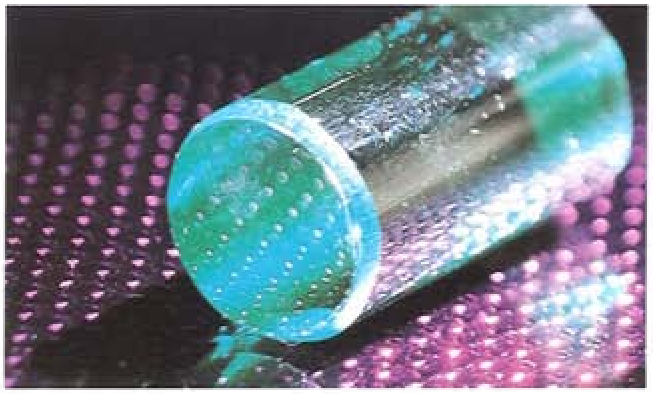
Cr:LiCAF and Cr:LiSAF: New Materials for Tunable Solid-State Lasers



Cr:LiCAF and Cr:LiSAF, two new laser materials recently discovered at LLNL, have properties that could lead to tunable solid-state lasers with dramatically improved performance.

ALTHOUGH dye lasers have dominated the market for tunable lasers for many years, there has been a continuing effort to develop new materials for tunable solid-state lasers. Tunable solid-state lasers would offer a number of important advantages over dye lasers, including a longer operating life, a longer energy-storage lifetime, more reliable and efficient flashlamp pumping, Q-switching (the sudden release of stored energy in a short pulse of light), flexible harmonic generation, and improved beam quality at high average power levels.

The commercial solid-state materials currently available—alexandrite ($Cr^{3+}:BeAl_2O_4$), titanium-sapphire ($Ti^{3+}:Al_2O_3$, or Ti:sapphire), and a selection of other materials (called F-center materials) that operate at cryogenic temperatures—all have some intrinsic limitations. Other tunable laser media have also been discovered, most of them based on the Cr^{3+} ion; however, the performance of many of these chromium lasers is substantially impaired because of excited-state absorption, color-center formation, or other parasitic absorption and loss mechanisms. Thus, the search for new materials continues.

Under the sponsorship of the Inertial Confinement Fusion (ICF) Program, and within a guided search for advanced ICF drivers, we recently discovered two new laser materials: $Cr^{3+}:LiCaAlF_6$ (Cr:LiCAF) and $Cr^{3+}:LiSrAlF_6$ (Cr:LiSAF).[1] These materials have properties that could lead to tunable solid-state lasers with significantly improved performance. In particular, Cr:LiCAF and Cr:LiSAF lasers:

- Can be efficiently pumped by flashlamps, diode lasers, or other lasers.
- Have demonstrated high laser efficiency (61% with laser pumping,

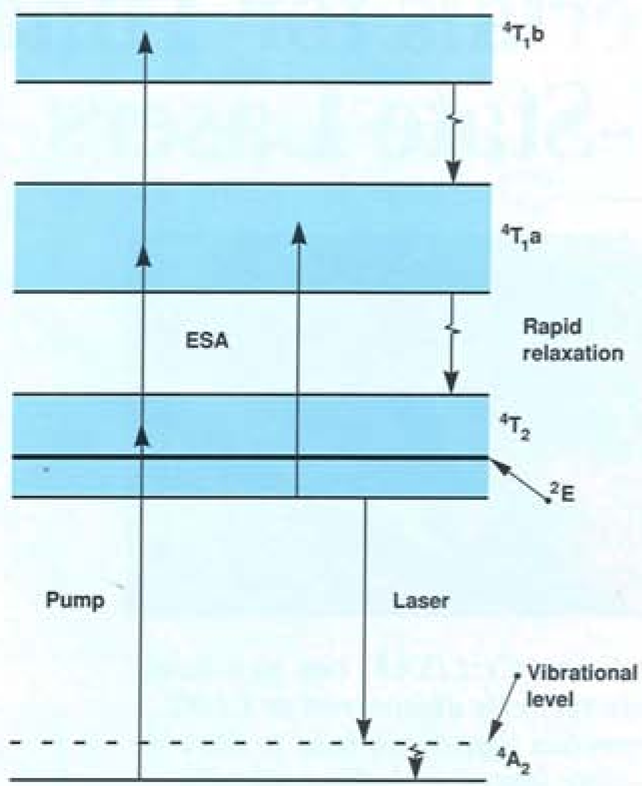


Figure 1. Energy levels of low-field Cr^{3+} showing the optical transitions involved in pumping, lasing, and excited-state absorption (ESA).

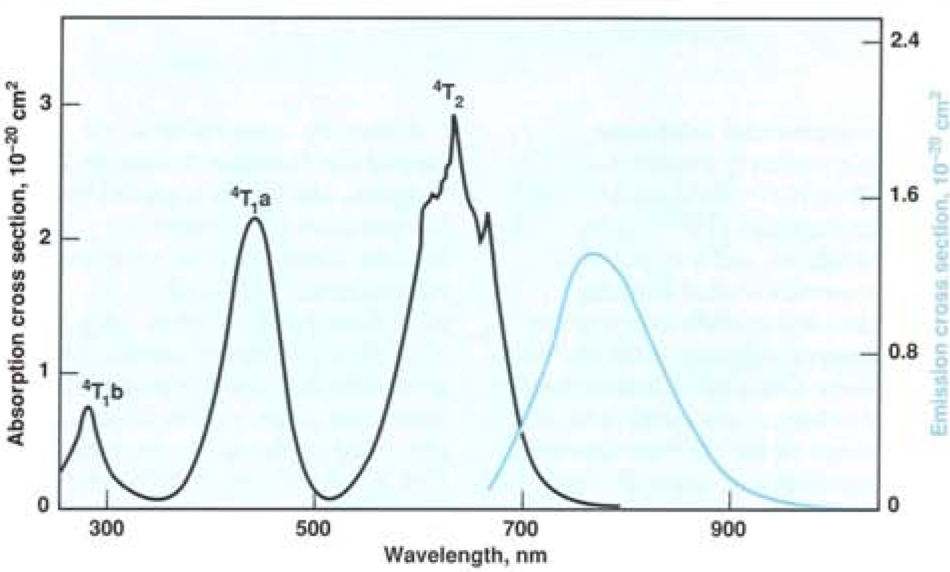


Figure 2. Typical absorption and emission spectra of Cr:LiCAF. Absorption bands in the red and blue leave a transparent region in the green (~500 nm) and provide for efficient absorption of pump light.

5% with flashlamp pumping).

- Offer a long energy-storage lifetime, which simplifies pumping requirements and makes the materials suitable for Q-switching and amplifier configurations (170 μs for Cr:LiCaAlF, 67 μs for Cr:LiSAF).
- Have a large gain bandwidth, allowing amplification of ultrashort (femtosecond) pulses.
- Have a large emission cross section for efficient extraction of stored energy.
- Are tunable from 730 to 1000 nm (red to infrared), and the frequency may be doubled to 365 to 500 nm (blue to green).
- Possess favorable thermo-mechanical properties, allowing for ease of thermal management and material fabrication.
- Are subject to very low thermal lensing, leading to good beam quality at high power levels.
- Have very low nonlinear indices ($n_2 \cong 0.4 \times 10^{-3}$ electrostatic charge units, or esu) and very high damage thresholds (>55 J/cm^2 at 10 ns), enabling transmission of undistorted high-intensity pulses through the material.
- Have a uniform distribution of the chromium ions, permitting very uniform and high chromium-doping levels throughout the laser medium.
- Have excellent optical quality, resulting in low loss and high output power.
- Require modest crystal growth conditions (melting point < 800°C).
- Are grown from inexpensive, nontoxic starting materials.

We have evaluated all of the important optical and physical properties of Cr:LiCAF and Cr:LiSAF and have found them to be excellent. Several laser configurations based on these new materials have been assembled at LLNL, other research institutions, and private companies. We are confident that Cr:LiCAF and Cr:LiSAF lasers will soon be widely used in a broad range of scientific, industrial, and defense applications.

Performance of Tunable Cr^{3+} Lasers

The performance of a laser material is determined by a combination of spectroscopic, thermal, and mechanical properties that affect laser efficiency, energy-storage lifetime, beam quality, and power-handling capability. We selected LiCAF and LiSAF as Cr^{3+} hosts because they would have very high laser efficiencies.

The electronic transitions between energy levels of Cr^{3+} that are used for optical pumping and lasing are shown in Figure 1. In tunable Cr^{3+} lasers, ions excited into the $^4T_2$ state by pumping in the red and blue absorption bands have a laser transition to the excited vibrational states of the ground $^4A_2$ level. This lasing scheme requires crystals in which the $^4T_2$ state (in its relaxed lattice configuration) is at a lower energy than the ^2E state (the upper laser level in ruby); such crystals are called "low field" hosts for Cr^{3+}. Excited-state absorption (ESA) originating from the upper laser level is also shown in Figure 1. ESA is an intrinsic process that reduces the efficiency of lasers. We have recently found that the severity of ESA in Cr^{3+} lasers can be mitigated by selecting a host crystal that provides a small substitutional site coordinated by a rigid framework of oxygen or fluorine ions.[2]

LiCAF and LiSAF were identified as promising host crystals on the basis of these criteria. Single crystals of these materials had never been grown synthetically before we selected them for use in Cr^{3+} laser applications. Thus, they represent "designer" laser materials.

Spectroscopic and Laser Properties

The absorption and emission spectra of Cr:LiCAF are shown in Figure 2. The absorption bands in the red and blue, which leave a transparent region in the green, give these Cr^{3+} materials a beautiful emerald green color (Figure 3) and, most important, provide for efficient absorption of pump light. In fact, calculations of single-pass pumping reveal that the pumping efficiency of Cr:LiCAF is about twice as high as that of typical neodymium-doped laser glass.[3] The absorption and emission spectra of Cr:LiSAF are broader and shifted to longer wavelengths than those of Cr:LiCAF, and the Cr:LiSAF absorption and emission cross sections are about

Figure 3. Cr:LiCAF has a beautiful emerald green color as a result of its absorption bands in the red and blue.

four times larger than those of Cr:LiCAF.

The lifetime of the upper laser level is 170 μs in Cr:LiCAF and 67 μs in Cr:LiSAF. Thus, these two materials complement each other. Cr:LiCAF has a better energy-storage lifetime. Cr:LiSAF has a higher emission cross section that permits better extraction of stored energy with short pulses without exceeding the damage thresholds of the laser elements and cavity optics.

We evaluated the laser efficiency (under continuous operation) of these two materials using the 647-nm line of a krypton ion laser to pump directly into the $^4T_2$ metastable state. The measured output power as a function of absorbed pump power is shown in Figure 4. The measured efficiency is 61%. The intrinsic efficiency is 86% (obtained by multiplying the measured efficiency by the ratio of the pump and laser wavelengths and correcting for passive loss in the crystal and laser resonator).

To place the performance of these new materials in perspective, we also investigated a number of the best Cr^{3+} laser materials (Table 1). The tuning ranges (or reported operating wavelengths) are also listed. The intrinsic laser efficiency is limited only by ESA and other pump-induced absorption processes (such as color-center formation), and thus provides a good criterion for judging the relative merit of the different materials. It is clear from Table 1 that LiCAF and LiSAF are two of the most efficient Cr^{3+} laser materials under continuous operation. We believe that ESA is a major reason for the lower efficiencies obtained with the other materials.

We also investigated the flashlamp-pumped laser performance of Cr:LiCAF using a rod of material (6.4 mm in diameter, 80 mm long) grown by Chai, Morris, and Long of Allied-Signal Corporate Research Center.[3] The rod was pumped by a single flashlamp in a close-coupled cavity. The early rods of Cr:LiCAF, grown by pulling from a melt, were quite lossy because of small scattering centers, and the best efficiency observed was only 1.6% (defined as the ratio of laser output energy to the electrical energy stored in the drive circuit). However, even with its high roundtrip scattering loss (49%), the Allied-Signal rod produced about 2 J of output energy in a ~100-μs long pulse. Improved material is now available and has led to much better performance. Recently, Chai, Stalder, and Bass (University of Central Florida) obtained up to 5% efficiency from Cr:LiSAF with flashlamp pumping.[4] This is comparable to the efficiency of a commercially available alexandrite rod of like dimensions under similar conditions.

Figure 4. Laser efficiency of Cr:LiCAF in terms of laser output power vs absorbed pump power. (Intrinsic efficiency is determined by multiplying the measured efficiency by the ratio of the pump and laser wavelengths and correcting for the passive loss in the crystal and laser resonator.)

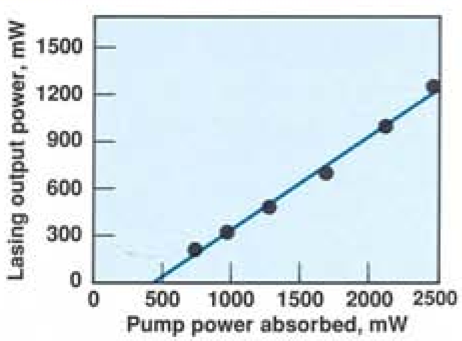


Table 1. Intrinsic laser efficiencies of chromium-doped laser materials.

Material	Lasing wavelength, nm	Intrinsic efficiency
$LiCaAlF_6$ (LiCAF)	720 to >840	0.86
$Be_3Al_2[SiO_3]$ (emerald)	720 to 842	0.86
$BeAl_2O_4$ (alexandrite)	701 to 850	0.76
$LiSrAlF_6$ (LiSAF)	780 to 1000	0.67
$BeScAlO_4$ (scalexandrite)	792	0.40
$Na_3Ba_2Li_3F_{15}$ (GFG)	786	0.34
$ScBO_3$	787 to 892	0.34
$Y_3Sc_2Al_3O_{12}$ (YSAG)	760	0.29

Thermal, Thermo-Optic, and Mechanical Properties

The performance of a solid-state laser material at high pulse energies or high average power is determined by its thermal, thermo-optic, and mechanical properties. The two problems encountered in high-power operation are (1) mechanical failure due to thermal stress and (2) degradation of beam quality caused by thermally induced changes in refractive index. The power level at which mechanical failure occurs is highest for materials with high fracture toughness, a low coefficient of thermal expansion, and good thermal conductivity. Good beam quality at high power, however, requires materials with low thermally induced changes in refractive index. We have measured these properties for LiCAF,[5] and although we have yet to measure them for LiSAF, we anticipate that they are similar in magnitude.

The fracture toughness and thermal conductivity of LiCAF are considerably smaller than the values found in the best oxide laser hosts, such as Nd:YAG, Ti:sapphire, and alexandrite (see Table 2). On the other hand, we have found that LiCAF (and possibly LiSAF) has very low thermal lensing in comparison with the oxide hosts.[4] For example, in a direct comparison of Cr:LiCAF and alexandrite in the same flashlamp-pumped cavity, the power of the thermal lens in Cr:LiCAF was seven times lower than that in an alexandrite rod with identical dimensions and a similar fractional absorption of light.

Crystal Growth and Optical Quality

Growing crystals of adequate size and optical quality is the most time-consuming and uncertain aspect of developing a new laser crystal. Cr:LiCAF was first grown synthetically at LLNL in 1987. We have been experimenting with various crystal growth processes. The first samples, grown by a zone-melting process, were small and lossy. In subsequent attempts,

Table 2. Qualitative comparison of various tunable laser systems.

Property	Cr:LiCAF	Cr:LiSAF	Alexandrite	Ti:sapphire	Nd:YLF	Nd:YAG	Dye (infrared)
Intrinsic efficiency	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent	Average
Storage lifetime	Excellent	Average	Excellent	Poor	Excellent	Excellent	Poor
Flashlamp absorption	Excellent	Excellent	Excellent	Poor	Poor	Poor	Average
Diode-laser absorption	Excellent	Excellent	Average	Poor	Excellent	Excellent	Average
Emission cross section	Average	Excellent	Poor	Excellent	Excellent	Excellent	Excellent
Thermal lensing (undesired)	Low	Low	Average	Average	Low	Average	High
Mechanical strength	Average	Average	Excellent	Excellent	Average	Excellent	Poor
Ultraviolet solarization (undesired)	Low	Low	Average	Average	Low	Average	High
Toxicity of materials	Low	Low	High	Low	Low	Low	High

crystals were pulled from a melt and grown by two variants of the Bridgman process. The as-grown crystals had micrometer-sized scattering centers, which have not yet been conclusively identified; the early crystals had scattering losses of several percent per centimeter.

Recently at LLNL, we have succeeded in nearly eliminating these defects in the crystals by a postgrowth annealing process. This annealing can be done on rods and slabs with centimeter-sized cross sections. The scattering losses of these annealed crystals are about 10^{-3} per centimeter, similar to the losses in good laser glass and crystals. We anticipate that Cr:LiCAF rods 1 cm in diameter and 10 cm long will soon be available with excellent optical quality.

In addition, large uniform doping with Cr^{3+} is possible in LiCAF and in LiSAF. The distribution coefficient of Cr^{3+} in LiSAF is very close to unity, and no significant reduction of crystal quality at high doping levels has been observed.[5] Therefore, the Cr^{3+} doping level can be tailored to provide the optimum pumping efficiency and uniformity for the desired application.

Cr:LiCAF and Cr:LiSAF vs Other Laser Materials

For tunable laser applications in the near-infrared (or frequency-doubled into the blue), Cr:LiCAF and Cr:LiSAF must compete with alexandrite, Ti:sapphire, and some dye lasers. Table 2 provides a qualitative rating of the important properties of these laser systems as well as for Nd:YLF and Nd:YAG.

It is clear that Cr:LiCAF and Cr:LiSAF excel for nearly all of the important properties. All of the solid-state laser materials have high intrinsic efficiencies, although the operating mode (continuous or pulsed) has a significant bearing on the actual laser efficiency. Table 2 shows that Cr:LiCAF and alexandrite both have low emission cross sections; for this reason, efficient fast-pulse extraction with Q-switching or amplifying is difficult with these laser materials. We also see that Ti:sapphire, in spite of its extraordinarily large tuning range (660–1170 nm), has an excited-state lifetime that is too short for efficient energy storage and thus cannot be pumped efficiently by flashlamps or diode lasers. Dye lasers do not have the capability of storing energy and are characterized by a very low saturation fluence; therefore, they are not well suited to many pulsed- and high-power applications. Cr:LiSAF has a better balance between excited-state lifetime and emission cross section and thus appears to have an advantage over the other materials.

In regard to average power capability, the major differences between fluoride hosts such as Cr:LiCAF and Cr:LiSAF, on the one hand, and oxide hosts such as alexandrite and Ti:sapphire, on the other, involve thermo-mechanical strength and thermal lensing. Table 2 shows that the mechanical properties of the oxides (alexandrite and Ti:sapphire) are clearly superior. However, it turns out that the oxide-based laser materials used in most applications possess mechanical properties that far exceed the necessary requirements. Thus, we expect that the mechanical properties of Cr:LiCAF and Cr:LiSAF will be satisfactory for nearly all applications.

Thermal lensing can severely degrade laser performance. Cr:LiCAF and Cr:LiSAF exhibit thermal lensing that is remarkably low, typically an order of magnitude lower than that exhibited by the oxide crystals. This feature is particularly useful for applications requiring high average power and high repetition rates.

In addition, Cr:LiCAF and Cr:LiSAF are relatively easy to handle. The starting materials for these crystals are nontoxic, unlike alexandrite (which contains a poisonous beryllium component) and many dyes (which are both toxic and inconvenient to handle). In addition, the materials for the LiCAF and LiSAF crystals melt at temperatures less than 800°C, whereas alexandrite and sapphire require temperatures greater than 1800°C. Obviously, the lower melt temperature for LiCAF and LiSAF greatly simplifies crystal growth conditions. Also, since LiCAF and LiSAF have distribution coefficients of unity, it is possible to grow large (>15-cm) boules of Cr:LiCAF and Cr:LiSAF with extremely large and uniform chromium-doping levels. (The distribution coefficient of the lasing ion is not unity for Nd:YAG, Ti:sapphire, or alexandrite, which limits the uniformity and doping levels in these materials.)

A direct comparison of Cr:LiCAF and Cr:LiSAF with alexandrite (the best Cr^{3+}-laser material currently available) clearly reveals the superiority of our new laser materials. Only very low chromium-doping levels (<0.3%) are possible with alexandrite, whereas very high levels (>40%) can be achieved with LiSAF with only modest chromium self-quenching of excitation energy. A higher doping level leads to more efficient flashlamp absorption and therefore a less costly pump system. We recently exploited this unique property by efficiently pumping a Cr:LiSAF laser at a wavelength of ~750 nm.[6] This is significant because powerful and efficient AlGaAs laser diodes operate at this wavelength, and they can be used to produce an efficient all-solid-state, diode-pumped tunable laser.

In addition, the emission cross section of Cr:LiSAF is much larger than that of alexandrite (4.8×10^{-20} vs 1.0×10^{-20} cm^2), leading to much more efficient pulsed energy extraction; this is a crucial parameter for laser amplifiers and Q-switched resonators. LiCAF and LiSAF also have much higher damage thresholds (>55 J/cm at 10 ns) and lower nonlinear indices (0.4×10^{-13} esu) than do alexandrite and the other oxide laser materials; these are important properties for high-peak-power applications. Lastly, alexandrite lasers must be operated at >80°C, whereas LiCAF and LiSAF can be operated at room temperature, eliminating the need for a cumbersome heater system.

Possible Applications of Cr:LiCAF and Cr:LiSAF

We anticipate that Cr:LiCAF and Cr:LiSAF will be most competitive in applications that require good beam quality at moderate power levels.[7] These new materials are very versatile: the level of chromium doping can be tailored to the specific application, the tuning range is substantial, and the energy-storage time and emission cross section support a variety of pulse formats and laser system configurations.

Numerous applications in basic science, industry, defense, and medicine are well suited to these new materials. Laser rangefinders and illuminators, undersea optical communications (frequency-doubled into the blue), spectroscopy, and pumping other lasers are examples of such uses. Another application being explored here at LLNL is the amplification of stretched femtosecond pulses, which are then recompressed to generate very high peak power from tabletop lasers. Such tabletop lasers can be used to study the physics of very high optical fields and to generate very high harmonics in the vacuum-ultraviolet region. The combination of broad gain bandwidth, long fluorescence lifetime, and adequate emission cross section make Cr:LiCAF and Cr:LiSAF ideally suited for this application.

Many of these applications are currently being pursued or seriously considered, both within the Laboratory and by outside organizations. In fact, nearly a dozen commercial laser manufactures have requested licensing rights from LLNL for these new materials. Several companies plan to grow the laser crystals, and others are interested in developing specific laser devices based on Cr:LiCAF or Cr:LiSAF for medical, scientific, manufacturing, or defense applications. The total market for tunable lasers is on the order of $25 million annually. We anticipate that Cr:LiCAF and Cr:LiSAF will support 10 to 20% of the market share within the next few years and may, in fact, generate a larger market.

Modern laser technology continues to be constrained by the limitations of the laser materials. In spite of the tremendous variety of electro-optics technologies currently applied in lasers, nearly all systems are based on one of perhaps half a dozen laser materials. Clearly, the creativity and ingenuity of scientists and engineers will be stimulated by the unique and exciting attributes of Cr:LiCAF and Cr:LiSAF.

Key Words: laser materials—Cr^{3+}:$LiCaAlF_6$ (Cr:LiCAF), Cr^{3+}:LiSrAlF6 (Cr:LiSAF); lasers—solid-state, tunable; material properties.

References

1. S. A. Payne et al., "$LiCaAlF_6$:Cr^{3+}: A Promising New Laser Material," *IEEE J. Quant. Electron.* **24**, 2243–2253 (1988); S. A. Payne et al., "Laser Performance of $LiSrAlF_6$:Cr^{3+}," *J. Appl. Phys.* **66**, 1051–1056 (1989).
2. J. A. Caird et al., "Quantum Electronic Properties of the $Na_3Ga_2Li_3F_{12}$:Cr^{3+} Laser," *IEEE J. Quant. Electron.* **24**, 1077–1099 (1988).
3. L. L. Chase et al., "Laser Performance and Spectroscopy of Cr^{3+} in $LiCaAlF_6$," in *OSA Proceedings on Tunable Solid State Lasers*, M. L. Shand and H. P. Henssen, Eds. (1989), Vol. 5, pp. 71–76.
4. M. Stalder, B. H. T. Chai, and M. Bass, "The Flashlamp-Pumped Cr:$LiSrAlF_6$ Laser," *Appl. Phys. Lett.* **58**, 216–218 (1991).
5. B. Chai, M. Mass, and M. Stalder, "Crystal Growth and Lasing Performance of Cr-Doped LiCAF and LiSAF Crystals," presented at Advanced Solid State Lasers Topical Meeting, Salt Lake City (March 5–7, 1990).
6. S. A. Payne et al., "Properties and Performance of the $LiCaAlF_6$:Cr^{3+} Laser Material," *Solid State Lasers* (SPIE Conf. Series, 1990), Vol. 1223, pp. 84–93.
7. S. A Payne et al., "752-nm Wing Pumped Cr:LiCAF Laser," *IEEE J. Quant. Electron.* **28** (4) (1992) (in press).
8. S. A. Payne, L. L. Chase, H. W. Newkirk, and W. F. Krupke, "Cr^{3+}-Doped Colquiriite Solid State Laser Material," U.S. Patent No. 4,811,349 (issued 7 March 1989).

For further information contact William F. Krupke (510) 422-5905 (left), Stephen A. Payne (510) 423-0570 (middle), or Lloyd L. Chase (510) 422-6151 (right).