_2O_3 \cdot 4.7Al_2O_3 \cdot 0.3Si_2N_2O)$[b]
YAS-4	Y,Al,Si?	$Y:Al:Si = 1.00:1.64:0.02$ $(3Y_2O_3 \cdot 4.9Al_2O_3 \cdot 0.1SiO_2)$
YAS-5	—	$Y:Al:Si = 1.00:1.56:0.12$ $(3Y_2O_3 \cdot 4.65Al_2O_3 \cdot 0.35Si_2N_2O)$

[a] Analysis on normal crystalline grains (about 0.5–1 μm).
[b] Analysis on large crystalline grains (about 20 μm).

some rather perfect crystalline grains could be found, as shown in Fig. 10, on which nearly the same ratio of Y : Al : Si with the one in YAS-3′ (or YAS-3) was obtained, as shown in Table II. Thus in our experimental conditions used, the limit of solubility of Si and N in YAG was near to $3Y_2O_3 \cdot 4.65Al_2O_3 \cdot 35Si_2N_2O$.

4. Conclusion

Solubility of Si in YAG in two compositions which were, respectively, located in two systems Y_2O_3–Si_2N_2O–Al_2O_3 and Y_2O_3–SiO_2–Al_2O_3 were determined by using EDX for qualitative analysis and electron probe X-ray microanalyzer for quantitative analysis. The results obtained proved that in the presence of N, Al can be substituted by Si, presumably with the simultaneous substitution of N for O. Otherwise, it will be difficult for substitution to take place. The limit of solubility of Si and N in YAG has also been determined by both solid state reaction and crystallizing from a Y/Al-rich silicate glassy matrix. Nearly the same results obtained by both methods proved that the limit composition of solid solution is close to $3Y_2O_3 \cdot 4.65Al_2O_3 \cdot 0.35Si_2N_2O$.

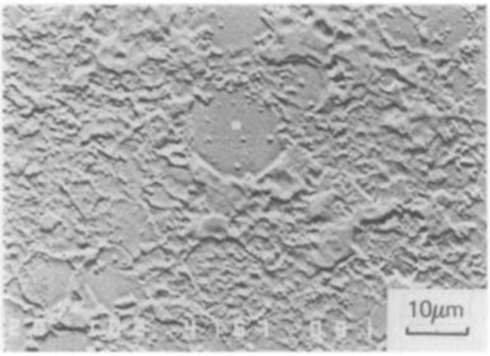


FIG. 10. Scanning electron micrograph of YAS-5 (backscattered electron image–composition), showing some perfect crystalline grains, which were chosen to be detected by electron microprobe.

Acknowledgments

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