

## RARE-EARTH DOPED PHOSPHATE GLASSES FOR NEODYMIUM LASER SYSTEMS POSSESSING A GREATLY ENHANCED PUMP POWER CONVERSION

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### ABSTRACT

Neodymium doped glasses, lasing at 1.06  $\mu\text{m}$  and excited by a Xe lamp, are of interest for numerous commercial and military applications. Dominant issues known to limit pump power conversion efficiency include solarization from the Xe lamp's UV spectral component, amplified spontaneous emission (ASE) from the  $\text{Nd}^{3+}$ , and the spectral mismatch in Xe output power with the strongest absorption bands of the  $\text{Nd}^{3+}$ . This work presents spectroscopic results and discusses the synergistic interactions found in a phosphate glass doped with  $\text{Ce}^{3+}$  to prevent solarization,  $\text{Sm}^{3+}$  to inhibit ASE, and  $\text{Eu}^{3+}$  to radiatively sensitize the  $\text{Nd}^{3+}$  absorbing the portion of the Xe emission spectrum previously unused. This triply doped system is shown to enhance the output power from the  $\text{Nd}^{3+}$  laser rod by 50 % over undoped analogs.

### INTRODUCTION

The laser cavity is one of the components in the solid state laser system and is used to filter the UV part of pump radiation and as well as to absorb any laser light that might lead to amplified spontaneous emission (ASE) on back-reflection through the gain region. In addition to these basic requirements, rare-earth dopants were added to this material in order to improve further the conversion efficiency of the pump energy. More specifically, we studied that inclusion of europium into a cerium and samarium codoped phosphate cavity glass that surrounds a Nd laser rod and xenon pump lamp in a 'figure-8' arrangement. Phosphate glasses were chosen because they possess a large glass formation region, are good host for fluorescent ions, and shows good thermo-mechanical and chemical properties. In addition to the  $\text{Ce}^{3+}$  that will be shown to prevent solarization, and the  $\text{Sm}^{3+}$  that limits ASE,  $\text{Eu}^{3+}$  was added to preferentially

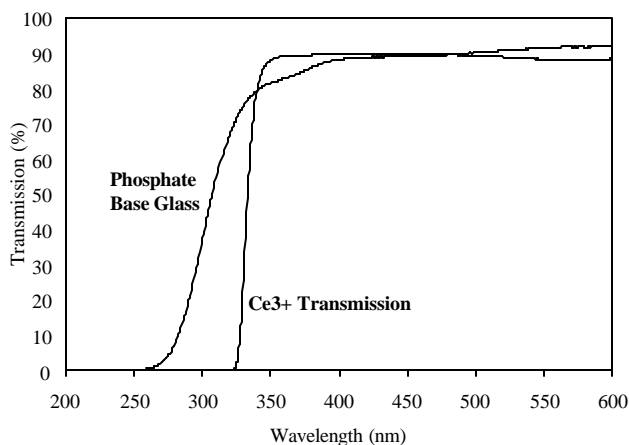


Figure 1.  $\text{Ce}_2\text{O}_3$  doped glass as antisolarant cutting off the pump lamp UV radiation below 325 nm.

absorb the pump light in the 300 - 500 nm region [1]. This was postulated to enable an increase in the overall pump power conversion efficiency since  $\text{Eu}^{3+}$  could absorb these energies that  $\text{Nd}^{3+}$  does not and radiatively emit at wavelengths overlapping the strongest absorption bands of the  $\text{Nd}^{3+}$ . The transferring of this unused energy by radiative sensitization to absorbable wavelengths by the laser material is the main point of this work.

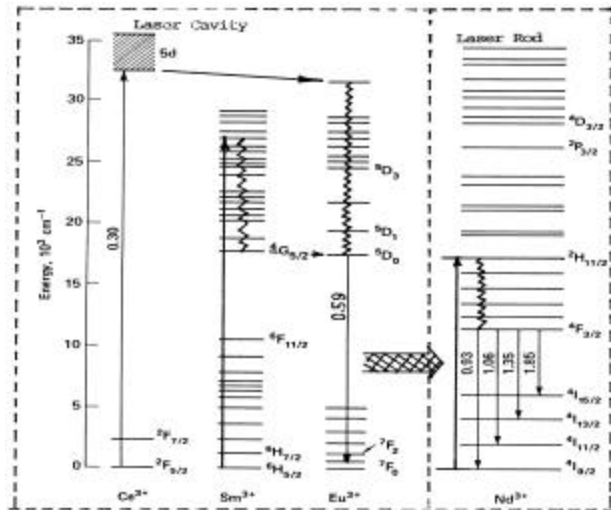
## EXPERIMENTAL

All rare-earth doped phosphate glasses were melted from high purity raw materials in platinum crucibles. A special bubbling technique was applied to remove the water from glasses [2]. A fining process was used to obtain a high order of homogeneity in the glass with the controlled atmosphere. After the fining process, the glass was gradually cooled down to the cast temperature and then was cast into a preheated aluminum mold. The annealing process took 18 hours to cool the glass down to the room temperature. The glass was cut into 2.54cm x 2.54cm x 1cm size with two parallel surface polished. All transmission and absorption spectra were measured by PE-Lambda 9 spectrophotometer and fluorescence and excitation spectra were measured using a PE-LS50B luminescence spectrometer.

## RESULTS AND DISCUSSION

### Preventing Solarization

The spectral properties of an optical material can be changed when it is exposed to short wavelength, near bandgap radiation. This is known as solarization and has the detrimental effect of lessening the transmission of pump or laser light through the host. UV antisolarants were studied to prevent color center formation.  $\text{Ce}^{3+}$  was found to be an excellent UV antisolarant because it possesses a strong and broad  $f-d$  absorption that overlaps the UV components of the Xe lamp (see Figure 1) [3]. For the europium doped glasses used to sensitive the laser material (discussed further below), the addition of  $\text{Ce}^{3+}$  was found to be doubly beneficial since the energy absorbed by the  $\text{Ce}^{3+}$  in preventing solarization was subsequently transferred to the  $\text{Eu}^{3+}$ . This was determined by measurement of the fluorescence properties of  $\text{Ce}^{3+}:\text{Eu}^{3+}$  doped glasses.



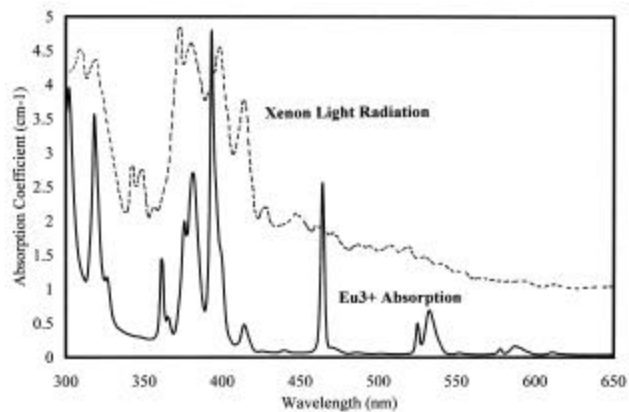
these glasses then was quantified for the prevention the ASE from any off-axis Nd<sup>3+</sup> laser emission (see Table 1). Sm<sup>3+</sup>, which has a large absorption cross section at 1064 nm and no absorption band overlap with Nd<sup>3+</sup> or the Eu<sup>3+</sup> that will be used to sensitize Nd<sup>3+</sup>, was found to provide the greatest overall benefit [4]. In addition, it was found to sensitize the Eu<sup>3+</sup> by the energy transfer from its <sup>4</sup>G<sub>5/2</sub> excited state to Eu<sup>3+</sup> <sup>5</sup>D<sub>0</sub> level (see Figure 2).

**Table 1. Laser Wavelength Absorber Selection to Prevent ASE in Laser Material**

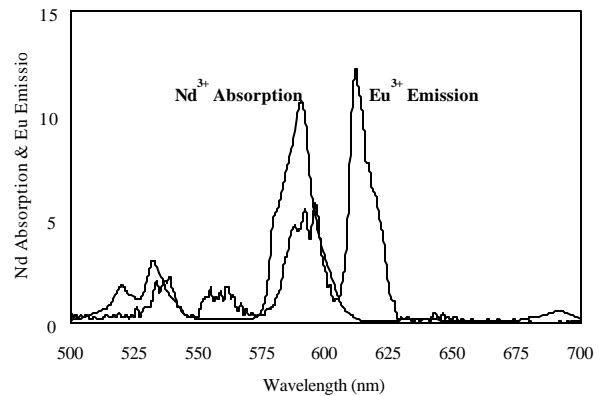
Doping Ion	Dy <sup>3+</sup>	Pr <sup>3+</sup>	Yb <sup>3+</sup>	Sm <sup>3+</sup>
Peak Wavelength (nm)	1092	1000	975	1070
Absorption Cross Section at 1064 nm (cm <sup>2</sup> )	1.77E-21	2.51E-22	9.11E-24	2.58E-21

*Radiative Sensitization of the Laser Ions*

The main radiative sensitizer ion was selected from the trivalent rare-earth ions including Ce<sup>3+</sup>, Pr<sup>3+</sup>, Sm<sup>3+</sup>, Gd<sup>3+</sup>, Tb<sup>3+</sup>, Dy<sup>3+</sup>, Ho<sup>3+</sup>, Eu<sup>3+</sup>, Er<sup>3+</sup>, Tm<sup>3+</sup>, and Yb<sup>3+</sup>, by measuring their absorption and fluorescence spectra and determining the spectral overlap to the Xe emission spectrum and the Nd<sup>3+</sup> absorption spectrum. Following these studies, Eu<sup>3+</sup> was selected due to its strong absorption in the UV region where Nd<sup>3+</sup> does not possess any bands (Figure 3) and its strong fluorescence at 550 – 600 nm which does overlap the strongest Nd<sup>3+</sup> absorption bands (Figure 4). Both of the Eu<sup>3+</sup> absorption and fluorescence mechanisms were studied to quantify better its energy level structure and relaxation dynamics in the phosphate host glass. The absorption spectrum of Eu<sup>3+</sup> in a phosphate glass arises from transitions to higher energy states from the <sup>7</sup>F<sub>0</sub> ground state and thermally populated <sup>7</sup>F<sub>1</sub> level. This thermally populated level is actually beneficial in this case since it permits a greater amount of the pump radiation to be absorbed and radiatively transferred to the



**Figure 3. Eu<sup>3+</sup> absorption overlap with the xenon pump lamp emission.**



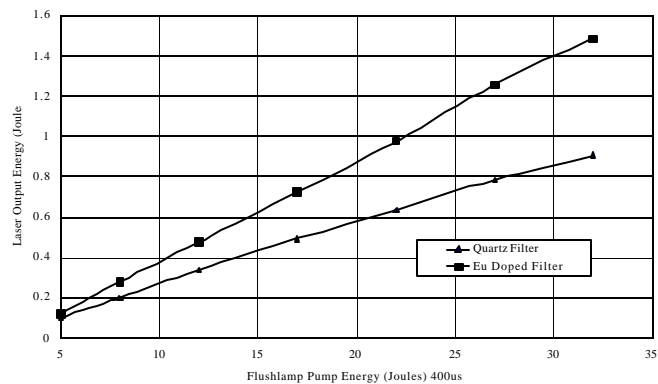
**Figure 4. Eu<sub>2</sub>O<sub>3</sub> (16 Mol.%) doped phosphate glass fluorescent spectrum (320 nm excitation) and Q-100 Nd phosphate laser glass (3 Wt.%, Kigre, Inc) absorption spectrum. Note overlap of Eu<sup>3+</sup> emission with Nd<sup>3+</sup> absorption.**

$\text{Nd}^{3+}$ .  $\text{Eu}^{2+}$  also was studied since its very strong and broad absorption bands ( $f - d$  transition with peak at 270 nm) would absorb most of the UV pump energy due to its large absorption coefficient. However, the difficulty reducing  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  without affecting the  $\text{Ce}^{3+}$  or  $\text{Sm}^{3+}$ , or the phosphate glass, made the use of divalent europium impractical.

Orange and red fluorescence was observed under Xe lamp excitation from transitions between the  $^5\text{D}_0$  excited state and the lower lying  $^7\text{F}_J$  ( $J = 1,2$ ) levels. Multiphonon relaxation processes limit radiative transitions from these higher  $\text{Eu}^{3+} ^5\text{D}_J$  energy levels to the lower energy states so the  $^5\text{D}_0$  is the only state that radiatively emits. These nonradiative relaxations are beneficial in the present case since the strong emission from the  $^5\text{D}_0$  state in phosphate glasses at 590 nm overlaps well the main absorption bands of  $\text{Nd}^{3+}$  in the laser host. Given the large energy gap of  $12.6 \times 10^3 \text{ cm}^{-1}$  between the  $^5\text{D}_0$  state and the next lower lying  $^7\text{F}_6$  state, there is a low negligible probability of nonradiative relaxations in phosphate glasses and a near unity quantum efficiency for the  $^5\text{D}_0$  emission. Further, inspection of the emission spectrum from the  $\text{Ce}^{3+}$  and  $\text{Sm}^{3+}$  glasses also doped with  $\text{Eu}^{3+}$  there appears to be no energy transfer back from  $\text{Eu}^{3+}$  to  $\text{Sm}^{3+}$  in the phosphate glass since only the  $\text{Eu}^{3+}$  emissions were observed.

### Laser Performance

Lastly, the phosphate glass codoped with  $\text{Ce}^{3+}:\text{Sm}^{3+}:\text{Eu}^{3+}$  was melted and its transmission, fluorescence, and excitation spectra were measured in order to evaluate its spectral properties in regards to serving as a Nd laser cavity glass. The codoped phosphate glass cavity was assembled in the Nd:YAG laser system to test its performance by measuring the power output at  $1.06 \mu\text{m}$  as a function of the Xe pump power. A 50% increase in pulsed laser output power was observed in this system when compared to quartz or Pyrex flowtubes (Figure 5). This is a remarkably large improvement in the conversion efficiency of the Xe pump energy and marks a highly valuable contribution to the materials engineering of laser systems.



**Figure 5. Eu:Sm:Ce codoped phosphate cavity glass sensitization laser performance test.**

### CONCLUSION

Rare earth doped phosphate cavity glasses for Nd:lasers were studied in order to enhance the conversion of pump power to the laser emission.  $\text{Ce}^{3+}$  was found to be an efficient antisolarant to limit color center formation from the UV components of the Xe pump lamp.  $\text{Sm}^{3+}$  was found to serve well as a selective wavelength absorber to prevent ASE.  $\text{Eu}^{3+}$  doped into the cavity glass was found to absorb strongly the Xe pump light that would normally be unused in the 300 – 500 nm ranges where the  $\text{Nd}^{3+}$  laser ion does not

absorb. Nonradiative relaxation of this absorbed energy to the  $\text{Eu}^{3+} \ ^5\text{D}_0$  state resulted in the efficient emission at wavelengths that overlapped the strong absorption bands of the  $\text{Nd}^{3+}$  and act as a radiative sensitizer. The  $\text{Ce}^{3+}$ , as antisolarant, and  $\text{Sm}^{3+}$ , as ASE inhibitor, were also found to sensitize the  $\text{Eu}^{3+}$  emission without energy back-transfer. A Nd:laser system surrounded by the  $\text{Ce}^{3+}:\text{Sm}^{3+}:\text{Eu}^{3+}$  triply doped phosphate cavity glass exhibited a 50% increase in its output and clearly shows the commercial potential of this work.

## REFERENCE

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