Recent Progress in the development of Neodymium doped Ceramic Yttria

Narasimha S. Prasad[a], Chris Edwards[a], Sudhir B. Trivedi[b], Susan Kutcher[b], Chen-Chia Wang[b], Joo-Soo Kim[b], Uwe Hommerich[c], Vijay Shukla[d], Rajendra Sadangi[d], and Bernard Kear[d]

[a]NASA Langley Research Center, 5 N. Dryden St., MS 468, Hampton, VA 23681-2199
[b]Brimrose Corporation, 19 Loveton Cir., Baltimore, MD 21152
[c]Hampton University, Department of Physics, Hampton, VA 23668
[d]State University of New Jersey, Rutgers, Center for Nanomaterials Research, School of Engineering, Busch Campus, 98 Brett Rd., Piscataway, NJ 08854-8058

ABSTRACT

Solid-state lasers play a significant role in providing the technology necessary for active remote sensing of the atmosphere. Neodymium doped yttria ($Nd:Y_2O_3$) is considered to be an attractive material due to its possible lasing wavelengths of ~914 nm and ~946 nm for ozone profiling. These wavelengths when frequency tripled can generate UV light at ~305 nm and ~315 nm, which is particularly useful for ozone sensing using differential absorption lidar technique. For practical realization of space based UV transmitter technology, ceramic $Nd:Y_2O_3$ material is considered to possess great potential. A plasma melting and quenching method has been developed to produce Nd^{3+} doped powders for consolidation into $Nd:Y_2O_3$ ceramic laser materials. This far-from-equilibrium processing methodology allows higher levels of rare earth doping than can be achieved by equilibrium methods. The method comprises of two main steps: (a) plasma melting and quenching to generate dense, and homogeneous doped metastable powders, (b) pressure assisted consolidation of these powders by hot isostatic pressing to make dense nanocomposite ceramics. Using this process, several 1" x 1" ceramic cylinders have been produced. The infrared transmission of undoped Y_2O_3 ceramics was as high as ~75% without anti-reflection coating. In the case of $Nd:Y_2O_3$ ceramics infrared transmission values of ~50% were achieved. Furthermore, $Nd:Y_2O_3$ samples with dopant concentrations of up to ~2 at. % were prepared without significant emission quenching.

Index Terms- Remote Sensing, solid-state lasers, ceramics, Neodymium doped yttria

I. INTRODUCTION

NASA is actively engaged in the development of space-based active remote sensing missions using Light Detection And Ranging (LIDAR) techniques. Under the ongoing Laser Risk Reduction Program (LRRP), the emphasis is on the development of reliable and robust lasers for LIDAR systems appropriate for space based platforms. One of the technical objectives of LRRP is to develop viable one micron laser based all-solid-state UV transmitter technologies generating dual wavelengths around 308 nm and 320 nm for ozone profiling using Differential Absorption Lidar (DIAL) scheme. Basic design considerations involved several practical orbital and environmental operational conditions. Accordingly, for operation during strong day light conditions, a highly efficient, single longitudinal mode, conductively cooled, and all-solid-state UV transmitter scheme has been developed. The scheme involves a Nd:YAG pump laser operating at 1064 nm that is coupled to a nonlinear optics arrangement comprising of an optical parametric oscillator (OPO) and a sum frequency generator (SFG) that generates >200 mJ/pulse [1]. In this case, the overall transmitter scheme is relatively complex.

To simplify the UV transmitter architecture, several approaches are being contemplated. One of the approaches that NASA is actively engaged in is the development of novel laser materials that could conveniently provide UV wavelengths. Solid state tunable lasers based on single crystalline medium have significantly contributed towards the development of technology necessary for active remote sensing of the atmosphere from terrestrial, airborne and space based platforms. However, many recent studies on diode-pumped solid-state lasers have focused on polycrystalline ceramic lasers because of the advantages that they have over single crystals in terms of shape, size, ease of fabrication, and control of dopant concentrations [2-10].

Significant strides have been made in the development of ceramic neodymium doped Yttrium Aluminum Garnet (Nd:YAG) material [2-5]. Neodymium doped Yttria (Nd:Y_2O_3) is another material that has attracted considerable attention due to its lasing wavelengths and excellent thermo-mechanical properties [6-11]. The specific Stark level splittings in Nd:Y_2O_3 provides two emission lines at 914 nm and 946 nm originating from the $^4F_{3/2} \rightarrow {}^4I_{9/2}$ transition. Unlike Nd:YAG, the Nd:Y_2O_3 gain medium, besides 1064 nm wavelength, is capable of generating 914 nm and 946 nm wavelengths which when tripled will provide wavelengths around 305 nm and 315 nm. These two wavelengths are particularly useful in ozone sensing using the DIAL technique. Nd:Y_2O_3 not only possesses the requisite peak wavelengths at 914 and 946 nm for $^4F_{3/2} \rightarrow {}^4I_{9/2}$ emission but also has a relatively large Stark splitting of the ground state that is somewhere between garnets and fluorides. It has emission cross-sections approaching those in Nd:YAG, and it has the smallest 1.06μm/0.94μm cross-section ratio of any Nd doped material commonly known. All of these characteristics make Nd:Y_2O_3 an excellent candidate for study toward applications for atmospheric ozone DIAL measurements [11].

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 [5-11]. Furthermore, the thermal conductivity and thermal expansion coefficients are very similar to those of YAG. According to certain conservative estimates, the thermal conductivity of Nd:Y_2O_3 is nearly twice that of Nd:YAG. However, the yttria single crystal has a high melting temperature (2430°C) and a structural phase transition at 2280°C. Thus, 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 recent years, Japanese researchers [2-10] have used polycrystalline ceramics as a new type of laser gain media. Ceramic materials can be processed/produced at temperatures that are about two-thirds their melting points. They can be produced in large sizes, a variety of shapes, and best of all, with dopant concentrations about an order of magnitude higher than those in single crystal materials. In case of a dopant like Yb^{3+} where emission concentration quenching effects are practically absent, it is possible to produce ceramic laser materials with higher concentration to generate efficient lasing. Finally, with the short fabrication time and its amenability to large scale production, the cost of ceramic laser materials could be much lower than traditional laser materials.

Production of ceramic laser materials in the USA is in its initial stages. Most of the optical ceramic activity had been focused at producing transparent window material with superior thermo-mechanical properties for applications at infrared wavelengths [12]. In recent years, we have made significant progress in producing ceramic laser materials. We have overcome two major challenges in this area: 1) production of transparent ceramic material and 2) achievement of homogeneous rare earth doping. We have successfully produced $Nd:Y_2O_3$ with emission characteristics as good as single crystalline material. The uniqueness of our approach is in producing rare earth doped ceramic powders using a plasma spray process, followed by consolidation in green body form and subsequent hot isostatic pressing (HIP) of these powders. Rare earth doping in this process is carried out in the far-from-equilibrium regime that results in powder in a metastable state. This powder can have doping levels much higher than via the sintering/diffusion process. Also, as the powder has experienced a high temperature during formation, it can be consolidated while retaining these higher doping levels.

In this paper, we report on the recent progress made in the development of $Nd:Y_2O_3$ ceramics as a solid-state laser material primarily for remote sensing applications of atmospheric ozone [13]. In Section 2, the development of ceramic $Nd:Y_2O_3$ by an unique processing methodology is presented. The production and characterization of metastable $Nd:Y_2O_3$ powder and transparent ceramic disks are discussed in Section 3. Further experimental results on the absorption and emission properties of undoped and Nd doped Y_2O_3 powders and ceramics are discussed in Section 4.

II. NEODYMIUM DOPED CERAMIC YTTRIA

We have developed a far-from-equilibrium or metastable processing method to enable production of multiphase nanocomposite ceramics [14,15]. The new process integrates two enabling technologies: (1) Far-from-equilibrium processing to produce homogeneous metastable powders, and (2) Hot Isostatic Pressing (HIP) to densify these metastable powders, while decomposing them into nanocrystalline or nanocomposite structures. Co-nucleation of nano-phases during the consolidation also limits their growth, thus creating a uniform nanocomposite structure. This method overcomes the difficulties inherent in the processing of high surface area nanocrystalline powders where unrestricted grain growth is a serious problem. Moreover, fine grain multi-phase ceramics may show superplastic flow, which improves densification.

In previous work [16-20], we investigated the feasibility of using $Nd:Y_2O_3$ composites to produce polycrystalline nano-grain ceramic laser material. The overall goal of our collaborative effort is to develop appreciable size ceramic $Nd:Y_2O_3$ laser materials with high Nd concentration quenching limits along with excellent optical quality. We have produced spherical non agglomerated and monodisperse metastable ceramic powders of undoped Y_2O_3 and $Nd:Y_2O_3$ with 1 at.% and 2 at.% Nd^{3+} ions. These powders were consolidated first to form cylinder/disk

shape green bodies by a hydraulic press and then further densified using hot isostatic processing to produce the ceramic yttria samples. We have found in our previous work that many times the resulting material was translucent. Usually the translucent nature was a consequence of porosity in the samples. These pores act as scattering centers in the sample and prevent reasonable transmission. Through improved processing techniques we were able to produce both undoped Y_2O_3 and $Nd:Y_2O_3$ ceramics that were transparent. We briefly describe the production method in the following Section.

III. Nd:Y_2O_3 SAMPLE PREPARATION

Previously, we utilized ceramic $Nd:Y_2O_3$ samples using Y_2O_3 + Nd_2O_3 powders of required stoichiometry [16,17]. To obtain highly transparent materials in a more efficient way, various modifications to this process were carried out [18-20]. This procedure yielded highly transparent ceramic samples and is described as follows.

Powder production

Using the Rutgers plasma process [16], we can dope the rare earth materials, i.e. neodymium at desired levels. This is because of the high temperatures involved. The experiments described here are conducted using a Sulzer-Metco 9MB, 80kW plasma system and quenching in water.

To further improve the powder quality, we have produced powder by injection of liquid chemical precursors (Yttrium nitrate and Neodymium nitrate dissolved in water) into a plasma. This new process uses a reaction tube, shown in Fig. 1. The reaction tube attachment makes provisions for rapid cooling, via expansion through a supersonic nozzle. The residence time and cooling in the plasma can be controlled by injecting extra cooling gas and by inserting an aerodynamic de-Laval nozzle in the reaction tube, which caused nanoparticles to nucleate from the vaporized gas stream. In preliminary trials, yields better than 95% have been obtained. Consolidation experiments on these powders will be described in a later work.

The microstructure and porosity of the samples were evaluated by optical microscopy. The phase composition of the powders and dense samples were analyzed by X-ray diffraction (Fig. 2). The analysis was carried out in a Siemens D5000 diffractometer, using $Cu_{K\alpha}$ radiation (40 kV, 30 mA), and JADE (version 7.0) for phase identification.

Powder consolidation

The consolidation process chosen for this work is HIP. The powders generated by the above process can be densified into parts with microstructures that can be controlled by varying the HIP conditions. The HIP schedule can be adjusted, as shown in Fig. 3, to control the exposure of the metastable powder to maximum temperature and the time required at maximum temperature to achieve full densification. As a result, the structure and porosity of the densified part can be controlled. During consolidation a steel HIP canister with a diameter of 25.4 mm (1") and length of 25.4 mm (1") was used. The canister was coated with Boron Nitride and filled with the powders produced. This container was then evacuated, at 300 $^\circ$C, and e-beam welded. Typical HIP schedules used for experiments are illustrated in Fig. 3 where pressure and temperature measurements taken during the HIP run are shown.

A low temperature hold enables thermal equilibrium in the material and a subsequent high temperature hold ensures a fully dense material. The low temperature hold and high temperature

hold can be seen in Fig. 3. Several experiments have been performed to identify the temperature window in which consolidation occurs. However, the starting materials need to be of high purity. For HIP to be effective, uniform starting powder sizes, high starting purities, and a wide processing window is necessary. In the case of undoped Y_2O_3 we have achieved transparency higher than in the case of doped material. This was primarily due to the fact that the size of the dopant powder used was not same as the Y_2O_3 powder, the densification was affected adversely by the powder size difference.

IV. OPTICAL CHARACTERIZATION

The optical properties of undoped and Nd doped Y_2O_3 powders and ceramic disks were determined through transmission, absorption, and emission spectroscopy. The preliminary ceramic samples were translucent in nature due to compaction/HIP problems. For efficient lasing, the ceramic material needs to be transparent at IR emission wavelengths with good optical quality. In our case optical quality implies achieving uniform dopant distribution and single phase characteristics, minimal porosity and grain size compatible with emission wavelengths for minimal scattering.

Powders:

Prior to preparing the transparent ceramic disks, we performed emission studies on powder samples using 800 nm diode laser excitation. As expected, undoped Y_2O_3 powders did not exhibit any near-IR emission. 1 at.% and 2 at.% Nd:Y_2O_3 powders samples showed intense Nd^{3+} emission lines in the ~900-1000 nm range ($^4F_{3/2}$->$^4I_{9/2}$), ~1050-1150 nm ($^4F_{3/2}$->$^4I_{11/2}$), and ~1300-1450 nm ($^4F_{3/2}$->$^4I_{13/2}$) (see Fig. 4) [6,11]. The linewidth of the emission features was limited by the resolution of the emission setup. As discussed earlier, the lines at 914 nm and 946 nm are of interest for UV ozone lidar applications. The emission lifetime of the 946 nm line was determined to be ~140 µs and ~80 µs for the 1 at % and 2 at % Nd:Y_2O_3 powder, respectively. The decrease in lifetime with higher Nd concentration is possibly due to concentration quenching. Some improvement of emission lifetime was achieved through annealing studies. For, example annealing the 2 at % Nd:Y_2O_3 powder at 1200ºC increased the lifetime to ~190 µs. Overall, the obtained Nd:Y_2O_3 powders exhibited shorter emission lifetimes then that `reported for Nd:Y_2O_3 bulk crystals (~300 µs) [11].

Ceramics:

Ceramic boules of undoped Y_2O_3 and Nd:Y_2O_3 (2 at.%) with dimensions of up to 1"diameter x 1" length were developed. From these boules, 0.9" x 1"x 2 mm slices were cut and polished. Figure 5a shows a photograph of a transparent undoped Y_2O_3 sample. An example of a transparent Nd:Y_2O_3 sample used in our measurements is shown in Fig. 5b. This figure also shows a translucent sample in the upper left corner for comparison.

The transmission curves of two ceramic samples over a range from 250-2000 nm are shown in Fig. 6. The undoped Y_2O_3 ceramic exhibited bandedge absorption at ~ 250 nm and an IR transmission as high as ~75 %. Note that the test samples were uncoated and hence the Fresnel losses are not accounted for. For Y_2O_3, the refractive index, n, is equal to 1.74 at 2000 nm, which leads to ~14% Fresnel reflection losses.

The Nd:Y_2O_3 ceramic sample showed a slightly reduced transmission with values of ~55% at IR wavelengths. In addition, this sample also revealed characteristic Nd^{3+} absorption lines in the

visible and near-IR spectral range. A high resolution absorption spectrum of the ceramic Nd:Y_2O_3 sample for the range from ~700-900 nm is shown in Fig. 7. The observed absorption features of Nd^{3+} ions are nearly identical to those reported for a single crystal of Nd:Y_2O_3 [11]. The peak absorption coefficient at ~821 nm was determined to be ~6 cm^{-1} with a linewidth of ~1 nm.

We then measured the emission spectra and lifetimes of un-annealed Nd:Y_2O_3 consolidated ceramic samples with 2 at.% Nd doping HIPed at 1400°C (see Fig. 8a). No significant spectral differences were observed for the emission from Nd:Y_2O_3 powders and ceramics. It is interesting to note, that the lifetime of the Nd:Y_2O_3 ceramic was more than twice as long as the powder sample [20] (see Fig. 8b). It appears that the ceramic formation process leads to a reduction of unwanted non-radiative decay losses. In an effort to further improve on the emission lifetime of Nd:Y_2O_3 ceramics, annealing experiments were carried out. The lifetime increased from ~230 μs before annealing to ~310 μs after annealing the sample at 1200°C for 36 Hr, which is very similar to the reported lifetime of Nd:Y_2O_3 single crystals [11]. Up to 2 at. % Nd:Y_2O_3 samples were prepared and no significant emission concentration quenching was observed. It appears, that higher Nd concentrations are possible, which would be important for applications in thin-disk lasers. Thus, in our work with ceramic Nd:Y_2O_3, we successfully achieved emission and lifetime characteristics that were comparable to those found in single crystal samples.

V. CONCLUSIONS

In summary, advances made in material processing techniques, have successfully led to the development of highly transparent ceramic materials. We have optimized the emission and lifetime characteristics of Nd:Y_2O_3 ceramics, comparable to single crystal Y_2O_3. Based on these results we have clearly established the feasibility of producing Nd:Y_2O_3 as a potential ceramic laser material. Ceramic Y_2O_3 with band-edge absorption of less then ~250 nm and uncoated sample transmission of ~75 % were developed. A transmission of greater than 50% for IR wavelengths was achieved for Nd:Y_2O_3 ceramics. The ongoing experiments involve further improving powder preparation to address segregation issues and to improve the transmission of Nd:Y_2O_3 ceramics. Also, up to 2" diameter boules are currently being prepared. Ceramic Nd:Y_2O_3 has enormous potential as a solid-state laser material for ozone and other trace gas detection and bio-chemical sensing applications.

VI. ACKNOWLEDGMENTS

REFERENCES

1. Narasimha S. Prasad, Upendra N. Singh, Floyd Hovis, Darrell J. Armstrong, "High energy single-mode all-solid-state, tunable UV laser transmitter," *Proc. of SPIE,* vol. 6214, 62140T, Laser Radar Technology and Applications XI; Gary W. Kamerman, Monte D. Turner; Eds. May 2006.

2. A. Ikesue, T. Kinoshita, K. Kamata and K. Yoshida, "Fabrication and optical properties of high performance polycrystalline Nd:YAG ceramics for solid-state lasers" *J. Am. Ceram. Soc*. vol. 78, pp.1033-1040, 1995.

3. A. Ikesue, Y. L. Aung, T. Taira, T. Kamimura, K. Yoshida, G. L. Messing, "Progress in Ceramic Lasers", *Annu. Rev. Mater. Res.* vol. 36, pp. 397-429, 2006.

4. J. Lu, J. Song, M. Prabhu, J. Xu, K. Ueda, H. Yagi, T. Yanagitani, A. Kudryashov, "High-power Nd: $Y_3Al_5O_{12}$ ceramic laser", *Jpn. J. Appl. Phys.* vol. 39, pp. L1048-1050, 2000.

5. J. Lu, K. Ueda, H. Yagi, T. Yanagitani, Y. Akiyama, A. Kaminskii, "Neodymium doped yttrium aluminum garnet ($Y_3Al_5O_{12}$) nanocrystalline ceramics: a new generation of solid-state laser and optical materials", *J. Alloys Compounds*, vol. 341, 220-225, 2002.

6. J. Lu, J. Lu, T. Murai, K. Takaichi, T. Uematsu, K. Ueda, H. Yagi, T. Yanagitani, A.A. Kaminskii, "Nd^{3+}: Y_2O_3 ceramic laser", *Jpn. J. Appl. Phys.*, vol. 40, pp. L1277-L1279, 2001.

7. 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:Y_2O_3 ceramic laser," *Appl. Phys. Lett.*, vol. 82, pp. 2556-2558, 2003.

8. J. Lu, K. Takaichi, T. Uematsu, A. Shirakawa, M. Musha, K. Ueda, H. Yagi, T. Yanagitani and A. A. Kaminskii, "Promising Ceramic Laser Material: Highly Transparent Nd^{3+}: Lu_2O_3 Ceramic," *Appl. Phys. Lett.*, vol. 81, pp. 4324, 2002.

9. Shirakawa, K. Takaichi, H. Yagi, J-F. Bisson, J. Lu, M. Musha, and K. Ueda, "Diode-pumped Mode-locked Yb^{3+}: Y_2O_3 Ceramic Laser," *Optics Express*, vol. 11, pp. 2911-2916, 2003.

10. J. Kong and D. Y. Tang, J. Lu, K. Ueda, H. Yagi, and T. Yanagitani," Diode-end-pumped 4.2 W Continuous Wave Yb: Y_2O_3 Ceramic Laser," *Opt. Lett*, vol. 29, pp. 1212-1214, 2004.

11. B. M. Walsh, J. McMahon, W. C. Edwards, N. Barnes, R. W. Equall, R. L. Hutcheson, *J. Opt. Soc. Amer. B,* vol. 19, pp. 2893-2903, 2002.

12. Harris, Daniel C., "Materials for Infrared Windows and Domes," SPIE Optical Engineering Press, Bellingham, Washington, 1999.

13. W.B. Grant, *Lidar for Atmospheric and Hydrospheric Studies in Tunable Laser Applications*, ed. F.J. Duarte, New York: Marcel Dekker, Inc., pp. 241, 1995.

14. H. Gleiter, "Nanocrystalline Materials'', *Progress in Materials Science*, vol. 33, issue 4, 1989 pp. 223-315.

15. R. W. Siegel, "Synthesis and Properties of Nanophase Materials'', *Mat. Sci. Eng. A: Structural Materials: Properties, Microstructure and Processing*, vol. 2, pp. 189-197,1993.

16. B.H. Kear, V. Shukla and R. K. Sadangi, "Metastable nanostructured materials and method for production of the same", Provisional patent application, October 2004.

17. R.K. Sadangi, V. Shukla and B.H. Kear, "Processing and Properties of $ZrO_2(3Y_2O_3)$–Al_2O_3 Nanocomposites*,"* Journal of Refractory metals and hard materials, Vol.23 pp 363-368 2005.

18. S.B. Trivedi, S.W. Kutcher, C.C. Wang, G.V. Jagannathan, K. jia, R. Rosemeier. "Solid-state ceramic laser material for remote sensing of ozone using Nd:Yttria" On-going Phase II

Contract #NNL06AA21C. Dec 2005 – Dec 2007. Sponsored by NASA Langley Research Center.

19. Narasimha S. Prasad, Sudhir B. Trivedi, Susan Kutcher, Chen-Chia Wang, G. Jagannathan, Uwe Hommerich, Vijay Shukla, Rajendra Sandangi, Bernard Kear. "Development of solid-state ceramic material using Nd:Yttria", Solid State Lasers XV: Technology and Devices. *Proc. of SPIE,* vol. 6100, pp. 287-296, 2006.

20. Narasimha S. Prasad, S. B. Trivedi, S. Kutcher, C.C. Wang, G. Jagannathan, U. Hommerich, V. Shukla, R. Sandangi, "Development of solid-state laser material using ceramic Yttria," *Proc. of SPIE*, vol. 5887, pp. 17-1 to 17-6, 2005.