

Development of ceramic solid-state laser host materials

Narasimha S. Prasad^{1a}, Sudhir Trivedi^b, Susan Kutcher^b, Chen-Chia Wang^b, Joo-Soo Kim^b,
Uwe Hommerich^c, Vijay Shukla^d, Rajendra Sadangi^d

^aNASA Langley Research Center, Laser Remote Sensing Branch, 5 N. Dryden St., MS 468,
Hampton, VA 23681;

^bBrimrose Corporation, 19 Loveton Circle, Baltimore, MD 21152;

^cDepartment of Physics, Hampton University, Hampton, VA 23668;

^dRutgers The State University of New Jersey, Department of Materials Science and Engineering,
School of Engineering, Busch Campus, 98 Brett Rd., Piscataway, NJ 08854-8058

ABSTRACT

Polycrystalline ceramic laser materials are gaining importance in the development of novel diode-pumped solid-state lasers. Compared to single-crystals, ceramic laser materials offer advantages in terms of ease of fabrication, shape, size, and control of dopant concentrations. Recently, we have developed Neodymium doped Yttria (Nd:Y₂O₃) as a solid-state ceramic laser material. A scalable production method was utilized to make spherical non agglomerated and monodisperse metastable ceramic powders of compositions that were used to fabricate polycrystalline ceramic material components. This processing technique allowed for higher doping concentrations without the segregation problems that are normally encountered in single crystalline growth. We have successfully fabricated undoped and Neodymium doped Yttria material up to 2" in diameter, Ytterbium doped Yttria, and erbium doped Yttria. We are also in the process of developing other sesquioxides such as scandium Oxide (Sc₂O₃) and Lutesium Oxide (Lu₂O₃) doped with Ytterbium, erbium and thulium dopants. In this paper, we present our initial results on the material, optical, and spectroscopic properties of the doped and undoped sesquioxide materials. Polycrystalline ceramic lasers have enormous potential applications including remote sensing, chem.-bio detection, and space exploration research. It is also potentially much less expensive to produce ceramic laser materials compared to their single crystalline counterparts because of the shorter fabrication time and the potential for mass production in large sizes.

Keywords: Solid-state lasers, ceramic laser host materials, Neodymium doped Yttria, Ytterbium Yttria, Erbium Yttria, Scandium Oxide, Lutesium Oxide

1. INTRODUCTION

NASA is involved in the development of various remote sensing technologies for global ozone monitoring, wind sensing, trace gas detection and hard target imaging. NASA has made significant investments in the development of Neodymium doped Yttria (Nd:Y₂O₃) since it is an attractive material for UV generation suitable for remote sensing of ozone. Nd:Y₂O₃ is capable of producing laser radiation at both 914 nm and 946 nm besides 1064 nm. When 914 nm and 946 nm emission lines are frequency tripled, they correspond to ~305 nm and ~315 nm, respectively and these two wavelengths are of particular interest for ozone detection by Differential absorption lidar (DIAL) technique. Besides ozone sensing, transparent ceramic Yttria is being considered for optical window applications for crew launch vehicles (CLVs) and crew exploration vehicles (CEVs). Ceramic Yttria material has the potential for use as an optical window in high temperature (>2400 C) and high pressure (>30,000 psi) environments. Space crafts will be subjected to these conditions during re-entry into the Earth's atmosphere. Yttria has spectral transmission range starting from 200 nm. Greater than 85% transmission coefficient over visible and near-IR spectral band has been obtained with uncoated materials. Investigation into tailoring of ceramic Yttria to avoid thermal shock and other deleterious properties is under way.

¹ Narasimha.s.prasad@nasa.gov ; phone: 757-864-9403

Recently, we presented our work on the development of Neodymium doped Yttria ($\text{Nd}:\text{Y}_2\text{O}_3$) as a solid-state ceramic laser material [1]. In the past, single crystal Nd doped Yttria effort was investigated for potential ozone lidar applications at NASA [2]. Compared to single crystals, ceramic laser materials offer several advantages in regard fabrication ease, shape, size, and control of dopant concentrations [3]. Currently, NASA has extended investigations into other ceramic materials. They include (a) Yb:Yttria (for high power 1 micron pump source for UV LIDAR applications), Er:Yttria (for 1.5 -1.6 micron source for wind sensing and various other remote sensing applications), Scandium Oxide and Lutesium Oxide. The latter two materials are considered instead of Yttria due to their better thermal conductivity properties. Scandium Oxide with high melting point and better thermal conductivity than Yttria is attractive for laser applications. One drawback could be that it's thermal conductivity is found to reduce with doping. Lutesium Oxide is also attractive since it has better thermal conductivity than Yttria but remains constant even after doping. In this paper, we present our initial results on the material, optical, and spectroscopic properties of the doped and undoped sesquioxide materials of interest. In Section 2, we briefly discuss fabrication process of ceramic Nd doped Yttria followed by its emission and lifetime measurements. In Section 3, initial results on Ytterbium doped Yttria and Erbium doped Yttria materials are presented. In Section 4, fabrication of Scandium Oxide and Lutesium Oxide disks are discussed. Section 5 summarizes our initial results and current efforts that are underway.

2. CERAMIC NEODYMIUM DOPED YTTRIA

The cubic Y_2O_3 single crystal has several favorable properties such as a refractory nature, stability, and optical clarity over a broad spectral range. Furthermore, the thermal conductivity and thermal expansion coefficients are very similar to those of yttrium aluminum garnet (YAG). However, single crystalline Yttria has a high melting temperature of 2430°C and a structural phase transition at 2280°C , making it is extremely difficult to grow large-sized high quality Yttria single crystals. It is, however, relatively easy to fabricate Yttria ceramics because the sintering temperature is about 700°C lower than the melting temperature.

In our work, we used a scalable production method to make spherical non agglomerated and monodisperse metastable ceramic powders of $\text{Nd}:\text{Y}_2\text{O}_3$ compositions. These compositions were then used to fabricate polycrystalline ceramic material components. Emphasis was directed towards obtaining a fine scale and homogeneous microstructure in the sintered fully dense product. When these metastable powders are consolidated, the grain growth can be limited and fine structures can be realized. Various grain growth inhibitors can be used. Researchers at Rutgers University have developed the transformation assisted consolidation (TAC) technique for obtaining nanograin size bulk ceramics for multiphase systems [4,5]. This process uses homogeneous metastable powders produced by a plasma melting and quenching process on the starting powder material. The method has been successfully applied to multi-component ceramic powders such as alumina/titania ($\text{Al}_2\text{O}_3/13\text{TiO}_2$) [6] and zirconia/Yttria/alumina ($\text{ZrO}_2(3\text{Y}_2\text{O}_3)-20\text{Al}_2\text{O}_3$). The rapidly solidified powder may be in the form of an extended solid solution phase, intermediate phase or amorphous structure depending upon composition and cooling rate. Pressure assisted consolidation of these metastable powders results in a fully dense structure comprised of the nanoscale mixture of two or more equilibrium phases. When the initial powder is segregation free, the final product will be homogeneous. This technique to produce doped ceramic powders is unique and differs from the conventional techniques, which use high temperature sintering and/or other chemical routes for doping. Grain growth can be controlled by varying the heat treatment schedule. Moreover, pressure also affects the transformation from metastable to equilibrium structure. By controlling the decomposition parameters, nanograin structures can be achieved in fully dense parts.

2.1 Production of metastable $\text{Nd}:\text{Y}_2\text{O}_3$ powder

The method used for producing metastable $\text{Nd}:\text{Y}_2\text{O}_3$ is depicted in Figure 1. The $\text{Y}_2\text{O}_3 + \text{Nd}_2\text{O}_3$ powder of required stoichiometry was prepared and added to de-ionized water to form viscous slurry. The slurry was ball milled for about two days to ensure proper mixing and homogeneity. The slurries were then spray dried in a Niro atomizer spray dryer at an intake temperature of 200°C and exhaust temperature of 70°C . The atomizing pressure was 2 atmospheres. The coarse spray-dried powder was then sieved to obtain particles with sizes ranging from 38 to 54 μm . The sieved powder was plasma sprayed in a Sulzer Metco plasma spray system twice to insure the proper melting of powder and doping of Y_2O_3 with Neodymium. This technique produces powder particles in a metastable state and, unlike normal melting, does not segregate the dopants. The level of doping that can be achieved is an order of magnitude higher than by precipitation methods.

We successfully produced (Nd:Y₂O₃) powders with 1at% and 2at% Nd concentrations using the techniques described above. Figure 2 is an optical micrograph of the grains of Yttria powder prepared by the double plasma spray technique. These powders were prepared by spray drying slurry of Neodymium and Yttria powders. After this step, the powders were heat-treated and plasma sprayed to produce powders in the metastable state. The powder grains can be seen in Figure 2 and are transparent. The individual grains are transparent and light pink in color indicating incorporation of Neodymium. X-ray diffraction indicated the presence of single phase cubic Yttria (see bottom right picture in Figure 4). In addition, for understanding the dopant behaviors, ceramic Yttria with Nd concentrations of 4at.wt.% and 8at.wt.% were also produced. No quenching for 4at% sample was observed. However, for Nd concentration of 8at.wt.% quenching was observed.

2.2 Formation of disk

The metastable powders were consolidated and pressed into a green ceramic disk, which was then subjected to hot isostatic pressing (HIP). HIP is a technique where application of pressure and temperature is applied to a powder or green compact enclosed in a container. Initially, we used Yttria and Neodymium doped Yttria compacts enclosed in steel cans. The cans were degassed and leak tested prior to HIP. The HIP cycle and cans are shown in Figure 3 where pressure and temperature are shown on the two y axes. In Figure 3, the bottom right picture shows a can after the HIP process is complete. In this picture, the deformation in the cylindrical can and the crimping used to seal and weld marks are visible.

We have now moved to sinter-HIP processing to avoid the problems we had with steel cans and to save the time and expense of processing cans. The containerless HIP works by first sintering the sample to a point where the pores are all closed and residual porosity is less than 5-8%. The outer portion of the sample acts like a virtual can and the HIP process can take place. The main problem with sinter-HIP is that grain growth occurs during the sintering step. The issues with environment control are more severe in containerless HIP as the contamination from the process furnace is possible. These issues are currently being investigated.

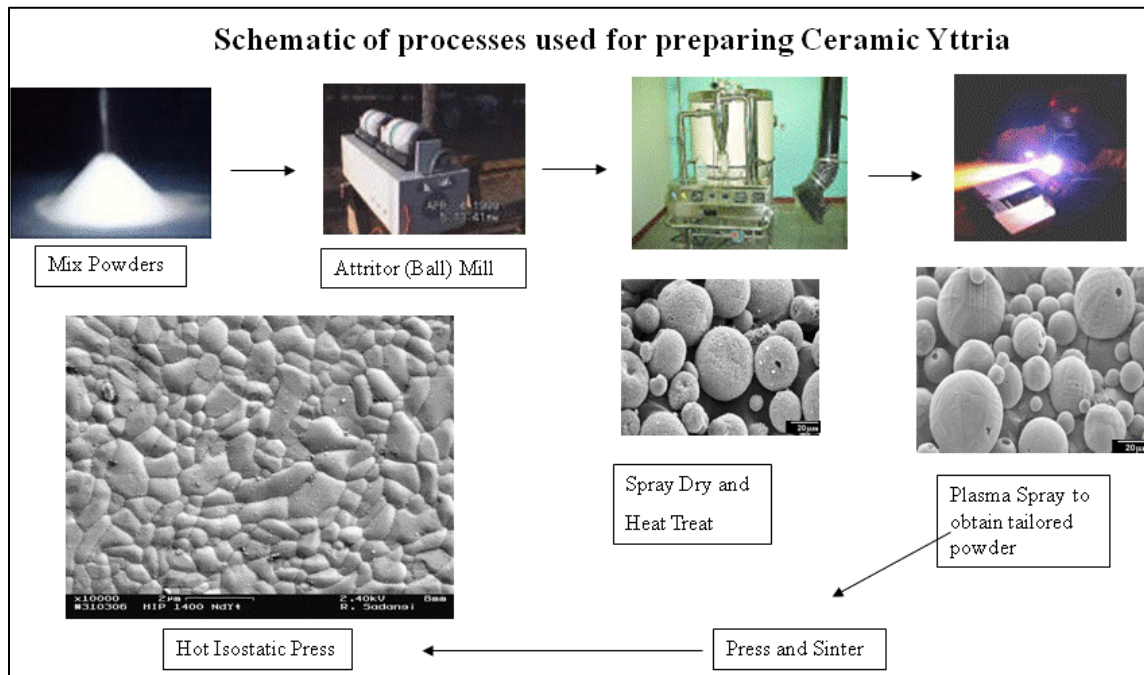


Fig. 1. Schematic of processes used for preparing ceramic laser materials.

Two inch diameter Ceramic Ytria samples were produced at two doping levels of 1at.wt.% and 2at.wt%. The ceramic samples cut out from the disk were mechanically very strong and translucent. Small portions of the sample were cut, polished and used for optical testing. From the SEM analysis of these samples, it was observed in the sample hipped at 1400°C that the pore level is low but the densification is not complete. In order to complete densification the disks were HIPPED at higher temperatures of 1650 °C and 1850 °C. X-ray diffraction results indicated the presence of single-phase cubic Ytria and there was no indication of phase separation or precipitates. Small samples were cut from these disks and polished, for further characterization. SEM pictures confirmed that the phase was cubic and there was no indication of phase separation.

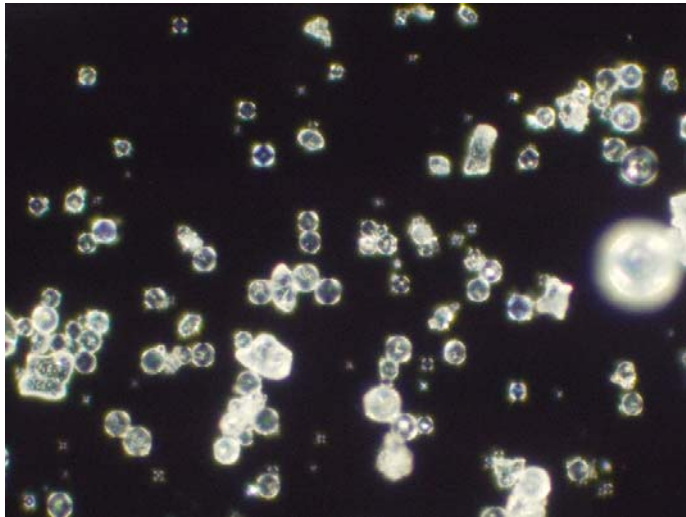


Fig. 2. Optical microscope pictures of double plasma sprayed Y₂O₃-Nd powder. The crystals are seen as transparent. Average powder size is 20 micrometers in diameter.

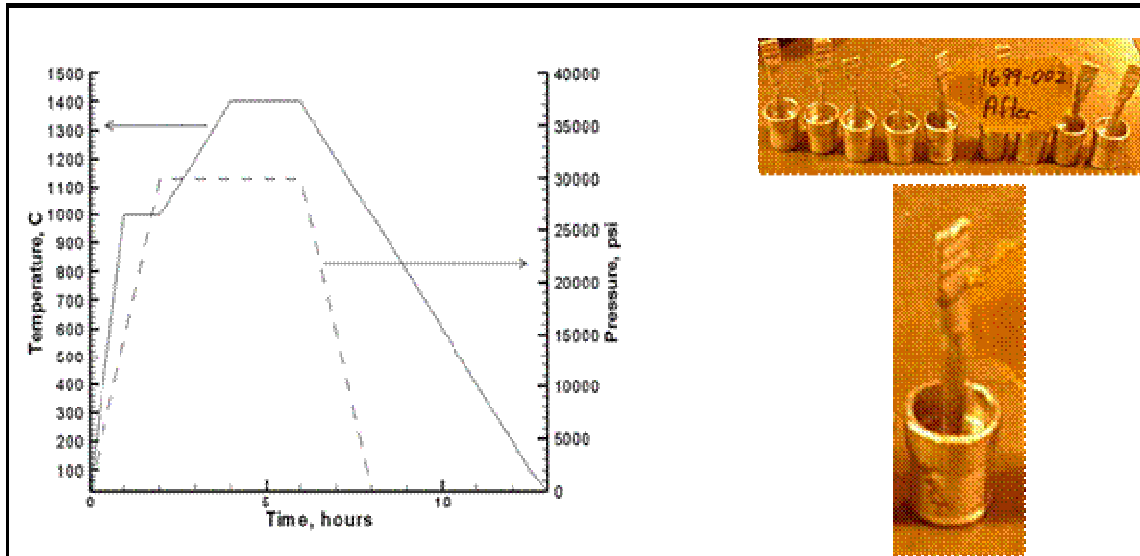


Fig. 3. The HIP cycle is shown in the left Figure. The top right picture shows cans used for HIP process. In the right bottom, the picture of can shows crimping and welding impressions after HIP process was completed.

2.3 Results of Nd doped Yttria fabrication

Several batch of doped and Nd:Yttria samples were produced and tested. We were successful in obtaining diffusion doped Nd:Yttria samples in sizes greater than 1" diameter. Figure 4 shows undoped doped and Nd doped samples X-Ray and transmission measurements. Here pictures of samples before and after pressing and annealing in oxygen atmosphere are shown. Up to 2" ceramic Yttria crystals were successfully produced. The transparent undoped Yttria samples were clear whereas the 1" diameter Nd doped Yttria samples had bluish tinge. As mentioned previously, 4at.wt% doping of Nd ions with no quenching was accomplished. When the doping level was increased to 8at.wt%, slight quenching was observed. X-Ray analysis of ceramic Yttria sample, shown in the bottom middle picture of Figure 4, indicates single phase characteristics.

Figure 5 shows the absorption spectra. The absorption curve and the corresponding transmission curve in the 700 nm to 950 nm wavelength range are shown. For absorption measurement, 1.6 mm thick sample was used. The absorption coefficient at 820.6 nm was $\sim 6.5 \text{ cm}^{-1}$. In Figure 6, the transmission spectrum of undoped and Nd doped Yttria are shown. In this graph, the blue curve is for the undoped ceramic Yttria sample while the red curve is for the diffusion doped Nd:Yttria. Greater than 85% transmission with uncoated samples was obtained without accounting for the Fresnel loss. For Yttria, the refractive index at 250 nm is ~ 2.05 ($\sim 24\%$ loss) and at 2000 nm, it is ~ 1.74 . The heat treatment was carried out at 1100°C . Hence, the diffusion doping of Nd in ceramic Yttria, along with the heat treatment, enhanced the transmission characteristics and, as such, pushed the bandedge close to 200 nm. The right picture in Figure 6 shows the emission spectra of 2 at.wt% doped Nd:Yttria using excitation at 800 nm. The peak emission obtained is at 1067 nm.

Figure 7 shows the transmission spectrum of ceramic Nd:Yttria and lifetime measurements. The decay constant obtained using 808 nm wavelength probe source is ~ 0.3 ms. This value is similar to that obtained for the single crystal Nd:Yttria [2]. In Figure 8, a comparison of emission spectra of single crystal and ceramic Nd:Yttria are shown. The characteristics of ceramic Nd:Yttria obtained is very similar to that of single crystal Nd:Yttria [2].

In Figure 9, a 2" diameter ceramic Yttria sample is shown. Some dark regions are still present in the sample. The non-stoichiometry, $\text{Y}_2\text{O}_{(3-x)}$, feature is due to reduction in Oxygen. The reason for the transmission loss in the two inch disk is that the structure is inhomogeneous. During HIP cycle the Yttria disk reaches full density and undergoes oxygen loss. This process is inhomogeneous and depends on the surrounding environment of the disk. When the sample is heat treated with oxygen, after the HIP process, for conversion back to stoichiometric Yttria, the inhomogeneous regions form pores and other defects and hence the transmission loss. The only way to avoid loss in the final sample is to avoid inhomogeneity, i.e. large departure from stoichiometry, during the HIP process. For obtaining highly transparent stoichiometric samples, a parametric study is being conducted to produce optimal environment for oxygen loss prevention.

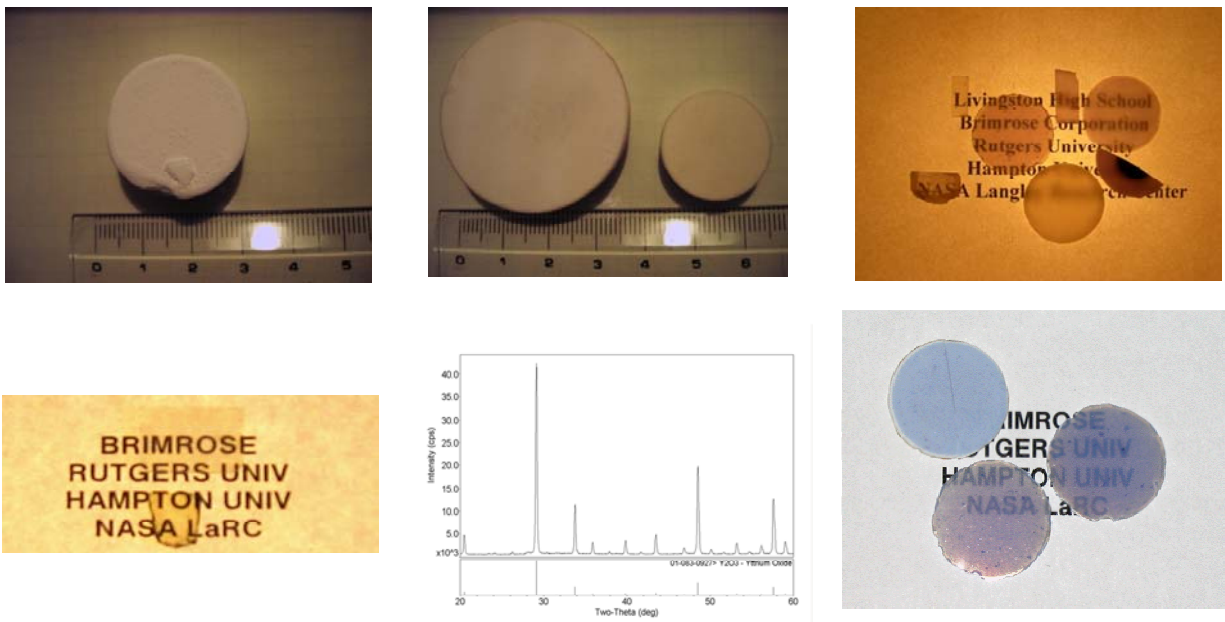


Fig. 4. Top Left: Pressed 1" diameter Yttria sample. Top middle: Yttria after vacuum sintering. Here 2" and 1" diameter samples are shown. Top right: Samples of undoped and doped Yttria samples. Bottom left: Highly transparent undoped Yttria samples. Bottom middle: X-ray diffraction of Yttria sample showing single phase characteristics. Bottom right: Transparent 1" diameter Nd doped Yttria samples.

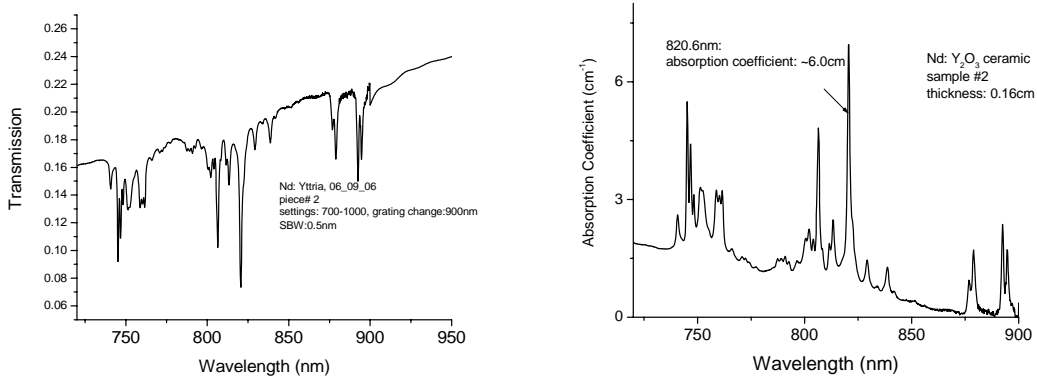


Fig 5. Absorption and transmission characteristics of ceramic Nd:Yttria. Top left: Transmission curve. Top right: The corresponding absorption curve. Sample thickness used was 1.6 mm

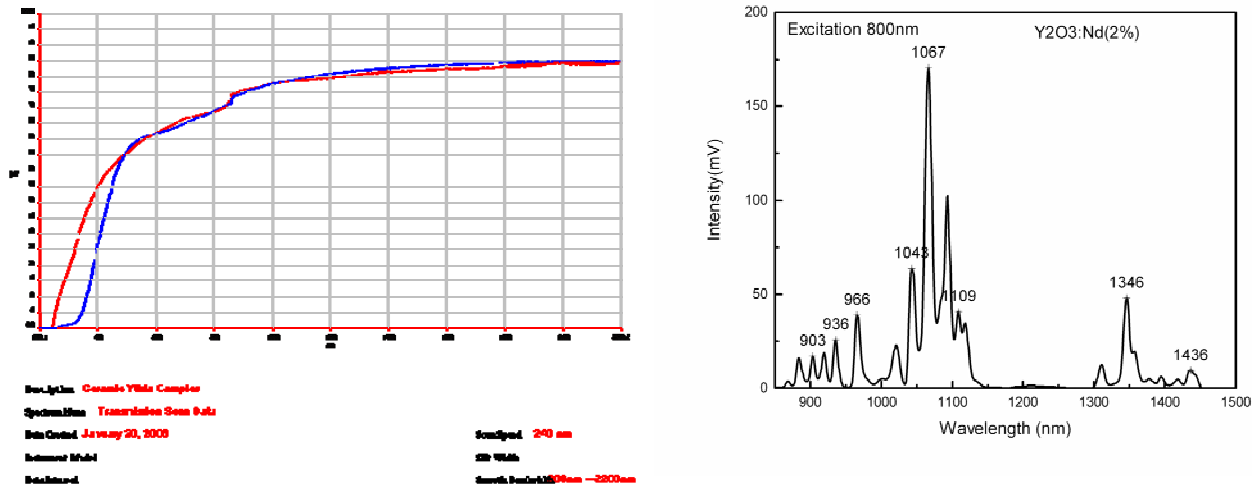


Fig. 6. Transmission and emission characteristics of ceramic Nd:Yttria. Left: Transmission curves for undoped and Nd doped ceramic Yttria. Blue Line is for undoped ceramic Yttria and the red line is for diffusion doped ceramic Nd:Yttria. Right: The emission characteristics of 2at.wt% Nd:Yttria with excitation at 800 nm. The peak wavelength is 1067 nm.

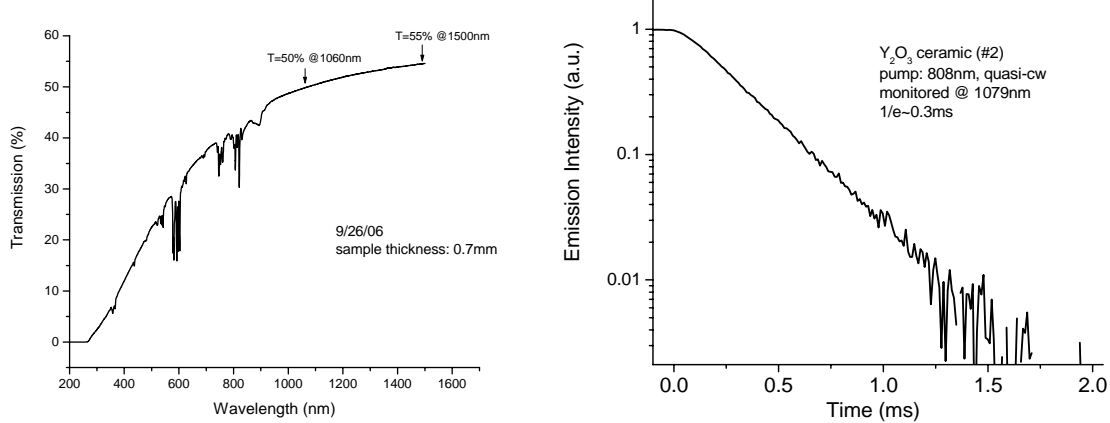


Fig. 7. Left: Transmission of Nd:Yttria sample of thickness 0.7mm. Right: Lifetime measurement results. Using 808nm pump, the decay constant is ~0.3 ms which is similar to that of a single crystal Nd:Yttria[2].

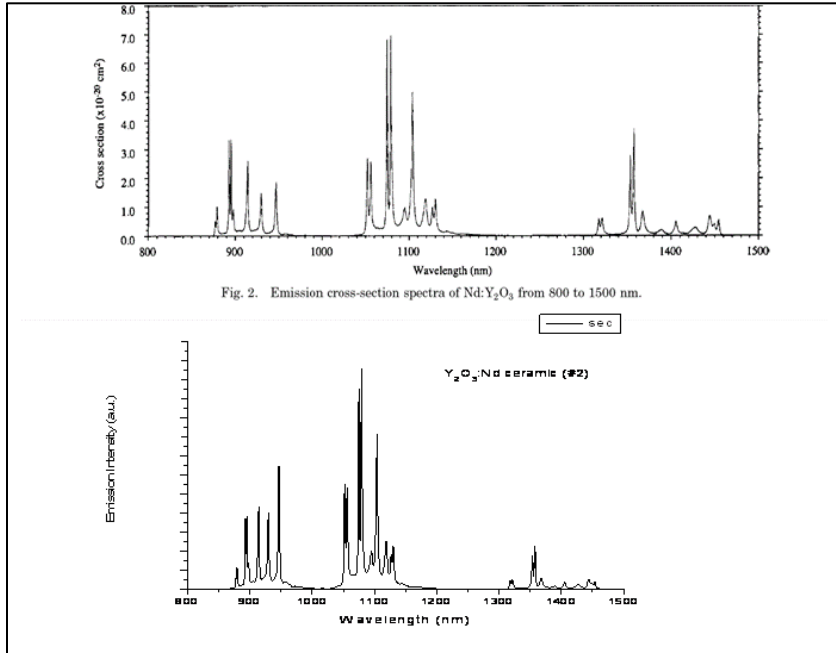


Fig. 8. Comparison of emission spectra from ceramic Nd:Y₂O₃ versus single crystal single crystal Nd: Y₂O₃ [2].

Fig. 9. Ceramic Yttria sample of 2" in diameter with dark regions due to oxygen loss.



3. YTTERBIUM AND ERBIUM DOPED CERAMIC YTTRIA

Alongside the development of ceramic Nd doped Yttria, Ytterbium and Erbium doped ceramic Yttria effort is being carried out using similar processes. We now present our initial results on Ytterbium and Erbium doped ceramic Yttria.

In Figure 10, pressed Yb doped ceramic Yttria samples are shown. For comparison, Nd doped Yttria samples are also shown. The lifetime and emission characteristics of Yb doped ceramic Yttria are shown in Figure 10. The decay constant of the pressed disk was 0.92 seconds. The spectrometer characteristics used for the measurements are given in the bottom left graph. The peak emission was at 1030 nm when excited at 920 nm wavelength source.

Figure 11 shows the emission and life characteristics of Erbium doped ceramic Yttria. The decay constant of the pressed disk monitored at 1541 nm was ~9.4 ms. The peak emission was at ~1530 nm when excited using a laser diode operating at 972 nm. The Erbium doped ceramic Yttria of 1" diameter test sample is shown in Figure 12.

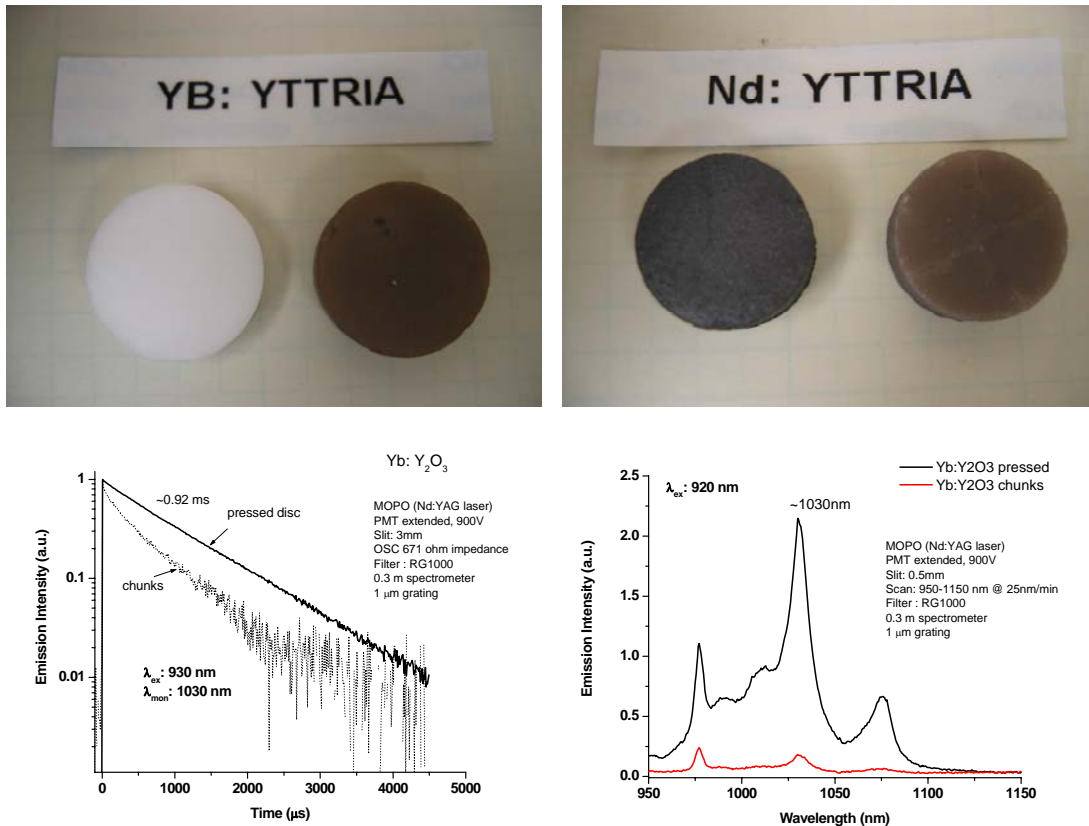


Fig. 10. Pressed Yb doped ceramic Yttria are shown in top right picture. Emission spectrum and lifetime measurements of Yb doped ceramic Yttria samples are shown in the bottom graphs. The decay constant of the pressed disk was 0.92 seconds. The peak emission was at 1030 nm when excited using a 920 nm wavelength source.

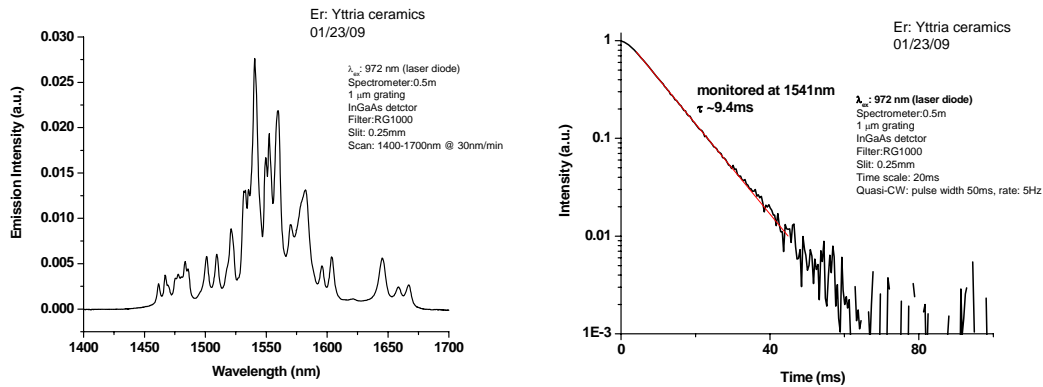


Figure 11. Emission Spectrum and Lifetime Measurements of Erbium doped ceramic Ytria samples. The decay constant of the pressed disk monitored at 1541 nm was ~ 9.4 ms. The peak emission was at ~ 1530 nm when excited at 972 nm source.

4. SCANDIUM AND LUTESIUM OXIDES

As indicated earlier, development of other potential sesquioxide materials including Scandium Oxide and Lutesium Oxide were taken up due to their thermal conductivity figures. Thermal conductivity of Scandium Oxide and lutesium Oxide are better than Ytria. As such, these materials could be used instead of Ytria for laser applications. In the case of Scandium Oxide, it is observed that the thermal conductivity decreases with doping. However, in the case of Lutesium Oxide, thermal conductivity remains constant with doping. Polished Scandium Oxide and Lutesium Oxide test samples of 1" in diameter are shown alongside Erbium doped ceramic Ytria in Figure 12. Currently, we are annealing these samples at 1450 C in the O_2 environment to replenish lost O_2 . In this case again, to obtain highly transparent and hence stoichiometric samples, a parametric study is being conducted for effective oxygen loss prevention.

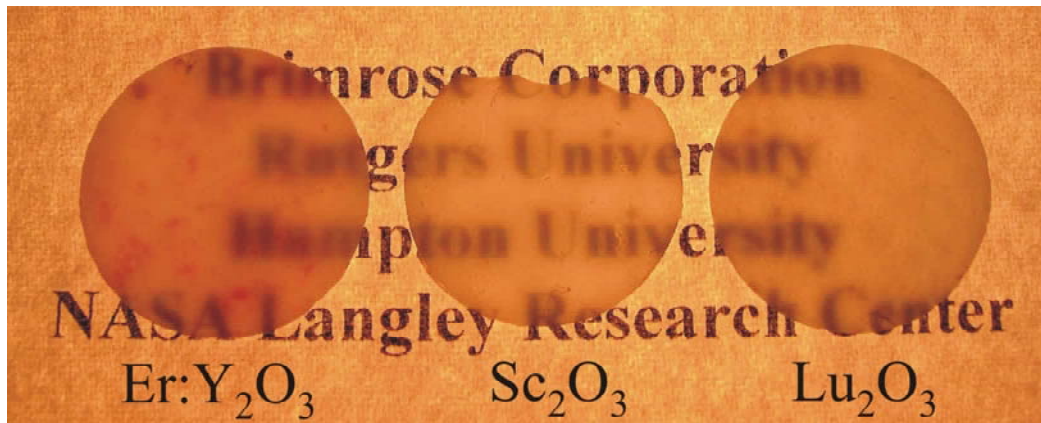


Fig. 12. Scandium Oxide and Lutesium Oxide test samples of sizes of 1" diameter. Erbium doped Ytria sample of 1" diameter is also shown.

5. SUMMARY AND CONCLUSIONS

We have demonstrated size scaling (up to 2 inch diameter) in undoped Yttria. We have successfully produced Ytterbium and Erbium doped ceramic Yttria with lifetimes compatible with single crystalline materials. Using a similar process, we also produced 1" transparent Scandium and Lutesium Oxide samples. These materials could provide better thermal conductivity characteristics than Yttria for laser development.

Our work in this area continues as we strive to develop larger samples with improved optical properties. We are experimenting with environmental controls and various heat treatments and HIP procedures, as well as with improving the control during the powder mixing process. Use of powders of higher purity will lead to a decrease in contamination and improved optical transmission. We are also in the process of developing other sesquioxides such as scandium Oxide (Sc_2O_3) and Lutesium Oxide (Lu_2O_3), which may provide improved thermal conductivity ceramic materials. Our goal is to develop materials that are suitable for solid-state lasing around 1.0 and 1.5 micron wavelengths.

REFERENCES

- [1] Prasad, N.S, Edwards, W.C., Trivedi, S.B., Kutcher, S.W., Chen-Chia Wang, Joo-Soo Kim, Hommerich, U., Shukla, V., Sadangi, R., Kear, B.H., Selected Topics in Quantum Electronics, IEEE Journal of Volume 13, Issue 3, May-June 2007 Page(s):831-837.
- [2] B.M. Walsh, J. McMahon, W.C. Edwards, N. Barnes, R.W. Equall, R.L. Hutcheson," Spectroscopic characterization of Nd:Y₂O₃: Application towards a differential absorption lidar system for remote sensing of ozone," *J. Opt. Soc. Am. B.*, vol. 19, pp. 2893-2903, 2002.
- [3] J. Kong, J.Lu, K. Takaichi,, T. Uematsu, K. Ueda, D.Y. Yang, D.Y. Shen, H. Yagi, T. Yanagitani, and A.A. Kaminskii. "Diode pumped Yb:Y₂O₃ ceramic laser" *Applied Physics Letters*, Vol. 82, Num. 16. pp. 2556-58 (2003).
- [4] J. Colaizzi, W.E. Mayo, B.H. Kear, S.-C. Liao. "Dense Nanoscale Single- and Multi-Phase Ceramics Sintered by Transformation Assisted Consolidation," *Intn'l J. Powder Metallurgy*, 37(1), 45, 2001. Winner of 2000 *MPIF Outstanding Technical Paper Award*.
- [5] "Transformation-Assisted Consolidation of Bulk Nanocrystalline TiO₂," S.-C. Liao, Y.-J. Chen, W.E. Mayo and B.H. Kear, *Nanostruct. Mater*, 11, pp. 553-557, 1999.
- [6] Kear, B H., Kalman, Z., Sadangi, R K. Skandan, G. Colaizzi, J. Mayo, W E. Plasma-sprayed nanostructured Al₂O₃/TiO₂ powders and coatings *Journal of Thermal Spray Technology*. v 9 n 4 Dec 2000. p 483-487.