Nanocrystalline Nd:YVO_4 Lasing Media

Chris Stoafer
Chemistry, California Polytechnic State University, San Luis Obispo

NNIN REU Site: Nanotech @ UCSB, University of California Santa Barbara
NNIN REU Principal Investigator: Prof. David Clarke, Materials Dept. University of California, Santa Barbara
NNIN REU Mentor: Matthew Chambers, Materials Dept. University of California, Santa Barbara
Contact: cstoafer@calpoly.edu, clarke@engineering.ucsb.edu

Abstract:

The goal of this project is to create neodymium doped yttria-vanadate crystals (YVO_4) using the ceramic method of production for potential use as a lasing medium. The method involves creating neodymium doped yttria stabilized zirconia and reacting them with $LiVO_3$ to produce nanocrystalline neodymium doped yttrium vanadate crystals (Nd:YVO_4). This reaction is expected to create crystals with higher concentrations of Nd in YVO_4 than bulk synthesis allows, which could potentially yield increased lasing efficiency.

Introduction:

One of the main limitations to improving solid-state lasers are the concentration limitations of the luminescent dopant in the lasing medium. The recent advancements in ceramic production of lasing media combined with the increased dopant levels achievable in nanocrystalline materials may provide a means to push the concentration limits.

This project uses a $LiVO_3$ flux technique to produce nanocrystalline neodymium doped yttrium vanadate (Nd:YVO_4) from a neodymium doped yttria-stabilized zirconia base in order to reach higher concentrations of neodymium than bulk synthesis allows. Such nanocrystals could then be combined and sintered into a single body.

Sacrificial Flux Crystal	%Nd Initially	%Nd After Flux
$(Nd_{.02}Y_{.07}Zr_{.91})O_{2x}$	2.0%	13.6%
$(Nd_{.02}Y_{.07}Zr_{.91})O_{2x}$	2.0%	13.7%
$(Nd_{.02}Y_{.20}Zr_{.78})O_{2x}$	2.0%	11.9%
$(Nd_{.02}Y_{.20}Zr_{.78})O_{2x}$	2.0%	12.6%

Table 1: ICP-AES results of HCl dissolution of neodymium flux products.

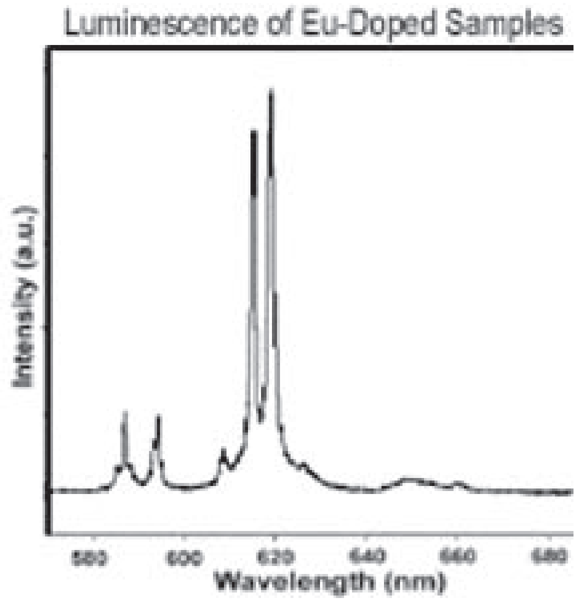

Figure 1: Eu:YVO_4 luminescence scan.

Higher concentrations of neodymium in the lasing medium may yield many benefits for this type of solid-state laser. For example, an increase in the efficiency of the lasing media may occur, allowing for more powerful lasers or smaller crystals and therefore more compact lasers. This could lead to a greater potential for laser applications and cheaper laser production.

Procedure:

This method required an yttria-stabilized zirconia (YSZ) precursor doped with rare-earth ions for the reaction to create the rare-earth ion doped YVO_4 (RE:YVO_4) crystals. Eu, which luminesces in the visible and whose spectra can be readily used to monitor changes in crystal structure, was used as well as Nd. TheYSZ was made with a precipitation method by mixing quantified amounts of zirconium acetate solution, yttrium nitrate, and the desired rare-earth ion nitrate (either europium or neodymium). This solution was then slowly added to concentrated ammonium hydroxide so the mixture would precipitate into nanocrystals. These nanocrystals were then collected by vacuum filtration, combined into a pellet and sintered.

This pellet was then placed into a platinum crucible with a proportion of $LiCO_3$ and V_2O_5, so that when they melted they

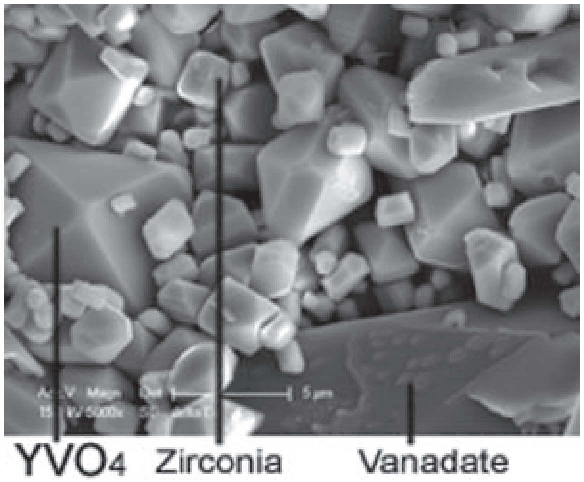

Figure 2: SEM of product mixture from Eu:YVO4 flux.

would form $LiVO_3$ and CO_2. This crucible was then heated to 1050ºC, where the $LiVO_3$ melted and reacted with the crystal pellet to create the RE:YVO_4 crystals, lithia, depleted zirconia and an excess vanadate. The water-soluble material (lithia and vanadate) was then removed with a water dissolution and the water-insoluble material was collected by vacuum filtration (RE:YVO_4 is water-insoluble). A luminescence plot was then taken of this sample to determine what wavelength of light the rare-earth ion emits when energized (Figure 1). An SEM image with an energy dispersive x-ray elemental map were taken to determine what compounds were in the water-insoluble material. A portion of this material was then dissolved in concentrated HCl to dissolve the RE:YVO_4. This solution was then analyzed with inter-coupled plasma-atomic emission spectroscopy (ICP-AES) to determine the concentration of the rare-earth ion in the crystal.

Discussion and Conclusions:

The luminescence plot of a sample made with europium showed significant peaks around 615 nm and 620 nm as seen in Figure 1. The spectrum is dissimilar to that seen in europium doped zirconias in that there is no peak observed at 580 nm, and the $^5D_0 \rightarrow {}^7F_1$ triplet centered at 590 nm in zirconia appears as two triplets centered at 585 nm and 595 nm; this result suggests that the rare-earth dopant is fully leached from the zirconia during the reaction. The SEM images (for example in Figure 2) showed a mixture of differently shaped nanocrystals and the energy dispersive x-ray results showed that YVO_4 crystals had been produced along with zirconia crystals, and some of the vanadate failed to dissolve (shown in Figure 3). The ICP-AES showed that the percent of the rare-earth ion (in this case neodymium) in the HCl-dissolvable material (Nd:YVO_4, but not ZrO_2, can be dissolved in HCl) was around 13%, which is much higher than the normal percentage in bulk-synthesized lasing media which is about 1%. These ICP-AES results indicate that the rare-earth dopant becomes concentrated in the YVO_4 crystals during processing, but since the YVO_4 crystals were not isolated there may have been some rare-earth ion leached from other phases in the sample, resulting in an over-estimate of dopant concentration in the YVO_4 crystals. The completed analysis gave some initial results about the success of our method, but more work needs to be done in order for these analytical techniques to be more accurate, and lasing efficiency has not yet been assessed.

Future Work:

The next step, to proceed in the analysis and development of this method, would be the isolation of the RE:YVO_4 crystals. More ICP-AES tests would then be run to determine the concentration of the rare-earth ion in the crystals. Following the ICP-AES analysis, the lasing efficiency of the crystals would then be measured and the method optimized to produce the highest lasing efficiency possible.

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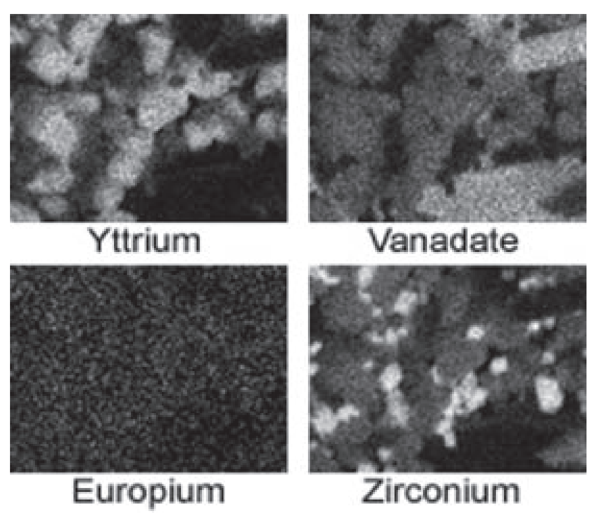

Figure 3: Energy dispersion x-ray of SEM sample.