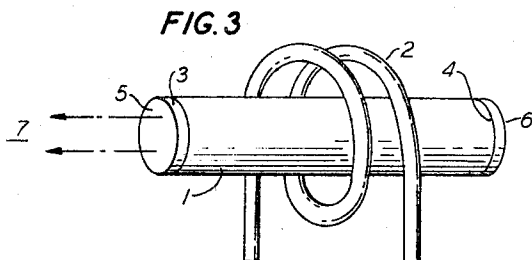
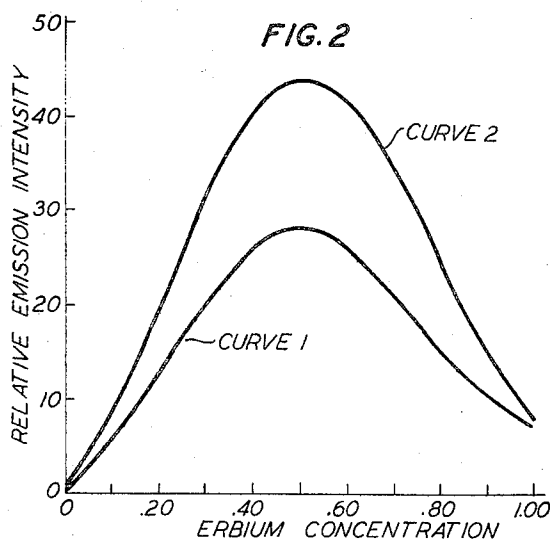
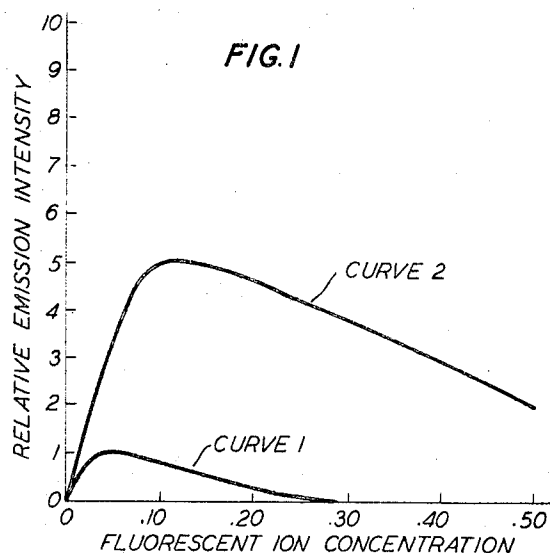


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FLUORESCENT GARNET COMPOSITIONS AND OPTICAL MASER DEVICES UTILIZING SUCH COMPOSITIONS

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Continuation-in-part of application Ser. No. 300,616, Aug. 7, 1963. This application Apr. 1, 1966, Ser. No. 539,462

7 Claims. (Cl. 331-94.5)

This application is a continuation-in-part of copending application Ser. No. 300,616, filed Aug. 7, 1963, now abandoned.

This invention relates to luminescent materials and to devices utilizing such materials. More specifically, the present invention relates to fluorescent compositions containing thulium and/or holmium ions in combination with erbium ions alone or with chromium ions. Still further, the invention relates to fluorescent compositions containing thulium in combination with erbium and ytterbium or in combination with erbium, ytterbium and holmium, alone or with chromium ions. Thus, the inventive compositions may be grouped in the following categories:

- (a) thulium+erbium
- (b) thulium+erbium+yterbium
- (c) holmium+erbium
- (d) holmium+thulium+erbium
- (e) holmium+thulium+erbium+yterbium.

Additionally, chromium may be present in each of the above-noted combinations.

In a preferred embodiment, the invention relates to fluorescent compositions in the garnet system including thulium, holmium, erbium and ytterbium ions.

In general, fluorescent materials evidence either lattice fluorescence or impurity ion fluorescence. In the former case, the fluorescence is a characteristic of the host structure while for the latter case, the fluorescence is attributable to impurity ions in the material, with the material per se merely acting as a host environment for such ions. The fluorescent ions generally contain unpaired electrons which emit radiation by photon processes in the course of returning to the ground state subsequent to excitation to higher energy states.

The list of fluorescent ions is extensive, as is the number of materials capable of providing a host environment for such ions. Commensurate with the art, trivalent rare earth ions exhibit characteristic frequencies at which fluorescence occurs. As noted in the book "Introduction to Luminescence of Solids," by H. W. Leverenz, 1950 Edition, page 98, such frequencies are essentially independent of environment. The intensity of fluorescence, however, is dependent on fluorescent ion concentration, excitation energy and host environment. Attempts by the art to increase fluorescent intensity have been primarily directed, therefore, to adjusting the preceding parameters. A limitation is imposed on the maximum intensities obtainable by this technique, however.

In accordance with the invention, a method has been discovered for removing the preceding limitation on the maximum emission intensities of thulium and holmium ions.

More particularly, it has been discovered that the emission intensities of fluorescent compositions containing thulium and holmium ions either singly or in combination are significantly enhanced by the further incorporation therein of erbium ions. The enhanced intensities result from an energy transfer mechanism whereby excitation energy is absorbed by the erbium ions and then transferred

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to the thulium or holmium ions. Since erbium ions absorb excitation energy over a greater useful frequency spectrum than thulium or holmium ions and, further, since the transfer of such absorbed energy to thulium and holmium ions is both permissible and efficient, the fluorescence of the thulium and holmium ions is substantially increased. Since the energy transfer mechanism between the erbium ions and the thulium and holmium ions is essentially environment independent, any environment in which thulium, holmium and erbium ions fluoresce will exhibit the enhanced emission characteristics of the invention.

Commensurate with the art, the energy level spectra of the erbium, thulium and holmium ions dictate that the host environments be essentially transparent to radiation in the wavelength range to at least 3.0 microns, the short wavelength range up to about 1.9 microns being the excitation energy range and the range from about 1.6 to 3.0 microns and greater being the emitted energy range. The latter range falls within the infrared energy spectrum, so suggesting the use of the inventive compositions in diverse infrared devices.

It has been determined that enhanced thulium fluorescence results when the fluorescent compositions contain at least 10 ions selected from the group consisting of (a) erbium and (b) erbium and ytterbium ions for every 100 thulium ions present in the composition. It has also been determined that enhanced holmium fluorescence results when the fluorescent composition contains at least 10 ions selected from the group consisting of (a) erbium, (b) erbium and thulium and (c) erbium, thulium and ytterbium ions for every 100 holmium ions.

Further, chromium ions may be added in an amount ranging from 0.1-1.0 percent of all the cations present in the case of thulium or holmium.

In a preferred embodiment of the present invention, it has been found that high fluorescent efficiency results in compositions of the general formula



wherein M may be yttrium, gadolinium, lutetium or mixtures thereof, Me may be trivalent gallium or aluminum, alone or in combination with chromium in an amount ranging from .16-1.6 atoms percent of the aluminum or gallium and the sum of $a+b+c+d+e$ equals 3, a ranging from 0.0-2.85, b , c and d ranging from 0.05-1.5 and e ranging from 0.001-1.0. A general preference has been found to exist for compositions wherein a ranges from 0.0-2.59, b ranges from 0.2-1.0, c ranges from 0.1-0.6, d ranges from 0.1-0.8 and e ranges from 0.01-0.6.

The invention may be more readily understood by reference to the accompanying drawing wherein:

FIG. 1 is a graphical representation, on coordinates of relative emission intensity against atom fraction fluorescent thulium and holmium ions, based on the total number of permissible cation sites per formula for the ions, showing the dependency of emission intensity on the concentration of fluorescent ions in fluorescent compositions of matter;

FIG. 2, on coordinates of relative emission intensity and atom fraction trivalent erbium, based on the total number of permissible cation sites per formula for erbium, is a plot showing the dependency of emission intensity on the concentration of erbium ions in thulium and holmium-containing fluorescent compositions of matter; and

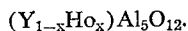
FIG. 3 is a perspective view of an infrared device utilizing compositions of the invention.

Referring more particularly to FIG. 1, there is shown the maximum emission intensities resulting from varying the fluorescent ion concentration in several fluorescent compositions of matter. In this figure, the ordinate measures the relative emission intensities of several garnet

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compositions with the abscissa indicating the thulium ion or holmium ion content of these compositions.

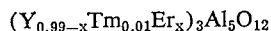
Curve 1 of the girues shows the effect of varying the thulium ion content in one composition having the empirical formula $(Y_{1-x}Tm_x)Al_5O_{12}$. Curve 2 of this figure shows the effect of varying the holmium ion content in another composition having the empirical formula



Commensurate with the understanding of the art, as the concentration of fluorescent ions in a host environment is increased, the emission intensity typically passes through a maximum and then decreases due to interactions between neighboring fluorescent ions. The most suitable concentration range for a given host environment is considered to be within the skill of the art. For the illustrative environments depicted in FIG. 1, inclusions of at least 0.0003 atom fractions trivalent thulium and holmium result in measurable emission intensities. On an atom percent basis, this corresponds to fluorescent compositions in which at least 0.03 atom percent of the cations present have been replaced by trivalent thulium or holmium ions. Measurable emission intensities result for holmium ion inclusions up to at least 0.50 atom fractions (50 atom percent). Similar considerations apply for thulium. Curve 1 of FIG. 1 is affected at high thulium concentrations by transfer to holmium impurities.

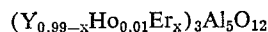
FIG. 2 of the drawing shows the enhancement in emission intensities realized by erbium ion inclusions in the holmium and thulium-containing garnet host environments of FIG. 1. Since the erbium-thulium and erbium-holmium energy transfer mechanisms are independent of environment, FIG. 2 is illustrative of the enhanced emission intensities, realized by erbium ion inclusions in all thulium and holmium-containing fluorescent compositions.

Curve 1 of FIG. 2 shows the effect of erbium ion inclusions in one thulium-containing host environment of FIG. 1 having the empirical formula



A comparison of FIGS. 1 and 2 shows that while the one atom percent thulium composition of curve 1, FIG. 1 exhibits a relative emission intensity of 0.29, erbium ion inclusions therein, as depicted by curve 1 of FIG. 2, permit the attainment of an emission intensity of about 29, an increase by a factor of 100 in intensity. Further, this emission intensity is greater by a factor of 30 than the maximum intensity of one that can be realized by optimizing the thulium ion concentration of the composition in accordance with the curve 1 of FIG. 1.

Curve 2 of FIG. 2 shows the effect of erbium ion inclusions in one holmium-containing host environment of FIG. 1 having the empirical formula



A comparison of FIGS. 1 and 2 shows that while the one atom percent holmium composition of curve 2, FIG. 1 exhibits a relative emission intensity of 1.2 erbium ion inclusions therein, as depicted by curve 2, FIG. 2, permit the attainment of an emission intensity in the order of 44, an increase by a factor of 36 in intensity. Further, this emission intensity is greater by a factor of 7 than the maximum intensity of 6 that can be realized by optimizing the holmium ion concentration of the composition in accordance with curve 2, FIG. 1.

To obtain the emission intensity curves of FIGS. 1 and 2, measurements were made on the noted compositions with a Perkin-Elmer high dispersion spectrometer adapted with a lead sulphide detector. Emission was excited by illuminating samples one inch long by one-eighth inch in diameter with a 3,000 to 8,000 Å. lamp through KG-3 filters. The measurements were made at 77° K. and the intensities are relative values of brightness of the emitting surface in units of power per unit of wavelength range.

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Referring to FIG. 3, there is shown a typical optical maser device utilizing a rod-shaped crystal 1 having the compositions disclosed herein. Pump energy is supplied by means of a helical lamp 2 encompassing rod 1 and connected to an energy source not shown. Lamp 2 is advantageously of a type which provides intense radiation over a broad band typically extending up to 1.9 microns. Xenon lamps are illustrative of this type. Ends 3 and 4 of rod 1 are ground and polished so as to be optically flat and parallel and are silvered so as to provide reflective layers 5 and 6. As indicated, layer 6 is completely reflecting while layer 5 is only partially reflecting so as to permit the escape of coherent radiation. Rod 1 during operation is typically maintained at liquid nitrogen temperature so as to facilitate the obtaining of a negative temperature state. A fuller description of devices of this type is found in the article entitled "Infrared and Optical Masers," pages 21-29 of the June 1961 issue of the Solid State Journal.

Optical masers of the general type illustrated in the figure have been operated utilizing as the active maser material compositions of the invention. Illustrative examples of such maser operation are given below.

Example I

An optical maser was operated using as the active medium calcium molybdate containing about 0.75 atom percent erbium, 0.50 atom percent thulium in place of calcium and 1.25 atom percent niobium in place of molybdenum. The device produced with a xenon pump intense coherent emission having a wavelength of approximately 1.91 microns at liquid nitrogen temperature. The threshold power required was 20 joules. In comparison, the threshold power was 60 joules for a similar composition not containing erbium. The lifetime of the excited thulium electrons in the crystal was approximately 0.9 millisecond.

Example II

An optical maser was operated using as the active medium calcium molybdate containing about 0.75 atom percent erbium, 0.50 atom percent holmium in place of calcium and 1.25 atom percent niobium in place of molybdenum. The device produced with a xenon pump intense coherent radiation having a wavelength of about 2.1 microns at liquid nitrogen temperature. The threshold power required was 100 joules. The lifetime of the excited holmium electrons was approximately 1.3 milliseconds. In comparison, the threshold power was 200 joules for a similar composition not containing erbium.

Example III

An yttrium aluminum garnet crystal of the present invention was grown by the flux technique described in copending application, Ser. No. 508,151 filed Nov. 16, 1965, by melting together 254.1 grams Y_2O_3 , 142.8 grams Yb_2O_3 , 143.4 grams Er_2O_3 , 116.1 grams Tm_2O_3 , 28.4 grams Ho_2O_3 , 880.9 grams Al_2O_3 , 3536 grams PbO , 4322 grams PbF_2 and 197 grams B_2O_3 in a one gallon size covered platinum container. The temperature of the system was raised to 1300° C. and cooling initiated at the rate of ½°/hour until a temperature of 950° C. was reached. Following, the flux was drained and the crystals cooled to room temperature. Finally, ⅜" rods were cut from the resultant crystals which were of the composition $Y_{1.5}Yb_{0.5}Er_{0.5}Tm_{0.4}Ho_{0.1}Al_5O_{12}$.

The resultant crystal was employed in an optical maser, producing (with a xenon pump) intense coherent emission having a wavelength of approximately 2.1 microns at liquid nitrogen temperature. The threshold pulse required was 3.5 joule inches at 77° K. For comparative purposes, the threshold pulse was 9 joule inches for a similar composition not containing ytterbium, 19 joule inches for a similar composition not containing ytterbium and erbium and 45 joule inches for a similar composition not containing ytterbium, erbium and thulium.

It is noted that the device discussed has been largely in terms of the most commonly reported maser design. Although such a design is easily fabricated, other configurations have been disclosed in the literature and are considered within the scope of the invention. The single crystal compositions depicted in FIGS. 1 and 2, for example, were made by the flux growth technique, a recent description of which is found in an article by J. W. Nielsen and E. F. Dearborn in *Physical Chemistry Solids*, 5,202 (1958). The Czochralski melt technique, a recent description of which is found in an article by K. Nassau and L. G. Van Uitert in the *Journal of Applied Physics*, 31, 1508 (1960), was utilized to prepare the compositions of Examples I and II.

Regardless of the process utilized to make the fluorescent compositions and, as understood by the art, it is desirable to minimize the amount of accidentally added rare earth ion impurity in order to insure consistent behavior. Such impurities are generally tolerated in amounts up to 0.01 percent of the principal active rare earth ions intentionally added. The nonactive ion impurity limits are not critical and ordinary reagent grade materials are utilized.

Charge compensation is required in many crystalline host lattices to compensate for the substitution of the trivalent erbium, thulium and holmium ions of the invention for the cations of the lattices. For example, two trivalent ions and a lattice vacancy substitute for three divalent cations. Compensation is also achieved by the further inclusion of compensating ions of the appropriate valency in the lattices. Illustratively, one sodium, lithium, rubidium, potassium or cesium monovalent alkali ion and one trivalent ion substitute for two divalent cations. One vanadium, niobium, tantalum or phosphorus pentavalent ion and one trivalent ion substitute for one hexavalent anion and one divalent cation of the lattice, respectively. One titanium or zirconium tetravalent ion and one trivalent ion substitute for one pentavalent anion and one divalent cation of the lattice, respectively.

Exemplary of the crystals grown by the various techniques are those having the empirical formulas: ABO_4 , where A is calcium, strontium, barium or lead and B is molybdenum or tungsten; ErC_2O_6 where C is titanium, tin, silicon, germanium or zirconium; $ErDO_3$ where D is aluminum, gallium, scandium, lanthanum, yttrium, boron, gadolinium or erbium; EF_2O_6 where E is calcium, magnesium, zinc, strontium, or barium, and F is niobium, tantalum, phosphorus, or vanadium; $Er_3G_5O_{12}$ where G is aluminum or gallium; $Er_2H_2O_7$ where H is titanium, tin, silicon, zirconium, or germanium; $I_2K_2O_7$ where J is calcium, magnesium, zinc, manganese or strontium and K is niobium, tantalum, phosphorus or vanadium; $ErAl_3O_{12}$; and ErL_3 where L is chlorine or fluorine.

One particular composition was grown by the Czochralski technique by mixing and melting at 1450 degrees centigrade, 170 grams $CaMoO_4$, 1.22 grams Er_2O_3 , 0.823 gram Tm_2O_3 and 1.32 grams Nb_2O_5 in an iridium crucible. A seed crystal was inserted into the top surface of the melt and was simultaneously rotated at 30 revolutions per minute and withdrawn from the melt at one-third inch per hour. The resulting calcium molybdate crystal had the composition and characteristics set forth in preceding Example I.

Another particular composition was grown by the flux technique by melting together 287 grams Er_2O_3 , 165 grams Y_2O_3 , 5.8 grams Tm_2O_3 , 254 grams Al_2O_3 , 2232 grams PbO and 2452 grams PbF_2 in a one gallon size covered platinum container. The charged container was located low in a vertical furnace so that its bottom remained cooler than the top of the melt. The temperature was raised to where the bottom of the charge was at 1200 degrees centigrade and then slowly cooled to 800 degrees centigrade. The resulting crystals were dissolved out with nitric acid. The crystals had the empirical formula

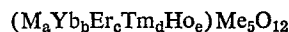
$(Er_{0.5}Y_{0.49}Tm_{0.01})_3Al_5O_{12}$, with the emission characteristic being shown in FIG. 1 of the drawing.

An illustrative process for forming polycrystalline fluorescent powders involves dissolving 6.92 grams $Er(NO_3)_3 \cdot 6H_2O$, 55.7 grams $Y(NO_3)_3 \cdot 6H_2O$, 2.3 grams $Tm(NO_3)_3 \cdot 6H_2O$ and 187.6 grams $Al(NO_3)_3 \cdot 9H_2O$ in water. The solution is evaporated to dryness. The resulting solute is slowly heated to 800 degrees centigrade and further heated at 1200 degrees centigrade for four hours to decompose the nitrates. The powders are then cooled and milled, resulting in a polycrystalline powder having the empirical formula $Er_{1.5}Y_{1.45}Tm_{0.05}Al_5O_{12}$. These powders are excited by radiation in the visible spectrum and produce fluorescence in the 1.91 microns region.

Although the invention has been described with reference to specific embodiments, the embodiments are to be construed as illustrative only and not as limiting in any way the scope and spirit of the invention as defined by the appended claims.

What is claimed is:

1. A fluorescent crystalline composition of matter of the general formula



wherein

M is selected from the group consisting of yttrium, gadolinium, lutetium and mixtures thereof,

Me is selected from the group consisting of gallium and aluminum,

a ranges from 0.0-2.85

b ranges from 0.05-1.5

c ranges from 0.05-1.5

d ranges from 0.05-1.5

e ranges from 0.001-1.0

and the sum of $a+b+c+d+e$ equals 3.

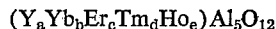
2. A composition in accordance with claim 1 wherein M is yttrium and Me is aluminum.

3. A composition in accordance with claim 1 wherein a ranges from 0.0-2.59, b ranges from 0.2-1.0, c ranges from 0.1-0.6, d ranges from 0.1-0.8 and e ranges from 0.01-0.6.

4. A composition in accordance with claim 1 wherein Me may include chromium in an amount ranging from 0.16-1.6 atoms percent thereof.

5. A composition in accordance with claim 3 wherein M is yttrium and Me is aluminum.

6. A coherent optical maser comprising a negative temperature medium consisting essentially of a composition having the general formula



wherein

a ranges from 0.0-2.85

b ranges from 0.05-1.5

c ranges from 0.05-1.5

d ranges from 0.05-1.5

e ranges from 0.001-1.0

the sum of $a+b+c+d+e$ equaling 3, characterized by at least three distinct energy levels, two of which have a separation in the frequency range of interest, means for pumping said medium with pump energy so that a population inversion is produced between said two separated energy levels and means for focusing said pump energy upon said negative temperature medium.

7. An optical maser in accordance with claim 6 wherein a ranges from 0.0-2.59, b ranges from 0.2-1.0, c ranges from 0.1-0.6, d ranges from 0.1-0.8 and e ranges from 0.01-0.6.

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