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Navy Case No. 77,756 **PATENT APPLICATION**
Inventors: Bowman et al

METHOD AND APPARATUS FOR PRODUCING HIGH BRIGHTNESS MID-IR FLUORESCENCE FROM PHOSPHOR MATERIALS

Background of the Invention

1. Field of the Invention

This invention relates to producing high brightness mid-IR fluorescence from phosphor materials.

2. Description of the Previously Published Art

Simple sources of broad band optical radiation have many applications. The most common of these devices are blackbody emitters, phosphors and light emitting diodes.

Blackbody sources are the simplest and most common of the broad band sources. They emit continuously over the entire ultraviolet, visible and infrared spectra with the distribution of power determined only by the emitters temperature. As the temperature of the emitter increases, the total output increases as well according to the Stefan-Boltzman Law and peak wavelength of the emission shifts to shorter wavelengths according to Wien's Displacement Law. As a result, the efficiency of blackbodies in the infrared is low, making blackbodies relatively weak emitters at wavelengths beyond 3 μm even at fairly high temperatures. Practical issues such as source lifetime restrict the emitter temperatures to less than 1000°K. Consequently, blackbody sources rarely produce more than 0.1 $W\text{-}cm^{-2}\text{-}\mu m^{-1}\text{-}sr^{-1}$. It is important to note the weak emission in the mid-infrared is a fundamental limitation of blackbody sources.

The other two types of broad band sources, light emitting diodes and phosphors, have become increasingly important alternatives to thermal sources in recent times. Many display and communications devices are based on these sources. These types of devices have important advantages over thermal sources for the spectral range over which they work. Light emitting diodes or phosphor based sources are generally longer lived and more efficient than thermal sources. However, until recently neither light emitting diodes nor phosphors could work effectively at wavelengths longer than about 3 μm. In the mid-IR, thermal sources have been the only broadband sources available. The invention described herein seeks to overcome this restraint on the spectral content of phosphor materials.

The present invention relates to a process of obtaining mid-IR radiation from a phosphor. The invention makes use of rare earths doped into low phonon energy solid state host materials. Such a process is novel and there appears to be no references disclosing the use of these materials to make superior mid-IR phosphor devices as disclosed herein.

Some of these host materials have been disclosed in the literature for use in other, significantly different devices than phosphors. As will be discussed in the next section, the use of these materials for lasers, superluminescent sources and amplifiers does not suggest their use as a phosphor. Before discussing those laser references, a brief comparison of lasers, superluminescent sources, amplifiers and phosphors and the physical principles behind their operation may help in understanding the basis of the difference.

Three processes characterize the interaction of light

and matter. These processes are absorption, spontaneous emission and stimulated emission. Absorption is the process whereby a photon excites matter from a state of lower energy to a higher energy excited state. Spontaneous emission is the process whereby a higher energy excited state of matter decays spontaneously to a state of lower energy, emitting a photon in the process. Stimulated emission is the process where a photon stimulates an excited state to decay to a state of lower energy, emitting an photon in the process. The net result is two photons with the same wavelength, phase and direction.

A laser (an acronym for Light Amplification by Stimulated Emission of Radiation) consists of a pump source and active medium within an optical resonator. In an idealized laser, the pump source excites a number of atoms of the active media into a higher energy excited state producing an inversion whereby the number of excited atoms is greater than the number of unexcited atoms. The excited active media emits some photons spontaneously inside the resonator at many different wavelengths. The resonator which consists of two reflective surfaces traps photons of a single wavelength and direction inside the resonator and within the active medium. Photons of other wavelengths are allowed to escape. The photons which are trapped in the resonator stimulate other excited atoms of the material to emit photons of the same wavelength and direction through the process of stimulated emission described above. The density of the photons in the cavity becomes very high. Some of the photons in the resonator are coupled out by allowing one of the mirrors in the resonator to be partially transmissive to the photons. The exiting photons constitute the useful laser emission of the laser. This emission can be characterized and described as being coherent (all photons are in the same direction, have the same wavelength and are in phase), narrow band (the photons

are the same or close in wavelength), and produced by the process of stimulated emission.

Superluminescent sources consist of an active medium and a pump source only. In a superluminescent source, the pump source excites a number of atoms of the active media into a higher energy excited state again producing an inversion. The excited active media again emits some photons spontaneously which stimulate other excited atoms to emit as they pass through the medium. In this case, unlike a laser, there is no build up of photons in a resonator cavity and the spectral profile is broader due to the wider range of wavelengths emitted by the spontaneously emitted photons. Note, however, that the emission which leaves the active media as superluminescent light is still narrower than the spontaneously emitted range and is dependent upon the gain profile of the transition. Consequently, similar to a laser, the exciting superluminescent light can be described as being narrow band and produced by the process of stimulated emission.

An amplifier operates similarly to a superluminescent source. It consists of an active medium and a pump source. In this case, however, the photons of the desired wavelength to be amplified are projected into one end of the medium from an external source and allowed to pass through the medium and stimulate excited atoms to emit photons as they travel through. Again, the light can be described as being narrow band and produced by the process of stimulated emission.

A phosphor, by contrasts, operates solely by the process of spontaneous emission. A phosphor consists of an active medium and a pump. The pump excites a number of atoms of the active medium into a higher energy state. Here, an inversion

is not necessary. The excited atoms emit photons spontaneously and these spontaneously emitted photons exit the media to produce the phosphorescent light. By contrast, this light is characterized as being incoherent, broad band, and produced by the process of spontaneous emission.

By the above description, we can see that there is a large difference between laser light, superluminescent light, amplified light and phosphorescence. We note also that the use of a material as a laser media, superluminescent light media or an amplifier media does not suggest its applicability as a phosphorescent media. To illustrate this difference, consider the tri-valent praseodymium ion doped into a low phonon host material of $LaCl_3$. The energy levels of Pr^{3+} are shown in Fig. 1. This is taken from Fig. 4 of an article by S. R. Bowman, Joseph Ganem, B. J. Feldman and A. W. Kueny entitled "Infrared Laser Characteristics of Praseodymium-Doped Lanthanum Trichloride," IEEE J. Quantum Electron., vol. 30, pp. 2925 - 2928, (1994). The diagram shows the observed laser and pump transitions, as well as the upconversion excitation of the upper laser level.

Ions which are excited to the $^3F_3$ state shown in Fig. 1 have a number of different states to which they can decay. The fraction of ions which spontaneously decay to each lower state is described by a branching ratio, β, which is a number between 0 and 1 where 0 indicates none of the ions in the excited state decay by that route and 1 indicates that all of the ions in the excited state decay by that route. The sum of all the β's from an excited state is equal to 1. For spontaneous emission, each ion decaying produces a photon. Thus, for a particular excited state, the higher the β for a particular transition, the stronger the light coming out at the wavelength of that transition. In the case of a laser, amplifier or superluminescent source, the

stimulated emission process changes the β of one transition to overwhelm the others,i.e., most of the ions decay by one decay route. In the case of spontaneous emission, the natural β determines the efficiency of the fluorescence. Thus, for a laser, high β is much less a factor than a phosphor. As an example, the transition $^3F_3 \Rightarrow {}^3H_6$ has been lased at 5 μm with good efficiency. For this transition, β is only 0.025. While this transition has been demonstrated as a laser, such a low β precludes its use as a phosphor source.

Chalcogenide glasses have been described in the literature. U. S. Patent No. 5,378,664 to Becker discloses a chalcogenide glass with Pr in the glass in at least 200 ppm. The chalcogenide glass, when formed into an amplifier for an optical fiber transmission system, efficiently amplified optical signals in the signal band of 1.3 microns. This use as an amplifier provides no indication of its behavior as a phosphor.

U. S. Patent No. 5,379,149 to Snitzer describes using rare earth doped low phonon glasses for lasers, amplifiers and superluminescent sources in the mid-IR range of 1.7 - 5 microns. However, all of these sources are stimulated emission devices which require optical gain to function. Phosphors, on the other hand, are spontaneous emission sources which do not have any optical gain and operate in a significantly different manner as discussed above. Again the three uses in this patent provide no suggestion of an phosphor use.

3. Objects of the Invention

It is an object of this invention to provide an important

new source of radiation in the mid-IR spectral region.

It is a further object of this invention to provide a phosphor which can work effectively at wavelengths longer than about 2 μm.

It is a further object of this invention to overcome the restraint on the spectral content of phosphor materials to provide a broad band spectrum.

It is a further object of this invention to provide mid-infrared phosphor materials which when optically pumped can generate high brightness, broad band incoherent optical sources in the 1 to 12 micron spectral range.

It is a further object of this invention to provide improved mid-infrared phosphor materials having the potential to be much brighter than currently available sources.

It is a further object of this invention to provide improved mid-infrared phosphor materials which will allow more compact optical systems with higher signal to noise ratios in the infrared.

It is a further object of this invention to provide improved mid-infrared phosphor materials which are mid IR sources that inherently are cooler and thus safer as well as requiring less power than comparable thermal sources.

It is a further object of this invention to provide improved mid-infrared phosphor materials having unique properties which will enable new applications for these IR sources.

These and further objects of the invention will become apparent as the description of the invention proceeds.

Summary of the Invention

This invention relates to finding a class of phosphors which extend useful fluorescence into the mid-IR with a wavelength of from about 2-12 microns. They are made of a host material which exhibits a low energy phonon spectra and a small amount of at least one rare earth element or rare earth compound doped in the host. When these phosphors are optically pumped to make them fluoresce they produce a bright, spontaneous infrared emission which is incoherent and broadband in the mid IR range with a wavelength from about 2-12 microns. The small amount of the rare earth element or rare earth compound can be either a dopant in the host or an integral part of a crystal of the host material.

These phosphors have an emission brightness which is greater than that of a blackbody emitting at a temperature less than 1000°K. The broadbandness of the emission can be further characterized as being broader than 10 wave numbers ($> 10\ cm^{-1}$). The host material preferably has a phonon energy of less than about 300 cm^{-1}. The preferred host materials are heavy tri-halide crystals and chalcogenide glasses. More preferred materials are tri-halide crystals, such as trichlorides and tribromides and especially lanthanum trichloride, and chalcogenide glasses, especially selenide glasses. Examples of rare earths are praseodymium, terbium, dysprosium, erbium, cerium, neodymium, thulium, and holmium. The amount of the rare earth element or rare earth compound which is doped in the host is to be an effective amount which can be quite small and on the order of

about 100 to 100,000 parts per million. Preferred host materials have an atomic structure which allows the rare earth ions to be easily introduced into the host material and these phosphors are transparent throughout the mid-IR range.

The phosphors can be used in a mid IR producing device by coupling a light source to the phosphor. A lens can be added and examples of light sources are an incandescent light, laser diodes and rare earth lasers. The bright, spontaneous infrared emission produced by these phosphors can be used for applications where more conventional UV, visible, or near IR phosphors are currently employed. Additional applications include remote sensing of pollutants or chemical processing, mid-IR spectrometers, covert marker or transponders, illuminator for IR imaging systems, free space communications sources, fluorescence based coolers, seed sources for IR lasers or OPO's, and medical diagnostic sensors.

Brief Description of the Drawings

Fig. 1 is an energy level diagram of Pr^{+3} doped $LaCl_3$ from a laser perspective.

Fig. 2 is an energy level diagram of Pr^{+3} doped $LaCl_3$ from a phosphor perspective.

Fig. 3. is a graph of mid-infrared emission of optically pump phosphors.

Fig. 4 is a diagram of an optically pumped fiber coupled Pr phosphor device.

Fig. 5 is a graph of a comparison of the brightness of phosphor with that of 1100°K blackbody source.

Description of the Preferred Embodiments

Optically pumping these specially selected mid-infrared phosphor materials generates high brightness, broad band incoherent optical sources in the thermal or mid-IR spectral range with about 2 to 12 microns wavelength. Infrared phosphor sources include those activated by rare earth ions and where the rare earth is contained within a host material which exhibits a low energy phonon spectra. This is key to extending useful fluorescence into the mid-IR.

For a phosphor to work well, the electronic state responsible for the fluorescence must have a high probability of decaying via radiation in the spectral band of interest. In more technical terms this means the active species must have a strong emission cross section and high branching ratio, β, for the wavelengths for the fluorescence spectral band.

Fig. 2. illustrates an energy level diagram for $Pr^{+3}:LaCl_3$ showing a possible pump transition for a phosphor process according to the present invention. The transition $^3H_5 \Rightarrow {}^3H_4$ is near 5 μm. The branching ratio for this transition as determined in our laboratory is 1 and thus this transition makes an excellent 5 μm phosphor. This transition illustrates again that although a transition in a material may be good for a laser it does not mean that it is good for use as a phosphor and vice versa. Here this transition is good for a phosphor; the transition exhibits a branching ratio of 1 and has been found to be a strong transition for use as a 5 μm phosphor. This transition would not, however, be a strong candidate for a stimulated emission device such as a laser which requires a

population inversion to achieve optical gain. Since the $^3H_4$ level is the ground state of the Pr^{3+} ions, a very high brightness pump source would be required in order to achieve inversion between the $^3H_5$ and $^3H_4$ levels for use as a laser.

We have found this situation to be typical among the rare earths. We have found that the first excited state has the highest branching ratio, making this the most likely candidate for a IR phosphor, but a poor candidate for a stimulated emission device.

Several tri-valent rare earths can exhibit these properties, if other decay mechanisms which compete with the fluorescence process can be controlled. For rare earth fluorescence in the mid-IR spectral region, however, there is a strong alternative decay route called multiple phonon quenching. In most rare earth doped materials, multiple phonon quenching rate overwhelms the mid-IR fluorescence rate making these materials useless as phosphors. Multiple phonon quenching rates depend exponentially on the maximum allowed phonon energy of the host phosphor material.

It is for this reason that use of a low phonon energy host material is very important. For materials with phonon energies on the order of about 300 cm^{-1} or less, the multiple phonon quenching rates can be quite low out to wavelengths as long as 12 μm. Examples of these low phonon energy host materials are heavy tri-halide crystals or chalcogenide glasses. Chalcogenide glasses are amorphous materials, which contain at least one constituent of group VI elements which include S, Se and Te. The common chalcogenide glasses include As_2S_3, $As_{12}Ge_{33}Se_{55}$, and As-Ge-S-Se system and we would expect good results with any rare earth

soluble chalcogenide. When these host materials are doped with the preferred rare earths, strong fluorescence in the mid-IR range can result. The amount of rare earth dopants is quite small and can be on the order of about 100 to 100,000 parts per million.

The phosphors described herein are an important new source of radiation in the mid-IR spectral region. As described above there are few alternative sources in this spectral range. These phosphors have the potential to be much brighter than currently available sources. These phosphors should allow more compact optical systems with higher signal to noise ratios in the infrared. These mid IR sources are inherently cooler and thus safer and they require less power than comparable thermal sources. This feature should enable new applications for these IR sources.

The examples below utilize a mid-IR phosphor based on trivalent praseodymium. However similar phosphors are possible with a number of interesting alternative rare earths such as, for example, terbium, dysprosium and erbium ions. When doped into one of the low phonon host materials and optically pumped in the near IR, each of these ions produces bright mid-IR fluorescence. As with praseodymium, each ionic species has a different spectral signature. Other rare earths that may be useful in the mid-IR phosphors are cerium, neodymium, thulium and holmium.

Each of these has one or more lower lying 4f excited states which should fluoresce efficiently due to a high branching ratio in the mid-IR. Variations in the phosphor characteristics are possible with different ionic densities. Phosphors are also possible which would use more than one of these rare earths as the active ions.

Absorbing sensitizer ions can also be added that would transfer energy from the optical pump to the active ionic species to improve performance. Examples of sensitizer ions are Tm, Nd, Cr and Er.

Other low phonon host materials for the rare earths phosphors include YCl_3, $LuCl_3$, $LaBr_3$, or LaI_3 and other chalcogenide glasses.

Many different pump sources and pumping schemes and geometrical configurations are also possible. See, for example, W. Koechner "Solid-State Laser Engineering" Springer-Verlag (1976).

The phosphor sources described herein could be used to provide mid-IR radiation for any application where more conventional UV, visible, or near IR phosphors are currently employed. Other potential applications for these sources include remote sensing of pollutants or chemical processing, mid-IR spectrometers, covert marker or transponders, illuminator for IR imaging systems, free space communications sources, fluorescence based coolers, seed sources for IR lasers or optical parametric oscillators (OPOs), and medical diagnostic sensors.

Having described the basic aspects of the invention, the following examples are given to illustrate specific embodiments thereof.

Example 1

This example illustrates phosphors made according to the invention.

Small amounts on the order of 1 to 100 parts per thousand of the rare earth praseodymium were doped into lanthanum trichloride ($LaCl_3$) crystals. In addition to having low phonon energies, these materials have several other properties that are desirable for a mid-IR rare earth phosphor host medium. They are transparent throughout the mid-IR and their atomic structures allow praseodymium ions to be easily introduced into the material.

The phosphors were optically pumped with a laser source tuned to one of the praseodymium near infrared ground state absorption bands at 1.5 μm, 1.6 μm and 2.0 μm. The emission spectra and fluorescence lifetime of the electronic metastable states of the Pr^{3+} ions were studied to determine their utility as mid-IR phosphor sources.

In the host materials described above, the Pr^{3+} ions were found to have a strong fluorescence line centered at 5 μm. As shown in Figure 3, the spectral shape of the line depends on the Pr density, but in general it extends from 3.5 to at least 5.5 μm where our detector response cutoff.

Example 2

This example illustrates the brightness of the Pr doped phosphors as compared to a black body source.

A Pr doped lanthanum trichloride crystal is optically pumped by a near infrared laser diode as shown in Figure 4. The crystal length is 3 mm, the diameter of the phosphor is 0.3 mm, and the pump has a power of 0.3 watt. The numerical aperture of the

pump has a power of 0.3 watt. The numerical aperture of the phosphor is 0.3. The pump source could emit at any of the near IR Pr absorption bands, but for this calculation, assume it emits at 2.0 μm. There are several Watt laser diodes which are currently commercially available in the 2 μm band and an example of one manufacturer is Spectrum Diode Labs. The pump light may be delivered to the phosphor using fiber and lenses. The phosphor may be configured as a bulk or waveguide emitter. Using the observed fluorescence spectra and reasonable assumptions about the optical coupling and fluorescence efficiency, the optically pumped phosphor would be as much as 100 times brighter than a hot blackbody source in the 3.5 to 6.5 μm range as shown in Fig. 5 which is a comparison of the brightness of the phosphor with that of a 1100°K blackbody source. This is a substantial improvement in the state-of-the-art infrared sources.

It is understood that the foregoing detailed description is given merely by way of illustration and that many variations may be made therein without departing from the spirit of this invention.

Abstract of the Disclosure

A phosphor is made of a low phonon energy host material and a small amount of either a rare earth or a compound of a rare earth. When the phosphor is activated by a light source which functions as an optical pump the phosphor emits light of highly enhanced brightness in the mid-IR range. Examples of host materials are heavy tri-halide crystals and chalcogenide glasses.

Figure 1

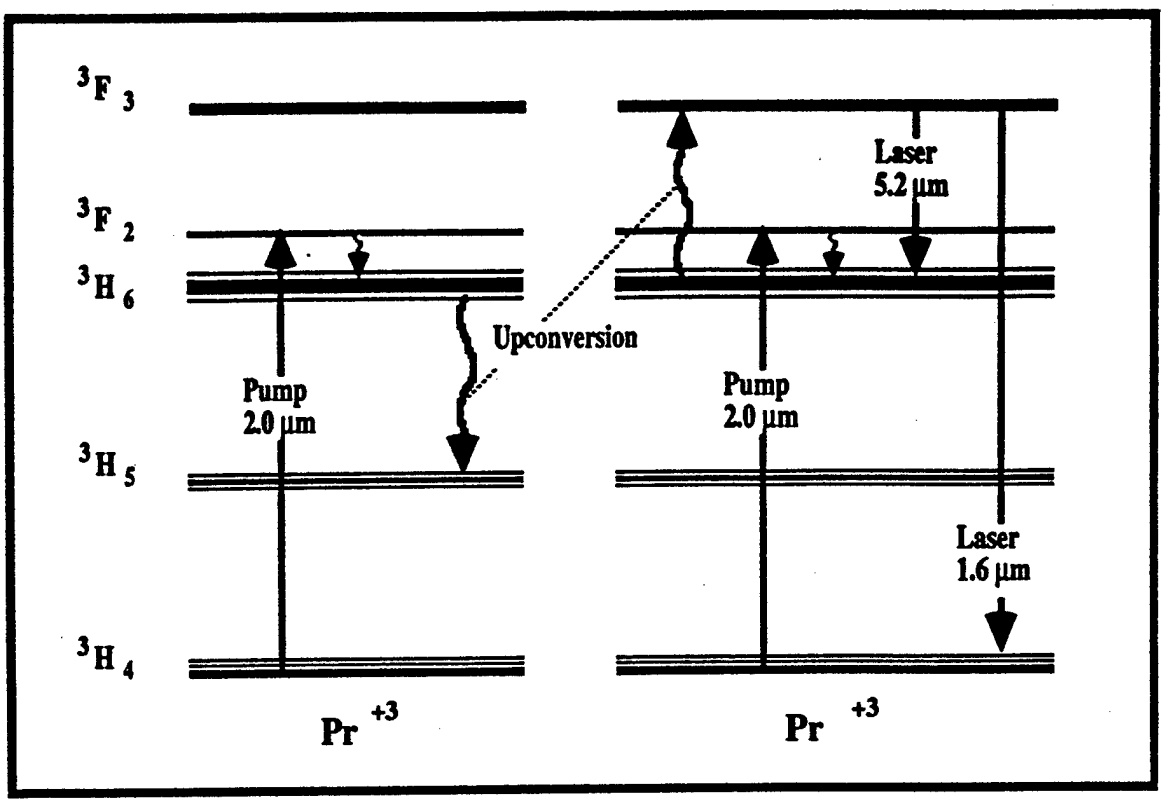

$^3F_3$
$^3F_2$
$^3H_6$
$^3H_5$
$^3H_4$
Pump
2.0 µm
Upconversion
Laser
5.2 µm
Pump
2.0 µm
Laser
1.6 µm
Pr^{+3}
Pr^{+3}

Figure 2

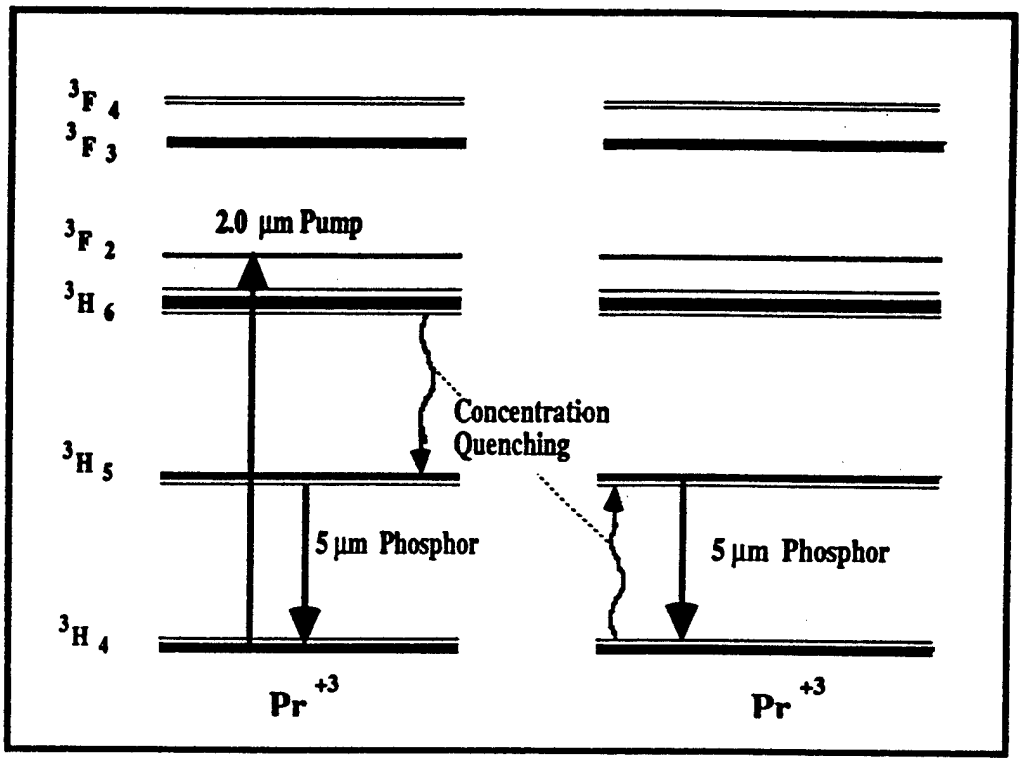

$^3F_4$
$^3F_3$
2.0 μm Pump
$^3F_2$
$^3H_6$
Concentration Quenching
$^3H_5$
5 μm Phosphor
5 μm Phosphor
$^3H_4$
Pr^{+3}
Pr^{+3}

Figure 3

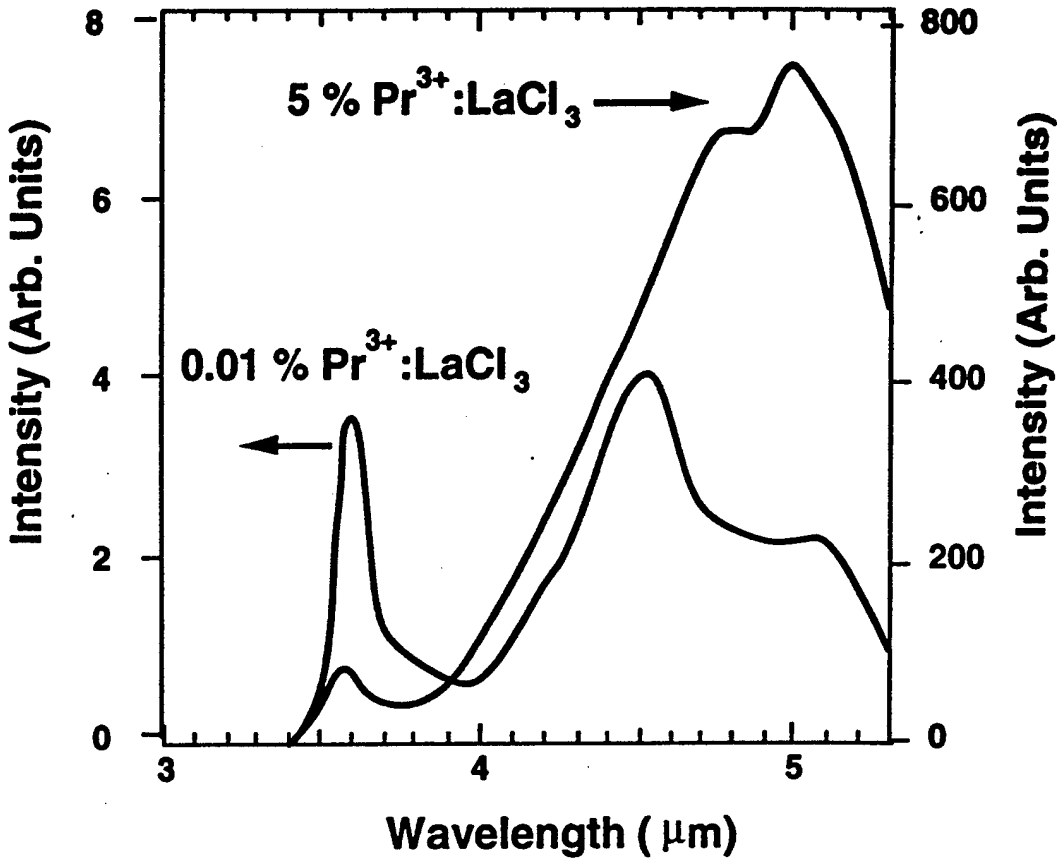

5 % Pr3+:LaCl3
0.01 % Pr3+:LaCl3
Intensity (Arb. Units)
Intensity (Arb. Units)
Wavelength (μm)
0
2
4
6
8
0
200
400
600
800
3
4
5

Figure 4

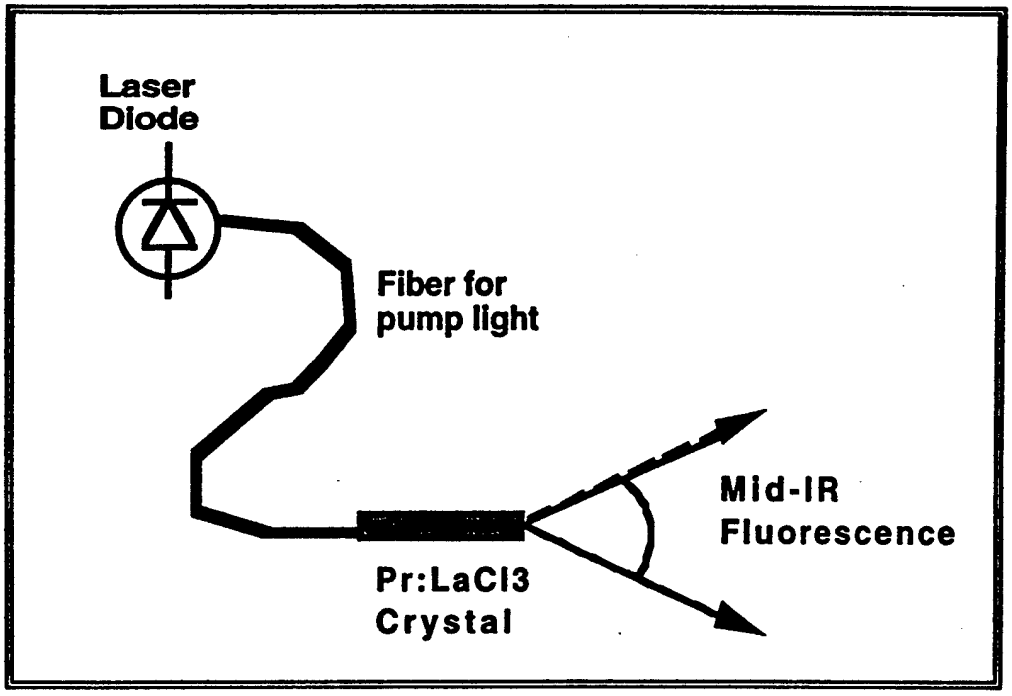
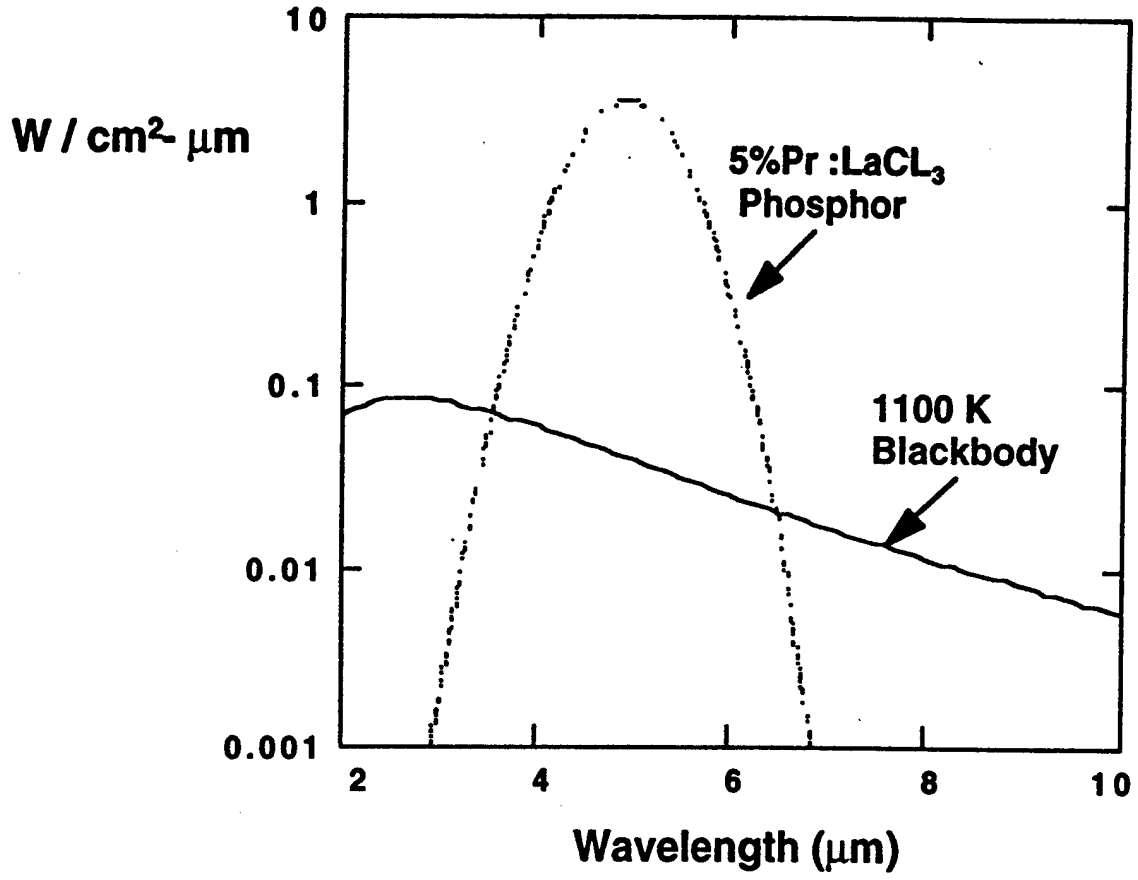

Laser
Diode
Fiber for
pump light
Mid-IR
Fluorescence
Pr:LaCl3
Crystal

Figure 5


W / cm2- μm
10
1
0.1
0.01
0.001
2
4
6
8
10
Wavelength (μm)
5%Pr :LaCL3
Phosphor
1100 K
Blackbody