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Influence of pore volume on laser performance of Nd : YAG ceramics

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For present study, 1.1 at % Nd-doped YAG ceramics with a controlled pore volume (150–930 vol ppm) were fabricated by a solid-state reaction method using high-purity powders. The scattering coefficients of Nd : YAG ceramics, obtained from Fresnel's equation, increased simply with increases in the pore volume. The cw laser output power of Nd : YAG ceramics was clearly related to the scattering coefficients of the specimens examined in the present works, which in turn were affected on the pore volume. The effective scattering coefficients of Nd : YAG ceramics with a pore volume of ~150 vol ppm were nearly equivalent to those of a 0.9 at %Nd : YAG single crystal by Czochralski method. As the exciting power was increased under excitation by an 808-nm diode laser, however, the laser output power of the Nd : YAG ceramics exceeded that of the Nd : YAG single crystal because of the fairly large amount of Nd additives. The lasing performance of the Nd : YAG ceramics changed drastically with change in pore volume. On the other hand, lasing performance was not affected by the existence of grain boundaries in the polycrystalline Nd : YAG ceramics.

1. Introduction

The most important four-level solid-state laser host, a YAG($Y_3Al_5O_{12}$) single crystal, uses the fluorescence of small content of Nd^{3+} ions in the wavelength of 1.064 μm as active species. In the recent years, Nd-doped YAG laser have been applied widely in medical operation [1–3] and various industrial capacities such as metal machining [4], marking in semiconductor process [5, 6].

Solid-state laser from both polycrystalline ceramics such as Nd doped Y_2O_3-ThO_2 ceramics created by Greskovich and Chernoch [7, 8] and Nd-doped YAG ceramics by present authors [9, 10] oscillated successfully using a xenon flash lamp and an 808-nm diode laser, respectively. Although the laser oscillation characteristics of Nd : YAG ceramics were nearly equivalent or superior to those of the Nd : YAG single crystal, the main source influencing beam scattering was not clearly identified.

A previous paper [11] reported beam scattering from the vicinity of the grain boundary. For the present work, Nd : YAG ceramics with pore volume controlled by the distribution of granulated powders were fabricated by a solid-state reaction method detailed previously [9, 10]. The scattering coefficient of the Nd : YAG ceramics were confirmed to change according to the above-described parameters. A laser oscillation experiment also was performed by diode laser excitation using Nd : YAG ceramics with various scattering coefficients.

2. Experimental

Starting materials for the present work were the same high-purity powders (>99.99 mass %) of Al_2O_3, Y_2O_3, and Nd_2O_3 used in the previous works [9–14]. Specimens were fabricated by weighed the starting powders to achieve an Nd content of 1.1 at % in the resultant YAG ceramics. The Al_2O_3, Y_2O_3, and Nd_2O_3 powders were mixed with 0.5 mass % of TEOS (Tetraethyl Orthosilicate) as a sintering aid, and the mixture then was milled for 12 h using high-purity Al_2O_3 balls. The milled slurry was dried using a spray dryer. To change the pore volume in Nd : YAG ceramics, the distribution of those granulated powders was controlled by adjusting the rotation speed of atomizer in the spray drier. The granulated, spherical powders, measuring <100 μm in diameter, were isostatically pressed at 140 MPa into disks 20 mm in diameter. The powder compacts were sintered at 1750 °C for 20 h under vacuum (1.3×10^{-3} Pa) using a high-vacuum furnace (model: WM-5010, Futeck Furnace Inc., Yokohama, Japan). The fabrication details are

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similar to those from previous works by same authors [9–14].

Disk specimens 10 mm in diameter, to be used for measuring scattering coefficients, were polished on both surfaces to resister below the average micro-roughness (Ra) of 2 nm, on a surface-roughness measuring equipment (model: TOPO-3D, WYKO Co., Tucson, AZ, USA). The transmission spectrum of each specimens was measured over the wavelength region from 400 to 1000 nm, using a spectrophotometer (model: U-3500, Hitachi Co., Tokyo, Japan) with a 0.5-nm slit width and a 120-nm/min scan speed.

Laser performance was measured using a cw laser oscillator pumped by an 808-nm diode laser (LD), similar to the equipment used in previous studies [11]. A specimen 10 mm in diameter and 5 mm thick (neither surface having an anti-reflection coating) was polished on both surfaces below the Ra of 0.2 nm micro-roughness to $\lambda/10$ ($\lambda = 632$ nm) flatness and to a parallelism of 10 s. A reflection mirror (100% reflection) and a half mirror (98% reflection) were situated in parallel on both sides of the specimen. A 0.9 at %Nd : YAG single crystal (Tokin Co., Sendai, Japan) by Czochralski (CZ) method was used for the optical reference for all measurements.

The scattering coefficient (an optical scattering loss) of the Nd : YAG ceramics and of an Nd : YAG single crystal were calculated as well as taken from the report by Sekita *et al*. [15]. The refractive indexes are used those data of YAG single crystal reported by Bond [16]. The scattering coefficient ($\alpha(\lambda)$) were calculated as follows.

$$\alpha(\lambda) = -t^{-1}\ln[I(\lambda)/I_0(\lambda)T(\lambda)^2] \qquad (1)$$

Details of above Fresnel's equation have been described in previous paper [11].

3. Results

Table I shows the specifications of samples used for optical measurements in present work. All specimens were sintered at 1750 °C for 20 h under vacuum. The specimens of A1 to A4, with changed spray-dry conditions (changes in the distribution of granulated powder) contained residual pores of approximately 150, 320, 680, and 930 vol ppm, respectively. The data for pore volume obtained by the present system were derived statistically by measuring 50 areas (each measurement area ~350 by ~500 μm) using a transmission microscope. The pores of each specimens measured almost several micrometers in diameter. The actual pore volume of Nd : YAG ceramics would be ~1/100 of the present value if the measuring method described by Imaeda [17, 18], using the transmission microscopy, were applied. The silicon contents of A1 to A4, as detected by ICP analysis, ranged from 310 to 350 mass ppm, respectively.

TABLE I Specification of specimens used in present work

Specimens	A1	A2	A3	A4
TEOS[a] (mass %)		0.5		
Sintering condition		1750 °C for 20 h		
Pore volume[b] (vol ppm)	150	320	680	930

[a]Tetraethyl orthosilicate.
[b]Measured by transmission microscopy.

Fig. 1 shows reflection microscope photographs of specimens A1 to A4 after thermal etching. The surfaces of all specimens are pore-free. The grain size distributions of the specimens differed slightly from one specimen to another.

Fig. 2 shows typical transmission microscope photographs of the A1 to A4 specimens. Residual pores (several micrometer in diameter) are revealed by open nicols in the depth direction of the specimens, and the perfect optical isotropy of all specimens also was confirmed by dark-field image under crossed nicols.

Fig. 3 shows a transmission electron microscope photograph and electron beam diffraction patterns of A1 specimen around the grain boundary. No extra grain boundary phase is present near the grain boundary, but some distorted layers (a few nanometer) are evident. On the upper and lower diffraction spots, the lattice in both grains near the grain boundary suggests the development of a single phase. The A2 to A4 specimens also show no extra grain boundary phase near the grain boundaries.

Fig. 4 shows the optical scattering coefficients (an optical scattering loss coefficients) of A1, A2, and A4 specimens and a 0.9 at %Nd : YAG single crystal were dependent on the measuring wavelength. The scattering coefficients decrease decreased with decreases in the pore volume and with the increases in the measuring wavelength. The scattering coefficients of the A1 specimen are nearly equivalent to those of the 0.9 at %Nd : YAG single crystal because of its low pore contents.

The surface roughnesses of both the single crystal and the polycrystalline ceramics were detected using a surface-roughness measuring equipment (measurement area ~230 by 230 μm). The Ra and P-V value (the difference between the highest and the lowest level on the polished surface) for the single crystal and the polycrystal specimens were 1.64 and 19.0 nm and 1.75 and 18.3 nm, respectively. The surface roughnesses of both the single crystal and the polycrystalline specimens were nearly equivalent, so that the actual surface losses of both specimens also were nearly equal.

Fig. 5 indicates the cw laser oscillation characteristics of specimens shown in Figs 2 and 3. The threshold and slope efficiency of Nd : YAG single crystal were 61 mW and 25.9%, respectively. The threshold and slope efficiency of A1, A2, A3, and A4 specimens are 97 mW and 30.6%, 134 mW and 10.7%, 172 mW and 6.4%, 218 mW and 4.5%, respectively. The laser output power of A1 specimen (with lowest pore volume) was lower than that of the Nd : YAG single crystal at lower exciting powers but exceed that of the Nd : YAG single crystal with increased exciting power. The laser oscillation characteristics of A1 specimen were nearly equivalent or superior to those of the Nd : YAG single crystal.

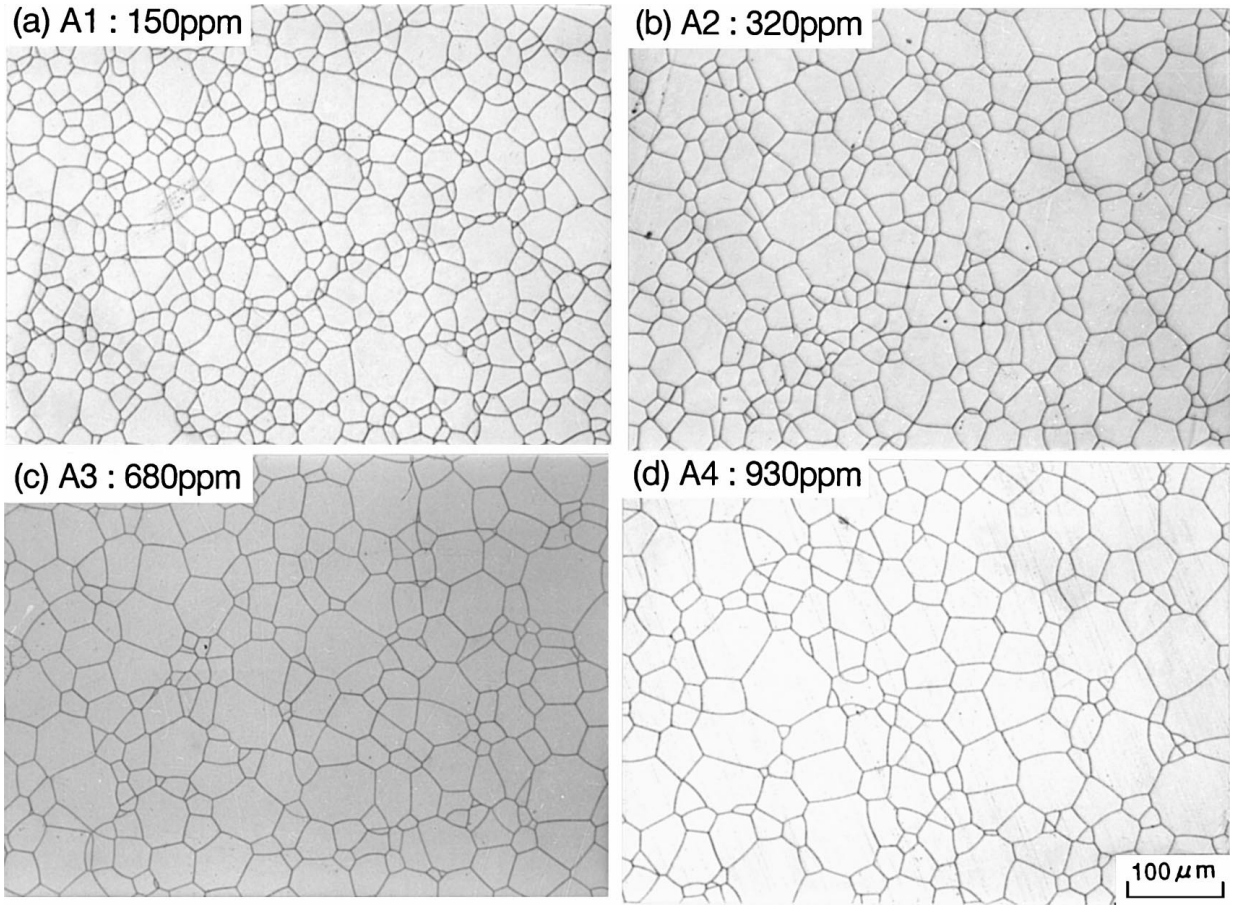

Figure 1 Surface of Nd : YAG ceramics with various pore volume after thermal etching.

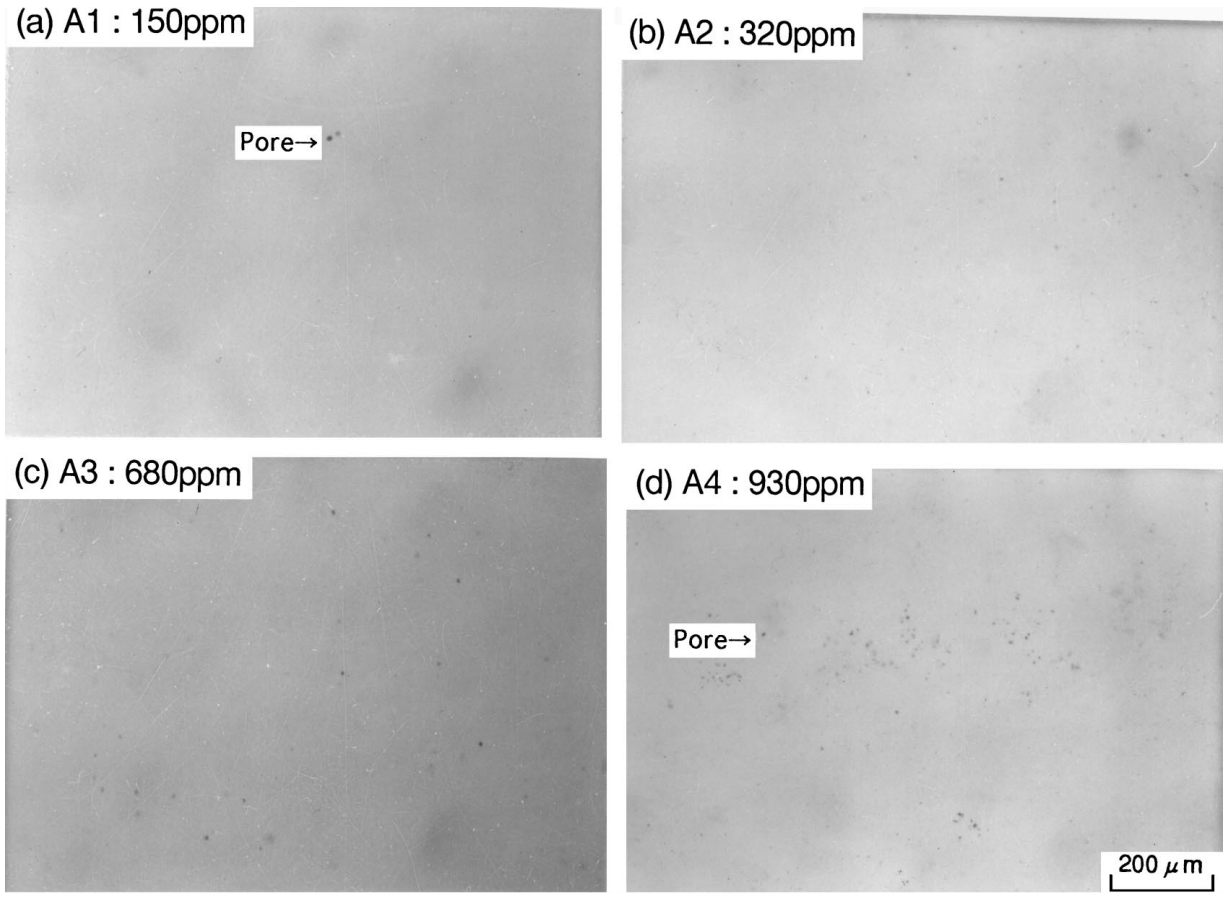

Figure 2 Transmission microscope photographs of Nd : YAG ceramics having various pore volume.

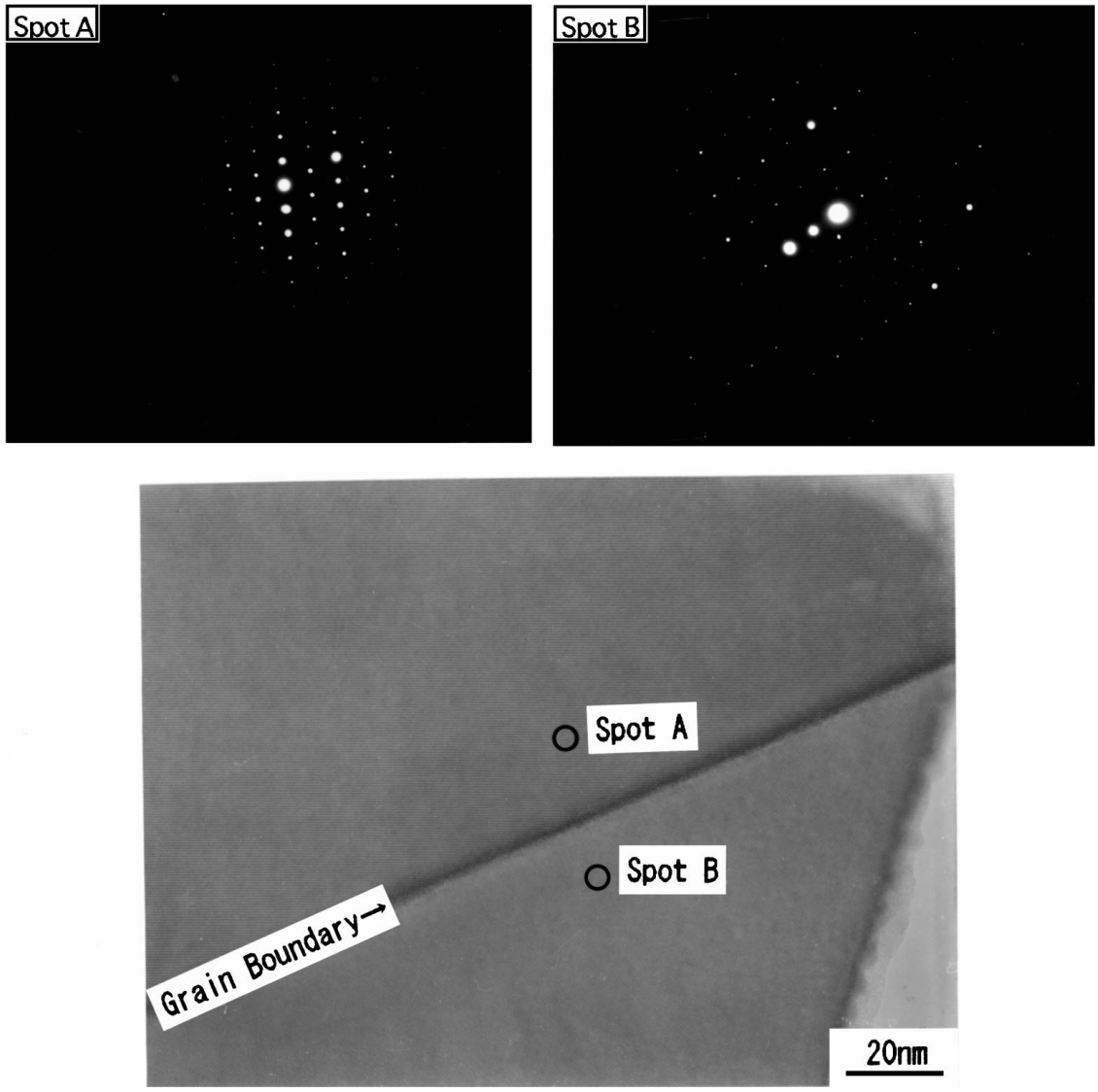

Figure 3 Transmission electron microscope photograph and electron beam diffraction patterns of the 1.1 at %Nd : YAG ceramics near grain boundary. No extra grain boundary phase is present up to vicinity of grain boundary. On upper and lower diffraction spots, each grain near grain boundary suggest to become single phase.

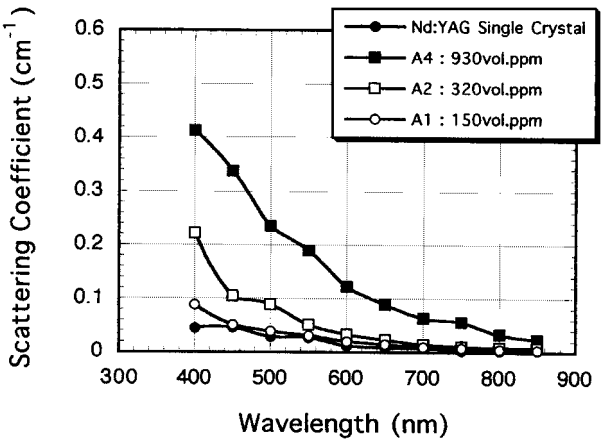

Figure 4 Dependence of absorption coefficients of Nd : YAG ceramics with various pore volume and Nd : YAG single crystal on measuring wavelength.

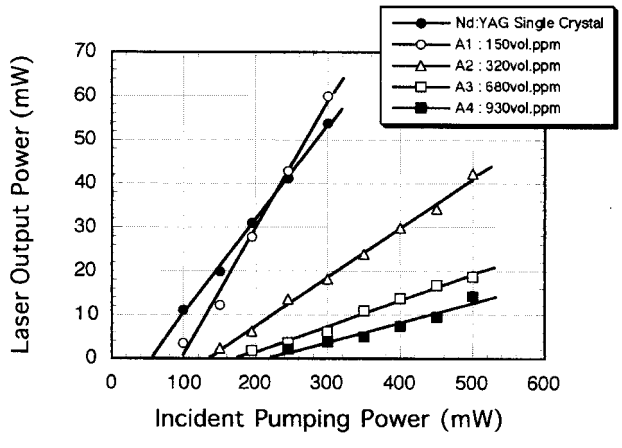

Figure 5 Laser output power vs. input energy for 0.9 at %Nd : YAG single crystal and 1.1 at %Nd : YAG ceramics with various pore volume excited by 808 nm diode laser.

Fig. 6 shows the relationships between laser performance (threshold and slope efficiency) and pore volume in the polycrystal specimens. At a pore volume below 150 vol ppm, the laser performance of the polycrystalline specimens nearly equaled that of the single crystal. The lasing performance (threshold and slope efficiency) of ceramics specimens thus is clearly attributable to pore volume.

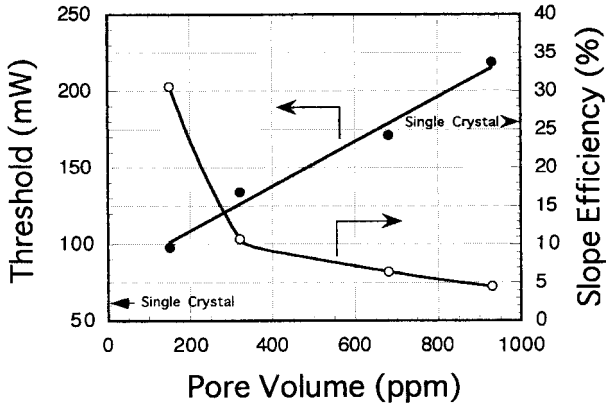

Figure 6 Affects of pore volume on laser performance of Nd : YAG ceramics.

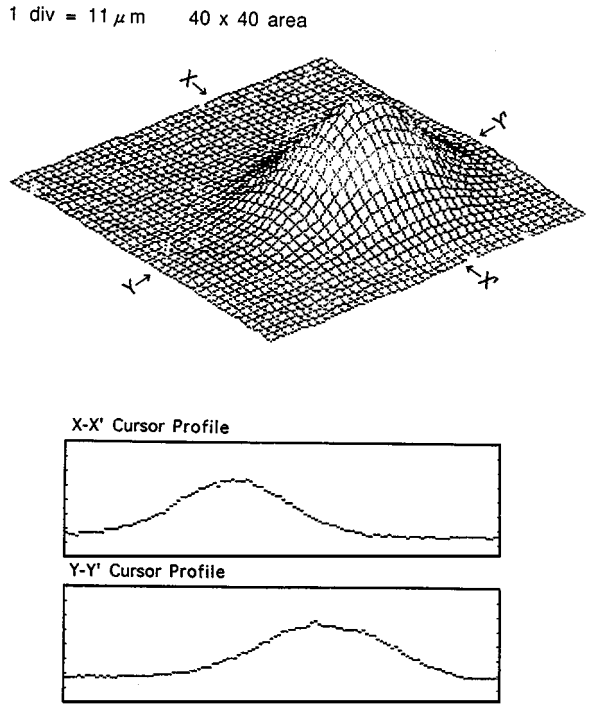

Figure 7 Laser beam profile of A1 specimen radiated from optical resonator.

Fig. 7 shows the laser beam profile (transverse mode) emitted from A1 specimen. The A1 specimen excited by diode laser oscillated an excellent laser beam, with a Gaussian distribution as good as high-quality single crystal, so that the beam mode emitted from polycrystalline ceramics was TEM_{00} (TEM = Transverse Electro-Magnetic Wave). The laser beam obtained from polycrystalline specimen thus had the best coherency in all transverse mode patterns. The quantity and quality of the laser beam from specimen A1, with many grain boundaries, was nearly equivalent to that of high-quality Nd : YAG single crystal.

Fig. 8 reveals the appearance of an Nd : YAG single crystal, as well as A1, and A4 specimens, irradiated by an He-Ne laser beam. Although no scatter was visible to the naked eyes in the single crystal, a few cases of scattering were seen in the A1 specimen and several in the A4. The position of the scattering center of He-Ne laser agreed with that of the pores, so that major optical scattering seems to have been caused by residual pores in the polycrystalline ceramics.

Fig. 9 shows the scattering center observed by transmission microscopy when the He-Ne laser was irradiated into polycrystalline ceramics (A4 specimen). The He-Ne laser beam scattered at the pore only, and an interferometory ring (scattering beam) generate from the interface between the host material (Nd : YAG grain) and the pore. Although pores did exist along the grain boundary, no scattered beams from the clean grain boundary of the Nd : YAG ceramics were observed under present measuring system.

4. Discussion

The optical losses and lasing efficiency from Nd, Cr-doped GSGG (gadlinium-scandium gallium garnet) and Nd-doped YAG single crystal have been reported by Carid *et al.* [19]. The laser performance of solid-state laser was attributed to both losses by the laser host and resonator insertion. If the same optical resonator were used in laser oscillation experiments, the laser output power would depend on the optical quality of the host materials.

Shiroki [20] has reported that the scattering of an Nd : YAG single crystal is caused by (1) pore, (2) inclusion, (3) double refraction by the stress, facet, and etc., (4) cluster (fine Nd : YAG particle). Commercial Nd : YAG laser rods were used in that work except for an optically heterogeneous part of the large ingot, but the scattering loss of high-quality laser rod was not zero.

Polarizing microscopy also confirmed that the optical anisotropic phase (inclusion and double refraction) was free in polycrystalline Nd : YAG ceramics. Transmission electron microscopy showed a perfect structure expanding up into the vicinity of the grain boundary. Actually, no clusters existed in the grain of polycrystalline Nd : YAG ceramics. The amount of scattering in the grain boundary only could not be measured in the present study, but the reason for the fairly small amount of scattering in polycrystalline ceramics must be considered.

Basically, the main structural differences between a ceramics and a single crystal are in the existence of the grain boundary and the absolute pore volume. If beam scattering is affected mainly by the grain boundary in polycrystalline ceramics, then scattering must be repeated continuously with every exciting beam (LD) and fluorescence beam (laser beam) that passes through the inside of the specimen. Such beams presumably could cross the grain boundary anywhere from several thousand to several ten thousand time; part of the beam proceeding through the ceramics would leak out. The total amount of beam leaking from the optical resonator would become enormous. Normally, the grain boundary of polycrystalline ceramics contains numerous dislocations, so that the density near the grain boundary is lower than that of inner grain. Because the refractive indexes between in the vicinity of the grain boundary and inner grain differ, scattering theoretically is stronger near the grain boundary. If the layer contained the dislocation is very thin, however, and the dislocation

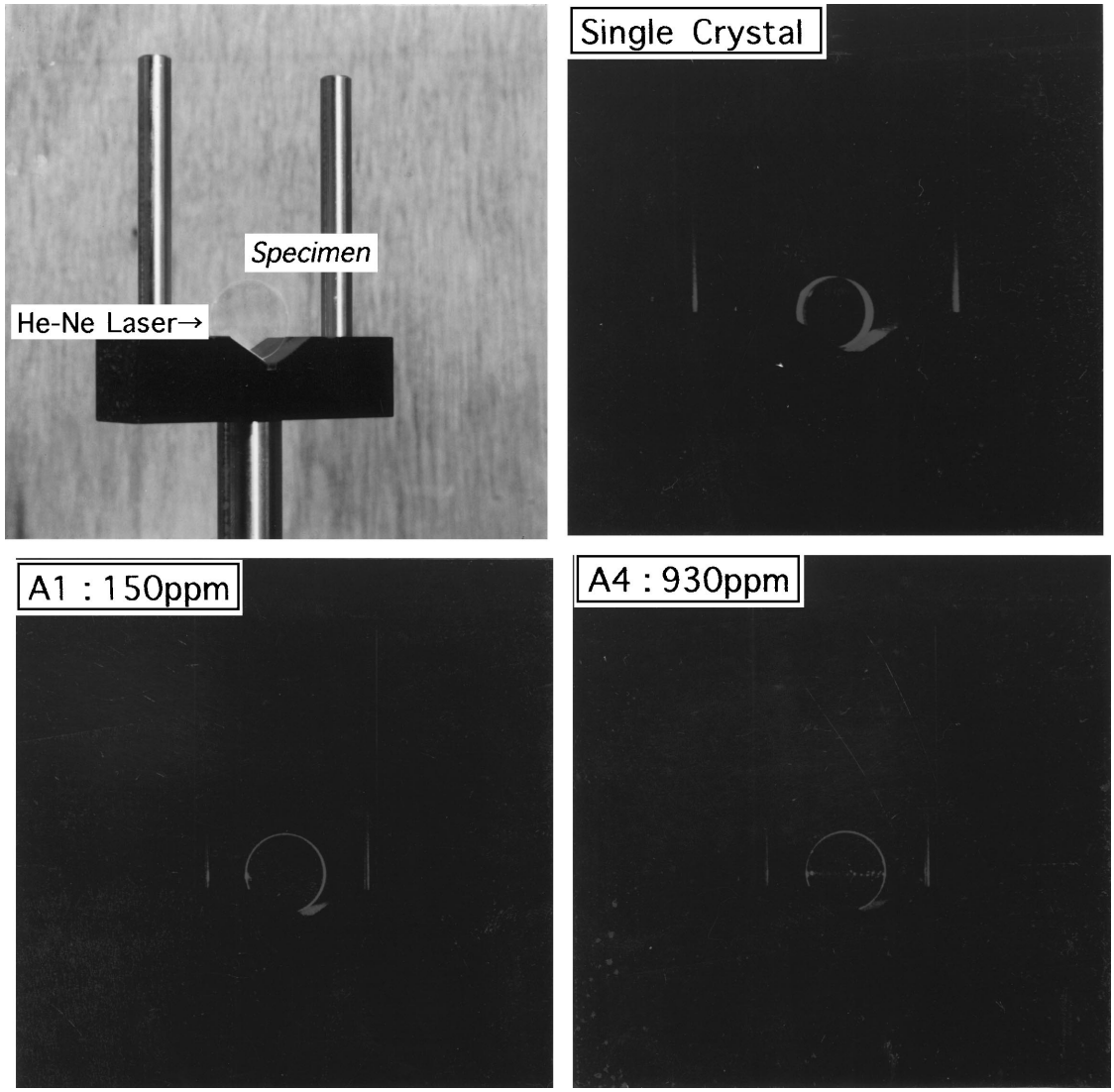

Figure 8 Photographs of Nd : YAG single crystal, A1, and A4 specimens irradiated by He-Ne laser beam (wavelength: 633 nm, intensity: 1 mW).

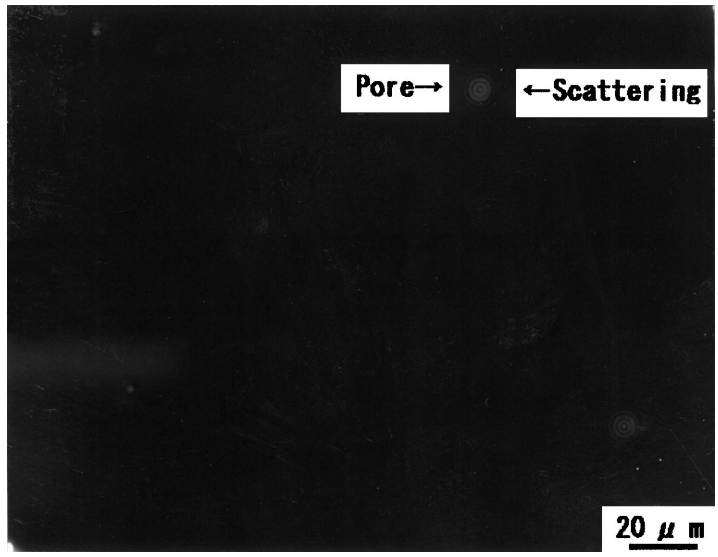

Figure 9 Transmission microscope photograph of A4 specimen irradiated with He-Ne laser beam. We can observe the only scattering beam from interface between Nd : YAG grain and pore.

density near the grain boundary is low, scattering from that layer should be extremely low. The density of lattice defects in a single crystal is higher than that in polycrystalline ceramics, as reported by Shirasaki *et al*. [21]. The scattering loss between the single crystal and the polycrystalline ceramics with lowest pore volume

was nearly equal in the present work. Scattering from the lattice defects of single crystal thus was comparable to that from dislocation near the grain boundary in polycrystalline ceramics, or both scattering amounts from the lattice defects of the single crystal and from dislocation near the grain boundary in polycrystalline ceramics were nearly negligible.

When the He-Ne laser was irradiated into the polycrystalline Nd : YAG ceramics, as shown in Figs 8 and 9, scattering seemed to be caused by the pores only. Even when the number of clean grain boundaries remained nearly constant, the scattering coefficient and laser performance of the polycrystalline Nd : YAG ceramics in relation to decreasing pore volume nearly equaled those of the Nd : YAG single crystal. In addition, effective laser oscillation with the best transverse mode (TEM_{00}) was performed successfully for the first time using specimen A1, with an actual pore volume of ∼1 vol ppm. The TEM_{00} mode of laser oscillation is known to be obtained through high-quality laser crystals and an excellent optical resonator. If the grain boundary of polycrystalline Nd : YAG ceramics contained scattering media, effective laser oscillation and the best coherence mode would not be achievable. The residual pores in ceramic therefore seem to be a major scattering center.

A close relationships exists between the quality of laser crystals and the threshold. The threshold of the single crystal was ∼60 mW in the present study, as shown in Fig. 6. The threshold of the polycrystalline Nd : YAG ceramics decreased with decreasing of pore volume. Interpolation from Fig. 6 implies that the threshold of perfect pore-free becomes ∼70 to ∼80 mW. That estimate is somewhat higher than the value obtained for a single crystal. The Nd concentration of YAG ceramics, however, is higher (0.2 at %) than that of a single crystal, so that the refractive index of the ceramics also is somewhat larger than that of a single crystal. No antireflection coating existed for either the single crystal or the ceramics during the present laser oscillation experiment, so that some scattering must have occurred continuously with every laser beam that passed though the surface of the specimen in the optical resonator. Because the surface loss (surface scattering) of specimen become too great in relation to the value of the refractive index, the threshold of the polycrystalline ceramics with a higher Nd concentration must have become too large. The difference in threshold between the single crystal and the polycrystalline ceramics with the lowest pore volume thus had no relation to optical quality. A detail experiment involving the parameters of the refractive index is necessary to validate that supposition.

In the end, it can be concluded that a clean grain boundary in Nd : YAG ceramics has almost no effect on lasing performance. A future paper will prove more definitively that the grain boundary in Nd : YAG ceramics affects neither laser characteristics nor optical scattering and that the laser ability of improved polycrystalline Nd : YAG ceramics is far superior to that of high-quality Nd : YAG single crystal by CZ method.

5. Conclusions

The important results obtained from the present study can be summarized as follows.

1. Optical scattering in Nd : YAG ceramics is caused by pores. When the pore volume becomes lower than 150 vol ppm, the optical scattering loss and the laser performance of Nd : YAG ceramics are nearly equivalent to those of high-quality Nd : YAG single crystal by the CZ method.

2. Clean grain boundaries in Nd : YAG ceramics cause hardly any increase in optical scattering or deterioration of laser performance.

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