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LS&T and CMS FY 2004 Feasibility Proposal 04-FS-006 - Ceramic Laser Materials Interim Report - June 8, 2004

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Interim Report – June 8, 2004

Thomas Soules (PI), Brady Clapsaddle (Co-PI), Kathleen Schaffers, Richard Landingham

I.   Introduction

The purpose of this memo is to give an update on our work on ceramic laser materials -- feasibility proposal 04-FS-006.

Transparent ceramic materials have several major advantages over single crystals in laser applications including, ease and robustness of manufacturing, large apertures, design flexibility, fracture toughness, high activator concentrations, uniformity of composition, no residual stress, and others discussed in the proposal. After a decade of working on making transparent YAG:Nd in 1995 Japanese workers demonstrated samples for the first time that performed as well in lasers as their single crystal counterparts. Since then several laser materials have been made and evaluated. For these reasons, developing ceramic laser materials is the most exciting and futuristic materials topic in today's major solid-state laser conferences.

The highlights and executive summary of our work to date are:

- Ordered a slab of transparent YAG:Nd from Konoshima Chemical Co. for evaluation in the SSHCL. Konoshima is the only company in the world currently making ceramic laser materials for sale. Our slab, the largest one made to date, will arrive within a week and will be evaluated in the SSHCL..
- Met with the inventor of the Konoshima laser ceramic, Dr. Takagimi Yanagitani, and discussed synthesis and performance of these materials in an all day session at LLNL on May 17.
- Made our first LLNL in-house nano-sized yttrium aluminum garnet by the CMS sol-gel process.
- Successfully sintering several samples of nano-particle YAG to near translucency.

In this report we will discuss each of the above items and include where relevant pictures or tables or references. In addition to reporting interim results this memo will serve as a reference and a place to put relevant data from subsequent samples throughout the study.

II.   Ordered Slab and Discussion with Konoshima

On March 2, 2004 we visited VLOC, a division of II-VI, Inc. in New Port Richey, Florida. VLOC received a contract from the JTO for ~ $500K to develop ceramic laser materials. They are splitting this money with the Pennsylvania State University. The group at Penn State under Dr. Gary Messing will work on the ceramic synthesis and VLOC will specify fabrication specs and do evaluation. VLOC (Dr. Tara Corso) later sent us two small (< 1cm) sample pieces of ceramic YAG:Nd at our request, one with 1 at % Nd and the other with 4 at % Nd, from Konoshima . We have performed XRD on one of the samples (1 at %Nd) and found that it was polycrystalline. We have not yet been able to observe the grain structure but will try carbon coating and looking at the edge next. We have also been unable to observe any sintering aid or grain growth inhibitor elements by EDAX. The EDAX shows only Y, Al and a trace of Nd which could be an impurity. Report is available from Ed. Lindsey.

We also contacted Konoshima through Biakowski International and ordered a 10x10x0.8 cm slab of YAG:Nd at a cost after negotiation of $10,000. The size was chosen to go directly into our diode-pumped SSHCL and will when shipped be the largest sample yet made. The concentration of Nd was chosen to absorb the radiation from the pump diodes in the thickness available. We were given a delivery date of 4 weeks and it looks like they will be on time with the sample arriving in the week of June 13, 2004.

At Biakowski/Konishima's request a visit to LLNL was arranged for May 17, 2004. This was an all day meeting with a talk and discussions and questions following.

The group from Konoshima/Biakowski included:

Dr. Takagimi Yanagitani (yanagitani@konoshima.co.jp), the inventor of the Konoshima process,

Mr. Takashi Shigeta (tshigeta@baikowski.co.jp) president of Baikowski Japan,

Mr. Q. Yuminami (qyuminami@baikowski.co.jp), sales manager for ceramics for Baikowski Japan, and

Mr. Justin Otto (baikjotto@aol.com) YAG US Sales manager for Baikowski International Corporation.

A presentation was given by Justin Otto of Baikowski International. Hard copies of the material presented are available from Tom Soules (3-9260).

Some of the technical tidbits from the meetings included:
1. 5 nine's purity starting materials are used. With several purification steps.
2. YAG precursors, yttrium aluminum carbonates are precipitated in DI water followed by washing and drying steps to achieve high purity. In the final step of preparing the starting materials the carbonates are calcined at 1100

C and dispersed in water with a dispersing agent. The particle surface at this point measures 10 m^2/g.

3. Ball milling and classification is used to obtain final particle size. ~ 50 % of the material is discarded.
4. The material is dispersed in water using a dispersing agent.
5. Pieces are cast using slip casting before sintering.
6. Sintering is carried out under vacuum, 10^-5 – 10^-6 torr at around 1800 C.
7. With their current furnace (they showed a picture) a sample up to 10x25 cm could be sintered. A much larger furnace capable of sintering 20 cum pieces could be purchased. Konoshima will send us the price of such a furnace in Japan.
8. Konoshima will guarantee a scattering loss of < 0.1 %/cm and will carry out 60,000 test laser shots before shipping. Shipping would be in 3 weeks.
9. It is more difficult for them to make thick samples. The sample being sent to us is 0.8 cm thick and they claimed to be able to go to 1.2 cm. Thicker samples would be made by first sintering the thin ones and then sintering them together to form one thicker monolithic piece.
10. After the initial vacuum sintering there are several additional sintering steps. Subsequent sintering steps are determined by analyzing the piece. Subsequent sintering steps may include hot pressing or hot isostatic pressing.
11. The following day, May 18, at the CLEO conference in San Fransisco, other groups discussed their work on ceramic laser parts.
    o Dr. Ueda pointed out that optical inhomogeneity was much less in ceramics and there was little internal residual stress. A dispersant should be used during slip casting. Bonding of two ceramic pieces by firing at 1800 C results in 17.7 micron diffusion of the activators. While during the bonding of single crystal diffusion lengths are only 3-4 microns. In heat pulse experiments, the ceramic has 3 times better thermal shock resistance than the single crystal.
    o Dr. Ikesue, the group competing with Konoshima, discussed a way to grow single crystals using ceramic powders. Sintering the powders to a seed crystal. SiO2 was using a a sintering additive.
    o The Center for Fine Ceramics in Japan presented a talk discussing composite structures. These were sintered at 1750-1780 C. Starting materials were 4 nine's yttria, alumina and neodymium oxide which were ball milled and spray dried. The powders were pressed into pills and the pills inserted into undoped YAG powder and the whole composite was pressed and then sintered. In this way using powders with different Nd concentrations structures with Nd graded from the center outward were also made.
    o A final talk was given on the use of a Konoshima composite ceramic with an undoped outside region serving as a light pipe to reduce stress due to thermal heating. A fiber bundle was directed at the edge and light was internally reflected to the Nd doped core.

Konoshima is clearly ahead of its competition. It is the only company selling ceramic laser materials.

III.   <u>In-house synthesis of YAG by the CMS sol-gel route</u>

Brady Clapsaddle developed the CMS procedure for making YAG nano-particle powder using the sol-gel route. This is illustrated schematically in the figure below.
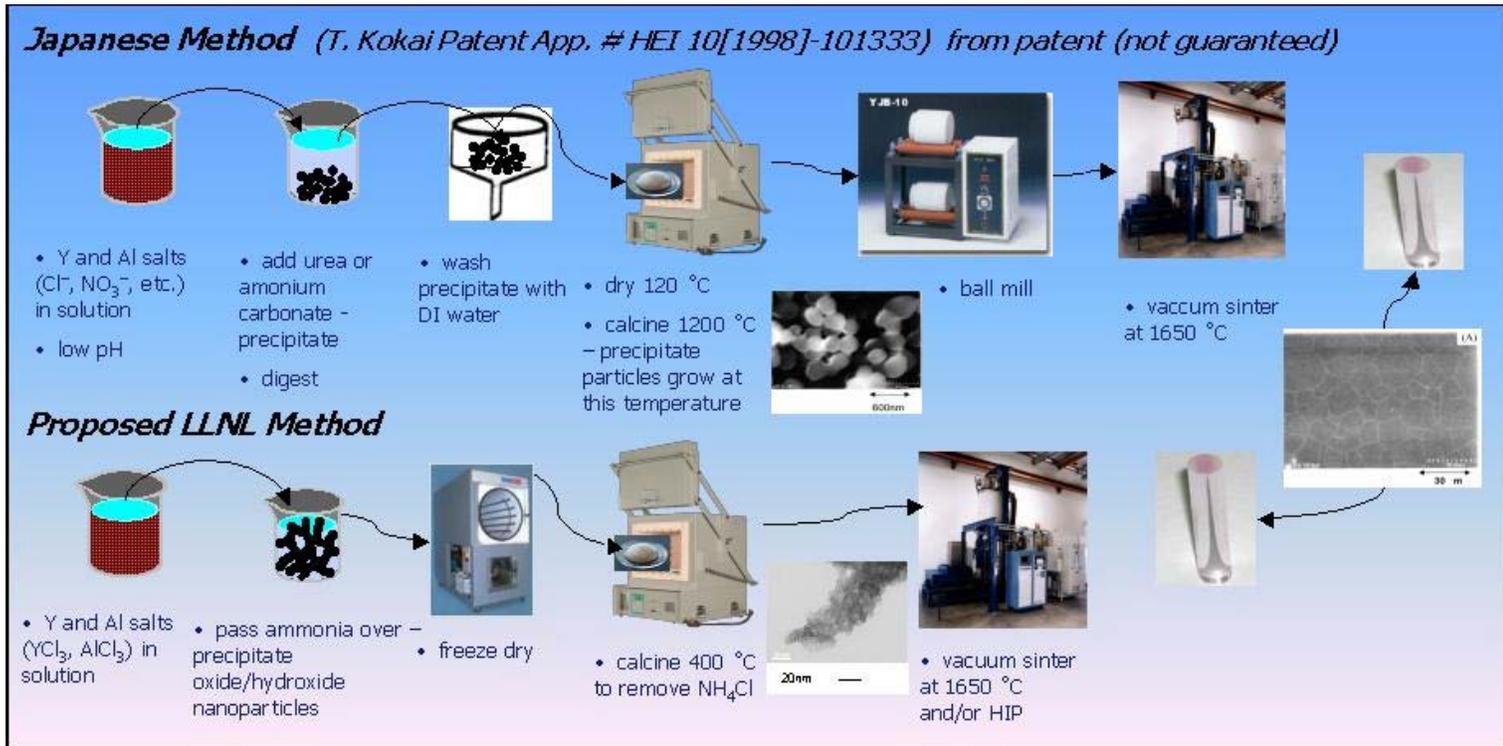
Also shown is a comparison with the Konoshima synthesis. Both involve a slow precipitation from an aqueous solution of soluble yttrium, aluminum and neodymium chlorides or nitrates. However while in the Konoshima process, ammonium carbonate, ammonium sulfate and/or urea is added dropwise to the aqueous solution with stirring to form the precipitate. In the LLNL process, ammonia is passed over or through the solution forming an oxide/hydroxide sol-gel. The advantages of the latter include the fact the ammonia gas does not introduce additional metal impurities while ammonium carbonate or sulfate may. Also the Konoshima precipitates, yttrium aluminum neodymium carbonates must be decomposed at high temperatures by calcining which causes sintering and requires additional steps, such as, ball milling to break up the sintered cake and reduce particle sizes. The LLNL sol-gel, on the other hand, is freeze-dried. Freeze drying also eliminates a difficult filtering and washing step. The freeze-dried material can easily be washed and filtered and again freeze dried. The result is a freely flowing powder that does not need to be ball milled.

The LLNL recipe is given below:

1. $AlCl_3 \cdot 6H_2O$ (56.28 g) and $YCl_3 \cdot H_2O$ (42.41 g; Y/Al = 3/5) were weighed into a 1 L, three-necked round bottom flask equipped with a mechanical stirrer and gas bubbler.

2. The salts were then dissolved in 400 mL of distilled/deionized water (resistivity = 18 Ω) while stiring.

3. A blanket of $NH_3(g)$ was then passed over the surface of the vigorously stirred salt solution through a tube connected to a $N_2(g)$ bubbler filled with a 28% solution of aqueous ammonia. The solution pH was monitored with pH paper as the $NH_3(g)$ slowly diffused into the salt solution.

4. A gelatinous solid was observed to form in the solution between pH 5 and 6. Stirring and $NH_3(g)$ diffusion was allowed to proceed until the solution pH reached 9 – 10 (12 – 24 hours), at which point the mechanical stirrer and $NH_3(g)$ bubbler were removed from the flask.

5. The solution was frozen for 3-4 days. Following freezing, the mixture was freeze-dried at 0.001 mbar to produce a fine powder consisting of amorphous yttrium and aluminum oxides and a large amount of ammonium chloride impurity.

6. The ammonium chloride (60 – 70 wt%) was removed by heating the powder to > 400 ˚C. Alternatively, the ammonium chloride can be removed by washing with water, filtering, and repeating the freeze-drying process.

7. The final, purified powder is then checked for ammonium chloride using infrared spectroscopy. The resulting amorphous, yittria/alumina powder was observed to be free-flowing and ready for further processing.

Several batches of 25 g have been made by Brady. Three processes for calcining the final freeze powder were used. Heating at 1000 C is air for ½ hour, heating in air at 475 C for ½ hr and no heating but rather washing out the ammonium chloride and then re-freeze drying. The XRD patterns below show that the material heated to 1000 C forms the YAG crystalline phase and no other phases are formed. When heated only to 475 C or less no crystal structure is apparent in the XRD suggesting that the yttrium aluminum oxide hydroxide is amorphous and there is no detectable ammonium chloride.
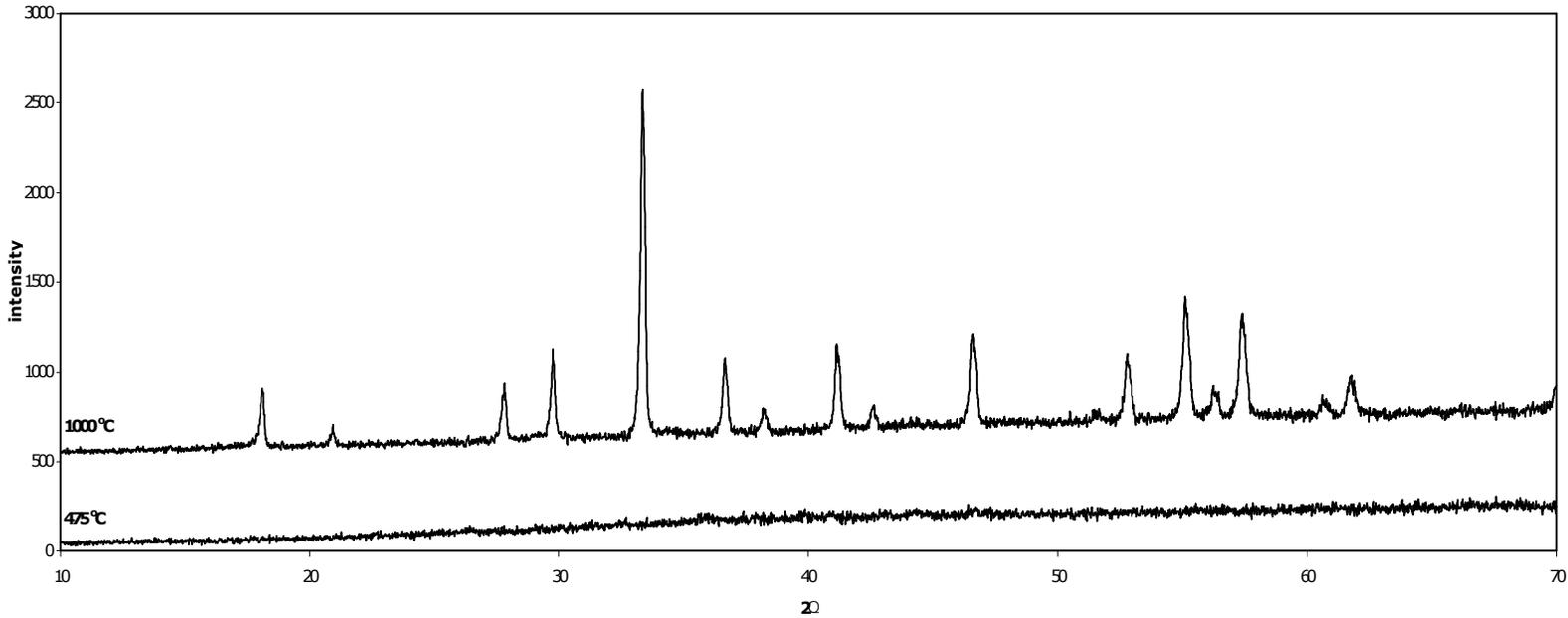
The XRD's show that the amorphous material will form the crystalline phase when heated to higher temperature.

The powder which was not heated at all but simply washed and re-freeze dried also showed good no ammonium chloride by IR. Adding AgNO3 which will form a AgCl precipitate if any chloride will be used as a more sensitive test for any remaining ammonium chloride.

The two heated samples were also submitted for particle size analysis and for SEM's. Hard copies are available from Tom Soules. The material that had been heated to 1000 C had a median particle size of 4.56 microns although the laser particle size analyzer used did not record submicron particles. The SEM pictures indicate that the particles are in fact agglomerates of much smaller crystalline grains. The material heated to 475 microns gave a median particle size of 5.47 microns but the SEM's show a lot of nanometer scale structure. Particles contain a lot of void space and under 2 K X SEM look like a random agglomeration of 'fuzz' under a microscope. Much of the detailed structure was on the order of nanometers. Some individual nano-sized particles were also seen. SEM pictures will also be obtained on the samples that were not heated but only freeze-dried and washed. These latter samples showed good flowability and will be used for subsequent sintering experiments.

IV.   Sintering Experiments

In order to start the sintering work prior to obtaining YAG nanoparticles from CMS, a commercial source for nano-particle YAG was found, MTI corporation. They supplied us with 200 g 70 nm median particle size 99.99 % purity YAG. The powder was cold pressed into four pellets, ~ 2 cm in diameter, by Richard Landingham and taken to Thermal Technologies which had a high temperature vacuum furnace for sintering.

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A set of three ~ 2 cm pills were fired for 12 hours at 10^-5 torr in the Thermal Technologies vacuum furnace. The picture above shows on the top a pressed pill that was not fired. The disk in the center of the bottom row was fired at 1750 C for 12 hrs. The one to the right at 1850 C and the one at the left was fired twice: first at 1650 C and then again at 1850 C. All three fired pills show definite sintering and some translucency. The pill fired at 1850 also shows visible grain growth and the pill fired twice shows significant grain growth.

Binders are often used to provide a more dense powder packing prior to sintering and allow the powder to be easily formed into a shape prior to sintering. For this reason in the next set of experiments water and Carbowax were investigated as binders. We also investigated the use of fine silica as a sintering aid.

The photograph below shows pictures of these samples after firing at 1750 C in at 10^-6 torr in the vacuum furnace at Thermal Technology Inc.
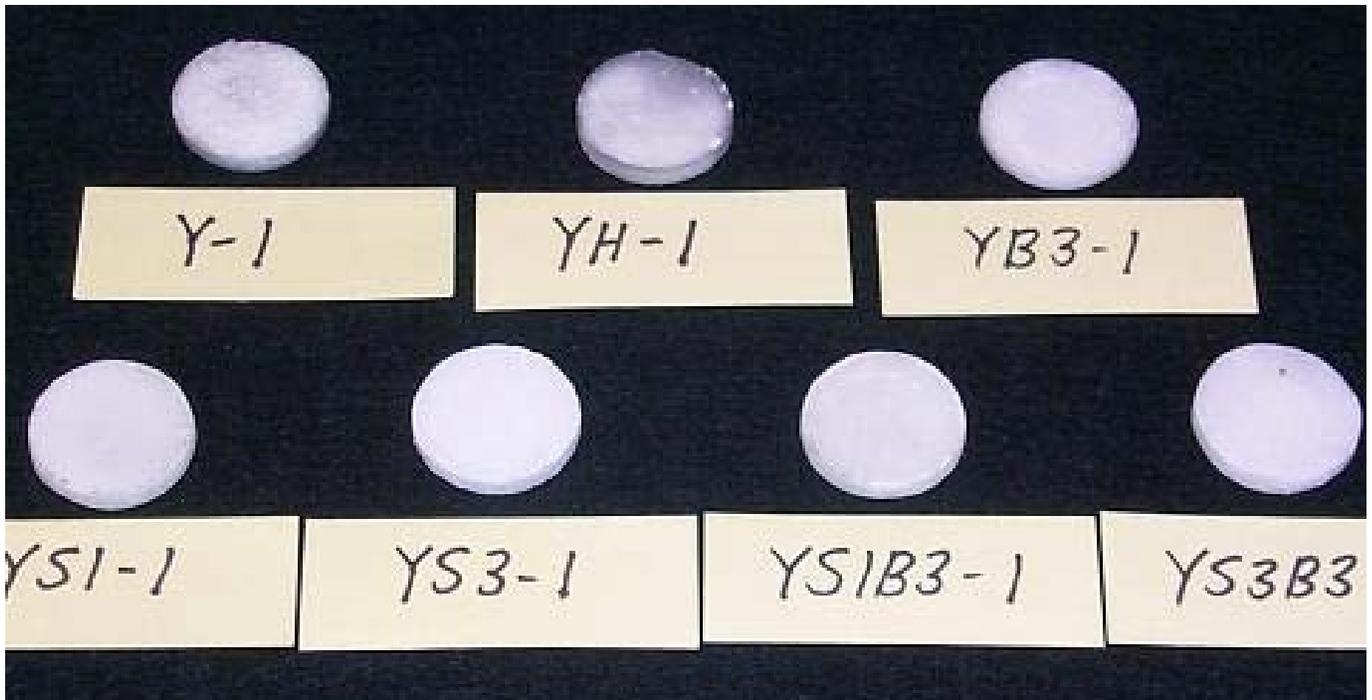
In order to keep track of these samples and the samples being made by Brady, the following is an Excel spreadsheet will be used going forward to track the process and performance of samples. A copy of the Microsoft Excell Sheet is attached. All samples going forward should be labeled.

Label	Starting Material	Source	Purity	Prec Agent	Wash	2nd Prec	Freeze Dry	Wash	Calcine T©	Sinter Temp	Atm	Time (hrs)	Hot Press	Temp	2nd Sinter	Atm	HIP	XRD	SEM	TEM	Density	Transparen
	YCl$_3$,AlCl$_3$	Aldrin	99	NH3			Y		1000									Y	Y			
	YCl$_3$,AlCl$_3$	Aldrin	99	NH3			Y		475									Y	Y			
	YCl$_3$,AlCl$_3$	Aldrin	99	NH3			Y	Y	none													
	nano-YAG	MTI	99.99							1650	10^-5	12			1850							Transl
	nano-YAG	MTI	99.99							1750	10^-5	12										Transl
	nano-YAG	MTI	99.99							1850	10^-5	12										Transl
Y-1	nano-YAG	MTI	99.99							1750	10^-6	12									94.1	Transl
YH-1	nano-YAG	MTI	99.99							1750	10^-6	12									92.5	Transl
YB3-1	nano-YAG	MTI	99.99							1750	10^-6	12									93.2	Transl
YS1-1	nano-YAG	MTI	99.99							1750	10^-6	12									92.6	White
YS1B3-1	nano-YAG	MTI	99.99							1750	10^-6	12									95.4	Transl
YS3-1	nano-YAG	MTI	99.99							1750	10^-6	12									94.8	White
YS3B3-1	nano-YAG	MTI	99.99							1750	10^-6	12									91.9	White

Richard Landingham also measured the density of the above samples by immersion and these are shown below. There is also room for comments and other descriptors on the spread sheet. At a later time the spread sheet will be put in a statistical analysis program to look for significant key input variables, etc.

YAG Nano Powder (MTI Corp.) Preparation for Vacuum Sintering													
Date-6/7/04													
Blend	As - pressed Green dimension				Calcined Condition (1000 C for 1/2 hr i					Sintered Condition			
ID	Dia.	Thick	Weight	Density	Dia.	Thick	Weight	Weigh	Density	Dia.	Thick	Weight	Density	Color
	(inch)	(inch)	(grams)	(gm/cc)	(inch)	(inch)	(grams)	Loss %	(gm/cc)	(inch)	(inch)	(grams)	(gm/cc)/%	
Dry powder														
Y-I	1.01	0.1558	5.017	2.477/54.4	1.005	0.156	5.02	0	2.48/54.4	0.85	0.135	4.932	3.93/86.4	T
Y-2	1.01	0.1492	4.89	2.521/55.4										
YH-1	1.01	0.1316	4.66	2.724/59.9	1.005	0.132	4.651	0	2.72/59.9	0.86	0.111	4.579	4.33/95.3	T
YH-2	1.01	0.1226	4.9	2.691/59.2										
YB3-1	1.01	0.11	3.887	2.732/65.2	1.005	0.11	3.796	2.34	2.67/58.6	0.86	0.099	3.75	3.99/87.7	T
YB3-2	1.01	0.16	5.744	2.762/66.0	1.005	0.16	5.592	2.65	2.69/59.1					
1.0 w/o SiO2														
YS1-1	1.01	0.1338	4.701	2.703/60.1						0.86	0.119	4.63	4.09/89.8	T/W
YS1-2	1.01	0.131	4.694	2.757/61.2										
YS1B3-1	1.01	0.132	4.779	2.785/67	1.005	0.132	4.67	2.28	2.72/60.5	0.86	0.116	4.632	4.18/92	T
YS1B3-2	1.01	0.133	4.8	2.776/66.8	1.005	0.133	4.675	2.6	2.70/60.1					
3.0 w/o SiO2														
YS3-1	1.01	0.141	4.97	2.71/61.5						0.87	0.12	4.854	4.15/91.3	W
YS3-2	1.01	0.1362	4.794	2.71/61.4										
YS3B3-1	1.01	0.133	4.745	2.75/67.2	1.005	0.133	4.63	2.42	2.68/60.8	0.87	0.113	4.561	4.14/91.1	W/T
YS3B3-2	1.01	0.135	4.81	2.717/66.6	1.005	0.135	4.678	2.56	2.65/60.1					
Y=YAG powder	H= H2O binder		B= 900 Carbowax Binder			S= SiO2 sintering aid								
T=translucent	W = White													

The results above show that the MTI nano-particle YAG pressed pills before sintering ranged from ~ 55 % theoretical density for the dry pressed pills to ~ 60 % when pressed with water to ~ 65 % when pressed with Carbowax binder. After sintering the dry-pressed pill was 86 % dense while the pills pressed with water or binder ranged from 90-95 % dense with no preference for either medium.

V.   Observations and Next Steps

Our accomplishments to date include obtaining significant background and detailed information on the transparent Konoshima ceramic process, as well as, samples for investigation. We have also ordered a large piece that will allow us to evaluate this material in our SSHCL. We have successfully synthesized nano-particle YAG by the sol-gel route. Finally we have successfully sintered nano-particle YAG to a density ~ 95 %. Clearly 95 % theoretical density is not sufficient for transparency which will require a density of 99.99%. We did not plan to reach the latter goal in our feasibility project.

However, going forward there are a number of actions that should enable us to reach higher densities and correspondingly higher transparency. The following are our near term plans:

1. To obtain higher level of purity in starting materials, one approach is to purchase 99.99 % pure rare-earth and aluminum oxides from Rhodia, Shin-Etsu, Molycorp or YuLong and Biakowski Int. respectively. These could then be dissolved in high purity nitric or hydrochloric acid. The addition of ammonia would bring the pH up until the sol-gel formed.
2. We will fire YAG samples made by the CMS sol-gel process. We will use samples that were freeze dried and washed but not calcined as these appear to have the best flowability and the least agglomeration.
3. We will look into the purchase of an air-jet mill and classifier. This would allow us to, without further contamination, reduce the particle sizes and break up agglomerates and also obtain fractions of different particle size of our room temperature sol-gel YAG. Particle size will no doubt effect the sintering and Konoshima hinted that they used only about 50 % of their starting material suggesting that they may also have classified their starting material.
4. The next step in sintering to increase density would be to hot press our samples. This can be done with the samples we have already sintered. Samples can be stacked to increase the efficiency of the hot pressing. This work would be contracted out at ~ $600 /sample. Subsequent sintering or hot isostatic pressings will also be tested.
5. A furnace originally purchased by LS & T and used by Onyx Optical has been returned to LS & T. This furnace is capable of reaching > 1700 C and is being set up. We may be able to do some of our own firing in air and perhaps with a muffle in an atmosphere or partial vacuum.