

Translucent Y3Al5O12 ceramics : something old, something new

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TRANSLUCENT $Y_3Al_5O_{12}$ CERAMICS : SOMETHING OLD, SOMETHING NEW

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ABSTRACT

A review is given of $Y_3Al_5O_{12}$ (YAG) powder preparation and the sintering of YAG powder compacts to translucency. The influence of processing parameters on the resulting microstructure and mechanical properties is discussed. Some preliminary new results on the optical properties and resistance to sodium corrosion are included.

INTRODUCTION

A number of ceramics are known to have a translucent (or even transparent) form. The most familiar example is aluminium oxide (Al_2O_3 or alumina) whose translucency was first reported by Coble (1). This material can be sintered with a limited amount of dopant and hot-pressed to transparency without any dope (2). Other oxidic materials that become translucent after either sintering or hot-pressing are $MgAl_2O_4$ (3,4), Y_2O_3 (5,6), BeO (7,8), MgO (7,9) and PLZT (10). Recently the nitrogen containing ceramics Alon (11), β -Sialon (12) and AlN (13) were also reported to become translucent when properly processed.

In patents concerned with hot-pressing of materials to translucency (14,15) yttrium-aluminium-garnet ($Y_3Al_5O_{12}$ or YAG) has been mentioned as a possibly useful optical ceramic. However, no actual examples were given. Nevertheless YAG is an interesting material, partly because it has a cubic crystallographic unit cell. This has two advantages. Firstly, there are no birefringence effects at the grain boundaries which might contribute to the effective absorption coefficient. Secondly, due to the absence of thermal expansion coefficient mismatch no grain boundary stresses arise. Moreover, the material is pseudo-isotropic in the elastic sense so that the grain boundaries are virtually stress-free when the material is in its ceramic form. Hence, ceramic YAG could be quite interesting from both the optical and

the mechanical point of view.

Originally, at the start of our investigations no references were found on ceramic YAG apart from some papers on powder preparation (16-18) and YAG formation (19-22). Much later a Russian patent (23) was discovered describing the sintering of YAG with the aid of a considerable amount of additives. This patent, too, mentioned translucency in the optical region, though without any supporting data.

In a series of papers we have reported the sintering of YAG to translucency (24-26) and some of the properties of the resulting ceramics (27,28). In the present paper we review the results obtained and add some perspectives.

POWDERS

In the course of the investigations several powder preparation routes were followed. Among these the 'flux' method appeared to be non-reproducible and the 'nitrate' and 'coprecipitation' method resulted in inhomogeneous distributions of Y and Al when tried on a larger scale. Only the 'mixed-oxide' and the 'modified sulphate' processes yielded suitable powders. The mixed-oxide powder was prepared from Al_2O_3 and Y_2O_3 mixed in the proper amounts in an agate ball mill and prefired in air. Typical specific surface areas obtained were $2 \text{ m}^2/\text{g}$ (24). In the modified sulphate process a (Al,Y) sulphate solution was spray-dried. This solution was prepared from an $\text{Al}(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ solution to which the proper amount of Y_2O_3 was added while the pH was kept constant at about 3 by the addition of H_2SO_4 . Calcining was usually done at about 1300°C . Single phase YAG powder (fig. 1), as checked with X-ray diffraction, was obtained, in this case with a specific surface area typically of $.5 \text{ m}^2/\text{g}$ (24,26). With the powders thus obtained it was necessary to add some dopant, either SiO_2 or MgO , to the powder to obtain full density and translucency. For the mixed-oxide powder SiO_2 was added before mixing of the constituents. For the addition of SiO_2 to the sulphate-derived powder, ortho-ethylsilicate was prereacted with H_2SO_4 and added to the Al solution. In the case of MgO , the proper amount of Mg acetate was dissolved in the sulphate solution prior to spray-drying or added to a slurry of YAG powder in ethanol. This slurry was subsequently dried and calcined (24).

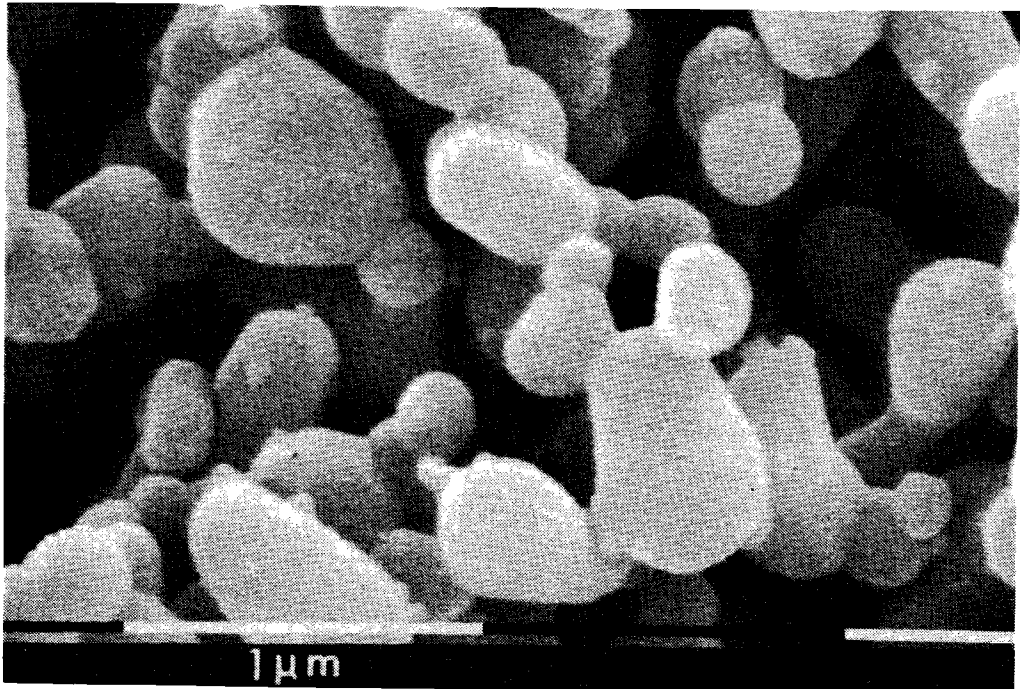


Fig.1 : SEM photograph of deagglomerated YAG powder prepared by the 'sulphate' process. Agglomeration was virtually absent : the average agglomerate size as determined with sedimentation analysis was equal to the sphere equivalent size as calculated from the specific surface area.

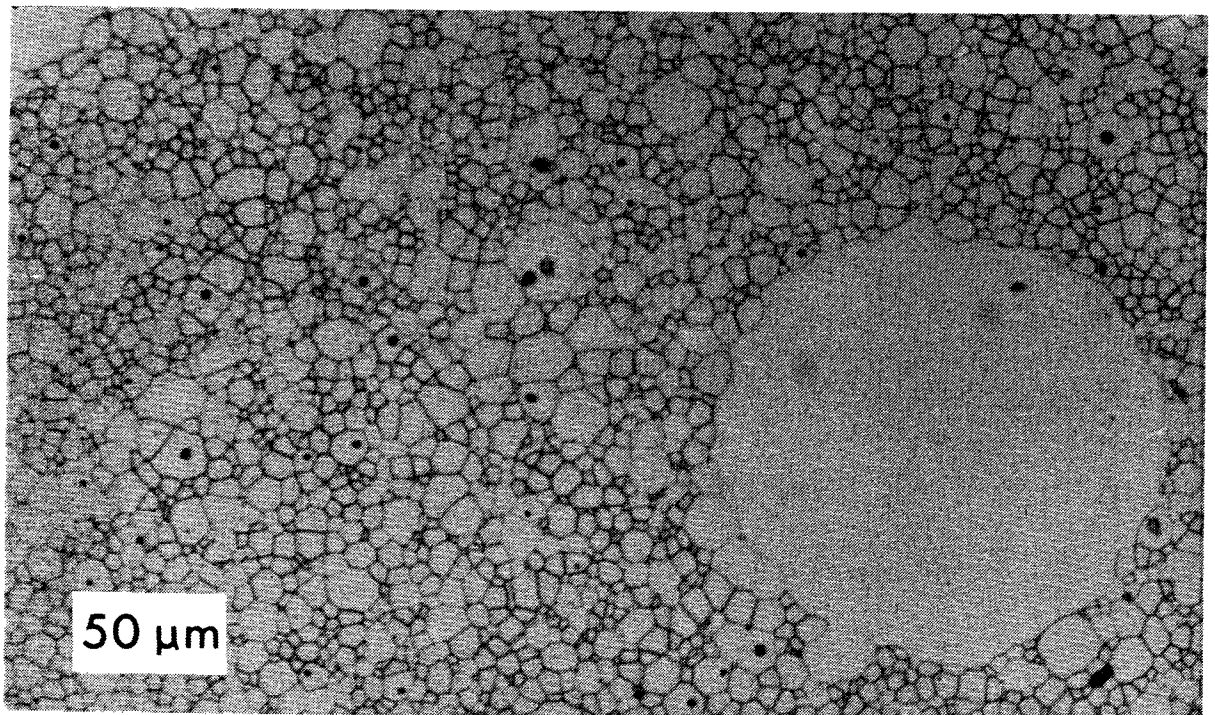


Fig. 2 : Microstructure of the YAG(mixed oxide powder) sintered in vacuum. Note the large grain due to the inhomogeneous dopant distribution.

SINTERING

Sintering was done in vacuum (24,25) or in a hydrogen atmosphere (25,26) at temperatures up to 1850 °C. The translucency of the final ceramic turned out to depend considerably on the pressure during (isostatic) compaction of the powder (26). When a high compaction pressure was used, a fully dense but non-translucent ceramic was the result. Lower compaction pressures yielded dense and translucent ceramics. No essential differences in microstructure could be detected, however. The appearance of translucency is probably due to a slightly higher final density. From the sintering experiments the strong impression was obtained that the dopants acted as a grain growth inhibitor. It is interesting to note that MgO has also been used as an inhibitor for liquid phase epitaxy (LPE) growth of garnets (29).

MICROSTRUCTURE

The ceramics prepared from the mixed-oxide powder usually had an inhomogeneous microstructure (fig. 2), probably due to the inhomogeneous distribution of the dopant. On the other hand, the ceramics sintered from the wet-chemically derived powder had a homogeneous microstructure with a grain size of a few micrometers when sintered under the proper conditions (fig. 3), i.e. with a sufficient amount of dopant and optimum sintering temperature. When powders were used without or with a too small amount of dopant, discontinuous grain growth was observed. Discontinuous grain growth is also observed when the firing temperature is too high; a too low sintering temperature results in a non-translucent ceramic.

Observations with a scanning electron microscope (SEM) equipped with an energy dispersive analyzer (EDX), showed that the ceramics fired in vacuum frequently contained Al-rich inclusions in spite of the fact that the powder was weighed out stoichiometrically. The Al-rich inclusions were also detected (fig. 4.) by transmission electron microscopy (TEM) experiments. Firing in hydrogen dramatically diminished the number of inclusions (26) to a level non-detectable with X-ray diffraction. These inclusions are thus due to the sintering process itself and not to inhomogeneity of the green body. One could have expected that these inclusions hinder the grain growth. It is therefore remarkable that the material sintered in vacuum at 1750 °C for 4 hours had an average grain size of about 3 μm , while material fired in

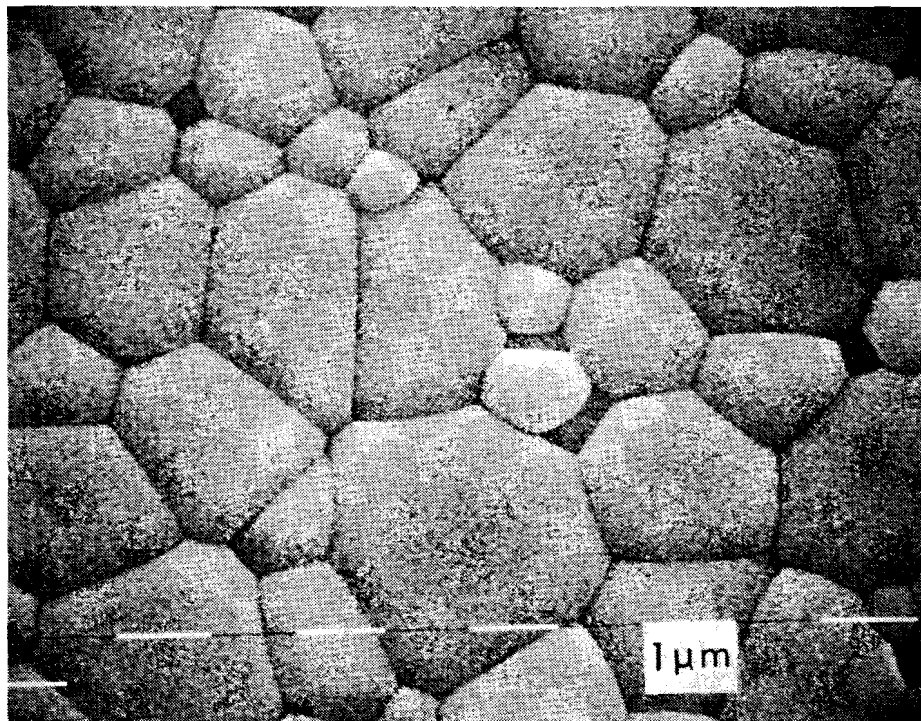


Fig. 3 : Microstructure of the YAG(sulphate-derived powder) sintered in hydrogen. A homogeneous microstructure with an average grain size of 1.5 μm is obtained.



Fig. 4 : Dark-field image of an Al-rich inclusion in a grain of YAG doped with 1200 wt ppm SiO_2 and sintered in vacuum. Note the strain-induced contrast contour around the inclusion.

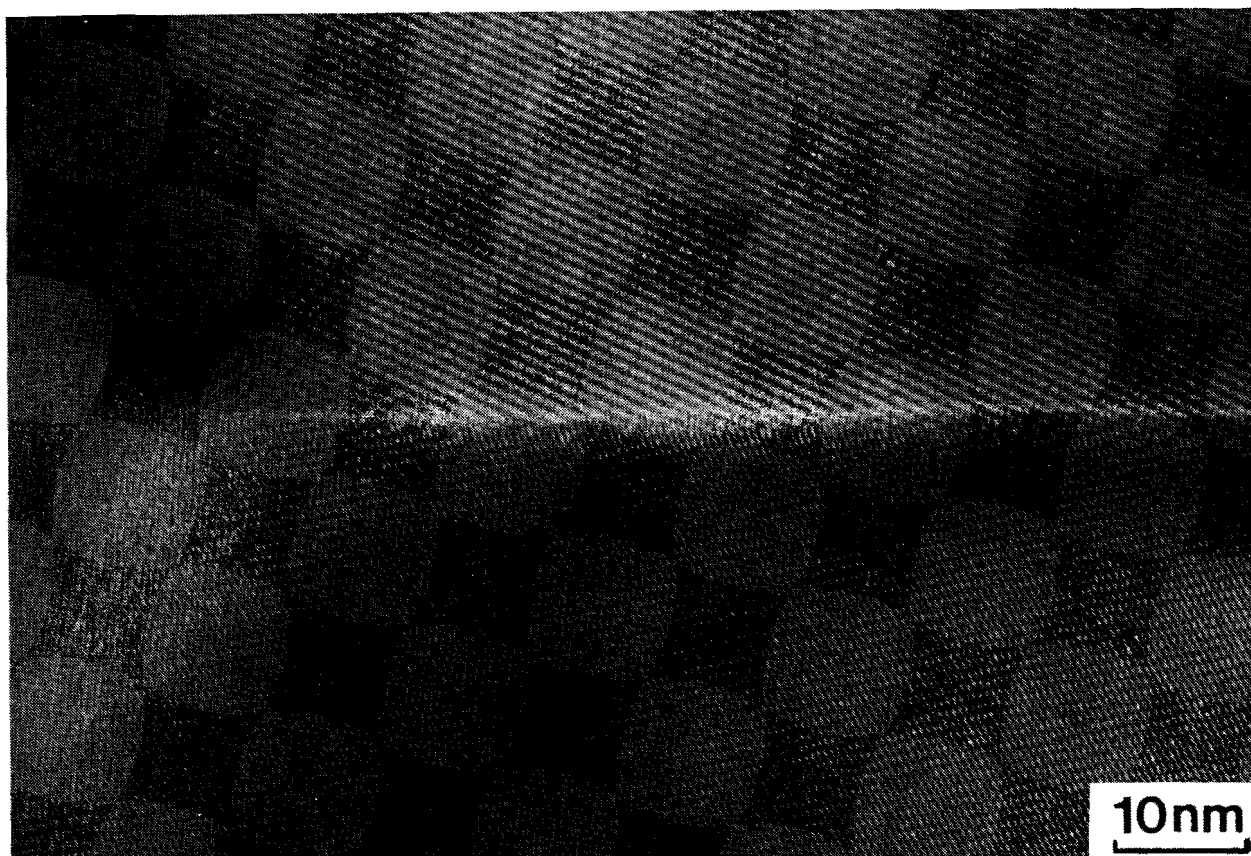


Fig. 5 : Lattice and Moiré fringes in three YAG grains in the ceramic doped with 500 wt ppm MgO and sintered in vacuum. Note the absence of lattice deformation up to the grain boundary.

hydrogen under the same conditions showed an average grain size of about 1.5 μm .

In the best known optical ceramic, Al_2O_3 , a slight amount of MgO (see e.g. ref. 2) is usually added in order to make the material translucent. The various opinions concerning the dopant behaviour presented in the literature seem to converge towards a MgAl_2O_4 second phase at the triple points at high dopant levels and to a slight segregation of MgO at the grain boundaries, probably as nonstoichiometric MgAl_2O_4 at discrete spots (see e.g. ref. 30). For YAG this aspect of dopant behaviour is also of importance. A first step was taken by studying the grain boundary structure (28) by TEM. From these studies on the material sintered in vacuum, it emerged that the material contained neither second phases at the grain boundaries as detectable

within the lattice resolution of the samples (better than 0.5 nm) nor second phases at the triple junctions (fig. 5). The probable absence of any grain boundary phase suggests that abnormal grain growth is inhibited by solid solution of the dopants in the host lattice. A most important observation was that the lattices of two adjacent grains showed no deformation whatsoever up to the grain boundary itself. This is in strong contrast with translucent Al_2O_3 where Carter et al. (31) detected a deformed boundary layer with a thickness of about 6 nm. Preliminary work on ceramics sintered in hydrogen yielded very similar results on the grain boundary structure.

ELASTICITY AND HARDNESS

Comparing the value of Young's modulus, E , for YAG sintered in vacuum (about 290 GPa) with those of Al_2O_3 (400 GPa) and Y_2O_3 (177 GPa) we note that YAG is stiffer than Y_2O_3 but more compliant than Al_2O_3 (27). However, there is only approximate agreement with the theoretical value (283 GPa) obtained by averaging the single crystal elastic stiffness constants. This difference is small but significant and is due to the Al-rich inclusions. These inclusions are stiffer than the YAG matrix, which results in a higher overall value of E . As expected, the experimental value for material sintered in hydrogen (284 GPa) is quite close to the theoretical value (27). Vickers indentations on YAG resulted in hardness values of about 18 GPa at 2 Newton load (27). A significant influence of the applied load was observed (Meyer index $n=1.8$) but surprisingly no definite influence of humidity in the environment. Knoop indentations yielded lower values of hardness, about 15 GPa at 2 Newton load. The hardness of YAG ceramics is thus somewhat less than for Al_2O_3 (about 20 GPa, Vickers 2 N load) and substantially higher than for Y_2O_3 (about 6 GPa, method unknown).

FRACTURE TOUGHNESS

Catastrophic failure is characterized by two parameters: fracture toughness, K_{Ic} , and strength, S_f . In brief, the fracture toughness represents an inherent resistance to fracture while the strength is determined by both the intrinsic behaviour and the mechanical defect structure of the material. A typical value of K_{Ic} for the vacuum-sintered YAG was $1.7 \text{ MPa}\cdot\text{m}^{1/2}$ (27), both for the SiO_2 and MgO doped material having a regular microstruc-

ture. Apart from deviations from this 'normal' value of K_{IC} due to deviations from the regular microstructure (27), an anomalous behaviour with temperature was also observed. It was shown that for vacuum-sintered YAG the value of K_{IC} revealed a maximum at about 600 °C, contrary to the expected continuous decrease with temperature as encountered e.g. with Al_2O_3 . Since additional energy dissipation, e.g. by grain boundary sliding due to a viscous, glassy grain boundary phase, as found in debased alumina, is ruled out by the TEM experiments, another explanation is called for. The effect could be explained by the presence of the Al-rich inclusions. A small increase in K_{IC} due to the higher toughness of the inclusions is expected, but is counteracted by the tensile stress field in the YAG matrix, caused by the Al-rich inclusions. At increasing temperatures the magnitude of this stress diminishes, thus toughening the material. The decrease at still higher temperatures is due to the normal decrease in E with temperature, probably intensified by a change in fracture mode from transgranular to intergranular. At room temperature a much higher value of K_{IC} is thus expected for a single-phase YAG ceramic like the one sintered in hydrogen. This has indeed been observed: a value of $3.1 \text{ MPa}\cdot\text{m}^{1/2}$ was reported (26). This value is even higher than expected from an extrapolation of the high temperature decrease of vacuum-sintered YAG to room temperature, suggesting that other effects are also involved. Nevertheless this value is still lower than the one usually obtained for translucent Al_2O_3 : about $4 \text{ MPa}\cdot\text{m}^{1/2}$. The fracture energy G ($=K_{IC}^2/2E$) on the other hand is comparable (about 35 J/m^2) due to the lower stiffness of YAG.

STRENGTH

In spite of the relatively low values of K_{IC} , reasonable strength values were obtained. For the vacuum-sintered material S_f values of about 410 MPa were measured (27). For hydrogen-sintered material a much higher value of 640 MPa was determined (26). The increase in strength is actually somewhat less than expected from the K_{IC} values. This is the more remarkable since the hydrogen-sintered ceramic has a somewhat smaller grain size (about $1.5 \mu\text{m}$) than the vacuum-fired material (about $3.0 \mu\text{m}$) which usually leads to a higher strength. Very likely the cause must be sought in small differences in surface damage due to the machining (parallel to the stressing direction with a 300 mesh diamond grinding wheel).

TRANSLUCENCY

From previous absorption measurements it was clear that the degree of translucency of the ceramics sintered from the mixed-oxide powder was comparable with that of typical translucent Al_2O_3 (24) which has an absorption coefficient A of about 2.0 mm^{-1} . On the other hand the values for the vacuum-sintered YAG doped with SiO_2 and MgO were 1.6 and 0.7 mm^{-1} respectively, indicating a substantial improvement. These experiments were done with a relatively wide aperture of 10 degrees (24). More recent experiments with an aperture of only 1.2 degree yielded A -values as follows: Al_2O_3 about 3 mm^{-1} , $\text{YAG}(\text{SiO}_2)$ 0.6 - 1.7 mm^{-1} and $\text{YAG}(\text{MgO})$ 0.5 - 1.7 mm^{-1} . While the values for the YAG remained about the same, those of alumina substantially increased. The high in-line transmission of YAG, together with the small width of the scattered light distribution, leads to a transparent ceramic (fig. 6), in contrast to the usual translucent Al_2O_3 ceramic (2).

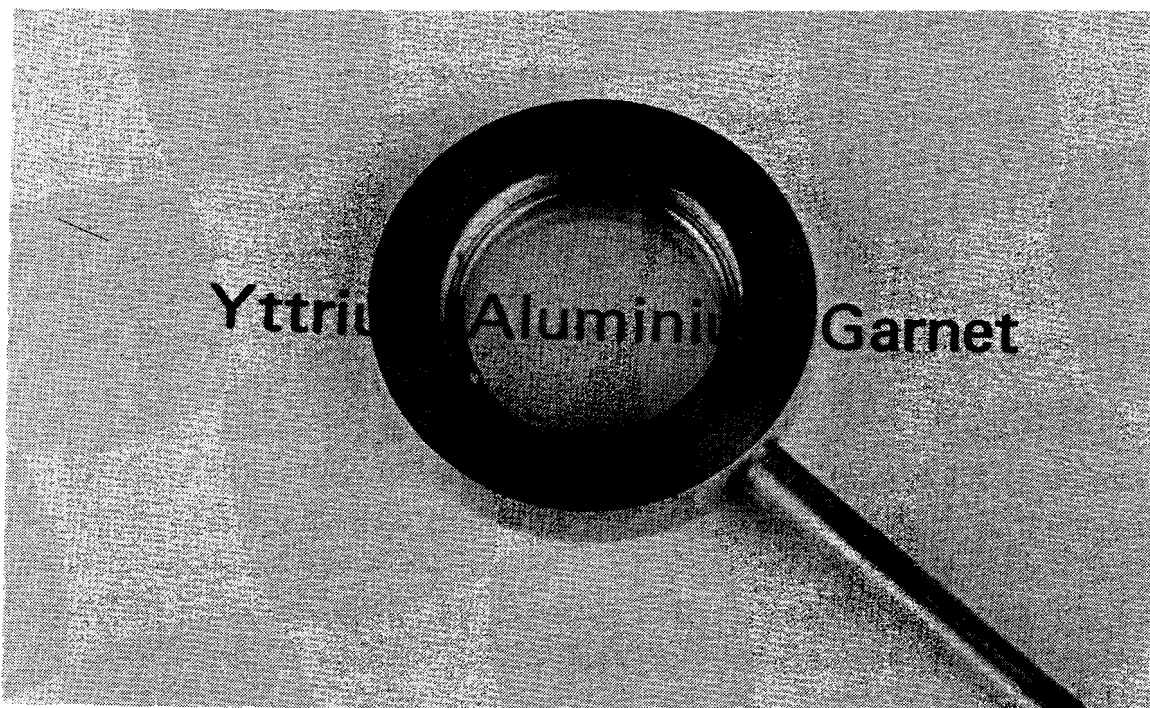


Fig. 6 : Translucent YAG with SiO_2 dopant disk of thickness $500 \mu\text{m}$ sintered in vacuum. The disk is actually a few millimeters above the paper, demonstrating the transparency of the material.

CORROSION

Resistance to corrosion from alkali metals is an important property to examine for further application of the YAG ceramic. A good resistance is expected from literature data (32) where for YAG a corrosion rate of 0.016 mm/year is reported for Li corrosion at 375 °C. By comparison, for Al₂O₃ rates higher than 12 mm/year were determined. To confirm this, corrosion experiments of a rather preliminary nature were done as described before (33). YAG samples were immersed in Na in a Mo container for 300 hours at 900 °C and examined afterwards in a SEM/EDX. After this treatment, YAG(SiO₂) had a corrosion layer thickness of about 3 μm. This layer consisted of at least two compounds, both containing Na, Al and Y. No penetration along grain boundaries was observed. Typical translucent Al₂O₃ (33) had a corrosion layer that was hardly detectable when vacuum sintered. However, at least 60 μm layer thickness and Na penetration along the grain boundaries resulted for alumina when sintered in hydrogen. After 100 hours at 1000 °C in Na, alumina shows a severe bulk corrosion. In contrast, YAG exhibited a corrosion layer thickness of only about 9 μm. The corroded layer has the same thickness on single-crystalline YAG. YAG(MgO) yielded very similar results. The influence of the sintering atmosphere (vacuum versus hydrogen) is also minor. Quite a different behaviour is thus observed for Al₂O₃ and YAG ceramics. It seems very likely that the penetration along the grain boundaries in the case of Al₂O₃ is facilitated by the grain boundary deformation observed by TEM (31). In any case, the good resistance to Na corrosion is a further positive aspect of the YAG ceramics.

FINAL REMARKS

From the foregoing it is clear that the optical and mechanical properties of the YAG ceramics as well as the corrosion resistance to Na make these materials promising in more than one respect. Careful processing, however, is necessary and awaits further attention.

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