A method is described to improve and produce purer Cr$^{4+}$-doped laser materials and lasers with reduced co-incorporation of chromium in any other valence states, such as Cr$^{3+}$, Cr$^{5+}$, and Cr$^{6+}$. The method includes: 1) certain crystals of olivine Structure with large cation (Ca) in octahedral sites such as Cr$^{4+}$:Ca$_2$GeO$_4$, Cr$^{4+}$:Ca$_2$SiO$_4$, Cr$^{4+}$:Ca$_2$Ge$_{x}$Si$_{1-x}$O$_4$ (where 0<x<1), and/or 2) high-temperature solution growth techniques that enable the growth of the crystals below the temperature of polymorphic transitions by using low melting point solvent based on oxide, fluoride and/or chloride compounds. Purer Cr$^{4+}$-doped laser materials are characterized by a relatively high concentration of Cr$^{4+}$-lasing ion in crystalline host that makes these materials suitable for compact high power (thin disk/wedge) NIR laser applications.
OTHER PUBLICATIONS


Petricevic et al., “Pulsed Laser Operation of Cr$^{3+}$:LiSeGeO$_4$ at 1.3 μm,” CLEO 97, CTuE7 9:30AM, pp. 77-78 (1997).


* cited by examiner
This patent application claims the benefit of U.S. Provisional Patent Application Ser. No. 60/633,441, filed Dec. 7, 2004, incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

This invention was made with government support under Grant No. NCC-1-03009 awarded by NASA and Grant No. W911NF0410023 from the U.S. Department of Defense. The government may have certain rights in this invention.

BACKGROUND


The Cr4+ ions in tetrahedral coordination are useful for realization of room temperature tunable solid state laser operation in the spectral range from 1.1 to 2 µm. Unfortunately, for all the materials listed above, the concentration of Cr4+ ions in the crystalline structure was lower than 0.1%, and chromium in other valence states (for example, Cr3+ and Cr5+) was present in those crystals. This led to complicated spectroscopic properties of the materials. As a result, the active media length in the laser devices was too high for at least some applications. This took these crystals out of consideration for small micro-laser development, where thickness of the laser element generally does not exceed a few mm in length.

BRIEF SUMMARY

One embodiment is a laser medium, comprising a single crystal of Cr4+:Ca4GeSi1-xO4, where 0<x<1. A variety of lasers can be formed using this laser medium.

Another embodiment is a single crystal of Cr4+:Ca4GeSi1-xO4, where 0<x<1 and the single crystal has at least 1 wt. % Cr4+. A variety of lasers can be formed using this laser medium.

Yet another embodiment is a method of making a laser medium. The method includes forming an undoped crystal substrate of Ca4GeSi1-xO4, where 0<≤x<1, and forming a layer of Cr4+:Ca4GeSi1-xO4, where 0<≤x<1, on the substrate by liquid phase epitaxy.

BRIEF DESCRIPTION OF THE DRAWINGS

Non-limiting and non-exhaustive embodiments of the present invention are described with reference to the follow-
cooled face of the disk 102 is transparent to pumping radiation and highly reflective for laser emission, the laser disk is mounted on a transparent heat sink 104 (e.g., a sapphire heat sink) and axial back pumping light 106 is directed through the transparent sapphire heat sink is applied.

In a modified version (FIG. 2) of the first configuration, the cooled face of the disk 102 in this embodiment, a wedge slab is optically coated to act as a total reflector, the wedge slab can be used as an active element to increase pump efficiency. The reflective coatings 108, 110 are on different components of the laser forming a resonator cavity 112. The disk 102 also includes an antireflective coating 114 on the surface that receives the pumping light 106.

The thin disk laser assembly designed for diode-pumped solid-state lasers was first put forward in 1992. It has been successfully applied to Yb:YAG lasers, [V. Andrea, B. Uwe, W. Klaus and G. Adolf. Proc. SPIE 2426 (1995), p. 501. U. Brauch, A. Giesen, M. Karwieski, Chr. Stewen and A. Voss. Opt. Lett. 20 (1995), p. 713], to generate high output power. A thin disc of the active material, with a thickness of a few hundred micrometers, was mounted on a heat sink, which resulted in only a small thermal lens because of the axial heat flow in the thin disk. Multiple absorption passes of the pump radiation through the ultra-thin laser crystal were usually needed for Yb or Nd-doped laser crystals because the crystal's optical density is low.

Cr4+-doped materials disclosed herein can have unusually high optical density providing a better opportunity for only single pass pumping process. Therefore, in at least some embodiments, a thin disk laser system design based on purely Cr4+-doped materials does not use complicated schemes to pump the thin disk by multiple absorption passes.

An estimation of number of absorption passes to be needed to pump a thin layer of Ca2GeO4 is described. Polarized absorption spectra, emission spectrum, and lifetime versus Cr concentration for Cr4+:Ca2GeO4 crystals are shown in FIGS. 3 and 4.

Absorption Coefficient:
From absorption spectra in FIG. 3:
@ 808 nm (Ellb, Pbnm) = 9 cm-1
@ 840 nm (Ellb, Pbnm) = 8 cm-1
@ 980 nm (Ellc, Pbnm) = 2 cm-1

Concentration Quenching:
Quantum efficiency (including temperature quenching), at 300K:
\[ \eta = \frac{W(77K)}{W(300K, wt \%) \times \text{rate of decay}} \]

where W is the rate of decay [sec^-1], W(77K)=40,000 sec^-1 (rate of decay at 77K and at low concentration (c<0.1 wt. %) was obtained from low-temperature measurements.) W(300K) is the rate of decay from room temperature measurements. (See FIG. 4.) The quantum efficiency is then calculated to be:
\[ \eta (0.1 \text{ wt. %}) = 50\% \]
\[ \eta (0.2 \text{ wt. %}) = 43\% \]
\[ \eta (0.5 \text{ wt. %}) = 37\% \]
\[ \eta (1.0 \text{ wt. %}) = 30\% \]

It was calculated that \( \eta (2.0 \text{ wt. %}) = 16\% \). Because this value is very low, it will not be considered.

A layer will absorb power, P, according to the following equation: \( P = P_o (1 - \eta (1 - 10^{-k n})) \), where k is the absorption coefficient (see FIG. 3), l is a length, and n is number of paths. Table 1 and 2 below show absorbed power in dependence on wavelength of pumping and number of paths for 100 μm and 200 μm layer of Ca2GeO4 doped with 1 wt. % of Cr4+. Efficiency is calculated as a product of quantum efficiency \( \eta_1 \) due to thermal and concentration quenching (listed above) and efficiency \( \eta_2 \) due to difference between energy of absorbed and emitted photons.

| Table 1
<table>
<thead>
<tr>
<th>Paths</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>Efficiency (( \eta_1 \times \eta_2 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>808 nm</td>
<td>Ellb</td>
<td>87%</td>
<td>98%</td>
<td>100%</td>
</tr>
<tr>
<td></td>
<td>830 nm</td>
<td>Ellb</td>
<td>84%</td>
<td>97%</td>
<td>99%</td>
</tr>
<tr>
<td></td>
<td>980 nm</td>
<td>Ellc</td>
<td>57%</td>
<td>60%</td>
<td>74%</td>
</tr>
</tbody>
</table>

As can be seen from Table 1, at pumping wavelengths of 808 nm and 830 nm, more than 80% of initial power is absorbed in a single pass through a 100 μm layer of Ca2GeO4 doped with 1 wt. % of Cr4+. The 200 μm layer absorbs almost 100% of pumping energy (98% and 97%) at 808 nm and 830 nm, and 60% at 980 nm.

A method for producing pure Cr4+-doped laser material without co-incorporation of chromium in any other valence state, such as Cr3+, Cr5+, Cr4+, and Cr6+ is discussed below. It will be recognized that there may be small amounts of chromium in these valence states. The method includes 1) forming certain crystals of olivine structure, such as Cr4+:Ca2GeO4, Cr4+:CaSiO4, Cr4+:CaGeSi2O7, and/or 2) high-temperature solution growth techniques, such as liquid phase epitaxy, that enable the growth of the crystals below the temperature of polymorphic transitions by using low melting point solvent based on oxide, fluoride and/or chloride compounds.

A method for producing a new and improved near infrared tunable disk mini-laser is also discussed. In at least some embodiments the laser uses only a single absorption pass of pumping radiation because of using the highly-doped Cr4+-doped laser material used as an active laser element/disk (e.g., a laser medium). Different laser systems utilizing different pumping procedures and employing purer Cr4+-doped laser materials are disclosed.

The present invention is also directed to the production and use of chromium-doped (Cr4+) materials, including high-concentration tetravalent chromium-doped (Cr4+) materials, for a variety of different types of laser including compact lasers in the near infrared spectral region.
In the past, the Cr\(^{4+}\)-doped materials (forsterite, YAG) always contained substantial amounts of chromium in other valence states, particularly Cr\(^{3+}\). As a result, creating a high concentration of tetravalent chromium laser ion in those materials was not possible. The length of crystalline laser elements to be used for these devices exceeded 5-10 mm which is often considered too big for compact lasers. Development of a number of new crystals belonging to olivine structure family opens the opportunity to build laser systems utilizing heavily-doped thin layers as an active media.

The crystal lattice of olivine contains a dispersion of occupied and unoccupied AX\(_4\) tetrahedra and BX\(_6\) octahedra groups formed by oxygen ions throughout the crystal as illustrated in FIG. 5. The BX\(_6\) groups are linked by edges into zigzag shaped rows that are separated by corridors containing no octahedral voids. The discrete AX\(_4\) groups are located at the site of occupied tetrahedral voids in this corridor (all of the other tetrahedral voids of the structure are unoccupied.) In the olivine structure Ge/Si ions occupy \(1/3\) of the tetrahedral interstices and metal ions (for example, calcium magnesium, iron, or manganese) occupy \(1/3\) of the octahedral voids.

In accordance with spectroscopic characteristics of Cr-doped, Ca-based olivines, Ca\(_2\)GeO\(_4\), Ca\(_2\)SiO\(_4\), and Ca\(_2\)Ge\(_x\)Si\(_{1-x}\)O\(_4\), there is no evidence of the presence of trivalent chromium (Cr\(^{3+}\)), as well as Cr\(^{2+}\), Cr\(^{5+}\), and Cr\(^{6+}\) in these materials. A feature of these doped Ca\(_2\)GeO\(_4\) crystals is a relatively high concentration of tetravalent chromium (Cr\(^{4+}\)) due, at least in part, to favorable structure characteristics of Ca\(_2\)GeO\(_4\). Although not wishing to be bound by any theory, it is believed that there are no suitable octahedral positions for trivalent chromium in the Ca\(_2\)GeO\(_4\) structure because of the large ionic radius of Ca\(^{2+}\) in octahedral positions, as well as the ionic radius of Ge\(^{4+}\) in tetrahedral coordination is close to the ionic radius of Cr\(^{4+}\) at the same site occupation. Cr\(^{4+}\) can also substitute for silicon. As a result, the substitution concentration of Cr\(^{4+}\) ions in Ca\(_2\)GeO\(_4\) can exceed considerably the maximum level of that in other Cr\(^{4+}\)-doped compounds. Since high active ion concentrations can be achieved without significant fluorescence concentration quenching, Cr\(^{4+}\):Ca\(_2\)GeO\(_4\) becomes a suitable material for diode pumping and fabrication of miniature laser and waveguide devices. For example, the tuning range of the materials described herein covers the very important 1.33-1.55 \(\mu\)m wavelength range.

One method of crystal growth to obtain Cr\(^{4+}\):Ca\(_2\)GeO\(_4\), as well as Cr\(^{4+}\):Ca\(_2\)SiO\(_4\), Cr\(^{4+}\):Ca\(_2\)Ge\(_x\)Si\(_{1-x}\)O\(_4\), is based on the Czochralski pulling technique that was modified for crystallization from high-temperature solution (flux). As an example, crystal growth of bulk Cr\(^{4+}\):Ca\(_2\)GeO\(_4\) crystals (boules) were carried out from CaF\(_2\)-based flux with Ca\(_2\)GeO\(_4\) concentration of about 70 wt. %. The Cr\(^{4+}\) concentration in the initial charge was varied from 0.5 wt. % to 1.5 wt. %. The parameters of crystallization used are listed below: growth direction—[100], temperature range—1300-1350 \(^\circ\)C, pulling rate—0.2-0.1 mm/h, seed rotation speed—60-20 rpm, and growth atmosphere—argon. Since the temperature interval of crystallization that exceeds 1300 \(^\circ\)C is usually considered a maximum temperature for platinum crucible under RF-heating conditions, an iridium crucible, 5.08 cm diameter by 5.08 cm high, with 2.0 mm thick wall and bottom, and nitrogen atmosphere were chosen for the Cr\(_2\)Ca\(_2\)GeO\(_4\) growth procedure. Fully transparent, dark green Cr\(_2\)Ca\(_2\)GeO\(_4\) crystals more than 15 mm in diameter and up to 60 mm long were grown under the growth conditions described above.

The ease of Cr\(^{4+}\) incorporation in Ca\(_2\)GeO\(_4\) crystalline structure also permits the use liquid phase epitaxy (LPE) to fabricate high quality high concentration, Cr\(^{4+}\)-doped thin films and layers on appropriate undoped substrates. Liquid phase epitaxy is a process in which a single crystal layer can be grown from a dilute molten solution on a flat oriented single crystal substrate. Typically, the growth is performed at constant temperature by dipping the substrate in a supersaturated melt solution in which the solute is melted in a "suitable" solvent. The melt is characterized by an equilibrium temperature (or saturation temperature). Generally at the thermodynamic equilibrium the solute concentration (or solubility) increases with the temperature. A decrease of the temperature below the saturation temperature (\(T_s\)) leads generally to the crystallization of a part of the solute.

For oxide materials, one example of the LPE process is the following: The constituents of the solution are melted in a platinum crucible at about 50-100 \(^\circ\)C above the saturation temperature. For example, the solution can include a CaCl\(_2\)—CaF\(_2\) flux with germanium oxide, silicon oxide, and chromium oxide in the desired stoichiometric amounts. Before growth, the melt is stirred to provide complete dissolution of solute components. The substrate is mounted horizontally on a platinum holder and preheated in the furnace. The substrate has an alternate rotation of 50-100 rpm with a change every 5-10 s. Before dipping, in order to limit the temperature fluctuations, the substrate is to stay a few minutes above the melt. During growth, the melt temperature is kept constant. After the growth a rapid speed rotation (800 rpm) should be used in order to eliminate the solvent droplets. Then the substrate is pulled out of the furnace slowly in order to avoid thermal stresses.

Crystalline surfaces obtained by LPE can be quasi-atmospherically flat depending on the structural perfection and misorientation of a singular oriented substrate surface. However, it is useful to adjust supersaturation to grow in the regular step-flow mode. Taking these prerequisites into account we have prepared [0 1 0] Cr\(^{4+}\)-doped Ca\(_2\)GeO\(_4\) films with "optically smooth" surface areas have been prepared on singular [0 1 0] Ca\(_2\)GeO\(_4\) faces. The Cr\(^{4+}\)-doped Ca\(_2\)GeO\(_4\) film 202, illustrated schematically in FIG. 6, was formed on substrate 204 at a deposition temperature range of 800-750 \(^\circ\)C using a cooling rate of 5 \(^\circ\)C/h and a deposition time of 10 h with 30 rpm substrate rotation. For example, by LPE it is possible to grow highly quality optical layers of Cr\(^{4+}\):Ca\(_2\)GeO\(_4\) on undoped Ca\(_2\)GeO\(_4\) substrate from CaCl\(_2\)—CaF\(_2\)-based flux. In some embodiments, the layers have a thickness of 50-200 \(\mu\)m and are grown at a temperature in the range of 750-800 \(^\circ\)C. Thus, these materials, Cr\(^{4+}\):Ca\(_2\)GeO\(_4\) as well as other Ca-based olivines are available to develop Cr\(^{4+}\)-doped layered structures for mini-lasers and planar waveguide lasers and amplifier applications by liquid phase epitaxy technique with sufficient concentration of Cr\(^{4+}\)-ions.

Generally, the single crystals have the formula Cr\(_n\): Ca\(_{2n}\)Ge\(_{1n}\)O\(_{4n}\) where 0\(\leq x\leq 1\). In some embodiments, 0\(\leq x<1\) or 0\(\leq x\leq 1\) or 0\(\leq x\leq 1\) or 0\(\leq x\leq 1\) or 0\(\leq x\leq 1\) or 0\(\leq x\leq 1\) or 0\(\leq x\leq 1\) or 0\(\leq x\leq 1\). In some embodiments, single crystals can have at least 0.05 wt. % Cr\(^{4+}\) and may have at least 0.1 wt. %, 0.5 wt. %, or 1 wt. % Cr\(^{4+}\) or more. In some embodiments, the single crystals have 1 to 5 wt. % Cr\(^{4+}\). A variety of lasers, including near infrared (NIR) lasers, can be formed using these materials, including, for example, lasers containing the arrangements schematically illustrated in FIGS. 1A, 1B, and 2. One example of a laser system that can be built as all solid state compact lasers with utilizing a thin Cr\(^{4+}\):Ca\(_2\)GeO\(_4\) disk is schematically illustrated in FIG. 2A. At the heart of the laser is a 100-\(\mu\)m thick Cr\(^{4+}\):Ca\(_2\)GeO\(_4\) disk 302 disposed on a transparent heat sink 304 (e.g., a
sapphire heat sink.) The disk is pumped with up to 300 W of 800-940 nm light from diode bars 306 (or any other suitable pumping light source.) For example, a laser diode stack consisting of a number bars can be used for pumping. Pumping light is delivered to the laser head by a planar waveguide 308. The radiation emitted by each bar was first collimated individually by a cylindrical microlens 310. A planar waveguide is used to shape the emitting beams of the laser diodes. Two cylindrical lenses 312 are used to focus the collimated diode laser beam into the planar waveguide. Using imaging optics consisting of cylindrical and spherical lenses after the waveguide, a homogeneous pumping line is obtained and coupled into the Cr\textsuperscript{4+}:Ca\textsubscript{2}GeO\textsubscript{4} disk crystal through a transparent heat sink 304. The dielectric mirror coatings 314, 316 on the disk itself define the resonator of the oscillator. The cooling face of the disk attached to sapphire is coated for high reflectivity at the laser wavelength (e.g., 1.3-1.5 \textmu m) and high transmission at the pumping wavelength (e.g., 800-940 nm), while the other side is high reflectivity coated for both wavelengths (95% reflectivity at 1.3-1.5 \textmu m, high reflectivity at 800-940 nm).

A second example is schematically illustrated in FIG. 7B, where a similar pump assembly (with laser diode bars 306, optics 310, 312, and waveguide 308) is used to pump Cr\textsuperscript{4+}:Ca\textsubscript{2}GeO\textsubscript{4} wedge 302 from its front surface. Heat management in the gain medium (wedge) is a central to successful operation of this laser and is provided by a heat sink 304 (e.g., a copper heat sink.) The wedge 302 includes a high reflective coating 314 on the back side near the heat sink 304 and an antireflective coating 318 on the front side. A coupler 320 is provided with a 95% reflective coating at the laser wavelength (e.g., 1.2-1.7 \textmu m).

In another embodiment schematically illustrated in FIG. 8, for pulsed operation, the near-IR light from the laser head (e.g., laser disk 402) can then be directed through series of dispersive mirrors 404, 404a to a semiconductor saturable absorber mirror 406 that induces passive mode-locking. The laser light can pass through a mirror 408 and a tuning element 410 to an output coupler 412.

An example of a waveguide laser device is schematically illustrated in FIG. 9. A pump diode laser 502 provide pumping light through a coupling optic 506 to a waveguide 504 made of the Cr\textsuperscript{4+} material described above. As an example, the waveguide has a coating 508 that is highly reflective at the laser frequency (e.g., 1.3-1.5 \textmu m) and highly transmissive at the pumping frequency (e.g., 0.8 to 1.0 \textmu m) and a second coating 510 that is 95% reflective at the laser frequency (e.g., 1.3-1.6 \textmu m.) It will be recognized that these examples of lasers and waveguide laser devices can include more or fewer components or can be modified in accordance with known configurations of lasers and other devices.

The above specification, examples and data provide a description of the manufacture and use of the composition of the invention. Since many embodiments of the invention can be made without departing from the spirit and scope of the invention, the invention also resides in the claims hereinafter appended.

What is claimed as new and desired to be protected by Letters Patent of the United States is:

1. A laser medium, comprising:
   a single crystal of Cr\textsuperscript{4+}:Ca\textsubscript{2}Ge\textsubscript{4}Si\textsubscript{4}O\textsubscript{4}, wherein 0<x<1.
   The laser medium of claim 1, wherein 0<x<0.9.
   The laser medium of claim 1, wherein 0.1<x<0.9.
   The laser medium of claim 1, wherein a concentration of Cr\textsuperscript{4+} in the single crystal is at least 0.5 wt. %.
   The laser medium of claim 1, wherein the laser medium has a thickness of no more than 200 \textmu m.
   A laser comprising the laser medium of claim 1.
   The laser of claim 7, wherein the laser medium is a thin disk or thin wedge of Cr\textsuperscript{4+}:Ca\textsubscript{2}Ge\textsubscript{4}Si\textsubscript{4}O\textsubscript{4}.
   The laser of claim 7, further comprising a heat sink attached to a surface of the laser medium.
   The laser of claim 7, further comprising a pump light source configured and arranged to provide pumping light to the laser medium.
   The laser of claim 10, further comprising a heat sink attached to a surface of the laser medium, wherein the heat sink is transparent to the pumping light and the pump light source is configured and arranged to direct the pumping light through the heat sink to the laser medium.
   The laser of claim 7, further comprising a tuning element to tune a frequency of light emitted by the laser medium.
   A laser medium, comprising:
   a single crystal of Cr\textsuperscript{4+}:Ca\textsubscript{2}Ge\textsubscript{4}Si\textsubscript{4}O\textsubscript{4}, wherein 0<x<1 and wherein the single crystal comprises at least 1 wt. % Cr\textsuperscript{4+}.
   The laser of claim 14 wherein the single crystal comprises at least 1 wt. % Cr.
   The laser of claim 14 wherein 0<x<0.9.
   The laser of claim 14 wherein x is 0.
   A laser comprising the laser medium of claim 14.
   The laser of claim 18, wherein the laser medium is a thin disk or thin wedge of Cr\textsuperscript{4+}:Ca\textsubscript{2}Ge\textsubscript{4}Si\textsubscript{4}O\textsubscript{4}.
   The laser of claim 14, wherein 0.1<x<0.9.
   The laser of claim 18 further comprising a pump light source configured and arranged to provide pumping light to the laser medium and a heat sink attached to a surface of the laser medium, wherein the heat sink is transparent to the pumping light and the pump light source is configured and arranged to direct the pumping light through the heat sink to the laser medium.
   The laser of claim 18, further comprising a pump light source configured and arranged to provide pumping light to the laser medium and a heat sink attached to a back surface of the laser medium, wherein the pump light source is configured and arranged to direct the pumping light to the laser medium through a front surface of the laser medium.

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