LASER DISCRIMINATION BY STIMULATED EMISSION OF A PHOSPHOR

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ABSTRACT

A method for discriminating sources of UV, near infrared and far infrared laser radiations has been discovered. This technology is based on the use of a single magnesium sulfide phosphor doubly doped with rare earth ions, which is thermally/optically stimulated to generate colors correlatable to the incident laser radiation. The phosphor, after initial charging by visible light, exhibits green stimulated luminescence when exposed to a near infrared source (Nd: YAG laser). On exposure to far infrared sources (CO₂ laser) the phosphor emission changes to orange color. A UV laser produces both an orange red as well as green color. A device using this phosphor is useful for detecting the lasers and for discriminating between the near infrared, far infrared and UV lasers. The technology is also capable of infrared laser diode beam profiling since the radiation source leaves an imprint on the phosphor that can be photographed. Continued development of the technology offers potential for discrimination between even smaller bandwidths within the infrared spectrum, a possible aid to communication or wavemixing devices that need to rapidly identify and process optical signals.

INTRODUCTION

Availability of large number of infra-red lasers has resulted in the development of very sensitive sensor materials which can detect these lasers. Techniques have been developed to coat these materials uniformly on flat surfaces and to detect the laser either in transmitting or reflecting mode. However, these sensors, though highly efficient in detecting these lasers are unable to discriminate between them. It is desirable in many applications in industry, communication and defense to discriminate, if possible, between the laser wave lengths. Here we present a scheme by which it is possible to discriminate between invisible near infrared, far infrared and UV lasers.

Infrared sensor phosphors are charged by visible or UV radiations prior to the detection of infrared rays. Under infrared illumination, the phosphor emits visible radiation, the upconversion takes place at the expense of charging radiation. Essentially the charging radiation raises the carriers into energetically higher trapping states, from where they are optically stimulated to detrap and recombine with the recombination centers which are generally the impurity ions in the lattice. The observed luminescence is characteristic of these centers. Rare earth ions have been found to be quite efficient recombination centers in these phosphors - the popular phosphors being the alkaline-earth chalcogenides.
MATERIAL PREPARATION

The best amongst alkaline-earth sulfides for laser discrimination, we found through our experiments [1,2], is magnesium sulfide (MgS) doubly doped with rare-earths. Samarium in combination with either Cerium (Ce) or Europium (Eu) or Terbium (Tb) are quite efficient dopants for the discriminator. The infrared detector and discriminator MgS doubly doped with rare earth ions was synthesized in two steps. Initially magnesium sulfate reduced to MgS at 800-850°C by carbon disulfide in the presence of flowing argon. The schematic of the system is shown in Figure 1. When the flowing argon is bubbled through carbon disulfide (CS2) it carries with it CS2 which reacts with anhydrous magnesium sulfate to reduce it to magnesium sulfide. The outflowing gases are passed through water which dissolves the sulfur dioxide produced during the reaction. Complete reduction of magnesium sulfate to magnesium sulfide took approximately 2 hours. Magnesium sulfide, thus obtained, is then doubly doped with Sm3+ and Ce3+ (or Eu2+ or Tb3+) by mixing the magnesium sulfide with Sm (in the form of Sm2O3) and Ce (in the form of Ce2O3) in concentration of 1 x 10⁻³ and 5x10⁻⁴ mole/mole respectively. The above components were thoroughly mixed by dry grinding in a mortar. Mixture was then fired in alumina boat placed in a quartz tube at a temperature of 950°C in an inert atmosphere of flowing argon. Argon was passed through concentrated sulfuric acid to remove any water vapors contained in it. Good phosphors were produced after 2 hours of firing.

In another experiment, MgS doubly doped with rare-earth ions was produced in a single firing. Anhydrous magnesium sulfate and the dopants in the form of oxides or chlorides were blended by stirring in a suspension of acetone on a hot plate at 100°C until most of the acetone has evaporated. The mixture is then placed on a drying oven at 200°C for 1 hour to evaporate the remaining acetone. Next this mixture is placed in alumina combustion boats and fired in a McDanel mullite tube in a tubular furnace at 800°C in an atmosphere of N2 or Ar bubbled through carbon disulfide. Complete reduction of sulfate to sulfide takes nearly two hours.

The samples are allowed to furnace cool in an inert atmosphere. The excess sulfur was washed out by immersing the sample in carbon disulfide. Sample is then ground to pass through a standard 200-mesh sieve. Magnesium sulfide doubly doped with rare earth ions was deposited on thin glass slides by the method of sedimentation. A slurry of magnesium sulfide was made in acetone by immersing the particulate matter settled on the slide was excess alcohol was removed by evaporation. Mixture was then fired in alumina boat placed in a quartz tube at a temperature of 950°C in an inert atmosphere of flowing argon. Argon was passed through concentrated sulfuric acid to remove any water vapors contained in it. Good phosphors were produced after 2 hours of firing.

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METHOD OF DISCRIMINATION

The sample is charged by appropriate visible or UV light. This raises the charged carriers into the traps in the material. Infrared radiation stimulates these carriers to detrapping and recombine with the charge of opposite sign at the recombination center giving out light characteristics of the center. Periodic recharging of the device is required because the trapped charge leaks away over a period of time on storage or is released by the incident infrared rays. For MgS doubly doped with Eu, Sm, the room light (≈500nm) is sufficient to charge it continuously. However for MgS:Ce, Sm near UV light (≈320nm) is required to charge it. When near infrared rays impinge on the MgS doubly doped with cerium and samarium, a green emission characteristic of cerium ion is observed. This phosphor responds to 850nm - 1400nm radiations as shown in figure 2. The peak response is around 1060nm. On the other hand 10.6µm can easily heat the phosphor and the resulting emission is orange characteristic of samarium ion (see figure 3). When a UV laser strikes the phosphor, it will emit both cerium characteristic green as well as samarium characteristic orange color. This property of MgS doubly doped with cerium and samarium lends itself to an application in laser discrimination between three groups of lasers lying in near infrared, far infrared and UV regions (see figure 4). By discerning the color of emission through a filter gating system, it is possible to discriminate between invisible near infrared, far infrared and UV lasers. It may be noted that in addition to these emission characteristics, infrared stimulated luminescence will appear as a burst and then decay with time.
and will require charging or respotting before detecting the subsequent signal. The temporal profile of this emission from the phosphor when subjected to UV irradiation will be similar to the incident UV laser. Moreover, the phosphor would not require any charging and would not decay as long as a steady UV laser is shining on it.

DEVICE SCHEMATIC

On the basis of above description, it is possible to design a laser discriminating device. The schematic of the proposed device is shown in figure 5. The phosphor sensor is continuously or periodically exposed to a charging radiation. When an unspecified laser strikes the phosphor, it stimulates the phosphor emission which is picked up by an optic fiber through a condenser. This optical signal can be directed through either the fiber 1 or fiber 2 by the help of a director. Signal from fiber 1 encounter an appropriate green interference filter, while the signal from fiber 2, an orange filter. Depending upon the nature of the incident laser, the optical signal will reach the photomultiplier (PMT) through either one of the fiber systems or through both of them. Setting on the director will give the information about the color of the emission and therefore, the nature of the laser can be deduced. For further temporal information, the output of the PMT can be coupled to an oscilloscope. If the incident laser is in near infrared further analysis of temporal profile of the emission can lead to subtle distinction in the wavelength of the laser.

EXPLANATION OF THE PHENOMENON

The phenomenon on which the laser discriminator works is as follows: the charging light separates the positive (hole) and negative (electrons) carriers and they are trapped into different sites. For example in Ce and Sm doped magnesium sulfide, after charging, the positive charge (hole) resides at cerium ion and the negative charge (electron) is captured by samarium ion. The near infrared laser optically stimulates electrons from samarium ion, which then, recombine with holes in cerium ion giving out a cerium characteristic green luminescence. On the other hand, far infrared laser such as 10.6μm carbon dioxide laser will heat the phosphor, thereby thermally stimulating the holes from the cerium which eventually recombine at samarium ion resulting in orange samarium emission. Under UV laser both cerium and samarium emissions are observed. These emissions will last as long as the UV laser is striking the phosphor. A model for optically stimulated luminescence (OSL) observed under near infrared laser and thermally stimulated luminescence (TSL) observed under far infrared laser (10.6μm) is shown in Figure 6.

SUMMARY

It is possible to synthesize magnesium sulfide doubly doped with cerium (or europium or terbium) and samarium and use it to discriminate between near infrared, far infrared and UV laser by a scheme presented in this paper.

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REFERENCES


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FIGURE 1. SCHEMATIC OF SYNTHESIS ARRANGEMENT

QUARTZ TUBE

800°C

ANHYDROUS MAGNESIUM SULFATE

ALUMINA BOAT

TUBULAR FURNACE

ARGON

CARBON DISULFIDE

WATER
FIGURE 2. STIMULATION SPECTRUM OF OSL EMISSION
Figure 3.

Optically Stimulated Emission
Intensity (arb. units)

MgS: Ce, Sm

THERMALLY STIMULATED EMISSION
OPTICALLY STIMULATED EMISSION

WAVELENGTH (nm)

400 450 500 550 600 650 700

0 1 2 3

INTENSITY (arb. units)
FIGURE 4. SCHEMATIC OF LASER DISCRIMINATION

**FIG. 4 (a)**

- CHARGING RADIATION
  - MgS:Ce$^{3+}$, Sm$^{3+}$
  - MgS:Eu$^{2+}$, Sm$^{3+}$
  - MgS:Tb$^{3+}$, Sm$^{3+}$

- NEAR INFRARED LASER
  - MgS:Ce$^{4+}$, Sm$^{2+}$
  - MgS:Eu$^{3+}$, Sm$^{2+}$
  - MgS:Tb$^{4+}$, Sm$^{2+}$

- Far Infrared Laser
  - MgS:Ce$^{3+}$, Sm$^{3+}$
  - MgS:Eu$^{2+}$, Sm$^{3+}$
  - MgS:Tb$^{3+}$, Sm$^{3+}$

**FIG. 4 (b)**

- CHARGING RADIATION
  - MgS:Ce$^{3+}$, Sm$^{3+}$
  - MgS:Eu$^{2+}$, Sm$^{3+}$
  - MgS:Tb$^{3+}$, Sm$^{3+}$

- FAR INFRARED LASER
  - MgS:Ce$^{4+}$, Sm$^{2+}$
  - MgS:Eu$^{3+}$, Sm$^{2+}$
  - MgS:Tb$^{4+}$, Sm$^{2+}$

- UV LASER
  - MgS:Ce$^{3+}$, Sm$^{3+}$
  - MgS:Eu$^{2+}$, Sm$^{3+}$
  - MgS:Tb$^{3+}$, Sm$^{3+}$
FIGURE 5. SCHEMATIC OF THE PROPOSED DEVICE
FIGURE 6. A MODEL FOR OBSERVED PHENOMENON