SOLID-STATE REACTIVE SINTERING OF POLYCRYSTALLINE ND:YAG CERAMIC LASER HOST MATERIALS USING AN 83 GHZ MILLIMETER WAVE SYSTEM

Ralph W. Bruce and Chad A. Stephenson
Physical Sciences Dept., Bethel College
Mishawaka, IN, USA

Arne W. Fliflet and Steven B. Gold
Plasma Physics Division, Naval Research Laboratory
Washington, DC, USA

M Ashraf Imam
Materials Science and Technology Division, Naval Research Laboratory
Washington, DC, USA

ABSTRACT

We are investigating the solid-state reactive sintering of polycrystalline Nd:YAG ceramic laser host materials using a high power millimeter-wave beam as the heat source. The starting powder is a mixture of commercially available alumina, yttria, and neodymia powders. The laser-quality results obtained using the solid-state reactive sintering approach and the same materials in a conventional vacuum furnace[1] provide a benchmark for our experiments, which are being carried out using the Naval Research Laboratory (NRL) 83 GHz Gyrotron Beam Material Processing Facility. One objective of our work is to determine the effect of millimeter-wave heating on processing variables such as temperature and hold time and on the microstructural properties impacting the laser host application. Another objective is to optimize the heating uniformity and efficiency of the process for future use in a manufacturing process. Initial experiments with 1-hour hold times have produced translucent samples whose microstructure is currently being evaluated. Longer processing times (up to 16 hours) were needed to achieve full transparency in a conventional furnace. Hold times longer than 1 hour were also investigated and will be reported.

INTRODUCTION

Single crystal Nd-doped YAG has been the most widely used solid-state laser material[2]. Current materials for solid-state lasers include single crystals of neodymium-doped YAG and neodymium glasses. While single crystals have high thermal conductivity and can operate at high powers, they are costly and limited in size and dopant concentration. Neodymium-containing glasses can be large with reasonable cost but have low thermal conductivity, thereby limiting average power. Significant advantages of transparent polycrystalline laser host materials for high energy laser (HEL) applications, compared to single-crystal materials, are reduced processing temperatures, greatly reduced processing times, elimination of facet and pore structures, and the possibility of higher dopant concentrations. In addition, polycrystalline laser host materials have good thermal conductivity, high mechanical strength, and can be fabricated into large and complex structures.

One of the challenges in developing polycrystalline laser host materials is the need for high quality starting powders doped with the rare earth lasing ion. These are generally not commercially available and often require costly powder preparation techniques. The solid-state reactive sintering of Nd:YAG is of particular interest in this regard because high-purity alumina, yttria, and neodymia

powders are commercially available. Moreover, Lee et al. (ref. 1) have shown that laser quality polycrystalline Nd:YAG can be produced by pressure-free solid-state reactive sintering in a conventional vacuum furnace and that the powder preparation requires only low-cost techniques such as ball milling[1].

Millimeter-wave processing has been shown to be an effective alternative to conventional vacuum furnaces for pressure-free sintering of low-loss oxide ceramic materials[3]. It involves direct volumetric heating of the ceramic powder. This often results in superior microstructure with fewer trapped pores, cleaner grain boundaries, and smaller grain size than conventionally sintered materials. These properties are critical to achieving high optical quality, transparent laser host materials. Other advantages of microwave processing include faster heating rates and the capability to sinter at lower temperatures than conventional heating, resulting in a shorter more efficient process[4].

A critical feature of millimeter-wave sintering is stronger coupling to laser host materials than conventional microwaves. Sesquioxides have very low rf loss and do not couple well at low frequencies (*e.g.* 2.45 GHz) compared to high frequencies (*e.g.* 83 GHz). The absorbed power per unit volume in a ceramic is proportional to the microwave frequency ω according to [5]

$$P_{absorbed}(\omega,T)=\frac{1}{2}\omega\varepsilon_0\varepsilon''(\omega,T)|E|^2 \tag{1}$$

where ε_0 is the free space permittivity, ε'' is the relative dielectric loss and E is the local rf field. Thus the power loss is a function of both the temperature T of the ceramic and the frequency; at a given frequency, oxide ceramics tend to be more absorbing at higher temperatures, and at a given temperature, an oxide ceramic is more absorbing at higher frequencies. The frequency dependence of the power absorption is an important motivation for processing low-loss ceramics at 83 GHz rather than at 2.45 GHz or 35 GHz.

We have therefore embarked on an investigation of solid-state reactive sintering of polycrystalline Nd:YAG ceramic laser host materials using an 83 GHz beam as the heat source. We are using the same materials and powder preparation techniques as discussed in ref. 1, so that the results of millimeter-wave processing can be directly compared with conventional vacuum sintering.

Equipment

The NRL gyrotron-based material processing facility (Fig. 1) features a 20 kW, CW (Continuous Wave), 83 GHz GYCOM gyrotron oscillator, which can generate between 1 W/cm^2 and 2 kW/cm^2 irradiance. The facility features a quasi-optical beam system for beam focusing and manipulation and an inner vacuum chamber for atmosphere control and vacuum processing. The gyrotron is operated via a fully automated computerized control system written in the LabVIEW™ platform with feedback from extensive *in-situ* instrumentation and visual process monitoring.

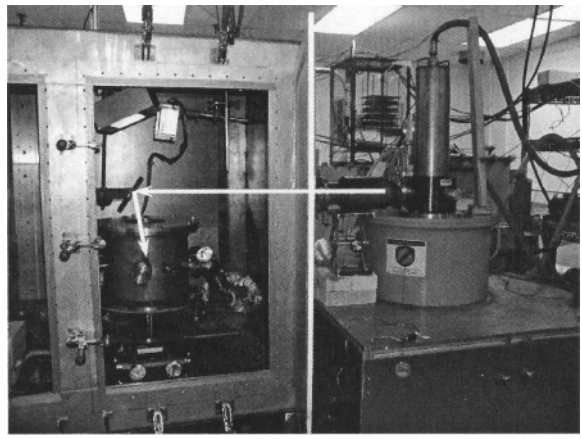

Figure 1. NRL 83 GHz gyrotron-based material processing facility. The millimeter-wave beam furnace is located inside the large processing chamber which serves to confine the millimeter-wave radiation. A 2-color pyrometer looks down on the furnace through a screen at the top of the processing chamber. The millimeter-wave beam exits the gyrotron horizontally (white arrow) and is deflected by a slightly concave mirror into the vacuum furnace through a quartz window.

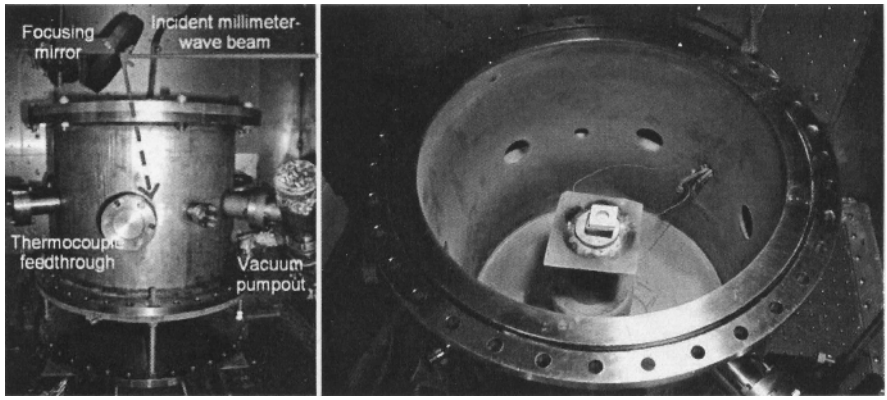

Figure 2. Millimeter-wave beam furnace. Side view [left], top view with lid including quartz vacuum window removed [right].

Experimental setup and processing

α-Alumina (AKP-50, Sumitomo, Japan), yttria (NYC Co., Tokyo, Japan) and neodymia (NYC Co., Tokyo, Japan) were obtained and mixed in the appropriate ratios to give 0, 1, 2 and 4 at. % Nd.

To this was added approximately 0.5% TEOS (Alfa, Ward Hill, MA) as a sintering aid. Ethyl Alcohol was then added to the mixture which was then ball milled for 16 hours. The milling media was high purity alumina balls. After milling, the slurry was dried and then hand-milled in an alumina crucible into a fine powder.

The green compacts were uniaxially pressed to approximately 53% theoretical density (TD). Some of these were then cold isostatically pressed (CIPed) to densities of approximately 61% TD. The ceramic work pieces were placed in an open or closed crucible and directly exposed to the 83 GHz beam which is focused to a roughly elliptical shape (approximately 1 cm by 4 cm) by the concave mirror. This type of beam is adequate for processing the small compacts currently being tested (diameter 5mm). Larger compacts will require a larger, more uniform beam. The crucible and the materials surrounding the workpiece (casketing) are chosen to provide thermal isolation and low temperature heating, and to reduce radiative losses to the cold-walled furnace. The ceramic work piece may be embedded in a setter powder and/or microwave susceptor. Zirconia is often used as a setter powder and other setter powders include boron nitride, alumina, and yttria. The beam power and intensity at sintering temperatures is a few kilowatts and a few 100 W/cm^2, respectively. The mirror position is adjusted during processing to optimize irradiation of the workpiece. The workpieces are processed in a small vacuum chamber (inner diameter 33 cm, height 28 cm) (Fig. 2) in a vacuum of between 25 and 100 milliTorr. The pressure is monitored for signs of outgassing during initial heating. The temperature is monitored by both an S-type thermocouple (platinum/platinum with 10% rhodium) situated near the sample and a remotely located two-color pyrometer.

The automated temperature controller elevates the sample temperature using feedback from the thermocouple or two-color pyrometer (by increasing the gyrotron voltage and consequently its output power) at a predetermined rate of approximately 10 - 20℃ per minute until it reaches the desire hold temperature. Typical hold time at temperature was approximately 1 hour, though some tests were conducted for a longer period. Final densities ranged from 57% for low-temperature and non-CIP'ed compacts to fully densified compacts. A summary of details is given Table I. A total of 45 samples were processed during this experimental effort.

Table I: Schedule of Processed Samples

83 GHz reactive sintering of Nd:YAG						**$Nd^{3+}:Y_3Al_5O_{12}$**	
6793-01 4 at. % Nd							
Sample	**Tempera-ture**	**Hold Time**	**at.% Nd**	**CIP**	**Density before CIP**	**Density after CIP**	**Final Density**
1	1800	15 min	4%	Yes			94%
2	1800	1 hour	4%	Yes		55%	99%
3	1700	1 hour	4%	Yes		54%	95%
4	1600	1 hour	4%	Yes		60%	90%
5	1900	1 hour	4%	Yes		57%	
6	1600	1 hour	4%	Yes	52%		98%
7	1700	1 hour	4%	Yes	54%	60%	99%
8	1800	1 hour	4%	Yes	54%	60%	93%
10	1800	2 hours	4%	Yes	54%	60%	
11	1750	75 min	4%	Yes	52%		
12	1750		4%	Yes	54%		
14	1750		4%	Yes	54%		

21	1700	1 hour	4%	No	53%		99%
22	1300	1 hour	4%	No	54%		
23	1500	1 hour	4%	No	54%		
24	1500	1 hour	4%	No	53%		
25	1500	1 hour	4%	No	52%		
26	1500	1 hour	4%	No	52%		
27	1500	30 min	4%	No			
28	1000	1 hour	4%	No	52%		59%
29	1100	1 hour	4%	No			68%
30	1500	1 hour	4%	No			74%
31	1200	1 hour	4%	No			61%
32	1300	1 hour	4%	No			62%
33	1400	1 hour	4%	No			57%
6793-02 2 at. % Nd							
Sample	**Tempera-ture**	**Hold Time**	**at.% Nd**	**CIP**	**Density before CIP**	**Density after CIP**	**Final Density**
1	1750	1 hour	2%	Yes		60%	99%
2	1700	1 hour	2%	Yes		61%	98%
3	1800	1 hour	2%	Yes		61%	100%
4	1750	1 hour	2%	Yes			100%
5	1800		2%	Yes			
6	1800	2 hours	2%	Yes			
7	1650	2 hours	2%	Yes			98%
8	1725	2 hours	2%	Yes			98%
6793-03 1 at.% Nd							
Sample	**Tempera-ture**	**Hold Time**	**at.% Nd**	**CIP**	**Density be-fore CIP**	**Density after CIP**	**Final Density**
1	1700	1 hour	1%	Yes		61%	98%
2	1750	1 hour	1%	Yes		63%	
6793-04 0 at. % Nd							
Sample	**Tempera-ture**	**Hold Time**	**at.% Nd**	**CIP**	**Density be-fore CIP**	**Density after CIP**	**Final Density**
1	1000	1 hour	0%	No			59%
2	1100	1 hour	0%	No			59%
3	1200	1 hour	0%	No			61%
4	1300	1 hour	0%	No			65%
5	1400	1 hour	0%	No			72%
6	1500	1 hour	0%	No			90%
7	1700	1 hour		Yes			
8	1750	1 hour		Yes			

Results and Discussion

One of the objectives of this work was to obtain results that would be comparable to obtained in ref. 1. To this end, a number of 0% Nd samples (Samples 6793-04, 1 to 2 and 4 to 6 in Table 1) were sintered after which XRD analysis was performed. The results are presented in Fig. 3, below. Whereas in the comparative study, all yttria and alumina was converted to YAG at a temperature of 1500 °C, there was still some evidence of the perovskite phase (YAP, denoted as P) at our measured temperature of 1500 °C.

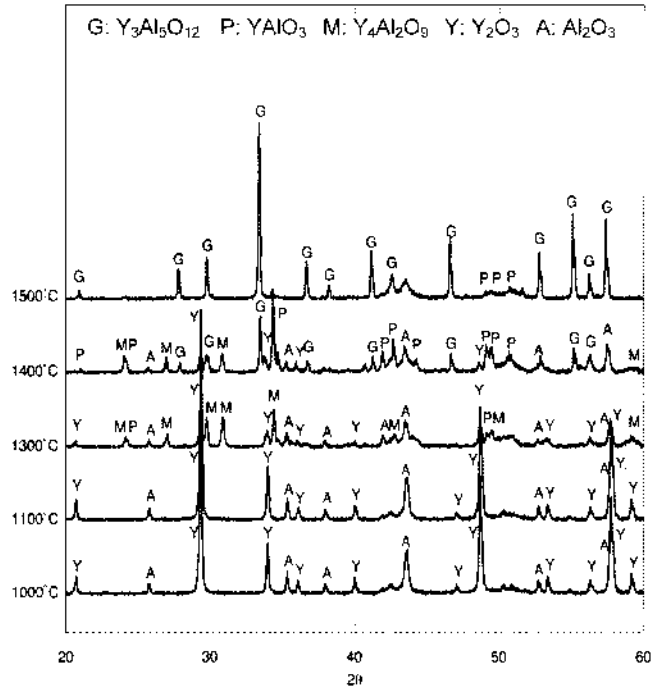

Figure 3. XRD of five samples of the 0 at.% Nd materials [Designated 6793-04 in Table 1]. The legend of the various peaks is given in the figure. Y and A are for the unchanged starting materials. M is the monoclinic phase of YA and begins to appear at 1300 °C or below but is gone by 1500 °C. P is the perovskite phase that begins to appear at 1300 °C and still evident at 1500 °C. The garnet phase, G, begins to appear at 1400 °C. Most of the material is converted to this phase by 1500 °C with a small residual of the perovskite phase.

Another objective of this study was to determine at what temperature full density would be reached. As given in Table 1, this was at approximately 1700 °C. XRD data for Sample 6793-02 (2 at. % Nd) is given in Figure 4, below. The garnet phase, G, is the only phase present at this temperature as was to be expected from the previous study. This is agreement with the results obtained in ref. 1. Yet it should be noted at this time, our results were usually obtained in 1 hour of hold time as contrasted to the 16 hours required by the reference study. Holds at the longer period of 2 hours did not show any significant gain in terms of increased densification.

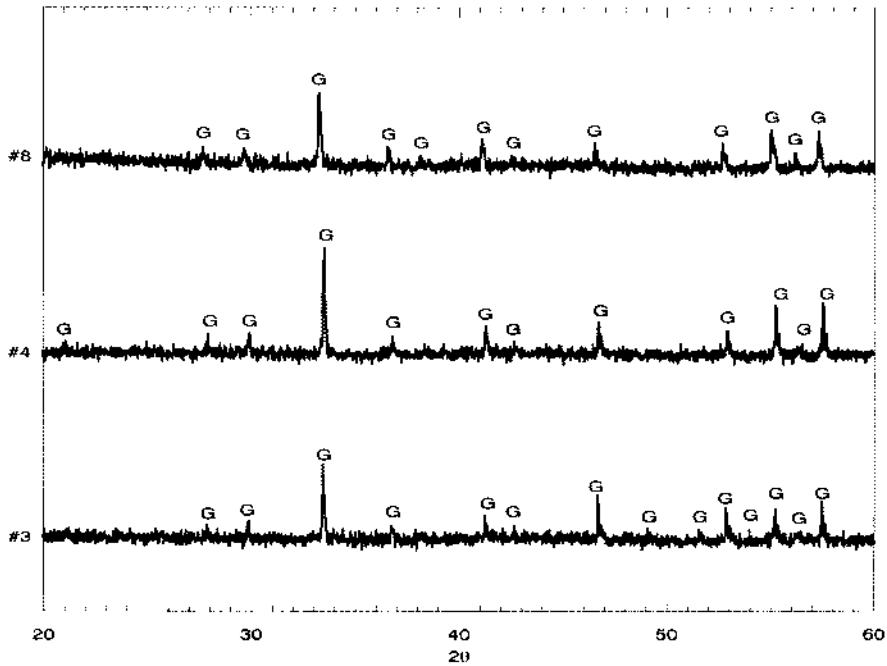

Figure 4. XRD of 2 at. % Nd:YAG. #3 was processed to 1800 °C with a hold time of 1 hour. #4 was processed to 1750 °C and #8 to 1725 °C with hold times of 1 hour.

Fundamental to this study was the obtaining of transparent materials. This was not accomplished to the degree desired but a high of translucency was in fact obtained. Figure 5 (left) shows an example of one of the more successful examples. This sample (6793-02 #4) is displayed with a light source from behind. Transmittance analysis was not performed. Analysis of the cause of the translucency was performed by looking at the microstructure using an SEM. This was performed on a sample similarly processed as was the foregoing sample. The result is shown in Figure 5 (right). The existence of pores gives rise to light scattering and a resultant non-transparent compact. It should also be noted that the grain sizes for our samples are on the order of 10 μm or less. The grain sizes for the reference study were on the order of 50 μm.

Notwithstanding the lack of transparency of the sample, the most important consideration in working with laser host materials is whether or not the Nd-doped material will in fact behave as a laser material. One critical indication of this is the measurement of the fluorescence lifetime once the material has been pulsed with the appropriate light source. Figure 6 shows the values we obtained for the 6793-02 (2 at. % Nd) samples. They compare very favorably with the results from other studies[6]. In particular, the reported values for polycrystalline Nd:YAG are 184 μs whereas the NRL material had an average value of 197 μs with 203 μs for the 1725 °C sample to 188 μs for the 1800 °C sample. This temperature dependency may or may not be significant and will be examined in future studies.

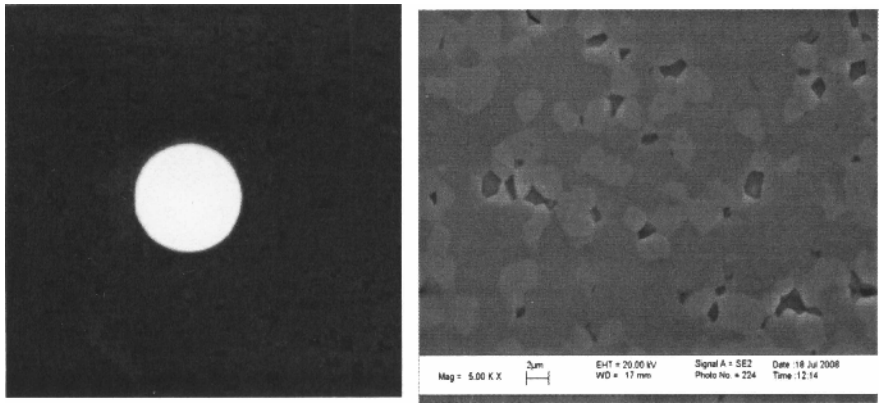

Figure 5. Left: Light transmittance from a back lit source showing translucency [Sample 6793-01 #2, 4 at.% Nd, sintered for 1 hour at 1800 °C]. Right: Micrograph of a similarly processed sample showing the presence of pores giving rise to light scattering [Sample 6793-01 #3, 4 at.% Nd, sintered for 1 hour at 1700 °C].

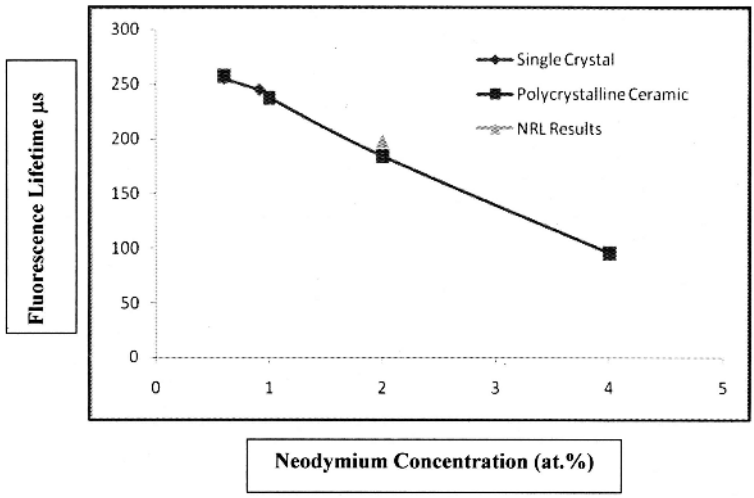

Figure 6. Fluorescence lifetime measurement of the 6397-02 samples 3, 4 and 8 compared to published results (ref. 6).

Conclusion

Translucent polycrystalline Nd:YAG samples , having fluorescence lifetimes consistent with published results, have been produced using the high-powered 83 GHz Millimeter-Wave Processing Facility at the Naval Research Laboratory. These early results indicate that this method of reactive sintering can produce viable material in significantly less time when compared to conventional ceramic processing techniques.

Acknowledgement

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