

Laser action in chromium-activated forsterite for near-infrared excitation: Is Cr^{4+} the lasing ion?

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Room-temperature pulsed laser action has been obtained in chromium-activated forsterite ($\text{Cr:Mg}_2\text{SiO}_4$) for excitation of the near-infrared absorption band of the system by the 1064 nm radiation from a Nd:YAG laser. The characteristics of laser emission are similar to those observed for 532 nm pumping. It is suggested that the laser action is due to a "center" other than the trivalent chromium (Cr^{3+}), presumably the tetravalent chromium (Cr^{4+}).

Recently, we reported¹⁻³ room-temperature pulsed laser action in chromium-activated forsterite ($\text{Cr:Mg}_2\text{SiO}_4$). The free-running laser output was centered at 1235 nm with a spectral bandwidth of 22 nm. The laser emission was stimulated by the 532 nm excitation of the green-red absorption band of the system. This absorption band, together with the one in the blue spectral region, originates from transitions between crystal-field-split states of the Cr^{3+} ion. The origin of the shallow absorption band spanning the 850–1200 nm wavelength range has not been determined with any certainty, and was tentatively attributed to other impurity ions.⁴ This absorption band overlaps a significant portion of the emission band of the system and inhibits laser action in that region. Identical absorption band has been observed in gadolinium scandium gallium garnet crystals codoped with trivalent chromium and neodymium ions ($\text{GSGG:Nd}^{3+}, \text{Cr}^{3+}$).⁵⁻⁷ The chromium ion in this crystal acts as an efficient sensitizer of Nd^{3+} emission, resulting in about a factor of two improvement in lasing efficiency relative to the Nd^{3+} :YAG crystal.^{8,9} The near-infrared absorption acts as a significant loss mechanism for Nd^{3+} emission in codoped GSGG crystal and impedes the full potential of the sensitization process. The "center" responsible for this infrared absorption has been considered to be a nuisance, and efforts have been made to get rid of this center by improving the crystal growth technique, or annealing the crystal in reducing atmosphere.¹¹ In this letter we report for the first time on laser action in chromium-doped forsterite pumped by 1064 nm radiation and present evidence that in chromium-doped forsterite the near-infrared active "center" is responsible for laser action. Absorption, emission, and lasing properties of this "center" are presented. We suggest that the center may be a Cr^{4+} ion in a tetrahedral site.

The absorption and fluorescence spectra of the center in the near-infrared spectral region are shown in Figs. 1 and 2, respectively. The room-temperature absorption spectrum is a double-humped band covering the 850–1200 nm wavelength range. The room-temperature fluorescence spectrum extends from 1000 to 1400 nm and peaks at 1140 nm. At liquid-nitrogen temperature both the spectra show a sharp zero-phonon line at 1093 nm followed by elaborately structured vibrational sidebands. A detailed analysis of the vibrational sidebands is out of the scope of the present letter and will be presented in a future publication. The fluorescence

lifetime is 15 μs at room temperature and 20 μs at liquid-nitrogen temperature.

The cavity arrangement used for obtaining laser action in $\text{Cr:Mg}_2\text{SiO}_4$ has been described elsewhere.¹ An identical arrangement was used in this measurement, except that the separation between the front and the back mirrors was 40 cm, and the pump beam was focused 5 cm in front of the sample by a 50 cm focal length lens. The fundamental and the second-harmonic emissions from a Q-switched Nd:YAG laser (Quanta Ray DCR-1) operating at a 10 Hz repetition rate were used for excitation of the near infrared and the visible bands, respectively. Pulsed laser action was readily observed for both the 1064 nm and the 532 nm pumping at or above the respective thresholds. To switch from one pump wavelength to the other, one merely had to change a filter in the beam path to transmit the desired wavelength and block the other. The amplitude and duration of the $\text{Cr:Mg}_2\text{SiO}_4$ laser pulse, as well as its delay with respect to the pump pulse, varied, as expected, with the pulse-to-pulse energy fluctuation of the pump pulses. However, for a similar level of excitation and within the time resolution of the experiment, there was no appreciable difference in the delay between the pump pulse and the output laser pulse for the two pump wavelengths. The laser thresholds and slope efficiencies for the two excitation wavelengths, 1064 and 532 nm, are shown in Fig. 3. The spectra of the free-running laser for pumping at 1064 and 532 nm are displayed in Figs. 4(a) and 4(b), respectively. Table I summarizes and compares

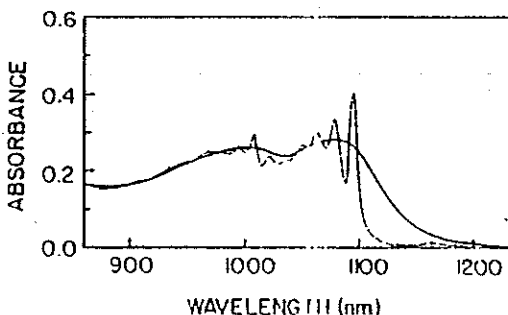


FIG. 1. Near-infrared absorption spectra of $\text{Cr:Mg}_2\text{SiO}_4$ at room temperature (solid line) and liquid-nitrogen temperature (broken line) for $E \parallel b$ axis. The crystal contains 0.04 at. % of Cr ions and has a thickness of 4.5 mm along the excitation direction.

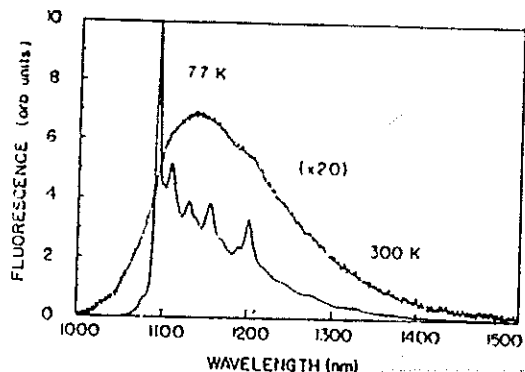


FIG. 2. Near-infrared fluorescence spectra of $\text{Cr:Mg}_2\text{SiO}_4$ at room temperature and liquid-nitrogen temperature for 1064 nm excitation.

the characteristics of laser emission for the two excitation wavelengths.

The data presented so far clearly indicate that the same center is active in laser action for both the 532 nm and 1064 nm excitations. For the 532 nm pumping there is a fast transfer of excitation from the levels directly pumped to the lasing level. The absorption at 532 nm and for that matter, the entire red-green band has been attributed to ${}^4A_2 \rightarrow {}^4T_1$ transitions in Cr^{3+} ion.^{1,10} If that is the case, then the Cr^{3+} ions act as a sensitizer, rapidly and efficiently transferring energy to the lasing center. However, the lasing center itself may have a higher lying absorption band that overlaps the Cr^{3+} absorption in the red-green spectral region. Similar contributions to absorption in this spectral region have indeed been suggested for Cr^{4+} in GSGG,¹¹ and for isoelectronic V^{3+} in corundum.¹² The growth of population in the lasing level for 532 nm pumping will then be due to vibrational nonradiative transitions which are very fast.¹³ Probably, both the interband nonradiative transitions, and the $\text{Cr}^{3+} \rightarrow$ lasing center energy transfer are effective in populating the lasing level for excitation in the visible. However, for the 1064 nm pumping, the lasing band is directly populated.

The key question that remains to be answered is, what is the origin of this lasing center. Trivalent chromium enters the forsterite crystal in two distinct sites, one with mirror ($M2$) and the other with inversion ($M1$) symmetry. Generally, the ions in the mirror sites are optically active. The

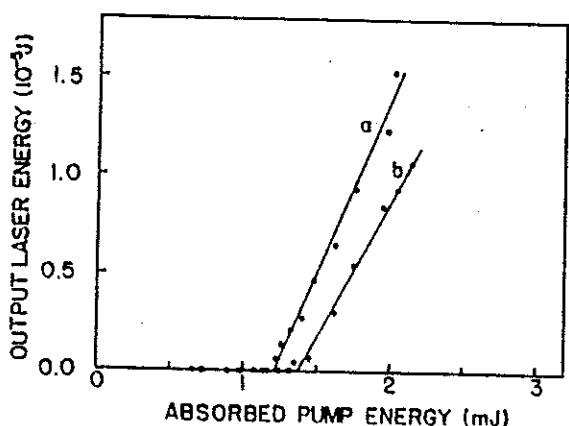


FIG. 3. Output energy of $\text{Cr:Mg}_2\text{SiO}_4$ laser as a function of input energy for (a) 1064 nm pumping and (b) 532 nm pumping.

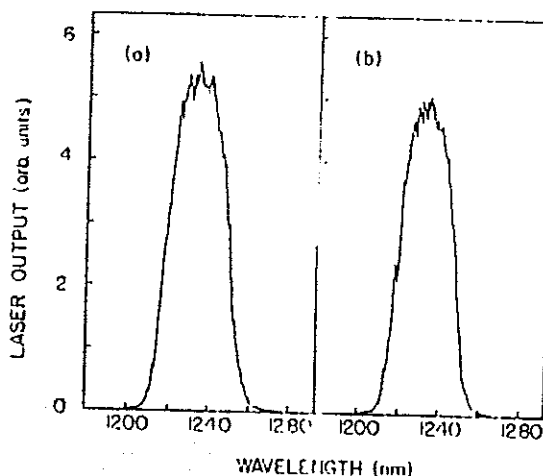


FIG. 4. Spectra of free-running $\text{Cr: Mg}_2\text{SiO}_4$ laser for (a) 1064 nm pumping and (b) 532 nm pumping.

polarized absorption spectra of chromium-activated forsterite have been analyzed¹⁰ in terms of Tanabe-Sugano formalism,¹⁴ and no infrared absorption band is predicted for Cr^{3+} ions in mirror sites. For Cr^{3+} ions in inversion sites, even ligand field-induced electric-dipole transitions are not possible. Dynamic interaction with lattice vibrations may result in transitory reduction of inversion symmetry, making transitions possible. However, such transitions are very weak and slow, as seen for Cr^{3+} ions in inversion sites in alexandrite, where the fluorescence lifetime is ~ 60 ms.¹⁵ The measured lifetime of $15 \mu\text{s}$ is too short for transitions within the states of a Cr^{3+} ion in inversion site. It is highly unlikely that the infrared absorption is due to the Cr^{3+} ions in inversion site.

Impurities other than chromium could be another possibility. Trivalent iron (Fe^{3+}) is a commonly occurring impurity in olivines, and exhibits a similar absorption band in the near infrared. However, the low-temperature spectrum of iron in olivine does not show the sharp-line structure as observed in chromium-activated forsterite.⁴ Chemical analysis of the sample did not indicate sufficient iron content to account for the observed absorption either.

A similar 850–1200 nm absorption band observed¹⁻⁷ in Nd,Cr:GSGG was first assumed⁶ to be due to Cr^{2+} , and finally has been attributed to Cr^{4+} centers.⁵ This band appears only in Cr-activated GSGG crystals and never in undoped or only Nd-doped crystals. The absorption coefficient of the band depends on the crystal growth condition and has been observed⁶ to vary over three orders of magnitude from a high of 2 cm^{-1} down to $1 \times 10^{-3} \text{ cm}^{-1}$ at 1061 nm, the

TABLE I. Properties of laser emission for the two excitation wavelengths.

Property	Value at the excitation wavelength of	
	1064 nm	532 nm
Lasing threshold (absorbed energy)	1.25 mJ	1.37 mJ
Slope efficiency	1.8%	1.4%
Spectral bandwidth (FWHM)	30 nm	27 nm
Center wavelength	1235 nm	1235 nm

wavelength for Nd laser emission. After a series of careful tests for impurities⁶ and analytical chemistry studies,⁵ these authors established a correlation between the strength of this absorption and the level of divalent calcium impurity in the sample. Divalent calcium appears as an impurity in scandium oxide, the starting material for growing GSGG. Also, to promote the growth of garnet crystals a small amount of calcium oxide is sometimes added to the melt. The working hypothesis here is that the Ca^{2+} causes Cr^{3+} to change to Cr^{4+} , and the Cr^{4+} ion on a tetrahedral site is responsible for the near-infrared absorption in question. In view of the similarities between the near-infrared absorption band in GSGG and forsterite, we tentatively assign the center in forsterite to Cr^{4+} ion as well. The role of Ca^{2+} is presumably played by Mg^{2+} in forsterite.¹⁶ Substitution for Si^{4+} in tetrahedrally coordinated sites is less frequent but possible,¹⁷ and may lead to tetrahedrally coordinated chromium ions in forsterite. Another possible identity of the lasing center may be the divalent chromium ion (Cr^{2+}) substituting for Mg^{2+} in the inversion (*M*1) site. It has been indicated that in distorted coordination sites, like the forsterite *M*1 site, Cr^{2+} may occur and be stable.^{18,19} According to the prediction of the crystal field theory such a center may account for the observed infrared absorption. The exact identification of the lasing center in chromium-activated forsterite still remains an interesting problem for further investigation.

Note added in proof. We have obtained cw laser action in chromium-activated forsterite by pumping the crystal with 1064 nm radiation from a cw Nd:YAG laser. By using a single-plate birefringent filter in pulsed mode, tuning over 1167–1345 nm has also been demonstrated.

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tional Aeronautics and Space Administration, and City College of New York Organized Research. Note: The submission date of this manuscript shows the priority of who obtained laser action in forsterite with the 1064 nm pumping first.

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