EMERALD—A NEW GEM LASER MATERIAL

This invited article describes the physics, current status, and potential of emerald as a new laser source.

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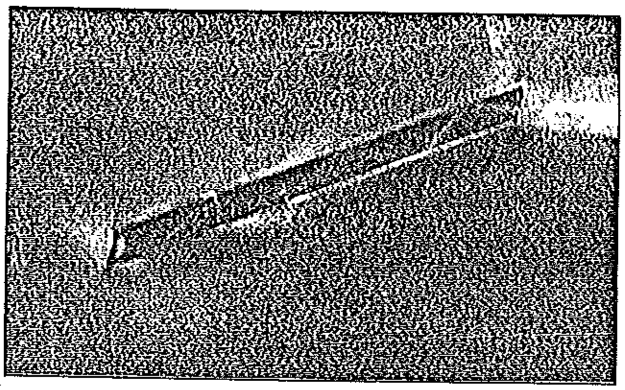

In the May 1983 *Laser Focus* Peter Moulton reviewed new developments in tunable solid-state lasers. Among the many listed materials, he pointed out the performance of chromium ions in different host crystals for suitable lasers. The operating wavelength range and lasing characteristics of Cr^{3+} ions in various hosts are sensitive to the particular crystal electric field. This is common to all transition metal ions in which the interaction of *d* electrons with crystal electric fields affects the matrix elements and energy levels.

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The chromium ion is the key behind the laser operation of two gem lasers: ruby and alexandrite, and also a promising new gem laser, chromium-doped beryl—commonly known as emerald. Already, tunable laser action has been achieved in flashlamp, laser pulse, and continuous-wave mode excitation with over 30% conversion efficiency.[1-3]

Background

Ever since alexandrite[4-6] was reported as a room-temperature-tunable laser material, researchers have been looking for other materials with similar properties with low crystal fields.[7-11] One candidate was emerald.

Recently, the authors at the Institute for Ultrafast Spectroscopy and Lasers at City College,[1-2] and M. L. Shand from Allied Corp.[3] reported laser action in emerald, a chromium-doped beryllium aluminum silicate (Cr^{3+} in $Be_3Al_2Si_6O_{18}$), and also demonstrated tunability of laser oscillation. The emission cross section [$\sigma_e = 1.4 \times 10^{-20}$ cm^{-2}] as well as gain characteristics of emerald were measured[3] to be approximately twice that of alexandrite ($BeAl_2O_4$:Cr^{3+}) and estimated[1,2] by calculations to be up to four times that of alexandrite. Emerald as a solid-state material appears to have the widest spectral bandwidth of any known laser material in which laser action has been achieved; this characteristic should permit the generation of subpicosecond pulses. Its modest gain and good energy storage capabilities should permit the generation of high peak powers. One of the important advantages of emerald as a laser medium is that it can work at elevated temperatures, a condition that increases the inversion population above the ground state. This property results in a major improvement in gain for the vibronic mode.

Properties of emerald associated with vibronic terminated transitions and temporal behavior of an optical phonon are of great interest in solid-state physics and nonlinear optics. Detailed knowledge of phonon properties is required for the computation of high power levels of line shape saturation, nonradiative loss processes, self-mode-locking, and "hole burning" in vibronic lasers.

These lasers are potentially important in technology as the basic elements of very broadband optical amplifiers and of tunable oscillators. The fundamental wavelength of emerald is, for example, ideal for the next generation of satellite laser ranging systems, which must use two optical frequencies to correct for atmospheric refraction. Such a laser might also be useful in space-borne altimeters that can measure sea state as well as surface pressure over the oceans. A high-peak-power emerald laser, combined with well-known nonlinear optical frequency-shifting techniques, would be an outstanding lidar transmitter for the measurement of atmospheric species distributions and temperature profiles.

Physics behind emerald

The basic concept of phonon-terminated transition of metal ions was proposed in the mid-1960s by McCumber[12] and experimentally observed first by Johnson et al. in Ni^{2+}-doped MgF_2.[13] The successful operation of alexandrite (Cr^{3+} in $BeAl_2O_4$) by Walling et al.[4–6] at room temperature as a tunable laser has led to the search for new crystals and glasses with broadband emission as potential laser materials. This has led us to renew research on emerald.[14–19]

Emerald is an excellent candidate for laser systems and ultrashort pulse generation. One of the important advantages of using emerald as a laser material is that it emits light over a very broad band (its fluorescence bandwidth at room temperature is 700–850 nm) and can thus be made tunable (see Figs. 1[a] and [b]). Another advantage is that it is a solid that may be Q-switched or mode-locked using dyes as saturable absorbers.

We feel that emerald is superior to alexandrite and ruby as a laser material for several major reasons (see Table 1):

- It has a weaker crystal field to act on energy levels of Cr ions, a significant advantage over other Cr-doped materials;
- Its higher gain—4 times greater than alexandrite—permits faster Q-switching and higher quality factor operation;
- As noted previously, the wide bandwidth of emerald will also enable the production of very short, high-intensity picosecond pulses, which are tunable in the visible and near-infrared.
- The broad absorption spectra of emerald (see Fig. 1[c]), which ranges from the visible up to 700 nm, allows the possibility of pumping by readily available flashlamps, or by suitable laser sources such as the krypton laser, and SHG and FHG from a YAG laser.

The laser action in emerald comes from the 4-level vibronic lasing model that is illustrated in Fig. 2. Because the upper laser level of emerald is phonon-coupled to the crystal lattice, raising the temperature increases the inversion population above the ground state. The result is a major improvement in gain with temperature for the vibronic mode. As noted previously, the crystal field that acts upon the energy states of the chromium ions in emerald is weaker than that of alexandrite and ruby. The crystal field parameters D_q for emerald, alexandrite, and ruby are about 1620 cm^{-1}, 1680 cm^{-1}, and 1820 cm^{-1}, respectively. The energy states modified by the crystal electric fields for emerald, alexandrite, and ruby are illustrated in Fig. 3. The most significant difference between emerald and other Cr-doped

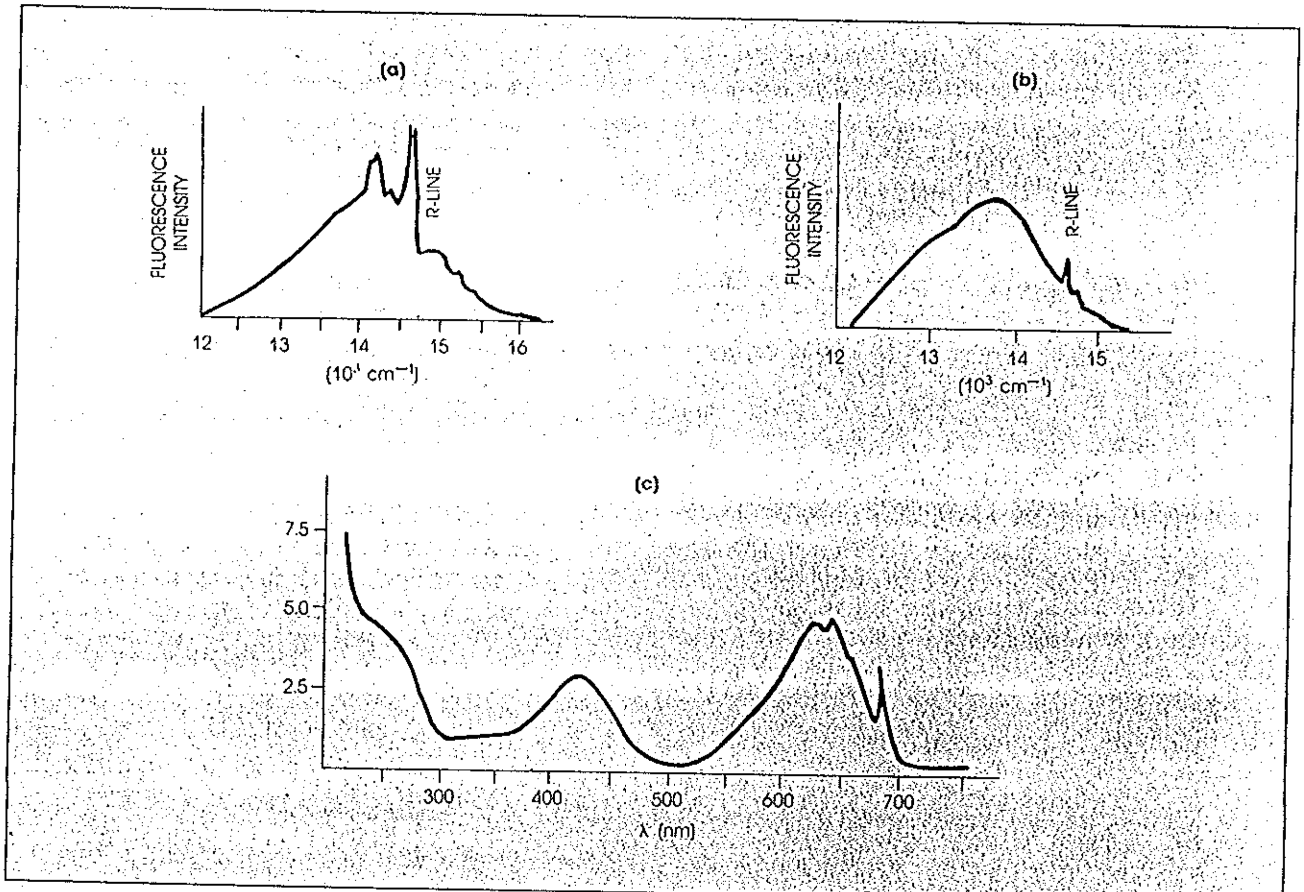

FIGURE 1. Room-temperature fluorescence of **(a)** alexandrite, **(b)** emerald, and **(c)** absorption spectra of emerald.

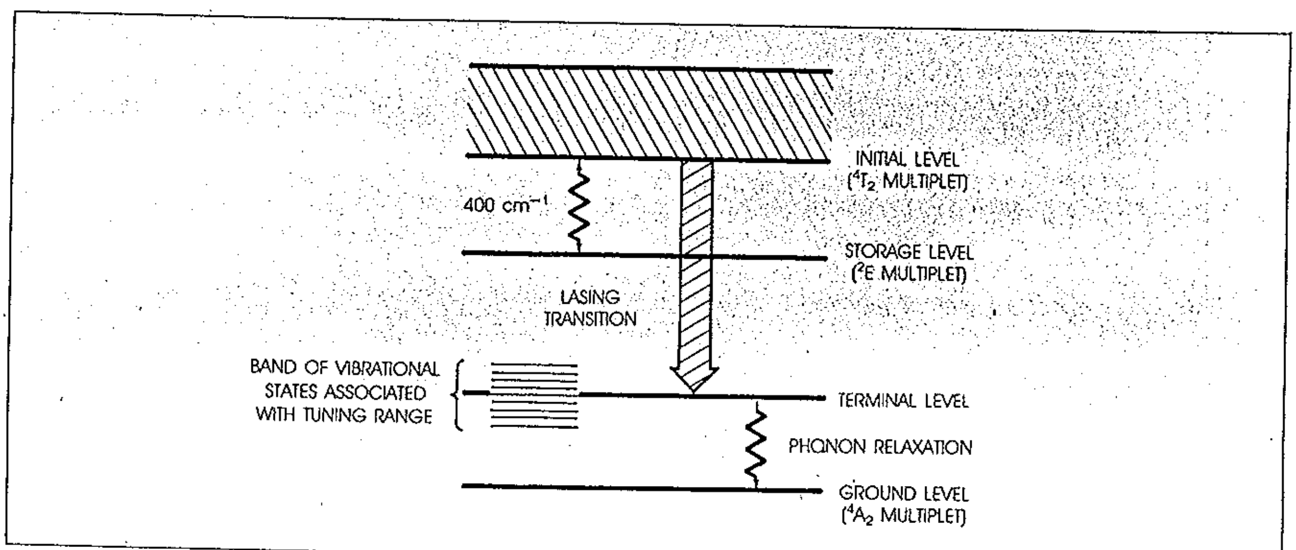

FIGURE 2. Vibronic lasing model.

materials is the smaller electric field surrounding the chromium ions. As a result, the two ^4T levels lie at slightly lower energies, closer to ^2E levels. The position of the ^2E band is essentially unaltered in these materials. In emerald the energy difference at room temperature between $^4T_2$ (responsible for broadband emission) and ^2E (R-line radiation) is about 400 cm^{-1}.[19] (This is in contrast to the energy differences [$^4T_2 - {}^2E$] for ruby[19] and alexandrite[6] of, respectively, 2300 cm^{-1} and 800 cm^{-1}.) This energy difference allows the repopulation of the $^4T_2$ level due to thermalization from the long-lived ^2E level. Therefore, emerald can have a relatively larger inversion of population of vibronic modes at room and higher temperatures. This increases the emission cross section, raising the gain and lowering the lasing threshold as compared with alexandrite and ruby lasers. In addition, the excited-state absorption measured by Fairbank et al. suggests little self-excited-state absorption by the laser emission.[14]

The nature of the excited state has an important consequence aside from determining the strength of the transition. Both the ground state $^4A_2$ and the excited state ^2E arise from the lower set of *d*-orbitals designated as t_{2g}, while the excited quartet $^4T_2$ has the configuration $t^2_{2g}e_g$. Since the e_g orbitals are pointed along the axes of the octahedron (at the ligands), one would expect that the promotion of an electron to an e_g orbital will result in a change of equilibrium internuclear distance between Cr^{3+} and its nearest neighbors. This will result in a distortion of the complex whenever the $^4T_2$

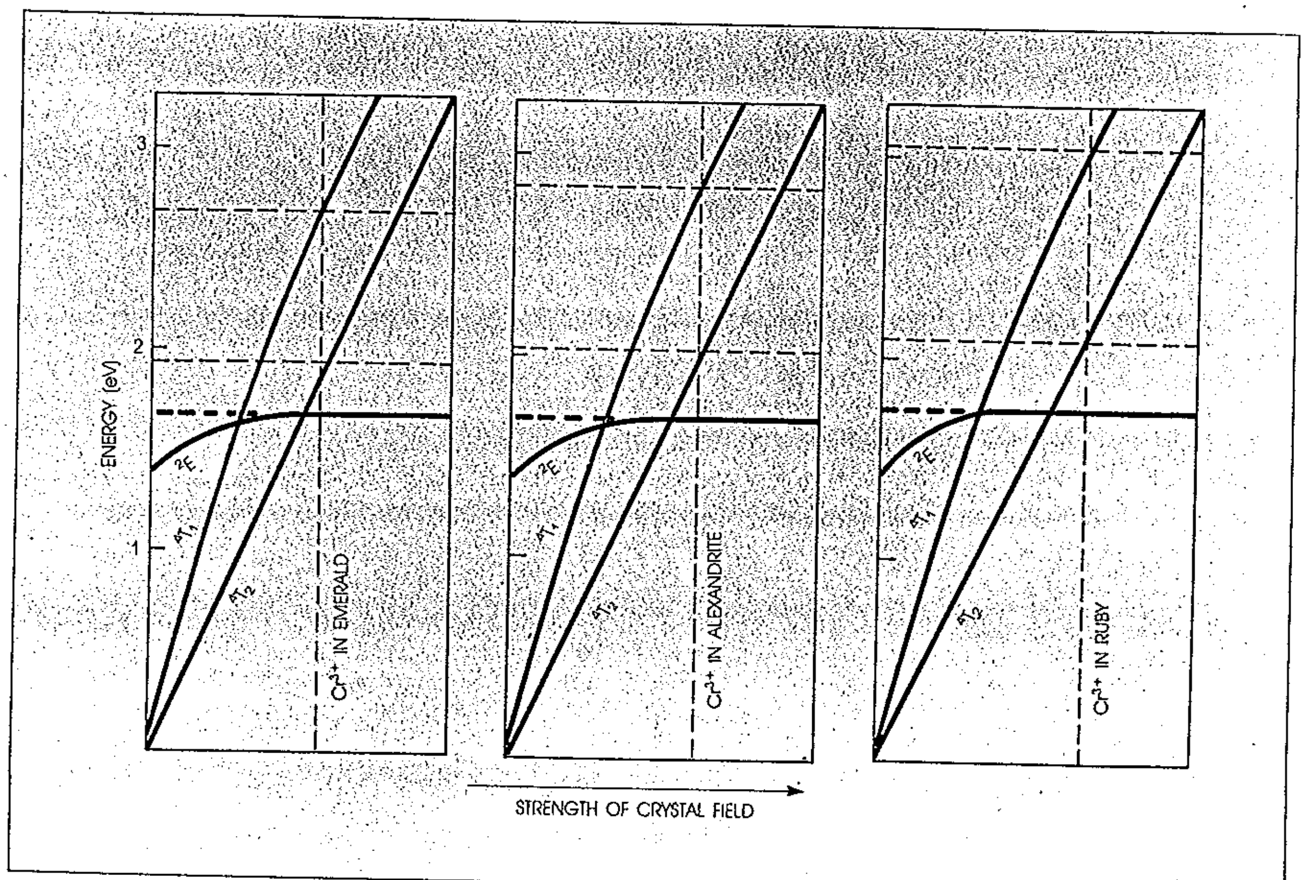

FIGURE 3. The energy states modified by the crystal electric fields for emerald, alexandrite, and ruby.

state is occupied. This distortion is, in fact, the principal reason why low-field materials (for which $^4T_2$ is the lowest excited state) show broadband fluorescence.[8]

Characteristics of emerald as a laser medium

Table 1 illustrates the lasing characteristics and thresholds of emerald and other laser materials. The calculated values are displayed in Table 1 for the number threshold N_{th} of ions required in the metastable state, fluorescence power P_f threshold for a standard laser cavity (length of optical resonator L = 20 cm and $\gamma = 2\%$ loss per pass), and the minimum absorbed pumped energy E_{min} required to achieve the threshold condition for standard losses (5% of the exciting light energy falls within the useful absorption band; 5% of this light is absorbed by the laser medium; the average ratio of laser frequency to the pump frequency is 0.5; and the lamp efficiency [optical output/electrical input] is 0.5). The theoretical lasing formulas are given at the top of the Table.

One can see from Table 1 that the optical energy needed for emerald to reach the lasing threshold is about 4 times smaller than in alexandrite, 270 times less than in ruby, and 28 times greater than in Nd^{3+}:YAG. Fluorescence tunability bandwidth over 1500 cm^{-1} is 250 times wider than Nd^{3+}:YAG and 1.5 times larger than alexandrite.

The physical properties of emerald are shown in Table 2. In Fig. 4(a), three hydrothermally grown crystals cut from a single ingot 4 cm long are displayed. In the Frontispiece/Fig. 4(b), a Brewster laser element of emerald in a slab configuration is shown. The red light emerging from the green crystal is a fluorescence trace after excitation by an argon laser line at 488 nm. Thus far, laser action was achieved using about 15-mm-long crystals in flashlamp and pulse modes and in a 4-mm sample by CW krypton laser excitation; typical beam energy is about 10 mJ and 10 mW, respectively.[21] In CW operation,

TABLE 1: COMPARISON OF THE LASING CHARACTERISTICS AND THRESHOLDS OF EMERALD AND OTHER LASER MATERIALS

Lasing Material	$N_{th}^{(4)} = \frac{8\pi\tau_0\eta^3\Delta\nu}{c\tau_c\lambda^2}$ $N_{th}^{(3)} = N_0/2$	$P_c = \frac{N_{th}h\nu}{\tau_0}$ [W/cm³]	$E_{min} = \frac{N_{th}h\nu}{\eta}$ [J/cm
Ruby 3-level λ = 694.3 nm $\Delta\nu$ = 11 cm^{-1} τ_0 = 3.10^{-3} sec	10^{19}	960	46[illegible]
Nd^{3+}:glass 4-level λ = 1.06 $\Delta\nu$ = 200 cm^{-1} τ_0 = 3.10^{-4} sec	9.10^{15}	5.6	2
Nd^{3+}:YAG 4-level λ = 1.064 $\Delta\nu$ = 6 cm^{-1} τ_0 = 5.5.10^{-4} sec	2.10^{15}	0.7	0
Alexandrite 4-level λA_{ve} = 720 nm $\Delta\nu$ = 1000 cm^{-1} τ_0 = 3.2.10^{-4} sec	1.6×10^{17}	140	7
Emerald 4-level λA_{ve} = 740 nm $\Delta\nu$ = 1500 cm^{-1} τ_0 = 6.5.10^{-5} sec	4.1×10^{16}	170	1

$N_{th}^{(4)}$ = population inversion density at threshold in the metastable state for a 4-level system.
$N_{th}^{(3)}$ = population inversion density at threshold for a 3-level system.
τ_0 = decay time associated with radiative laser transition
η = refractive index.
$\Delta\nu$ = the width of the gain linewidth at room temperature
τ_c = cavity lifetime — the time at which the energy is lost in the laser cavity.
c = speed of light.
λ = lasing wavelength.

TABLE 2: PHYSICAL AND OPTICAL PROPERTIES OF EMERALDS

Chemical composition	$Be_3Al_2(SiO_3)_6$:Cr^{3+}
Crystallographic character	Flattened hexagonal prismatic habit
Refractive index	1.570–1.576
Birefringence	0.005–0.006
Optic character	Uniaxial-negative
Pleochroism	Dichroic, strong green & bluish green
Dispersion	0.014
Hardness	7½–8
Specific gravity	2.67–2.69
Effect of heat	Fuses with difficulty to a glass
Effect of acid	Resists all but hydrofluoric
Degree of transparency	Highly transparent to translucent
Cr^{3+}-doped concentration	0.001–1%
Grade	Optical grade
Sizes	Slabs 20×50 mm; rods 3.5×45 mm

emerald will compete with the mode-locked dye lasers.

According to Dr. Richard Mandel of Vacuum Ventures, Inc., our supplier of hydrothermally grown emerald crystals, it is possible with existing equipment to grow about 100 emerald crystals 4–5 cm long per year, assuming a 15% yield. With the improvement of existing equipment, it may be possible to grow laser-grade crystals as long as 10–12 cm by this method. So far, problems still exist with the optical quality. When light travels parallel to the crystal growth planes, beam breakup occurs due to the inhomogeneity of the index of refraction. To minimize this effect, the beam should be directed parallel or perpendicular to the *c*-axis. This can be accomplished in a slab configuration, as shown in the Frontispiece. All of our lasing achievement to date has been made with type A class, gem quality crystals. Technological improvements in growing methods (being pursued by Allied Chemical[21]) are needed to obtain laser-quality crystals. This problem was common in the early 1960s with ruby crystals as well as with the first crystals of alexandrite.[4] Currently, emerald crystals are grown by the flow fusion method (Gilson, Switzerland) and by synthesis under

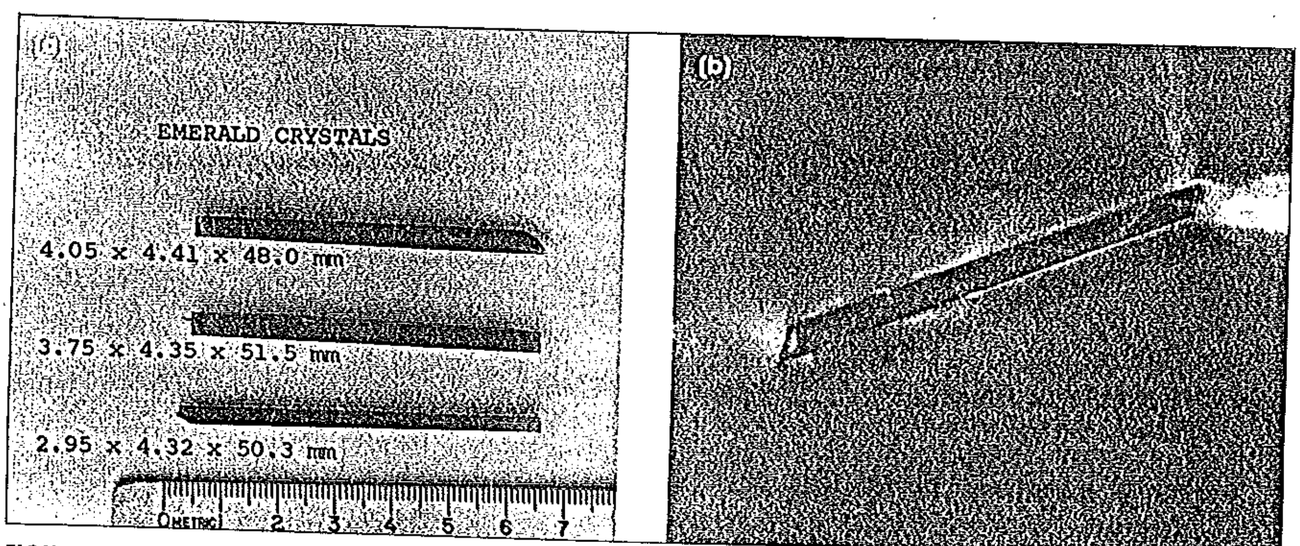

FIGURE 4.(a) Typical emerald crystals cut from a larger slab boule and before polishing; **(b)** Total internal reflection of blue argon line at 488 nm inside emerald, creating red path of fluorescence (slab geometry).

high pressure.[20] *(For a report by J. C. Walling on Allied Corp.'s activities and progress in alexandrite, and preliminary work in emerald,* *see p. 213.*—**Ed.**)

Conclusion

Emerald, a new wideband tunable laser, has ideal characteristics for fast Q-switching and ultrafast pulse generation by mode-locking. This material improves its performance at elevated temperatures instead of stopping laser action as in many others. It is our hope that developments in this area of research will prove our claims.

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