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(54) **SUBSTRATE DESIGN FOR OPTIMIZED PERFORMANCE OF UP-CONVERSION PHOSPHORS UTILIZING PROPER THERMAL MANAGEMENT**

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(21) Appl. No.: **12/171,005**

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**Related U.S. Patent Documents**

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| | Filed: | **May 7, 2004** |

U.S. Applications:

(63) Continuation-in-part of application No. 09/919,130, filed on Jul. 31, 2001, now Pat. No. 6,844,387, and a continuation-in-part of application No. 09/919,131, filed on Jul. 31, 2001, now Pat. No. 6,654,161, which is a continuation-in-part of application No. 09/448,657, filed on Nov. 24, 1999, now Pat. No. 6,327,074.

(60) Provisional application No. 60/109,837, filed on Nov. 25, 1998.

(51) **Int. Cl.**

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| ***G02F 1/355*** | (2006.01) |
| ***G11C 13/04*** | (2006.01) |

(52) **U.S. Cl.** ........................................ **359/326**; 365/151

(58) **Field of Classification Search** .................. 359/326; 365/151; 524/130, 132, 403, 413

See application file for complete search history.

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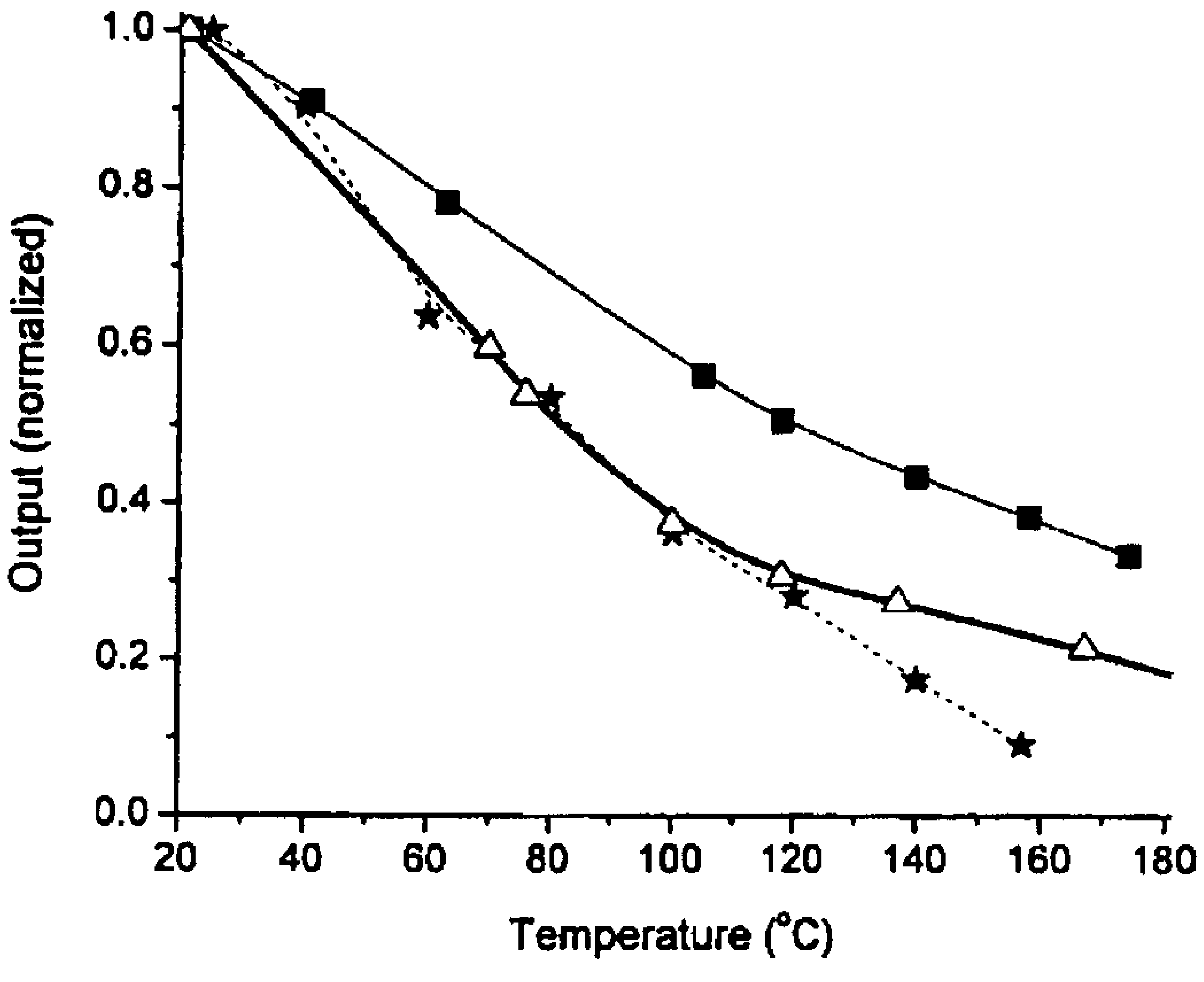
(57) **ABSTRACT**

Methods and compositions for using an up-conversion phosphor as an emitting material in a reflective displays and Polymer compositions for display mediums, and blue green red (BRG) display mediums. Roles of the pumping duration and character on the temperature and the efficiency of the up-conversion process in (Ytterbium, Erbium or Thulium) co-doped fluoride crystals are set forth. Methods, compositions and display mediums for using up-conversion phosphors in both reflective and transmissive displays in which the substrate and pixel shapes are designed to maximally remove heat deposited in the emitting material and thereby improve the efficiency of up conversion.

**44 Claims, 2 Drawing Sheets**



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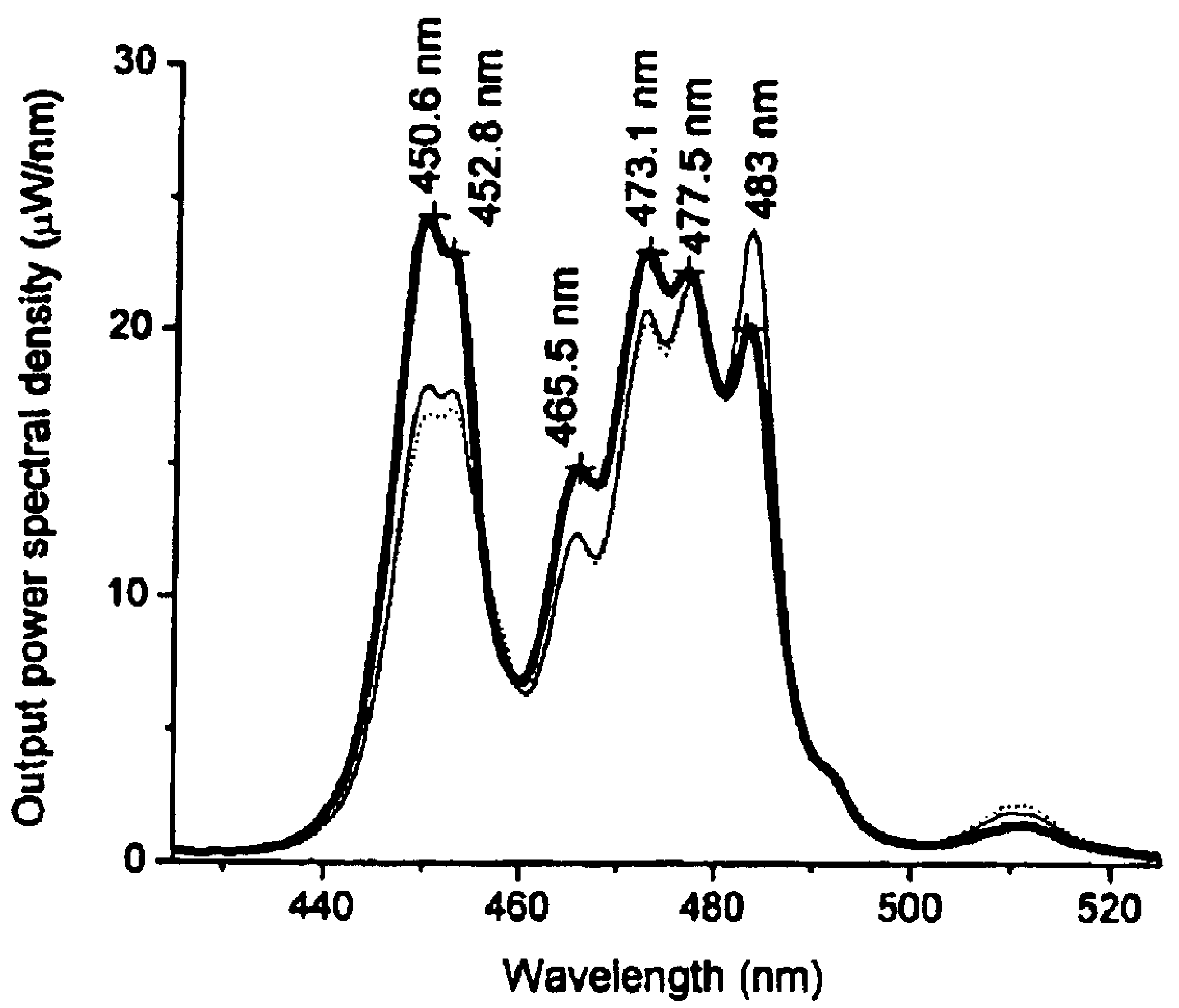


Figure 1

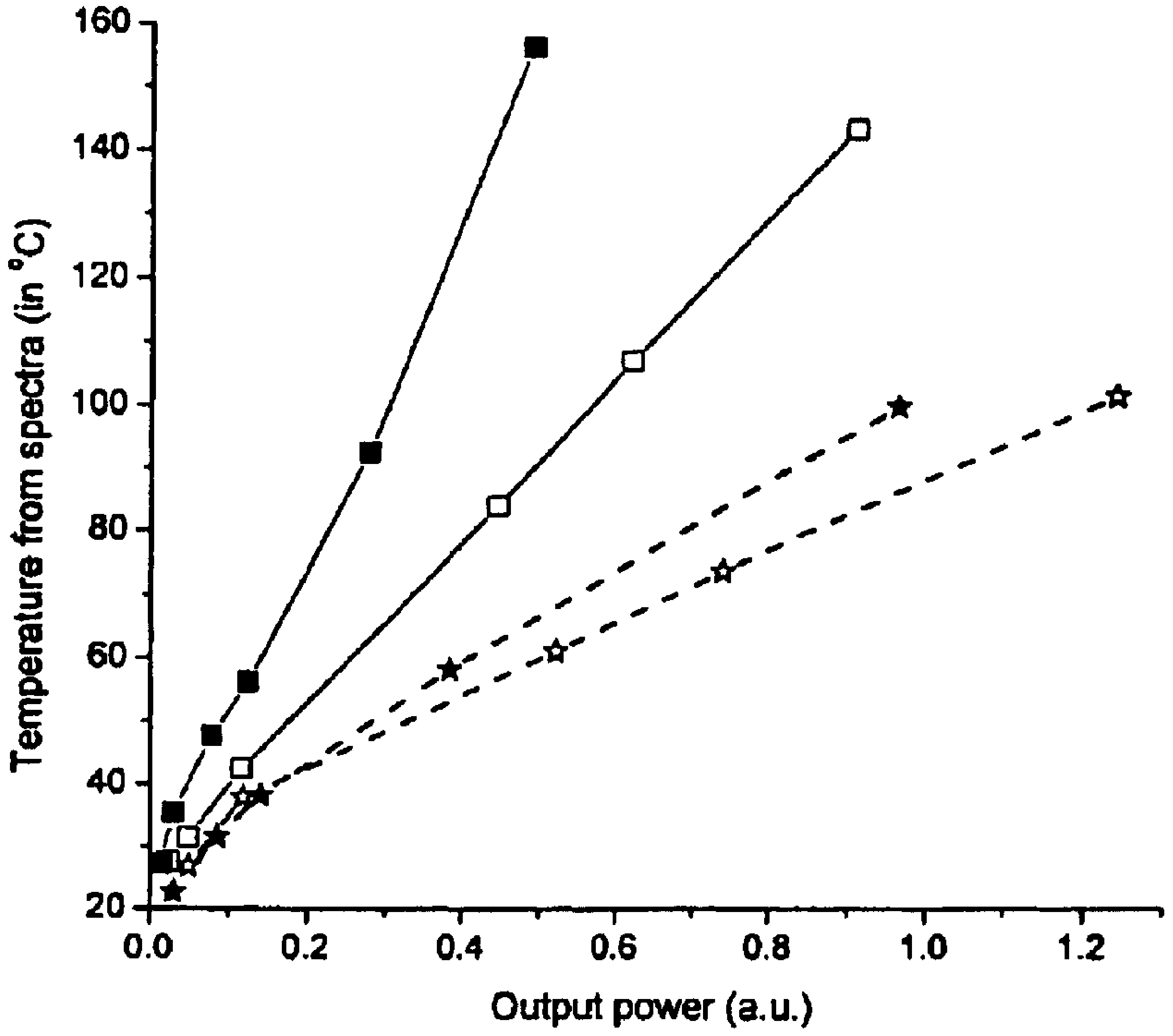
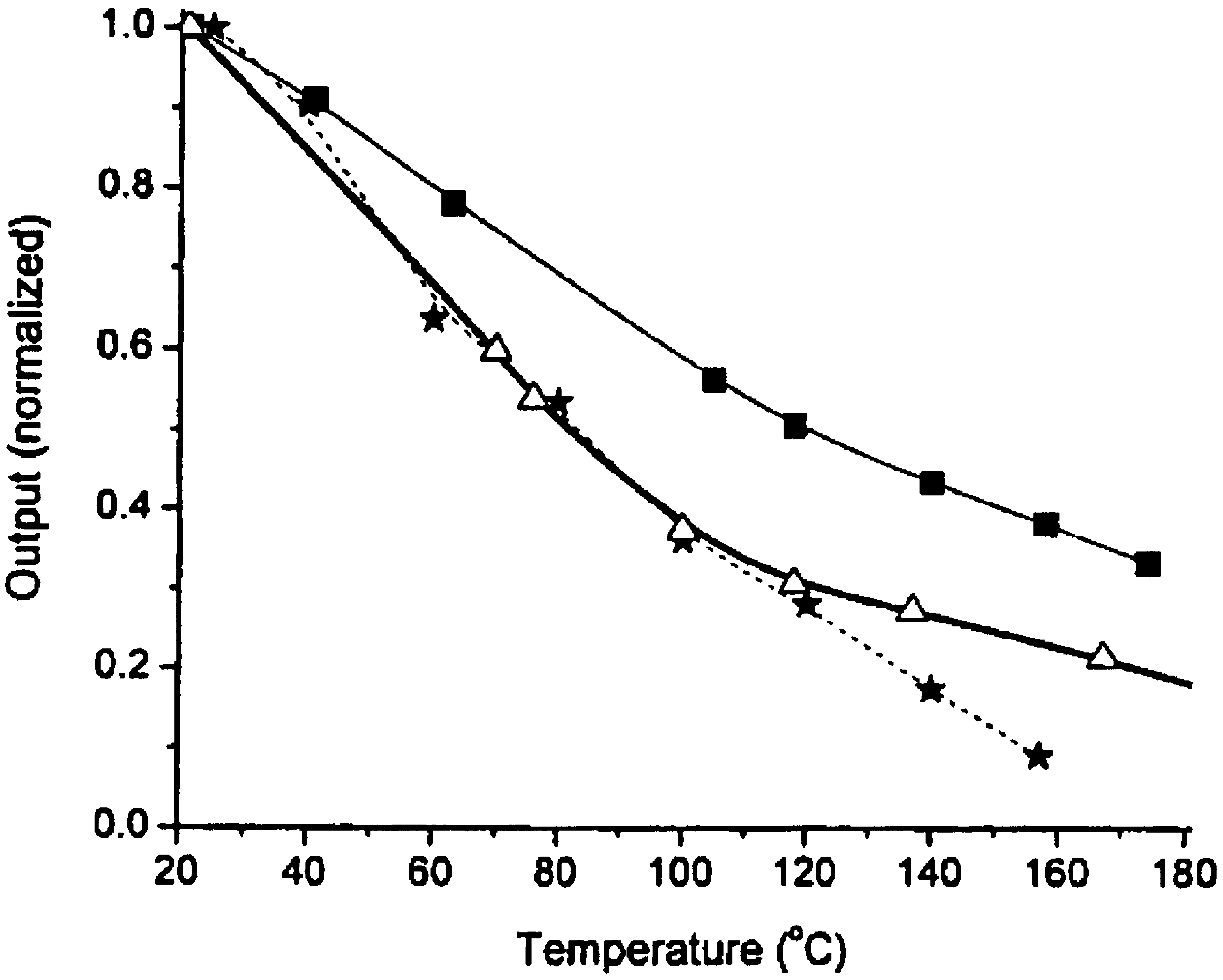


Figure 2



Output (normalized)
1.0
0.8
0.6
0.4
0.2
0.0
20
40
60
80
100
120
140
160
180
Temperature (°C)

Figure 3

# SUBSTRATE DESIGN FOR OPTIMIZED PERFORMANCE OF UP-CONVERSION PHOSPHORS UTILIZING PROPER THERMAL MANAGEMENT

**Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.**

[This invention is a ] *This is a reissue application of U.S. application Ser. No. 10/841,188 filed May 7, 2004, now issued as U.S. Pat. No. 7,075,707, which is a* Continuation-In-Part of U.S. applications Ser. No. 09/919,130 filed Jul. 31, 2001, now issued as U.S. Pat. No. 6,844,387 and Ser. No. 09/919,131 filed Jul. 31, 2001, now issued as U.S. Pat. No. 6,654,161, which are Continuation-In-Part applications of U.S. application Ser. No. 09/448,657 filed Nov. 24, 1999, now U.S. Pat. No. 6,327,074, which claims the benefit of priority to U.S. Provisional Application 60/109,837 filed Nov. 25, 1998.

This invention was funded in part under U.S. Army Contract DAAD199910220.

## FIELD OF INVENTION

This invention relates to the up-conversion efficiency of donor-acceptor doubly doped crystals dispersed in a stabilized polymer or other passive hosts and in particular to a class of fluoride crystals co-doped with ytterbium and erbium or thulium to provide composites and methods for use in luminescent displays.

## BACKGROUND AND PRIOR ART

Displays using liquid crystals have been proposed for generating color displays (see for example, U.S. Pat. Nos. 5,359,345 and 5,724,062 to Hunter). However, these patents require arranging individual pixels in rows and corresponding columns, (column 4, lines 36–39). The devices described can be expensive and complicated to manufacture, and can have narrow angular view ranges with low brightness. Additional display systems have been proposed with similar problems to those described above (see for example, U.S. Pat. No. 4,791,415 to Takahashi; U.S. Pat. No. 4,871,231 to Garcia, Jr.; U.S. Pat. No. 5,184,114 to Brown; U.S. Pat. No. 5,192,946 to Thompson et al.; and U.S. Pat. No. 5,317,348 to Knize).

Several patents have been proposed for displays using two-frequency up-conversion fluorescence (see for example, U.S. Pat. Nos. 5,684,621; 5,764,403; 5,914,807; 5,943,160; and 5,956,172 all to Downing). The Downing '403 patent appears to be the most relevant to the subject invention. Downing '403 is primarily concerned with embodiments where the use of different layers for red, green and blue emitters, abstract, FIG. **6**, and briefly describes some mixing of only crystal type materials in a single display media. However, for the single display media, Downing '403 uses nanometer sized particles, column 4, lines 33+, column 9, lines 42–45, which would inherently be difficult to form, handle and disperse in a display medium.

Other relevant known patents such as U.S. Pat. No. 5,003,179 to Pollack; 5,051,278 to Paz-Pujalt; U.S. Pat. No. 5,154,962 to Mertens et al.; U.S. Pat. No. 5,245,623 to McFarlane; U.S. Pat. No. 5,622,807 to Cutler; U.S. Pat. No. 5,846,684 to Paz-Pujalt et al. also fail to overcome the problems with the other patents described above.

The concept of frequency up-conversion (UC) of infrared-to-visible light in rare-earth (RE) doped materials was reported more than forty years ago for the first time. The efficiency that was observed or expected for this process was low in singly doped media, but it was quickly noticed that the mechanism could be made one or two orders of magnitude more efficient by using ytterbium (Yb) as a sensitizer ion in addition to the active ion: erbium (Er), holmium (Ho), or thulium (Tm). Efficient UC materials were extensively investigated, as they could be used for several potentially useful photonic applications, such as in UC lasers (visible lasers that are pumped by infrared diode lasers), or in display applications. However, because no powerful source existed in the 980-nm region in order to excite those up-converters, no practical product came out of the research. With the development of powerful 980-nm diode lasers lead by the telecommunication industry, a technology that appeared to be too inefficient in the past now has legitimate practical applications.

It has been noticed in the past that pumping conditions caused heating of the material and that higher efficiencies were obtained with low duty cycle excitation. It was also reported that for a same average input power, higher efficiencies were expected in pulsed excitation mode than in continuous wave (cw) excitation due to the quadratic nature of the process. The effect of the pumping conditions for display applications of UC materials need to be understood, as several technologies might be used to form the image. The infrared source can either be scanned (vector-addressed or raster-scan), or the image can be directly projected using Digital Micromirror Devices (MEMS) such as in the Texas Instrument Digital Light Processing (DLP™) technology. In the latter case the materials would be undergoing pulse-excitation, whereas they would be quasi-continuously excited in the second case.

As earlier noted, the development of powerful diode lasers emitting near 980-nm by the telecommunication industry is an enabling technology that allows up conversion to be used in displays. In the past no good pump source was available. Now these diodes provide for practical applications when the efficiency of up-conversion materials are enhanced to provide useful levels of fluorescence.

## SUMMARY OF THE INVENTION

A primary objective of this invention is to provide an inexpensive display medium for two and possibly three dimensional displays.

A secondary objective of this invention is to provide a transparent polymer (plastic) containing particles doped with rare earth ions for use as display medium for two and three dimensional displays.

A third objective of this invention is to provide homogeneously dispersed rare earth doped crystalline particles in a polymer and illuminated with light with wavelength near 980 nm so illuminated and provided with thermal management to result in enhanced luminescence efficiency.

A fourth objective of this invention is to provide a display medium for the up-conversion of 980-nm light to the visible for two and three dimensional displays.

The invention can be used with up-conversion displays with specific applications for two and three dimensional displays such as those described in parent patent application Ser. No. 09/448,657 filed Nov. 24, 1999, now U.S. Pat. No. 6,327,074, by the same assignee as the subject invention and of which is incorporated by reference thereto.

Novel display media according to this invention includes a method for using an up-conversion phosphor as the emitting material in a reflective display comprising the step of designing the shape of said display to maximally remove any heat developed in the emitting material whereby the emittance level of said phosphor is markedly increased.

Further objects and advantages of this invention will be apparent from the following detailed descriptions of the presently preferred embodiments which are described in the following text.

## BRIEF DESCRIPTION OF THE FIGURES

FIG. **1** shows emission spectra of approximately 0.4% Tm, approximately 25% Yb:YLF with the sample holder made of acrylic resin.

FIG. **2** shows the temperature of the emitting powder for various output powers in a sample of approximately 0.4% Tm, 25% Yb:YLF.

FIG. **3** shows the normalized output power from the red, green and blue up-conversion materials as a function of temperature.

## DETAILED DESCRIPTION OF THE INVENTION

Before explaining the disclosed embodiment of the present invention in detail it is to be understood that the invention is not limited in its application to the details of the particular arrangements shown since the invention is capable of other embodiments. Also, the terminology used herein is for the purpose of description and not of limitation.

It has been found in accordance with this invention that pumping with pulses as either by the irradiation or scanning process in a display, and providing proper means for thermal management of the emitting materials, both contribute to making efficient up-conversion displays with diode laser pumping attractive for display applications. This disclosure explains the techniques to achieve the desired higher efficiency.

As previously described, the subject invention can be used with up conversion displays with specific applications for two and three dimensional displays such as those described in parent patent applications U.S. application Ser. Nos. 09/919,130 and 09/919,131 both filed Jul. 31, 2001, now U.S. Pat. Nos. 6,844,387 and 6,654,161, respectively, and Ser. No. 09/448,657 filed Nov. 24, 1999, now U.S. Pat. No. 6,327,074, all to the same assignee as that of the subject invention and all of which are incorporated herein by reference thereto.

Table 1 is a list of various crystals and co-dopants and central wavelengths of the bands of visible emission detected following excitation with a diode laser source operating at approximately 968 nm.

TABLE 1

| Doping ion | | Peak emission wavelength (nm) | | |
|---|---|---|---|---|
| $Yb^{3+}$+ | Crystal host | blue | green | Red |
| $Tm^{3+}$ | $NaYF_4$ | 450, 475 | | 647, 698 |
| | KYF | 481 | | 652 |
| | YLF | 483 | | 648 |
| | $LuPO_4$ | 475 | | 649, 704 |
| $Er^{3+}$ | $NaYF_4$ | 411 | 540 | 660 |
| | KYF | | 550 | 654, 670 |
| | YLF | | 541, 549 | 654, 668 |
| | $LuPO_4$ | | 526, 550 | 657, 667 |
| $Ho^{3+}$ | $NaYF_4$ | | 540 | 648 |
| | KYF | | 544 | 658 |

Table 1: Visible emission of Tm, Er and Ho after Yb excitation in different hosts

In Table 1, $Yb^{3+}$ refers to ytterbium, $Tm^{3+}$ refers to thulium, $Er^{3+}$ refers to erbium, $Ho^{3+}$ refers to holmium, $NaYF_4$ refers to crystal sodium yttrium fluoride, and the supercript **3+** refers to the triply ionized state of the atom. Referring again to Table 1, KYF is short for $KYF_4$ and refers to crystal, potassium yttrium fluoride. YLF is short for $YliF_4$ and refers to the crystal, yttrium lithium fluoride. $LuPO_4$ refers to the crystal, lutetium orthophosphate.

The crystals and dopants listed in Table 1 are illustrative of a few of the combinations that can be used. Other lanthanide (rare earth) atoms in the **3+** state can also be used as dopants. For example, $Nd^{3+}$, $Pr^{3+}$, $Ce^{3+}$ and the like, can also be used. There can be other oxide and flouride crystals that can serve as host crystals. Transition metal dopants such as but not limited to $Cr^{3+}$, $Ti^{3+}$ and the like, can serve as dopants in these host crystals as well. Additionally, other crystals and activators that can be used for this invention can include those listed from pages 171 to page 311 listed in Laser Crystals by Alexander Kaminski, (Springer Verlag, New York) SBN 0-387-09576-4, 1981. These crystals and their activators can include but are not limited to the following described activators and crystal combinations.

Activator $Pr^{3+}$ and crystals can include: $LiYF_4$, $Ca(NbO_3)_2$, $CaWO_4$, and $SrMoO_4$.

Activator $Nd^{3+}$ and crystals can include: $LiYF_4$, $LiYO_2$, $LiNbO_3$, $LiNbP_4O_{12}$, $CaF_2$, $SrF_2$, $BaF_2$, $LaF_3$, $CeF_3$, NaF, $NaCaYF_6$, $NaCaCeF_6$, $NaNdP_4O_{12}$, $YF_3$, CaYF, SrYF, $CeO_2$, $GdF_3$, $YF_3$, $LuF_3$, $CdF_2$, $KY(MoO_4)_2$, $KY(WO_4)_2$, $KNdP_4O_{12}$, $KGd(WO_4)_2$, $CaMg_2Y_2$, $CaAl_4O_7$, $CaAl_{12}O_{19}$, Activator $Nd^{3+}$ and crystals can include: $LiYF_4$, $LiYO_2$, $LiNbO_3$, $LiNbP_4O_{12}$, $CaF_2$, $SrF_2$, $BaF_2$, $LaF_3$, $CeF_3$, NaF, $NaCaYF_6$, $NaCaCeF_6$, $NaNdP_4O_{12}$, $YF_3$, CaYF, SrYF, $CeO_2$, $GdF_3$, $YF_3$, $LuF_3$, $CdF_2$, $KY(MoO_4)_2$, $KY(WO_4)_2$, $KNdP_4O_{12}$, $KGd(WO_4)_2$, $CaMg_2Y_2$, $CaAl_4O_7$, $CaAl_{12}O_{19}$, $CaSc_2O_4$, $Ca_3(VO_4)_2$, $Ca(NbO_3)_2$, $CaMoO_4$, $CaWO_4$, $SrA_{12}O_7$, $SrAl_{12}O_{19}$, $SrMoO_4$, $SrWO_4$, $Y_2O_3$, $YAlO_3$, $Y_3Al_5O_{12}$, $Y_2SiO_5$, $YP_5O_{14}$, $Y_3Sc_2Al_3O_{12}$, $Y_3Sc_2Ga_3O_{12}$, $YVO_4$, $Y_3Ga_5O_{12}$, $(Y, Lu)_3Al_5O_{12}$, $Ba_{0.25}Mg_{2.75}Y_2$, $LaBe_2O_5$, $La_2O_3$, $LaAlO_3$, $LaP_5O_{14}$, $LaNbO_4$, $CeP_5O_{14}$, $NdAl_3(BO_3)_4$, $NdP_5O_{14}$, $Gd_2O_3$, $GdAlO_3$, $GdP_5O_{14}$, $GdScO_3$, $Gd_3Sc_2Al_3O_{12}$, $Gd_3Sc_2Ga_3O_{12}$, $Gd_3Ga_5O_{12}$, $Gd_2(MoO_4)_3$, $LuAlO_3$, $Lu_3Ga_5O_{12}$, $PbMoO_4$, $Bi_4Si_3O_{12}$, $Bi_4Ge_3O_{12}$, $LiLa(MoO_4)_2$, $Li(Nd, La)P_4O_{12}$, $Li(Nd, Gd)P_4O_{12}$, $LiGd(MoO_4)_2$, $NaLa(MoO_4)_2$, $NaLa(WO_4)_2$, $Na_3Nd(PO_4)_2$, $Na_5Nd(WO_4)_2$, $Na_3Gd(WO_4)_2$, Na(Nd, Gd), $Ka(MoO_4)_2$, $K_3Nd(PO_4)_2$, $K_3$(Nd, La), $K_3Nd(MoO_4)_4$, $K_5Bi(MoO_4)_4$, $CaY_4(SiO_4)_3O$, $Ca_{0.25}Ba_{0.75}$, $CaLa_4(SiO_4)_3O$, $CaLa(PO_4)_3O$, $CaGd_4(SiO_4)_3O$, $YScO_3$, $Y_2Ti_2O_7$, $ZrO_2$—$Y_2O_3$, $Ba_2MgGe_2O_7$, $Ba_2ZnGe_2O_7$, $(Nd, Sc)P_5O_{14}$, $(Nd, In)P_5O_{14}$, $(Nd, La)P_5O_{14}$, $(Nd, Gd)Al_3$, $LuScO_3$, $HfO_2$—$Y_2O_3$, $Bi_4(Si, Ge)_3O_{12}$, $Ca_5(PO_4)_3F$, $Sr_5(PP_4)_3F$, and $La_2O_2S$, $CeCl_3$, $Pb_5(PO_4)_3F$.

Activator $Ho^{3+}$ and crystals can include: $LiYF_4$, $Li(Y, Er)F_4$, $LiNbO_3$, $CaF_2$, $LiHoF_4$, $BaY_2F_8$, $Ba(Y, Er)_2F_8$, $HoF_3$, $CaF_2$, $YF_3$, $ErF_3$, $NaCaErF_6$, $K(Y, Er)(WO_4)_2$, $KGd(WO_4)_2$, $Ca(NbO_3)_2$, $CaMoO_4$, $CaWO_4$, $YAlO_3$, $Y_3Al_5O_{12}$, $Y_2SiO_5$,

$YVO_4$, $Y_3Fe_5O_{12}$, $Y_3Ga_5O_{12}$, (Y, Er)$Al_3$, (Y, Er)$_3Al_5O_{12}$, $LaNbO_4$, $GdAlO_3$, $Ho_3Al_5O_{12}$, $Ho_3Sc_2Al_3O_{12}$, $Ho_3Ga_5O_{12}$, $Er_2O_3$, $ErAlO_3$, $Er_2SiO_5$, $Er_3Sc_2Al_3O_{12}$, $ErVO_4$, (Er, Tm, Yb)$_3$, (Er, Lu)$AlO_3$, $Yb_3Al_5O_{12}$, $LuAlO_3$, $Lu_3Al_5O_{12}$, NaLa$(MoO_4)_2$, $CaY_4(SiO_4)_3O$, $SrY_4(SiO_4)_3O$, $SrLa_4(SiO_4)_3O$, $ZrO_2$—$Er_2O_3$, $Ba_2NaNb_5O_{15}$, and $Ca_5(PO_4)_3F$.

Activator $Er^{3+}$ and crystals can include: $LiYF_4$, $LiErF_4$, $CaF_2$, $BaY_2F_8$, Ba(Y, Er)$_2F_8$, $LaF_3$, $YF_3$, $ErF_3$, K(Y, Er)$(WO_4)_2$, $KGd(WO_4)_2$, $CaAl_4O_7$, $Ca(NbO_3)_2$, $CaWO_4$, $YAlO_3$, $Y_3Al_5O_{12}$, (Y, Er)$_3Al_5O_{12}$, $GdAlO_3$, $Er_3Al_5O_{12}$, (Er, Lu)$_3Al_5O_{12}$, $Yb_3Al_5O_{12}$, $LuAlO_3$, and $Lu_3Al_5O_{12}$.

Activator $Ni^{2+}$ and crystals can include: $MgF_2$, $MnF_2$, and MgO. Activator $V^{2+}$ and crystals can include: $MgF_2$. Activator $Co^{2+}$ and crystals can include: $MgF_2$, $KMgF_2$, and $ZnF_2$. Activator $Yb^{3+}$ and crystals can include: $CaF_2$,:$Nd^{3+}$, $Y_3Al_5O_{12}$, $Y_3Ga_5O_{12}$, (Y, Yb)$_3Al_5O_{12}$, $Gd_3Sc_2Al_3O_{12}$, $Gd_3Ga_5O_{12}$, (Yb, Lu)$_3Al_5O_{12}$, $Lu_3Al_5O_{12}$, $Lu_3Sc_2Al_3O_{12}$, and $Lu_3Ga_5O_{12}$. Activator $Sm^{2+}$ and crystals can include: $CaF_2$, $SrF_2$. Activator $Dy^{2+}$ and crystals can include: $CaF_2$, $SrF_2$. Activator $Dy^{3+}$ and crystals can include: Ba(Y,Er)$_2F_8$. Activator $Tm^{2+}$ and crystals can include: $CaF_2$.

Activator $Tm^{3+}$ and crystals can include: $CaF_2$, $SrF_2$, $ErF_3$, $NaCaErF_6$, $LiNbO_3$, $Ca(NbO_3)_2$, $CaMoO_4$, $CaWO_4$, $YAlO_3$, $Y_3Al_5O_{12}$, $YVO_4$, (Y, Er)$Al_3$, (Y, Er)$_3Al_5O_{12}$, $GdAlO_3$, $Er_2O_3$, $ErAlO_3$, $Er_3Al_5O_{12}$, (Er, Yb)$_3Al_5O_{12}$, (Er, Lu)$AlO_3$, $Lu_3Al_5O_{12}$, and $ZrO_2$—$Er_2O_3$.

Activator $U^{3+}$ and crystals can include: $CaF_2$, $SrF_2$, and $BaF_2$. Activator $Pr^{3+}$ and crystals can include: $LaF_3$, $LaCl_3$, $LaBr_3$, $PrCl_3$, and $PrBr_3$. Activator $Cr^{3+}$ and crystals can include: $BeAl_2O_4$, $Al_2O_3$, and $Y_3Al_5O_{12}$. Activator $Eu^{3+}$ and crystals can include: $Y_2O_3$, $YVO_4$. Activator $Gd^{3+}$ and crystals can include: $Y_3Al_5O_{12}$.

Some of the dopant-host combinations can also emit useful infrared light through excitation by absorption of a single photon. This invention can also include systems that emit infrared light by this process of down-conversion(e.g. absorbing a high energy photon and emitting one of lower energy) as well as systems that are excited by such two photon processes as up-conversion(e.g. absorbing more than one low energy photons and emitting one or more higher energy photons).

The rare earth doped crystalline particles are dispersed in a passive polymer host that can be comprised of a copolymer of alkyl acrylate or alkyl methacrylate and a dialkyl vinylbenzylphosphonate, alkyl vinylbenzylphosphonic acid monoester, or vinylbenzylphosphonic acid. The ratios of the acrylate or methacrylate to the phosphonate can range from approximately 95:5 molar ratio to approximately 20:80 molar ratio, respectively. Luminescent heavy metal ions such as rare earth compounds (for example, $NaYF_4$:ErYb) loading in the host polymer matrix can range from approximately 5 up to approximately 80 weight percent. Stabilization of the dispersed heavy element luminophores can be accomplished through complexation with the phosphoryl moieties.

One can prepare the crystals as approximately 10 μm size particles and disperse them in a phosphorylated polymethylmethacrylate (p-PMMA) host. This results in a display medium that can be formed to any desired shape, e.g., as a pixel, can be transparent or not, as desired, and can be affixed to any desired substrate; preferably a heat conductive substrate capable of maximally heat removal.

In this disclosure of the invention, the role of temperature on the efficiency of our up-conversion materials is set forth as well as the effect of various substrate materials, pumping rates and duration on the performance of three of our best

performing up-conversion (UC) materials. The materials used for the up-conversion material are characterized by color: green (Yb, Er doped sodium yttrium fluoride or Yb,Er:$NYF_4$): red (Yb, Br doped yttrium fluoride or Yb,Er:$YF_3$); and, blue (Yb, Tm doped yttrium lithium fluoride or Yb,Tm:$YLF_4$).

The results of the investigation are hereafter set forth.

The performance of the blue up-conversion material was altered when pumping with a continuous source compared to when using short pulse excitation. An early analysis that solved the rate equations numerically illustrated that this behavior could be explained when temperature-dependent transfer and cross-relaxation rates were included. In order to better understand thermal effects, the emission spectra obtained for the three color up-conversion materials when pumped with various intensities and pulse durations was recorded. Reference should now be made to FIG. **1** where a typical result for the blue emitter is shown. Emission spectra of approximately 0.4% Tm, approximately 25% Yb:$YLF_4$. The sample holder was made in acrylic. Three conditions of excitation were used: bold line corresponds to continuous pumping, the thin line represents approximately 5 ms pulse at a repetition rate of approximately 30 Hz, and the dotted line represents approximately 2 ms pulse at a repetition rate of approximately 30 Hz. The output luminance in the blue was the same in the three excitation conditions (approximately 58 mLm). The output power was the same in the three excitation conditions.

The peaks at approximately 463 nm and approximately 481 nm originate from the same upper energy level but different Stark splittings sub-levels. Those sub-levels are thermalized and the spectral distribution is therefore a signature of the temperature inside the sample. It can be shown from FIG. **1** that the temperature of the sample is much higher when continuous pumping is used than when pulsed excitation is used.

By using a hot plate and a thermocouple, the emission spectra after excitation with a low energy pulse the emission spectra can be recorded (no heating due to the excitation) at different pre-determined temperatures. From those measurements, one can determine the temperature in the sample at different output powers for various pump durations.

Reference should now be made to FIG. **2** which shows the resulting temperatures for two types of powder holders: acrylic and copper. The temperatures of the emitting powder for various output power in a sample of approximately 0.4% Tm, approximately 25% Yb: $YLF_4$ was recorded to establish if the nature of the holders was significant. Two sample holders were used: acrylic(solid lines) and copper(dashed lines). The solid symbols correspond to cw(continuous wave) excitation, the hollow symbols are for an approximately 30 Hz, approximately 5 ms pulse. The powder was contained in a cylinder hole of approximately 750 micron diameter, approximately 500 micron deep. There are two conclusions that can be drawn from that plot: first, for a given output power (or brightness), the temperature reached when pumping continuously is higher than when a short excitation pulse is used. Second, using a substrate that extracts the heat produced (high heat diffusion coefficient) significantly reduces the heating of the powder.

Finally, the total output power as the temperature of the sample was measured. The results are shown in FIG. **3** for the three red, green and blue (RGB) emitters in which the normalized output power from the red, green and blue up-conversion materials as a function of temperature are plotted. FIG. **3** shows normalized output power at low incident pump intensity from the red(thin line and solid stars), green(thin line and solid squares), and blue(thick line and hollow triangles) up-conversion materials as a function of temperature.

Through the green phosphor is only slightly affected by heating, the blue and the red emitters' performance greatly diminish when operated at the temperature reached when no thermal management is included in the design of a display. Experimental results show that lowering the operating temperature is the key to optimizing up-conversion materials performance. As shown by the graph of FIG. **3**, the three color up-conversion material has a maximum normalized output at a temperature of approximately 20 C when the same pulse excitation is applied to the three color up-conversion material. Preliminary simulations using Femlab™ show that using a material with high heat-diffusion-coefficient such as metals (copper) for reflective displays or chemical vapor deposition (CVD) diamond for both reflective and transmissive displays, as a substrate, reducing the pixel size to less than approximately 250 microns, and using pixels in the form of inverted cones to hold the up converting medium, will enable the use of up-conversion materials at temperatures within approximately 20° C. of room-temperature which can be considered approximately room temperature.

Photonic displays based on up-conversion materials have numerous advantages that make the technology appealing: the phosphors emit very narrow lines (~40 nm wide) which produce a very wide color gamut (That is, they define area of the color response diagram much greater than that of conventional cathode ray tube phosphors) and saturated colors, high-brightness (several kCd/m$^2$) can be achieved without damage to the phosphors, and no vacuum nor high-voltage is required. However, improving the materials' efficiency is paramount to making this technology able to compete with existing display technologies. In this work, one important step was identified in order to optimize the performance of the up-conversion phosphors: using heat-conductive substrate such as copper or aluminum or CVD diamond will reduce the operating temperature of the powder and improve the efficiency (efficiency is the ratio of the light power output of the display to the total power input to the display) of the display.

While the invention has been described, disclosed, illustrated and shown in various terms of certain embodiments or modifications which it has presumed in practice, the scope of the invention is not intended to be, nor should it be deemed to be, limited thereby and such other modifications or embodiments as may be suggested by the teachings herein are particularly reserved especially as they fall within the breadth and scope of the claims here appended.

We claim:

**1**. A method for using an up-conversion phosphor as an emitting material in a reflective display comprising [the step of]:

[designing] *configuring* a shape of said display to hold said up-conversion phosphor;

pumping said display from a source with an intensity and a duration to excite said up-conversion phosphor; *and*

[selecting] *configuring* said display to maximally remove any heat developed in the up-conversion phosphor in the emitting material during said pumping to optimize a performance of said up-conversion phosphor, wherein the luminescent efficiency of said up-conversion phosphor is substantially increased.

**2**. The method according to claim **1** wherein said reflective display is a pixel.

**3**. The method according to claim **1** wherein said reflective display is a substrate.

**4**. The method according to claim **3** wherein said reflective display is heat conductive.

**5**. The method according to claim **3** wherein said reflective display is copper.

**6**. The method according to claim **3** wherein said reflective display is aluminum.

**7**. The method according to claim **3** wherein said reflective display is chemical vapor deposition (CVD) diamond.

**8**. A method for using an up-conversion phosphor as an emitting material in a transmissive display comprising the step of:

designing a shape and material of said display to maximally remove any heat developed in the emitting material when pumped with an intensity and a duration, wherein the luminescent efficiency of said up-conversion phosphor is substantially increased.

**9**. The method according to claim **8** wherein said transmissive display is a pixel.

**10**. The method according to claim **8** wherein said transmissive display is a substrate.

**11**. The method according to claim **8** wherein said transmissive display is heat conductive.

**12**. The method according to claim **8** wherein said transmissive display is copper.

**13**. The method according to claim **8** wherein said transmissive display is aluminum.

**14**. The method according to claim **8** wherein said transmissive display is chemical vapor deposition (CVD) diamond.

**15**. A blue green red (BRG) display medium comprising:

(a) pixels having a blue, a green and a red emitter dispersed on a high heat conductive substrate; and,

(b) means for pulsing said pixels with a beam of light with wavelength near approximately 980 μm, wherein said high heat conductive substrate provides thermal management to optimize performance of said pixels to emit appropriate blue, green and red luminescence when pumped with the 980 μm wavelength beam of light.

**16**. The blue green red (BRG) display medium according to claim **15** wherein said means is by short pulse excitation.

**17**. An up conversion display comprising:

a three color up-conversion material having three different emitters;

a heat-conductive substrate *configured* to reduce the operating temperature of the three color up-conversion material, wherein the substrate has a shape *configured* to hold the three color up-conversion material; and

a pumping source [for providing] *configured to provide* a pulse having an intensity and a duration for exciting the three color up-conversion material, wherein the three color up-conversion material and the pulse intensity and pulse duration are selected to optimize the up-conversion process to emit the three colors and improve the efficiency of the display.

*18. The up conversion display recited in claim 17, wherein said substrate comprises copper.*

*19. The up conversion display recited in claim 17, wherein said substrate comprises aluminum.*

*20. The up conversion display recited in claim 17, wherein said substrate comprises chemical vapor deposition (CVD) diamond.*

*21. The up conversion display recited in claim 17, wherein the up-conversion material comprises a green up-conversion material.*

*22. The up conversion display recited in claim 21, wherein the green up-conversion material comprises at least one of Yb, Er doped sodium yttrium fluoride, and Yb,Er:NYF*$_4$.

*23. The up conversion display recited in claim 17, wherein the up-conversion material comprises a red up-conversion material.*

*24. The up conversion display recited in claim 23, wherein the red up-conversion material comprises at least one of Yb, Er doped yttrium fluoride and Yb,Er:YF*$_3$.

*25. The up conversion display recited in claim 17, wherein the up-conversion material comprises a blue up-conversion material.*

*26. The up conversion display recited in claim 25, wherein the blue up-conversion material comprises at least one of Yb, Tm doped yttrium lithium fluoride and Yb,Tm:YLF*$_4$.

*27. The up conversion display recited in claim 17, wherein the three color up-conversion material having three different emitters further comprises a passive polymer host.*

*28. The up conversion display recited in claim 27, wherein the passive polymer host comprises at least one copolymer, comprising:*

*residues of alkyl acrylate or alkyl methacrylate; and*

*residues of dialkyl vinylbenzylphosphonate, alkyl vinylbenzylphosphonic acid monoester, or vinylbenzylphosphonic acid.*

*29. The up conversion display recited in claim 27, wherein the molar ratio of the residues of alkyl acrylate or alkyl methacrylate to the residues of dialkyl vinylbenzylphosphonate, alkyl vinylbenzylphosphonic acid monoester, or vinylbenzylphosphonic acid is from about 95:5 to about 20:80.*

*30. A method for using an up-conversion phosphor as an emitting material in a reflective display comprising:*

*configuring said display with a heat-conductive substrate to hold said up-conversion phosphor; and*

*pumping said display from a source with an intensity and a duration to excite said up-conversion phosphor and to enable removal of heat developed in the up-conversion phosphor during said pumping, thereby increasing the luminescent efficiency of said up-conversion phosphor.*

*31. The method recited in claim 30, wherein said substrate comprises copper.*

*32. The method recited in claim 30, wherein said substrate comprises aluminum.*

*33. The method recited in claim 30, wherein said substrate comprises chemical vapor deposition (CVD) diamond.*

*34. The method recited in claim 30, wherein the up-conversion material comprises a green up-conversion material.*

*35. The method recited in claim 34, wherein the green up-conversion material comprises at least one of Yb, Er doped sodium yttrium fluoride, and Yb,Er:NYF4.*

*36. The method recited in claim 30, wherein the up-conversion material comprises a red up-conversion material.*

*37. The method recited in claim 36, wherein the red up-conversion material comprises at least one of Yb, Er doped yttrium fluoride and Yb,Er:YF3.*

*38. The method recited in claim 30, wherein the up-conversion material comprises a blue up-conversion material.*

*39. The method recited in claim 38, wherein the blue up-conversion material comprises at least one of Yb, Tm doped yttrium lithium fluoride and Yb,Tm:YLF4.*

*40. The method recited in claim 30, wherein the method is used on a three color up-conversion material having three different emitters and a passive polymer host.*

*41. The method recited in claim 40, wherein the passive polymer host comprises at least one copolymer, comprising:*

*residues of alkyl acrylate or alkyl methacrylate; and*

*residues of dialkyl vinylbenzylphosphonate, alkyl vinylbenzylphosphonic acid monoester, or vinylbenzylphosphonic acid.*

*42. The method recited in claim 41, wherein the molar ratio of the residues of alkyl acrylate or alkyl methacrylate to the residues of dialkyl vinylbenzylphosphonate, alkyl vinylbenzylphosphonic acid monoester, or vinylbenzylphosphonic acid is from about 95:5 to about 20:80.*

*43. A method of using a three color up-conversion material having three different emitters and a pumping source in a reflective display, comprising:*

*configuring said display with a heat-conductive substrate to reduce the operating temperature of the three color up-conversion material, wherein the substrate has a shape configured to hold the three color up-conversion material; and*

*pumping said display to provide a pulse having an intensity and a duration for exciting the three color up-conversion material, wherein the pulse intensity and pulse duration are selectable to substantially optimize the up-conversion process to emit the three colors and improve the efficiency of the display.*

*44. A photonic display device, comprising:*

*at least one up-conversion material comprising:*

*at least one activator;*

*at least one co-dopant; and*

*a passive polymer host;*

*a heat conducting substrate for thermal management; and*

*a pumping source.*

* * * * *

UNITED STATES PATENT AND TRADEMARK OFFICE

# CERTIFICATE OF CORRECTION

PATENT NO. : RE42,389 E
APPLICATION NO. : 12/171005
DATED : May 24, 2011
INVENTOR(S) : Rapaport-Zoubir et al.

Page 1 of 2

It is certified that error appears in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Title page, item (57), under “Abstract”, in Column 2, Line 4, delete “(BRG)” and insert -- (BGR) --.

Column 1, lines 10-22, delete “[This invention is a ] *This is a reissue application of U.S. application Ser. No. 10/841,188 filed May 7, 2004, now issued as U.S. Pat. No. 7,075,707, which is a* Continuation-In-Part of U.S. applications Ser. No. 09/919,130 filed Jul. 31, 2001, now issued as U.S. Pat. No. 6,844,387 and Ser. No. 09/919,131 filed Jul. 31, 2001, now issued as U.S. Pat. No. 6,654,161, which are Continuation-In-Part applications of U.S. application Ser. No. 09/448,657 filed Nov. 24, 1999, now U.S. Pat. No. 6,327,074, which claims the benefit of priority to U.S. Provisional Application 60/109,837 filed Nov. 25, 1998.

This invention was funded in part under U.S. Army Contract DAAD199910220.” and

insert

-- *CROSS REFERENCE TO RELATED APPLICATIONS*
*This is a reissue application of U.S. application Ser. No. 10/841,188 filed May 7, 2004, now issued as U.S. Pat. No. 7,075,707, which is a* Continuation-In-Part of U.S. applications Ser. No. *09/919,130* filed Jul. 31, 2001, now issued as U.S. Pat. No. 6,844,387 and Ser. No. *09/919,131* filed Jul. 31, 2001, now issued as U.S. Pat. No. 6,654,161, which are Continuation-In-Part applications of U.S. application Ser. No. *09/448,657* filed Nov. 24, 1999, now U.S. Pat. No. 6,327,074, which claims the benefit of priority to U.S. Provisional Application 60/109,837 filed Nov. 25, 1998.
*STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT*
This invention was funded in part under U.S. Army Contract DAAD 199910220. --.

Column 8, line 33, in Claim 15, delete “(BRG)” and insert -- ([BRG]*BGR*) --.

Column 8, line 42, in Claim 16, delete “(BRG)” and insert -- ([BRG]*BGR*) --.

Column 8, line 44, in Claim 17, delete “up conversion” and insert -- [up conversion]*up-conversion* --.

Column 8, line 58, in Claim 18, delete “*up conversion*” and insert -- *up-conversion* --.

Signed and Sealed this
Fourteenth Day of August, 2012

David J. Kappos

David J. Kappos
*Director of the United States Patent and Trademark Office*

Column 8, line 60, in Claim 19, delete "*up conversion*" and insert -- *up-conversion* --.

Column 8, line 62, in Claim 20, delete "*up conversion*" and insert -- *up-conversion* --.

Column 8, line 65, in Claim 21, delete "*up conversion*" and insert -- *up-conversion* --.

Column 9, line 1, in Claim 22, delete "*up conversion*" and insert -- *up-conversion* --.

Column 9, line 3, in Claim 22, delete "*fluoride,*" and insert -- *fluoride* --.

Column 9, line 4, in Claim 23, delete "*up conversion*" and insert -- *up-conversion* --.

Column 9, line 7, in Claim 24, delete "up conversion" and insert -- up-conversion --.

Column 9, line 10, in Claim 25, delete "*up conversion*" and insert -- *up-conversion* --.

Column 9, line 13, in Claim 26, delete "*up conversion*" and insert -- *up-conversion* --.

Column 9, line 15, in Claim 27, delete "*up conversion*" and insert -- *up-conversion* --.

Column 9, line 18, in Claim 28, delete "*up conversion*" and insert -- *up-conversion* --.

Column 9, line 25, in Claim 29, delete "*up conversion display recited in claim 27,*" and insert -- *up-conversion display recited in claim 28,* --.

Column 9, line 51, in Claim 35, delete "*fluoride, and Yb,Er:NYF4.*" and insert -- *fluoride and* $Yb,Er:NYF_4$. --.

Column 10, line 6, in Claim 37, delete "*Yb,Er:YF3.*" and insert -- $Yb,Er:YF_3$. --.

Column 10, line 13, in Claim 39, delete "*Yb,Tm:YLF4.*" and insert -- $Yb,Tm:YLF_4$. --.