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K. I. Schaffers
S. A. Payne

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Crystal Growth of Optical Materials for Advanced Lasers

Kathleen I. Schaffers and Stephen A. Payne

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During FY96, two specific projects have been addressed, Yb-doped fluoroapatite (Yb:S-FAP) and Cr:ZnSe crystals, which are being used as the gain media to develop diode-pumped solid-state lasers (DPSSL). Both materials have unique properties for near infrared to mid-infrared applications. However, as with most new materials, there are defects in the crystals that create optical losses and reduce the efficiency of the lasers. Therefore, the source of the losses in the crystals has been studied and techniques have been developed to reduce and/or eliminate defects to aid in the growth of high optical quality crystals to increase laser efficiency.

Yb:S-FAP [Yb³⁺:Sr₅(PO₄)₃F]

Yb:S-FAP and its derivatives have been targeted as candidates for use as diode-pumped solid-state lasers (DPSSL) for high average power applications. Specifically, these crystals have been chosen as the gain media for the development of the Mercury Laser which is a gas-cooled-slab (GCS) DPSSL.¹ The scope of this project was to produce high-quality crystals for initial testing and for future implementation in laser systems. Yb³⁺-based lasers have only recently been studied in the laser community, therefore, the Yb:S-FAP crystals are not yet commercially available and had to be grown and studied at LLNL.

Crystals of Yb:S-FAP are grown by the Czochralski method where a crystalline Yb:S-FAP seed is inserted into a molten mixture of the material components for growth. At the appropriate temperature and gradients, crystallization onto the seed will begin and a crystal is then slowly pulled from the melt at approximately 1 mm/hr while rotating at 20 rpm. Typical boule sizes are up to 1 inch in diameter by 7" in length.

Two distinct defects can be present in as-grown boules of Yb:S-FAP: cloudiness from precipitation of starting components at the growth interface and core-type defects. During FY96 we developed a high-temperature post-growth annealing process that has been successful in alleviating the cloudiness that appears in as-grown boules. In this process, the crystal is suspended over the melt surface for up to 7 days in a temperature zone of the growth furnace that is ~300°C below the melting point. By using this technique, it has been possible to produce crystals with < 0.1%/cm optical scattering losses and < ~1%/cm impurity absorption losses at the emission wavelength (1047 nm) of the laser. While these specifications are adequate for efficient laser operation, additional improvements may be possible.

To further study and understand the source of the defects, a series of experiments have been performed to anneal away the cloudiness in alternative atmospheres, including SrF₂, inert (argon), and slightly oxygen rich; all have proven inadequate. The cloudiness worsened for the SrF₂ and oxygen rich cases and there was only a slight improvement in the argon atmosphere. One explanation for these results is that some component of the Yb:S-FAP melt is diffusing into the boules. However, it has been shown that the temperature for annealing is likely the most important parameter. Core defects are another issue that must be addressed to make more efficient use of the boules that are grown. These defects manifest themselves as "hair-like" streamers, about 1-10 mm in length, that begin at approximately 4-5 cm down the boule, and spread out in a "pyramid" formation down the length of the boule (Figure 1). In addition, the number of defects appear to increase with Yb concentration in the melt. This statement is supported by Scanning Electron Microscopy (SEM) X-

ray analysis of a core defect where the dominant component was measured to be Yb-based, likely Yb_2O_3 or YbOF . Experimental data suggests that there is a stoichiometry problem that develops in the melt over time as the crystal is growing. The improvements realized by adding excess SrF_2 to the starting melt composition imply that the vaporization of SrF_2 at 1810°C from the melt surface creates an imbalance in composition and therefore the left over components precipitate out of the melt as core defects to maintain the correct stoichiometry. This important conclusion, based on the FY96 work, has significantly improved the potential for reducing and/or eliminating these defects in Yb:S-FAP crystals.

Figure 1

High-quality crystals of La-doped S-FAP have also been grown for use as end caps for Yb:S-FAP crystals used in a study for the Laser Isotope Separation (LIS) program to predict the potential of replacing the copper vapor lasers with a DPSSL. These end caps eliminated problems with cracking from thermal stresses in the laser rods and allowed the success and completion of this phase of the project.

In addition, for many applications, the absorption band [full width at half maximum (FWHM) $\cong 5$ nm] of Yb:S-FAP is too narrow for ideal pumping efficiency at 900 nm when using large, low-cost diode arrays (FWHM $\cong 6$ -8). This nonideal overlap only utilizes approximately 75% of the available pump power which increases the number and cost of the diodes required for the laser designs. Therefore, we attempted to broaden the absorption band of the Yb crystals to better accommodate the performance of the diode arrays while simultaneously maintaining all other favorable laser and materials properties for efficient operation at high peak power. To accomplish these goals, crystals of $\text{Yb:Sr}_{5-x}\text{Ba}_x(\text{PO}_4)_3\text{F}$ were grown where $0 \leq x \leq 5$.² Spectroscopic analysis of these mixed crystals shows that with increasing Ba in the Yb:S-FAP lattice, the absorption linewidth broadens from 5 nm for $x = 0$ to 13-15 nm for $x = 1$ and 2, with a continuous increase for intermediate concentrations (Figure 2a). This increase is more suitable for diode pumped lasers. The emission spectra were also studied to predict the effect of Ba on the ability to extract energy from the gain media. What we see is that for Ba concentrations from $x = 0$ to $x = 2$, there tends to be a continual decrease in emission cross-section or intensity by only about a factor of two (Figure 2b). These initial results predict that the $\text{Yb:Sr}_{5-x}\text{Ba}_x(\text{PO}_4)_3\text{F}$ crystals will offer the laser designer the ability to essentially "dial in" the properties required for different laser systems by modifying the Ba concentration.

Figure 2a

Figure 2b

$\text{Cr}^{2+}:\text{ZnSe}$

The second phase of the FY96 work was centered around Cr^{2+} -doped II-VI materials, such as $\text{Cr}:\text{ZnSe}$ and $\text{Cr}:\text{ZnS}$, which have been critical to the development of a tunable, diode-pumped mid-infrared laser. This novel class of Cr^{2+} lasers exhibit good efficiency and broad tunability in the 2 to 3 μm range when pumped with long-wavelength 1.65-1.8 μm InGaAsP laser diodes.³ The production of highly-doped, low optical loss $\text{Cr}:\text{ZnSe}$ and $\text{Cr}:\text{ZnS}$ crystals to improve laser performance has been the focus of the materials part of the project. Optical losses tend to be 10-20%/cm which significantly reduces laser efficiency.

There are three growth techniques available that have produced samples that lase: the Bridgman method, Seeded Physical Vapor Transport (SPVT),⁴ and diffusion doping.⁵ SPVT material appears to provide the best optical quality and lowest losses to date, but doping to high Cr^{2+} concentrations is not straightforward. Bridgman grown crystals tend to have large parasitic losses due to inclusions and/or voids which have been reported to be attributed to selenium-rich or metal-rich precipitates.⁶ Diffusion-doping, however, appears to be promising since both single crystal and fine-grained polycrystalline window material can be used; window material provides a unique opportunity since it can be obtained in very large size pieces with low impurity levels.

We have concentrated on diffusion doping which is a relatively simple solid-state technique to diffuse Cr vapor into crystals. The process entails sealing a ZnSe or ZnS crystal into an evacuated quartz ampoule with CrSe powder. This ampoule is then heated in an isothermal furnace at a temperature that sublimates the CrSe , creating a Cr atmosphere around the ZnSe crystal (Figure 3). By adjusting the diffusion time and temperature, control can be maintained over the Cr concentration achieved in the crystal. This process has generated approximately 3x higher doping in crystals than has been previously achieved by the Bridgman or SPVT methods. However, one complication that arises is that diffusion occurs at temperatures high enough to cause selective evaporation of the host crystal thus altering the stoichiometry so that production of defects is likely. By incorporating excess Zn vapor into the

diffusion ampoule to counteract evaporation from the crystal, we have been able to reduce the optical losses by over 50%.

The progress achieved to date on improving the optical quality and increasing the doping concentration of Cr in both ZnSe and ZnS has made a significant impact on the performance of the laser. Efficiencies are expected to increase further as this project continues and higher quality crystals are achieved as well as optimization of the laser geometry.

Figure 3

During FY96, we have studied and grown crystals of Yb:S-FAP, Yb:Sr_{5-x}Ba_x(PO₄)₃F, La:S-FAP, and Cr²⁺:ZnSe, for use as the gain media for diode-pumped solid-state laser architectures. The cloudiness in as-grown boules of Yb:S-FAP has been alleviated by a post-growth annealing process and the investigation of the core defects have led to a better understanding of their origin and possible methods of reducing or eliminating them to improve the quality of the crystals. By adding Ba to the Yb:S-FAP lattice [Yb:Sr_{5-x}Ba_x(PO₄)₃F] we have effectively increased the absorption linewidth to better accommodate diode-array pump performance. Finally, diffusion doping of Cr into ZnSe and ZnS host materials has proven a useful method for increasing the doping concentration and the addition of Zn into the process has led to ~50% lower losses in the crystals.

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