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(54) **COMPOSITE PHOSPHORS BASED ON
COATING POROUS SUBSTRATES**

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(57) **ABSTRACT**

A composite material is provided including a phosphor material of at least one of among hafnium oxide, niobium oxide, tantalum oxide or zirconium oxide as a conformal coating on a porous substrate, the composite characterized as exhibiting photoluminescence at room temperature. Also provided is a composite material including a phosphor material of at least one of among hafnium oxide, niobium oxide, tantalum oxide, zinc oxide or zirconium oxide as a conformal coating on a porous substrate, the composite characterized as exhibiting photoluminescence at room temperature and as having a broad emission spectrum having a width at 1/2 maximum greater than 80 nm.

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Related U.S. Application Data

(60) Provisional application No. 61/063,154, filed on Jan. 30, 2008, provisional application No. 61/063,153, filed on Jan. 30, 2008.

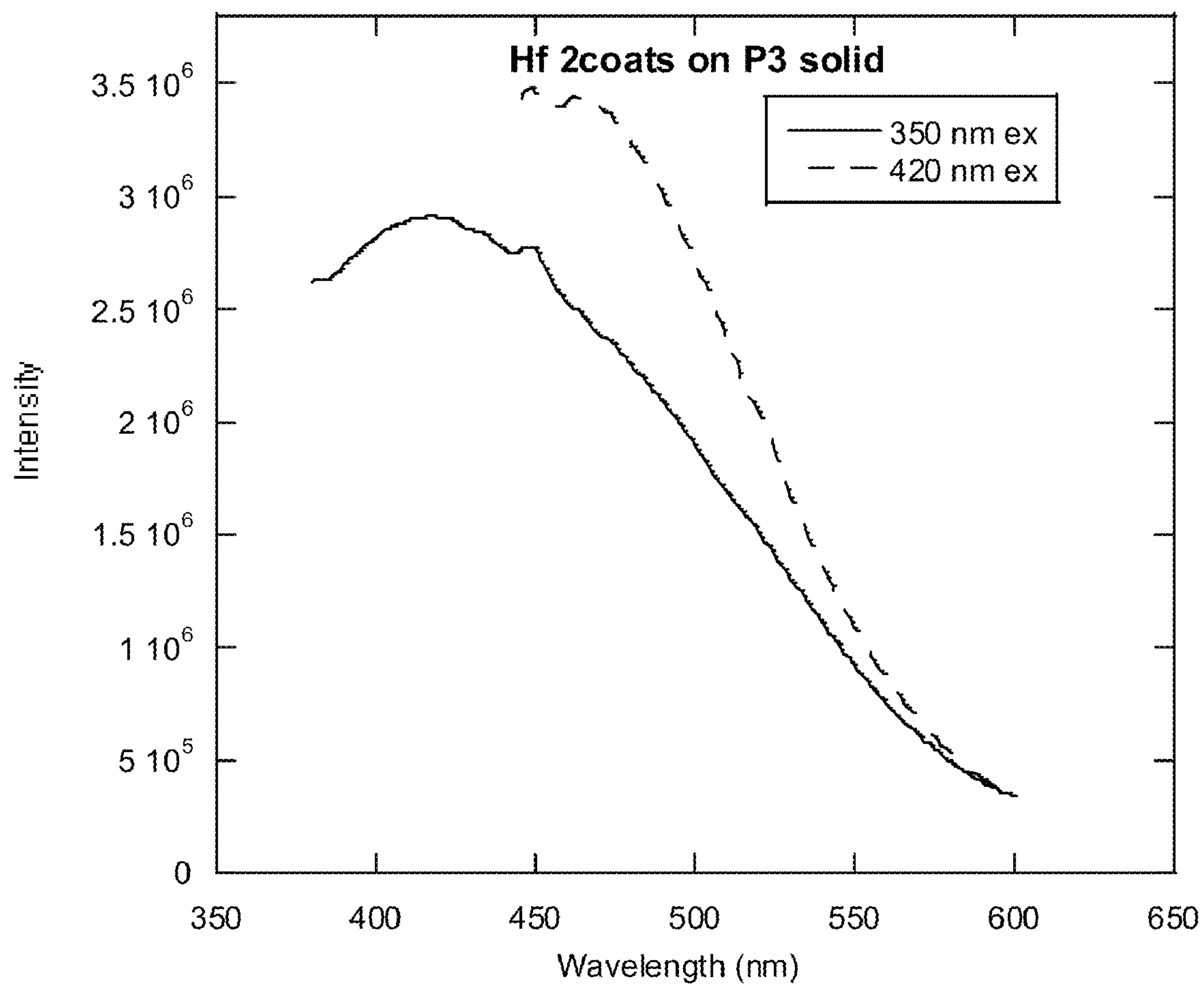


Fig. 1

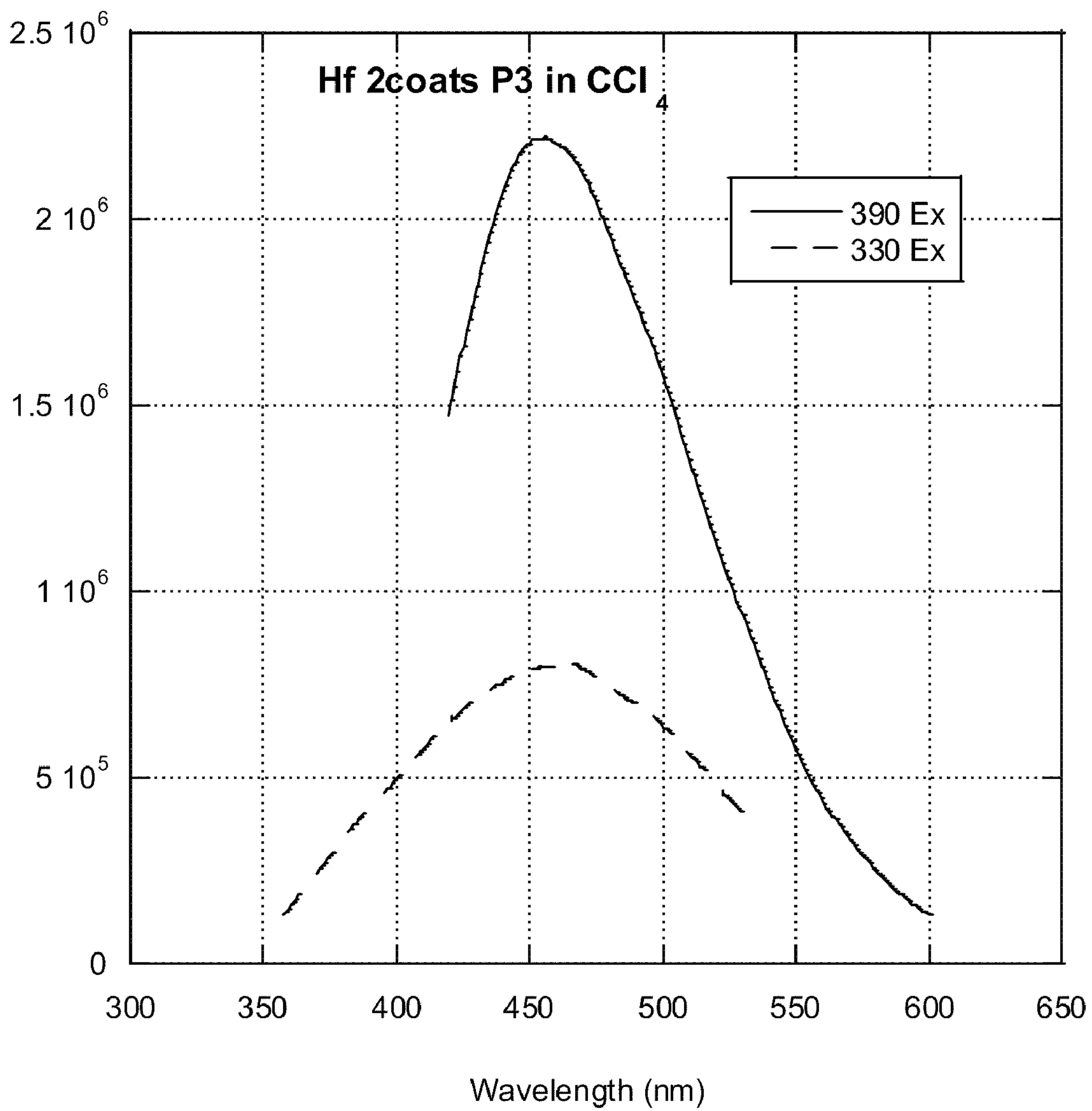


Fig. 2

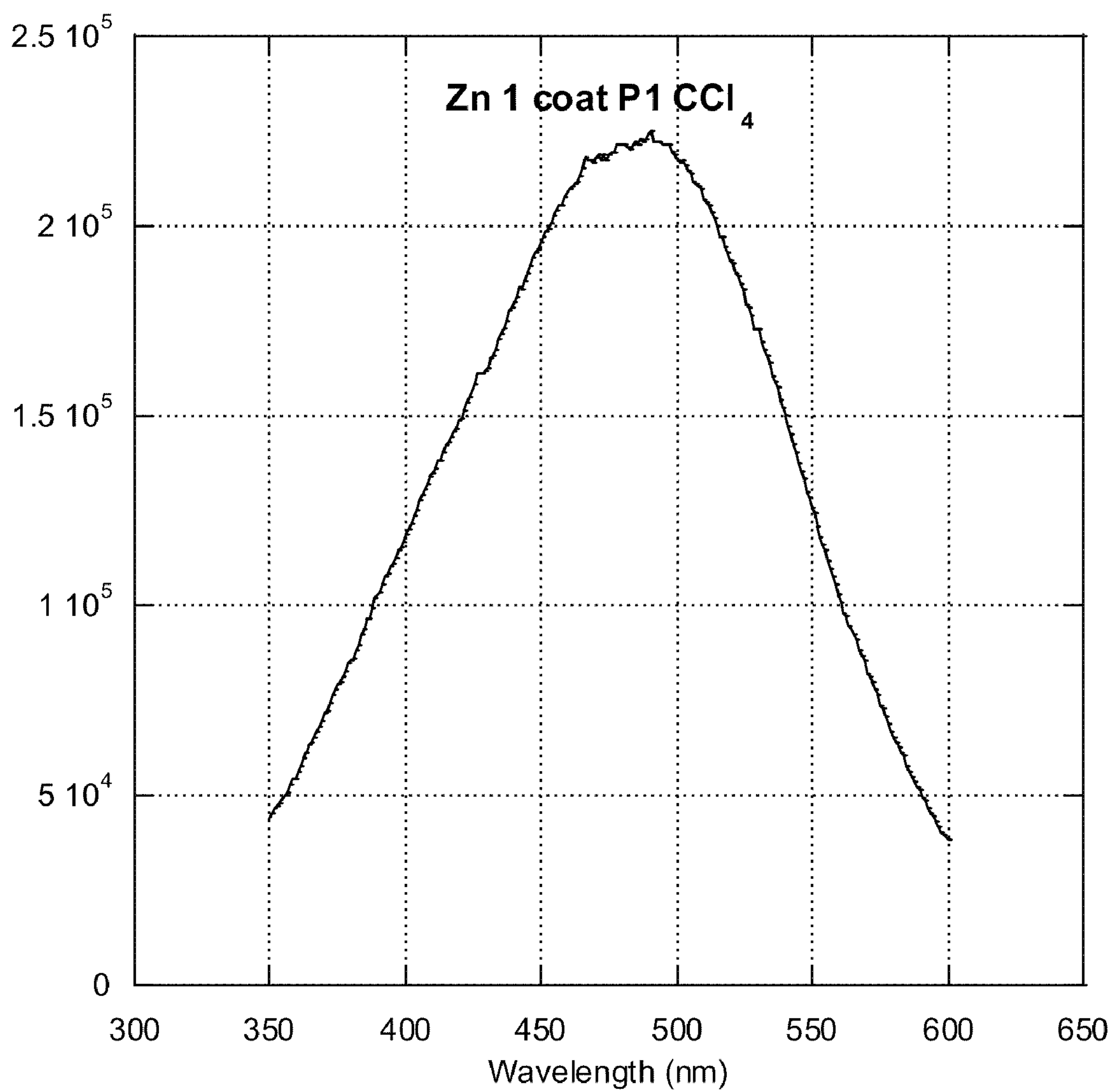


Fig. 3

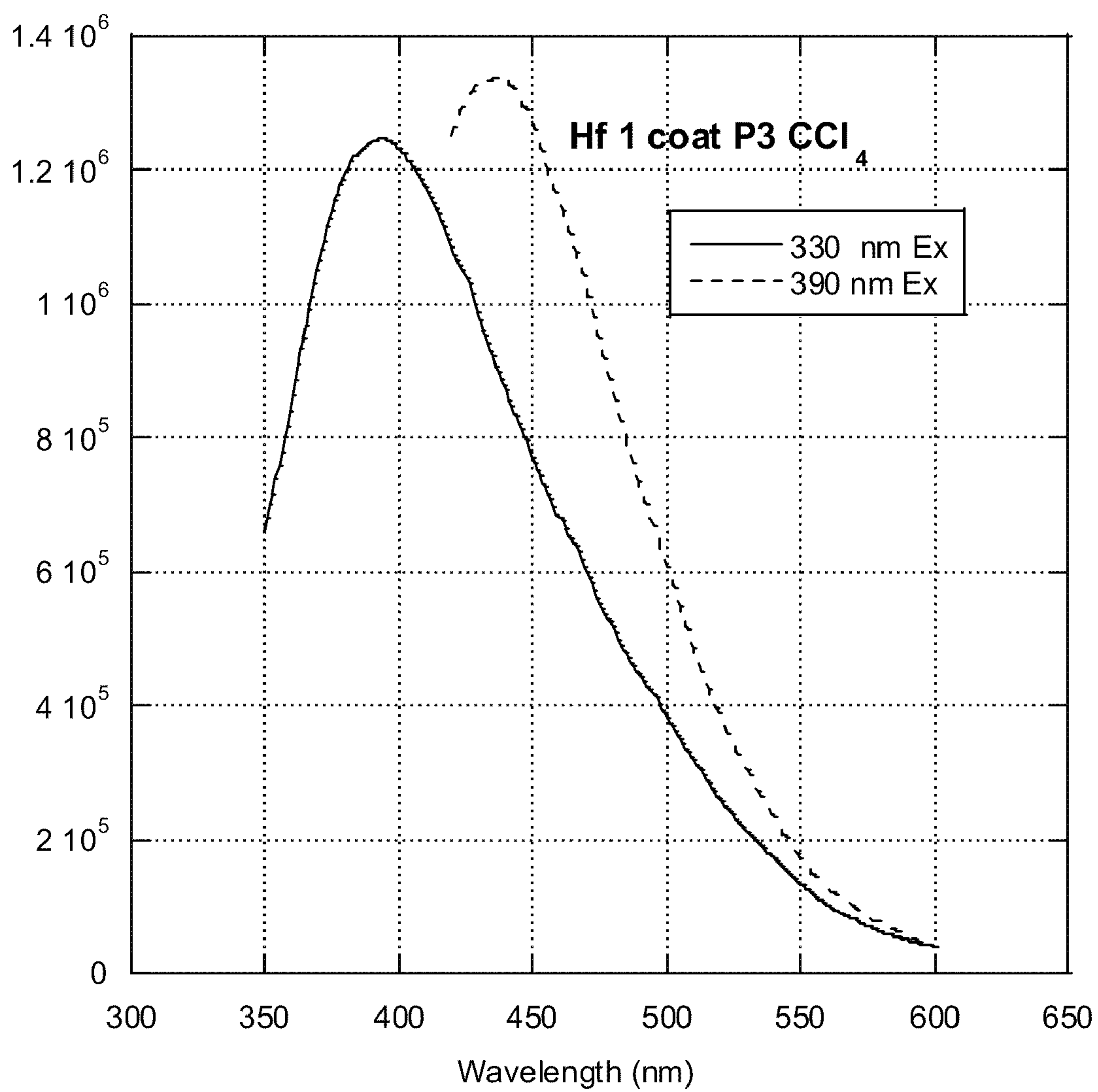


Fig. 4

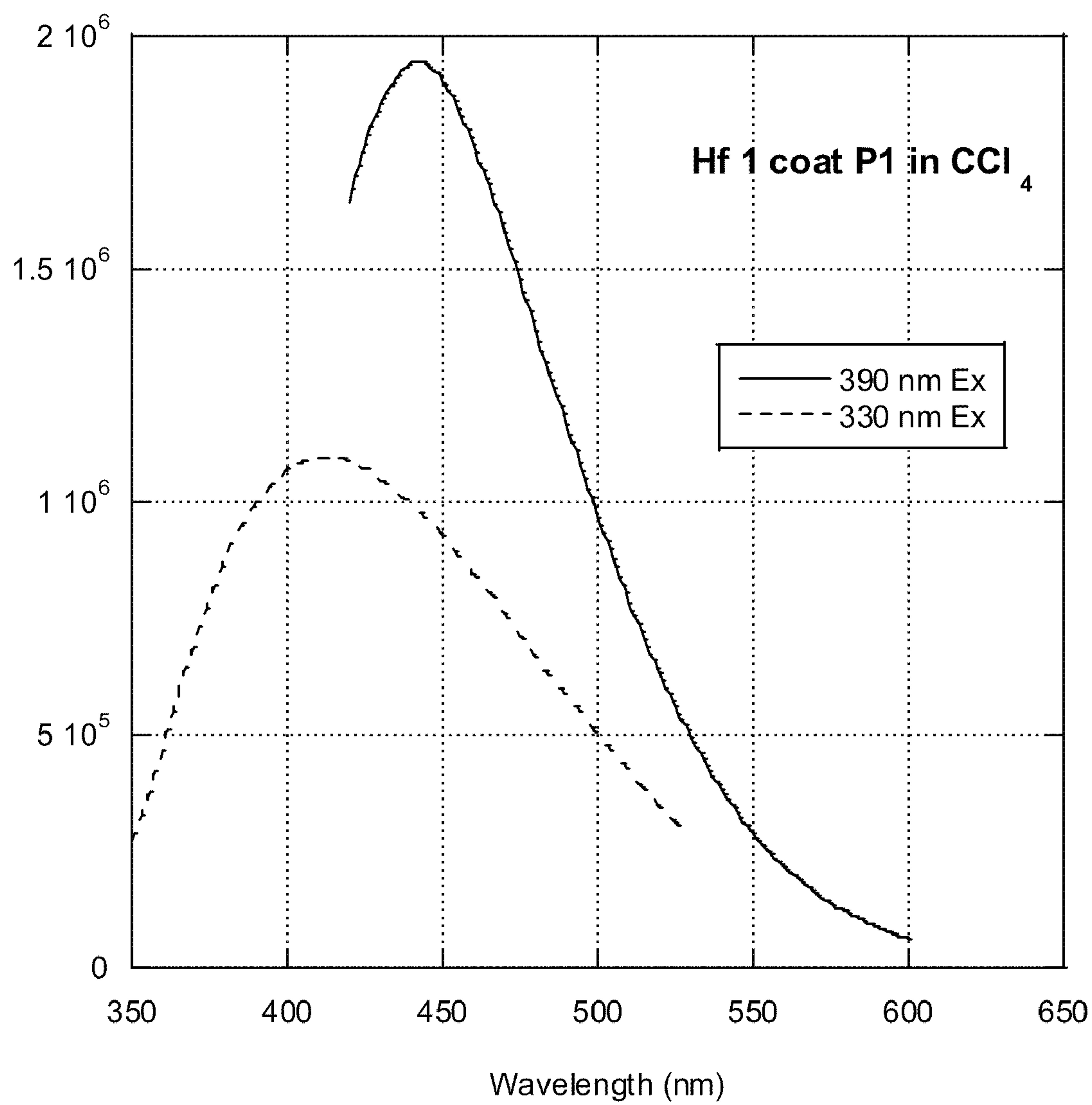


Fig. 5

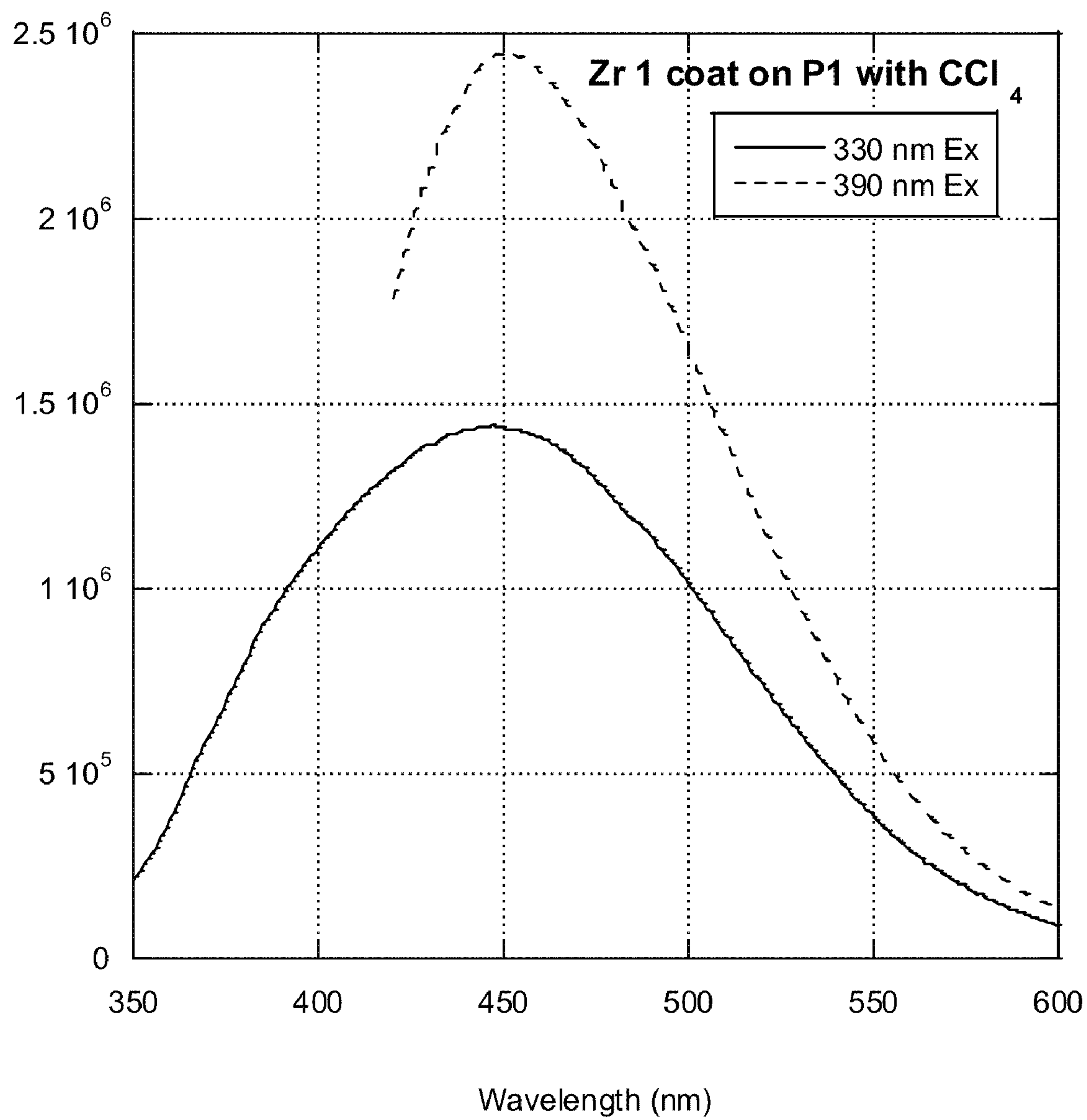


Fig. 6

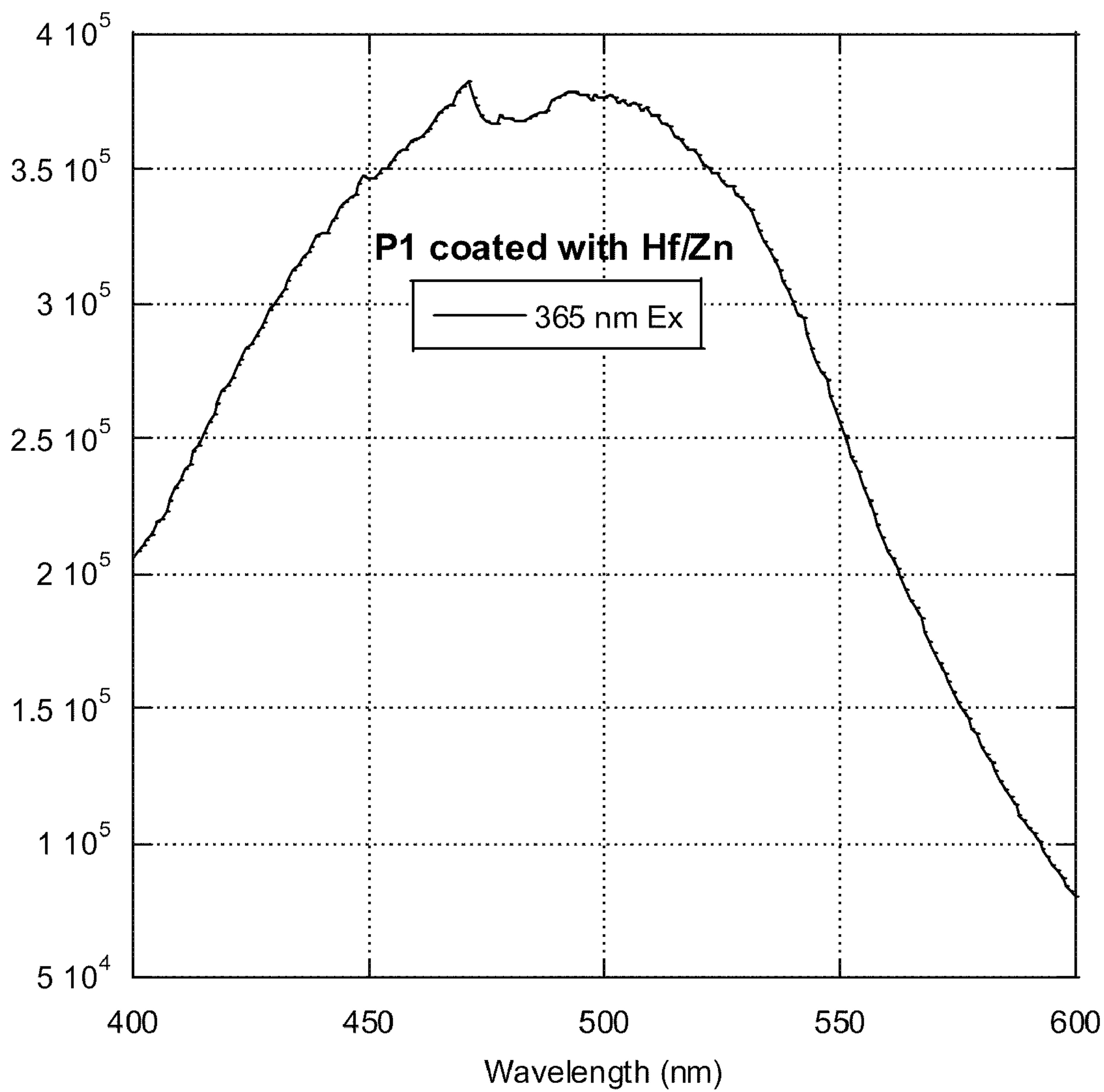


Fig. 7

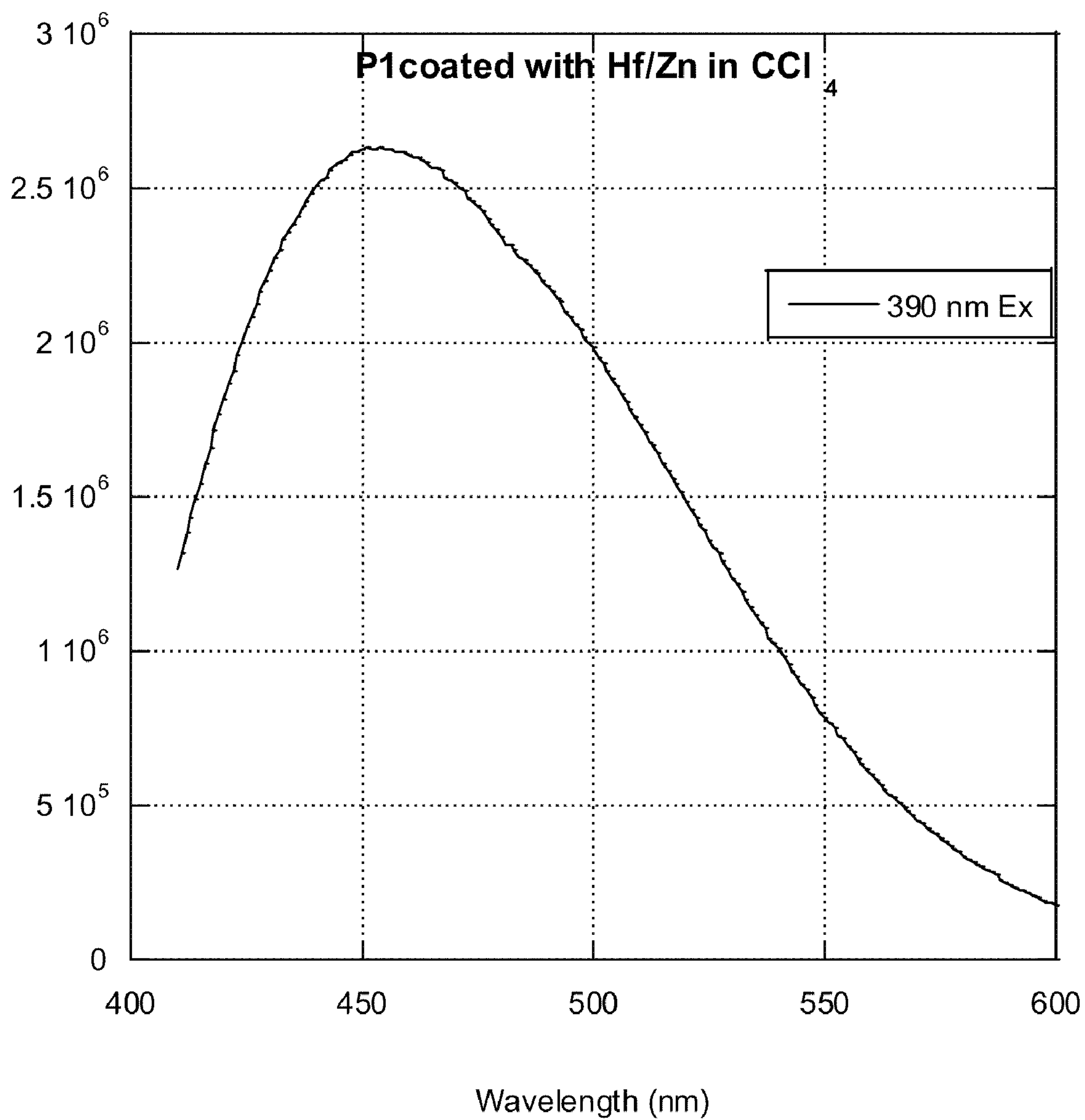


Fig. 8

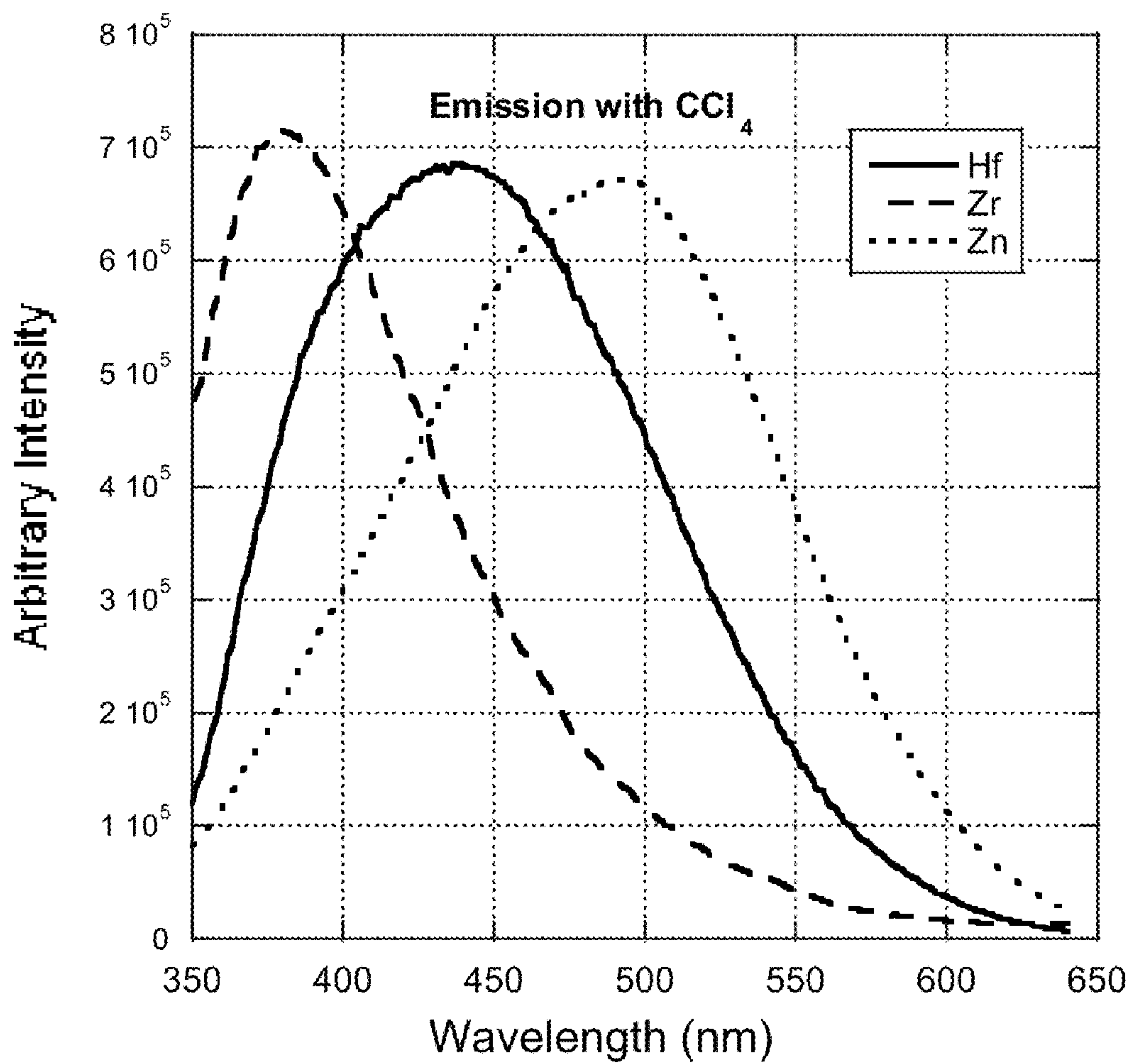


Fig. 9

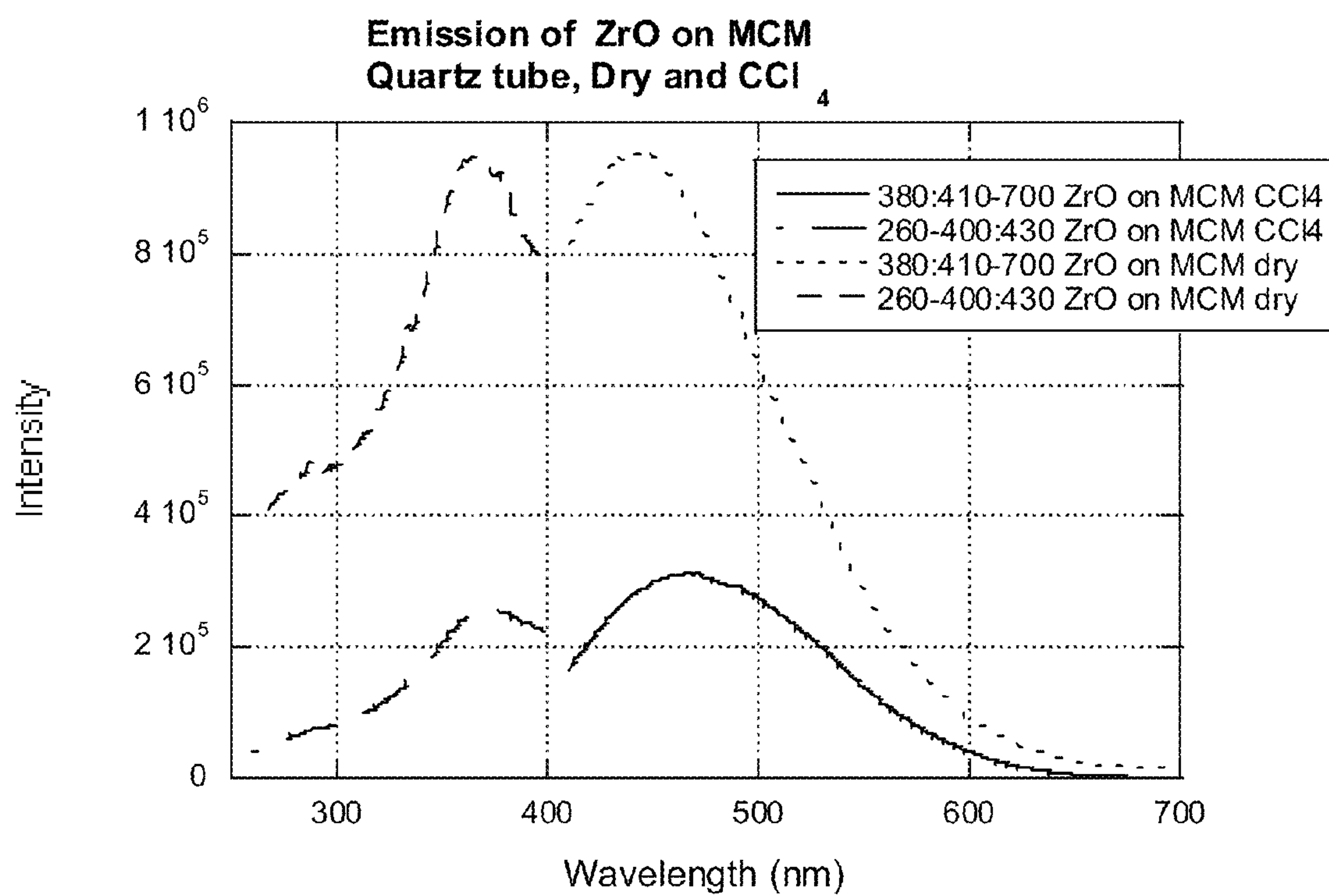


Fig. 10

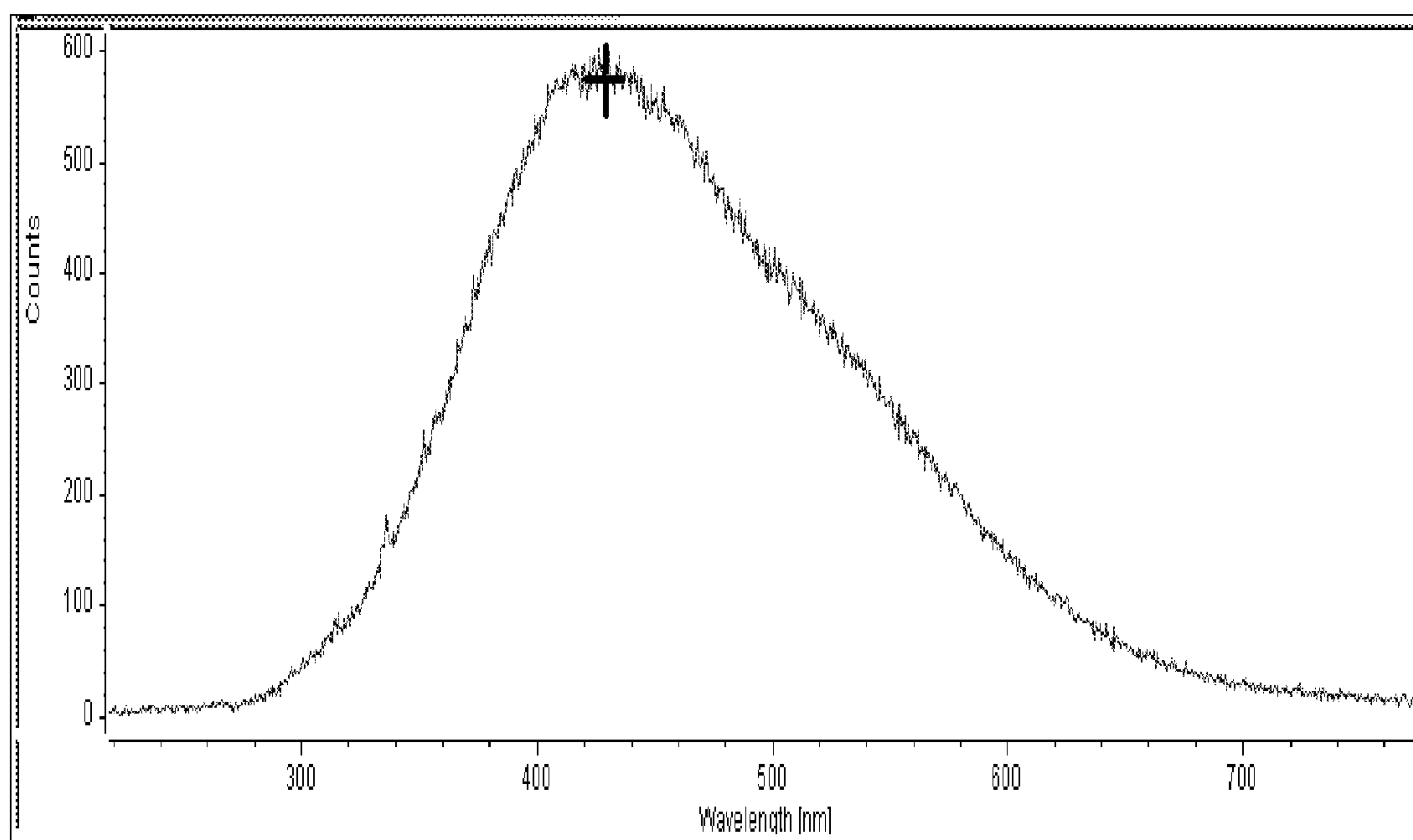


Fig. 11

COMPOSITE PHOSPHORS BASED ON COATING POROUS SUBSTRATES

RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Ser. No. 61/063,154 entitled "Composite Phosphors Based on Coating Porous Substrates," filed Jan. 30, 2008, and U.S. Provisional Application Ser. No. 61/063,153 entitled "Polymer-Assisted Deposition of Conformal Films on Porous Materials," both hereby incorporated by reference.

STATEMENT REGARDING FEDERAL RIGHTS

[0002] This invention was made with government support under Contract No. DE-AC52-06NA25396 awarded by the U.S. Department of Energy. The government has certain rights in the invention.

FIELD OF THE INVENTION

[0003] The present invention relates to a new series of metal oxide phosphors having a broad emission in the visible light region. In particular these phosphors can be deposited onto silica inverse opal structures or silica-based zeolites. The phosphors can be deposited as films by a polymer assisted deposition technique and can result in a luminescent composite material.

BACKGROUND OF THE INVENTION

[0004] Phosphors find applications in many LED devices. Thin films of phosphors are used in many imaging and LED applications from radiation detection to solid state lighting. The key properties of phosphors include quantum yield, stability, emission wavelength and lifetime. In particular for LEDs the efficiency of conversion of high energy blue excitation light to the white light is a key factor for the overall LED efficiency. Phosphors are an integral part of any LED, and unfortunately contribute significantly to efficiency losses. The loss mechanisms include fundamental losses innate to the phosphor conversion material (nonradiative decay paths that lead to reduced quantum yields) and reduced extraction efficiency. The reductions in extraction efficiency include radial emission from the phosphor and wave guiding at interfaces. Phosphors are often applied in an epoxy layer over the high energy emitting GaN light source. If smooth layers are applied effective wave guiding can occur that channels light to the sides of the device. Efforts have been made to reduce this effect through surface roughening but extraction efficiencies remain at or near 60% in the best cases. Typically phosphors are only available as powders or as thin film coatings.

[0005] One of the major obstacles in the development of high efficiency systems is loss due to wave guiding when thin film phosphors are used. Thin films help to minimize losses from self absorption, but the planar interface between the phosphor layer and other layers in the device lead to interfaces with different refractive indexes. At these interfaces all light from the phosphor that hits the interface at an angle $>$ than the critical angle as defined by Snell's Law is effectively reflected at the surface and wave guided to the edges of the film. One way to avoid this problem is to place the phosphor as a thin film on a three dimensional structure with vertical structures that allow the light to propagate in the desired direction. As the surface area of the 3-dimensional structure

increases more phosphor can be excited resulting in higher light yield. Nanoporous structures offer great potential, but they are very difficult to coat. These nanoporous structures can include porous alumina anodiscs that consist of a honeycomb structure with straight channels having pore diameters from 20 to 200 nm, porous inverse opals structures having well defined connected cavities that can be readily controlled to the hundreds of nanometers, and well known silica-based zeolite systems such as MCM-41 with pores on the dimensions of 3 to 100 nm in diameter. All of these structures have high surface areas but the nanometer scale porosity with openings or cavities less than about 1000 nm make them very difficult to coat by traditional line-of-site techniques.

[0006] Over the past 10 years, photonic crystal ("PC") structures have emerged as perhaps the ultimate platform for microdevices that can manipulate light in all three dimensions. These artificial microstructures consist of a periodic repetition of dielectric elements, which creates forbidden and allowed energy bands for photons. PCs represent a major new frontier in optoelectronics due to their ability to coherently manipulate light. This manipulation is essential for enabling new concepts such as producing negative indices of refraction, tailoring the photonic density of states, controlling spontaneous emission rates, and modifying and controlling blackbody radiation. It has been predicted [Shanhui Fan, et al., Phys. Rev. Lett. 78, 3294 (1998)] that a weakly penetrating etched photonic lattice on the surface of an LED can suppress all lateral modes, causing the light to be emitted primarily in the vertical direction.

[0007] PCs have been restricted to a subset of materials that can be formed in the sol-gel processing. Inverse opals represent one common form of PC in which a metal oxide is formed around closed-packed monodisperse polymer beads, and then the beads are subsequently removed by heat treatment to yield a metal oxide with interconnected cavities that reflect the size of the polymer beads. It is not possible to make PCs from just any material, which limits their potential properties. Coating is one way to add functionality, but traditional techniques such as pulsed laser deposition ("PLD") and chemical vapor deposition ("CVD") cannot coat the complex porous structures. Sol-gel can penetrate the pores but does not result in conformal coatings since metal oxide oligomers form in the bulk solution. The primary technique used for effective coating of 3-D materials such as inverse opals structures is atomic laser deposition ("ALD"). ALD is limited in that thicker coatings require many steps and only single component coatings can be readily applied. PAD can deposit conformal coatings of complex metal oxides on nano-structured 3-D supports.

[0008] PAD is a unique alternative coating method based on solutions that access the interior of porous substrates. The coating solution used in PAD is made by adding the metal precursor to the polymer. The polymer actively binds the metal, encapsulating it to prevent chemical reactions that may lead to undesired phases of metal oxide. PAD is a low-cost chemical solution method and effectively eliminates problems such as uneven distribution of the metal oxide on the substrate, unwanted reactivity of the metal resulting in the formation of undesired phases, and the difficulty of obtaining the desired metal/metal ratios when coating a substrate with more than one metal oxide. The PAD technique is a bottom-up growth technique that enables coating complex 3-D structures.

[0009] New thermally stable phosphors with high quantum yields and/or short lifetimes are highly desirable. These phosphors can be used in solid state lighting where broad emissions that mimic the solar spectrum to generate warm white light are highly advantageous. They can also be used as scintillator for radiation detection where a combination of high quantum yields, short lifetimes and emission bands that matches the PMT detector sensitivity are all figures of merit.

[0010] Chemical solution deposition techniques have been generally viewed as less capital intensive (see, Lange, "Chemical Solution Routes to Single-Crystal Thin Films", *Science*, vol. 273, pp. 903-909, 1996 and Schwartz, "Chemical Solution Deposition of Perovskite Thin Films", *Chemistry of Materials*, vol. 9, pp. 2325-2340, 1997). Also, chemical solution techniques are not generally limited to flat surfaces.

[0011] A scintillator is a material that is transparent in the scintillation or emission wavelength range and that responds to incident radiation by emitting a light pulse. From such materials, generally single crystals, it is possible to manufacture detectors in which the light emitted by the crystal that the detector comprises is coupled to a light-detection means and produces an electrical signal proportional to the number of light pulses received and to their intensity. Such detectors are used especially in industry for thickness or weight measurements and in the fields of nuclear medicine, physics, chemistry and oil exploration. A family of known scintillator crystals widely used is of the thallium-doped sodium iodide Tl:NaI type. This scintillating material, discovered in 1948 by Robert Hofstadter and which forms the basis of modern scintillators, still remains the predominant material in this field in spite of almost 50 years of research on other materials. However, these crystals have a scintillation decay which is not very fast. A material that is also used is CsI that, depending on the applications, may be used pure or doped either with thallium ("Tl") or with sodium ("Na"). One family of scintillator crystals that has undergone considerable development is of the bismuth germanate ("BGO") type. The crystals of the BGO family have high decay time constants, which limit the use of these crystals to low count rates. A more recent family of scintillator crystals was developed in the 1990s and is of the cerium-activated lutetium oxyorthosilicate Ce:LSO type. However these crystals are very heterogeneous and have very high melting points (about 2200 degrees Celsius). The development of new scintillating materials for improved performance is the subject of many studies. One of the parameters that it is desired to improve is the energy resolution. This is because in the majority of nuclear detector applications, good energy resolution is desired. The energy resolution of a nuclear radiation detector actually determines its ability to separate radiation energies which are very close. It is usually determined for a given detector at a given energy, such as the width at mid-height of the peak in question on an energy spectrum obtained from this detector, in relation to the energy at the centroid of the peak. The smaller the value of the energy resolution, the better the quality of the detector.

[0012] Nevertheless, lower values of resolution are of great benefit. For example, in the case of a detector used to analyze various radioactive isotopes, improved energy resolution enables improved discrimination of these isotopes. While thin film scintillators have limited utility in applications where energy resolution is needed in radiation detection, they have major applications in imaging systems such as X-ray imaging device.

[0013] X-ray imaging devices in which the scintillator for converting an X-ray into visible light, or the like, and the imaging devices for receiving the visible light, or the like, are used in combination and more particularly a resolution-variable X-ray imaging device whose resolution can be changed as occasion demands and an X-ray CT apparatus. As the X-ray imaging device for capturing an image by visualizing an X-ray, there are some devices that can sense directly an X-ray and others that can visualize an X-ray by using the scintillator and then capture an image by using the imaging device such as CCD, or the like. In this case high quantum yield and very short lifetimes are desirable.

[0014] Conventional neutron detectors typically include devices that operate as ionization chambers or proportional counters. Each of the available methods demonstrates different strengths, but all share the common goals of high neutron efficiency, minimum gamma-ray sensitivity or gamma/neutron discrimination. Other systems, including scintillators doped with ^6Li , or ^{10}B , have been examined with mixed results. One of the prime difficulties in these systems is the gamma-ray rejection characteristics of the system. In addition, many of the detector materials are air and water sensitive or the scintillators employ heavy elements that limit gamma-ray rejection or have slow response times thanks to the long relaxation times. Scintillators have the added complication that often single crystals are required to avoid light loss, making it difficult to add large amounts of boron or lithium to increase the neutron cross-section absorption. While there are obvious advantages to the use of solid-state neutron detectors, to date these are outweighed by their disadvantages. Coating scintillators onto three dimensional structures which can then be filled with neutron stopping material may provide a new class of neutron detector.

SUMMARY OF THE INVENTION

[0015] To achieve the foregoing and other objects, and in accordance with the purposes of the present invention, as embodied and broadly described herein, the present invention provides for a new series of phosphors including oxides of hafnium ("Hf"), zirconium ("Zr"), zinc ("Zn"), tantalum ("Ta"), or niobium ("Nb") deposited as thin conformal films onto porous metal oxide supports. The resulting composites can have the property of observable photo-luminescence ("PL") at room temperature.

[0016] The present invention further provides for a new series of phosphors composed metal oxide mixtures containing at least one of the following: Hf, Zr, Zn, Ta, or Nb deposited as thin conformal films onto porous metal oxide supports. The resulting composite has the property of observable photo-luminescence ("PL") at room temperature. In particular porous silica structures serve as the substrate. Further, the emission band of the resulting phosphors is generally very broad having a width at $\frac{1}{2}$ max of greater than 80 nm.

[0017] This invention further involves filling a porous substrate with a homogenous solution, said solution containing a soluble metal precursor and a soluble polymer in a suitable solvent, to form a polymer and metal containing layer thereon, said polymer characterized as having metal binding properties, and heating said substrate in a controlled atmosphere at temperatures and for time characterized as sufficient to remove said polymer from said polymer and metal containing layer and form a conformal film on the porous support.

[0018] The resulting coated porous structure has observable PL at room temperature and maintains porosity which may be subsequently filled with a liquid, gel, or solid. Filling the cavities with materials of refractive index that match the substrates refractive index can lead to enhanced light output which is important for many applications.

[0019] The invention also includes a light-emitting device comprising a mesoporous silicon or silica support structure having pores, an interior surface, and an exterior surface, and a conformal metal-oxide-containing film that coats said interior surface and exterior surface of said mesoporous silicon or silica support structure without substantially blocking the pores of said mesoporous silicon support structure.

[0020] The invention also includes a radiation detector having a light-emitting device that comprises a mesoporous silicon or silica support structure having pores, an interior surface, and an exterior surface, and a conformal metal-oxide-containing film that coats said interior surface and exterior surface of said mesoporous silicon or silica support structure without substantially blocking the pores of said mesoporous silicon support structure.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] FIG. 1 shows the emission spectra of a hafnium-containing solid composite phosphor from Example 5 upon 350 and 420 nm excitation.

[0022] FIG. 2 shows the emission spectra of a hafnium-containing solid composite phosphor from Example 5 filled with CCl_4 upon 330 and 390 nm excitation.

[0023] FIG. 3 shows the emission spectra of a zinc-containing solid composite phosphor from Example 7 filled with CCl_4 upon 330 nm excitation.

[0024] FIG. 4 shows the emission spectra of a hafnium-containing solid composite phosphor from Example 4 filled with CCl_4 upon 330 and 390 nm excitation.

[0025] FIG. 5 shows the emission spectra of a hafnium-containing solid composite phosphor from Example 2 filled with CCl_4 upon 330 and 390 nm excitation.

[0026] FIG. 6 shows the emission spectra of a zirconium-containing solid composite phosphor filled with CCl_4 upon 330 and 390 nm excitation.

[0027] FIG. 7 shows the emission spectra of a hafnium-zinc-containing solid composite phosphor from Example 12 upon 365 nm excitation.

[0028] FIG. 8 shows the emission spectra of a hafnium-zinc-containing solid composite phosphor from Example 12 filled with CCl_4 upon 390 nm excitation.

[0029] FIG. 9 shows emission spectra of hafnium, zirconium and zinc oxide on silica inverse opal filled dry and filled with CCl_4 .

[0030] FIG. 10 shows emission spectra of zirconium oxide on silica MCM-41.

[0031] FIG. 11 shows emission spectrum from HfO_2 coated inverse opals irradiated with Mo $K\alpha$ radiation.

DETAILED DESCRIPTION

[0032] The present invention describes a new class of phosphors that have desirable characteristics for a variety of applications including LEDs, solid state lighting, scintillation-based imaging, and scintillation-based detection of radiation. A series of new phosphors have been prepared by coating nanoporous substrates with metal oxide coatings using the PAD process, for example 2 coats of hafnium oxide on 360

nm silica inverse opals gives bright emission, as shown in FIG. 1. The substrates coated include silica inverse opals, and the silica zeolite MCM-41. Coating the nanoporous substrates via PAD with Hf, Zr, Ta, Nb, or Zn solutions or a solution mixture of more than 1 metal containing Hf, Zr, Ta, Nb, or Zn produces a thin conformal coating on the porous material. Filling the pores with index-matched material increases the light output. The filling of the pores reduces the light scattering. FIG. 2 shows the 360 nm pore diameter silica inverse opals coated with 2 coats of hafnium filled with carbon tetrachloride. When zinc oxide is coated on the 320 nm pore diameter silica inverse opals and the pores are filled with carbon tetrachloride the emission, seen in FIG. 3, is at much lower energy. Interestingly, the number of coats also has an effect on the emission maxima. When the 2 coats of hafnium is applied onto 360 nm pore diameter silica inverse opals the emission maxima for 390 nm excitation is ~455 nm, see FIG. 2. When the only 1 coat of hafnium is applied onto 390 nm pore diameter silica inverse opals the emission maxima for 390 nm excitation is ~440 nm, see FIG. 4. The size of the pores also has an effect. When hafnium is coated onto 320 nm pore diameter silica inverse opal the emission maxima for 330 nm excitation is ~410 nm, see FIG. 5. Whereas, the hafnium coated onto 360 nm pore diameter silica inverse opal the emission maxima for 330 nm excitation is ~390 nm, see FIG. 5. Zirconium coated onto inverse opals with a pore diameter of 320 nm, give an emission maxima of 450 nm, seen in FIG. 6. The porous substrates coated with Hf, Zr, Ta, Zn and a 50:50 mixture of Zn and Hf all show strong PL at room temperature, as shown in FIG. 7. Filling the pores of the mixed hafnium-zinc material with an index-matched solvent as shown in FIG. 8 also results in increased light output. The photoluminescent material may include a single phosphor or multiple phosphors mixed together. The structure of the conformal film can be amorphous, composite, polycrystalline, nanocrystalline, or microcrystalline depending upon the chemistry of the solution, the substrate used for the film deposition and growth and the post-thermal treatment conditions. Hafnium oxide has been proposed as a potential high refractive index layer for coatings in a variety of materials and is used as an optical coating on glass, but it has never been shown to significant visible PL at room temperature. The observation of visible PL at room temperature for films of Hf, Zr, Ta, and Nb oxide films is unprecedented to our knowledge. Zinc oxide has long been known to have observable PL at room temperature via oxygen defects that lead to emissive states at energies below the bandgap of ZnO. Zinc oxide has also been deposited by a variety of techniques including spray pyrolysis and ALD onto many substrates including silica inverse opals. All of these materials show two emission bands: a blue band centered near 380 nm and a second green (structured) band centered near 540 nm. In general the green band is less intense than the blue band. Strong PL is typically only observed when the ZnO is prepared in a reducing atmosphere.

[0033] In particular Hf, Zr, Ta, Nb, Zn and combinations with more than one metal in combination such as Hf:Zn can be deposited as oxide films onto nanoporous structures or can be deposited onto various photonic crystal structures such as an inverse opal structure. The resulting composite materials are luminescent at room temperature with broad emission bands greater than 80 nm at 1/2 the maximum. The exact emission spectrum of each element is different as shown by

FIG. 9. This is important for white light applications and for matching photomultiplier tubes.

[0034] In the present invention the zinc oxide coated porous silica materials are unique in their structure as evidenced by the PL. In these new materials the PL shows only one extremely broad emission band centered near 490 nm with a bandwidth at $\frac{1}{2}$ max of 150 nm. At $\frac{1}{2}$ the maximum emission intensity the emission band is 150 nm wide extending from 400 to 550 nm. This type of emission from ZnO has not been observed before to our knowledge. Another unique feature of these composite ZnO phosphors is that they can be prepared by simple annealing in air. No reducing atmosphere is required for strong PL at room temperature.

[0035] Similar broad emission from defect sites below the bandgap energy of either the substrate or the coating is observed with Zr, Hf, Ta and a 1:1 mixture of Hf:Zn. All of the resulting phosphors show intense PL at room temperature with quantum yields greater than about 0.05. The lifetime of the hafnium coated silica inverse opals is extremely short at less than about 5 ns (the resolution of the instrument used). The combination of the short lifetime with a high quantum yield and a thermal stability of at least 500° C. is extremely rare in a phosphor system. Many metal oxide phosphor systems such as europium have microsecond or millisecond lifetimes that limit their applications. Organic phosphors with intense singlet to singlet state emission can have high quantum yields and very short lifetimes but they are not thermally stable at temperatures greater than about 250° C. and they are often toxic. Many of the phosphors described here are based on simple metal oxide coatings that should limited or no adverse health effects. Emission from coated porous silicon (silica) new with no examples of titanium, zirconium, hafnium, tantalum or niobium coated silica producing photoluminescence ever being reported. The effect is not just restricted to inverse opals. MCM-41 when coated with these metals also emits light, when excited, as seen in FIG. 10.

[0036] The present invention uses a soluble polymer to assist in the deposition of the desired metal containing film. The process can be referred to as a polymer assisted deposition ("PAD") process. Inclusion of a soluble polymer with a single metal precursor or multiple metal precursors promotes better distribution of the materials during the deposition. The metal bound polymer solution can be completely infused into a porous material by simple capillary action. This effect can be enhanced by exposing the porous material to the solution and then reducing the pressure in the system (by placing it in a partial vacuum) to cause the solution to fill the porous volume of the substrate. The volume of the metal bound polymer solution should not be significantly greater than the volume of the porous substrate. The solvent and polymer can be removed subsequently by heating at sufficiently high temperatures to first eliminate the solvent and then the polymer and leave a conformal metal containing film. By using a soluble polymer in conjunction with one or more metal precursors, single or mixed compound/complex metal containing films can be prepared. In one embodiment, the overall process can be an aqueous process that can be organic solvent free. Formation of the metal containing film depends upon the proper selection of precursor and atmosphere during heating. The polymer cannot only control the desired viscosity for the process, but also binds the metal ions to prevent premature precipitation and formation of metal oxide oligomers. As the solvent is removed the polymer bound metal will preferentially stick to the walls of the porous support when there are

good adhesive forces between the polymer and the porous support. The results are found to be a homogeneous distribution of the metal precursors in the solution and the formation of conformal metal containing films throughout the porous support. PAD can grow highly conformal films with no clogging of the porous structure and minimal loss in surface area.

[0037] The heating of the polymer and metal layer is generally carried out in air for simple metal oxide films, but can also be carried out under a variety of controlled atmospheres such as reducing atmosphere to maintain lower oxidation states in the films.

[0038] By the process of the present invention, the metal containing film may be prepared with an amorphous structure or a nanocrystalline structure, polycrystalline structure or crystalline structure by suitable treatment after deposition of the polymer and metal containing layer upon a substrate or by suitable selection of the substrate. Such amorphous or polycrystalline structures may be preferred for some applications, while crystalline structures are required for some phosphors to emit light efficiently.

[0039] The metal oxide-containing films of the present invention are conformal films, i.e., they are homogeneous films throughout the internal pores of the porous supports that do not greatly reduce the surface area by clogging pore openings.

[0040] In one embodiment of the present invention the porous substrate can be an inverse opals structure based on an oxide framework. The oxide framework can consist of silica, borate, zirconium oxide, titanium oxide and the like. The size of the cavities of the inverse opals framework can be varied from hundred of microns down to tens of nanometers.

[0041] In one embodiment of the present invention the porous substrate can be a porous silica zeolite. The size of the pores can be varied from 100 nm down to 3 nanometers depending on the framework structure.

[0042] The starting solution can be deposited on a desired substrate by infusion as a result of capillary forces, infusion through reduced pressure and the like. After deposition of the starting solution on a substrate, the deposited coating must be heated under a suitable atmosphere at high temperatures of from about 250° C. to about 1300° C., preferably from about 400° C. to about 1200° C. for a period of time sufficient to remove the polymer and to form only the metal containing film. Heating times may be varied and may be longer depending upon the thickness of the deposited film.

[0043] The coating is done by simply adding a volume of solution that is less than or equal to the volume of the porous support used. The solution wets into the pores by capillary action. Alternatively a reduced pressure atmosphere can be used to drive the solution into the porous substrate

[0044] The post-thermal treatment conditions such as post-annealing temperature and ambient change in a wide range depending on the objectives of the materials deposited. For most of the phosphors described here there thermal treatment was carried out by heating in air at a ramp rate of 10° C./min to 120° C., held for 1 hour, heated at a ramp rate of 10° C. to 450° C., held for 1 hour, and then heated at a ramp rate of 10° C. to 500° C., and held for 1 hour. The material was then allowed to cool to room temperature. In one embodiment of the present invention the resulting porous nanostructure with the metal containing coating from the PAD deposition may be subsequently filled with a liquid, gel or solid. The conformal coating does not fill the pore volume so that the pores may be filled with a subsequent step to add functionality including

high Z materials for gamma-ray absorption, boron containing materials for neutron absorption, materials with a refractive index to match the substrate in order to increase the light output of the phosphor and the like.

[0045] It has been found that not all materials have this photoluminescence. Coating of other high refractive index metal oxides such as tungsten and bismuth onto the inverse opals does not yield material with PL at room temperature. In addition the inverse opals themselves have no PL at room temperature.

[0046] Preliminary results from irradiation with X-Rays show that P1 gives no response, while the Hf coated P1 yields PL upon X-ray irradiation. These results indicate that these new phosphors are potential scintillators for radiation detection.

[0047] The coating of hafnium, zirconium, titanium and zinc on the silica inverse opals, which are an ordered nanoporous structure made up of mesoporous silica, and the mesoporous silica in the form of MCMs, results in a new material composition that emits light when excited with light of any energy greater than 420 nm. The potential utility of the coated silica inverse opals as scintillators in radiation detection is shown in FIG. 11 where the light emission is stimulated by X-ray radiation.

[0048] The present invention is more particularly described in the following examples which are intended as illustrative only, since numerous modifications and variations will be apparent to those skilled in the art.

[0049] Examples A-F describe the preparation of metal-containing solutions used in the deposition and formation of the metal containing films, e.g., metal oxide containing films. Examples 1-12 describe the synthesis of the composite phosphor materials in accordance with the present invention. Polyethyleneimine was obtained from BASF as a water free, branched, polymer with an average MW of 50,000. Water was deionized via reverse osmosis (having a resistivity >16 Ohms).

Example A

[0050] A hafnium coating solution was prepared by mixing 1.0 g of HfOCl_2 (ALDRICH, 99.99% pure), 1.0 g K_2EDTA (ALDRICH, 99.995% pure), and 1 gram BASF polyethyleneimine polymer in deionized (18 M Ω) H_2O . The resulting solution was filtered through a 0.45 micron filter, diluted to 200 mL with nano pure water, and purified by Amicon filtration with a 3,000 MW cut-off filter. The final concentrated solution was 144 mM hafnium, determined by ICP/AES. The potassium concentration was 11 mM, also determined by ICP/AES.

Example B

[0051] A hafnium coating solution was prepared by mixing 2.0 g of HfOCl_2 (ALDRICH, 99.99% pure), 2.0 g HEDTA (ALDRICH, 99.995% pure) and 2 grams BASF polyethyleneimine polymer and concentrated ammonium hydroxide, NH_4OH (Fisher) in deionized (18 M Ω) H_2O . The resulting solution was filtered through a 0.45 micron filter, diluted to 200 mL with nano pure water, and purified by Amicon filtration with a 3,000 MW cut-off filter. The final concentrated solution was 163 mM hafnium, determined by ICP/AES. This

solution was rotovapped to further concentrate it, resulting in a final concentration of 250 mM hafnium.

Example C

[0052] A zinc solution was prepared by mixing 3.7 g zinc nitrate hexahydrate, $\text{Zr}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, (ALPHA AESAR, 99.998% pure), 5.0 g HEDTA (ALDRICH, 99.995% pure) and 5 grams BASF polyethyleneimine polymer in deionized (18 M Ω) H_2O . The resulting solution was filtered through a 0.45 micron filter, diluted to 200 mL with nano pure water, and purified by Amicon filtration with a 3,000 MW cut-off filter. The final concentrated solution was 179 mM zinc, determined by ICP/AES.

Example D

[0053] A zirconium solution was prepared by mixing 2.04 g of Zirconyl Nitrate, $\text{ZrO}(\text{NO}_3)_2$, (Aldrich 35 wt % Zr), 2.0 g HEDTA (Aldrich 99.995% pure) and 2 grams BASF polyethyleneimine polymer and concentrated ammonium hydroxide, NH_4OH (FISHER) in deionized (18 M Ω) H_2O . The resulting solution was filtered through a 0.45 micron filter, diluted to 200 mL with nano pure water, and purified by Amicon filtration with a 3,000 MW cut-off filter. The final concentrated solution was 225 mM zirconium, determined by ICP/AES.

Example E

[0054] A bismuth solution was prepared by mixing 3.0 g bismuth nitrate hydrate, $\text{Bi}(\text{NO}_3)_3 \cdot \text{X}\text{H}_2\text{O}$, (ALPHA AESAR, 99.999% pure), 2.0 g HEDTA (ALDRICH, 99.995% pure) and 2 grams BASF polyethyleneimine polymer in deionized (18 M Ω) H_2O . The resulting solution was filtered through a 0.45 micron filter, diluted to 200 mL with nano pure water, and purified by Amicon filtration with a 3,000 MW cut-off filter. The final concentrated solution was 153 mM bismuth, determined by ICP/AES.

Example F

[0055] A tungsten solution was prepared by mixing 3.0 g of sodium tungstate, and 3.0 grams BASF polyethyleneimine polymer in deionized (18 M Ω) H_2O at pH 7 (by addition of HCl). The resulting solution may be pH adjusted to >4 by addition of an ammonium hydroxide solution. The solution was filtered through a 0.45 micron filter, diluted to 200 mL with nano pure water, and purified by Amicon filtration with a 3,000 MW cut-off filter. The final concentrated solution was 211 mM tungsten, determined by ICP/AES.

Example 1

[0056] Silica inverse opals were coated with hafnium oxide using the PAD method of coating. 334 mg of the solution from example A was diluted with 105 mg of deionized (18 M Ω) H_2O . The solution was then dropped onto 30 mg of P1 photonic inverse opals in a 20-mL scintillation vial. The vial was rotated to ensure total coverage of the inverse opals by the coating solution. The coated inverse opals were then rotovapped under negative pressure in order to cause the solution to penetrate the cavities within the photonic inverse opals and remove excess water.

[0057] When the inverse opals appeared dry, the inverse opals were transferred to a ceramic crucible. The inverse opals were then annealed in air with the following heating program:

The temperature was ramped to 120° C. at 10°/min and held for 1 hour.

The temperature was ramped to 450° C. at 10°/min and held for 1 hour.

The temperature was ramped to 500° C. at 10°/min and held for 1 hour.

Example 2

[0058] P1-Silica inverse opals with one coat of Hf were prepared as follows. SiO₂ inverse opals were coated with hafnium oxide using the PAD method of coating. Two hundred mg of the solution from example B was diluted with 100 mg of deionized (18 MΩ) H₂O. The solution was then dropped onto 32 mg of P1 photonic inverse opals in a 20-mL scintillation vial. The vial was rotated to ensure total coverage of the inverse opals by the coating solution. The coated inverse opals were then rotovapped under negative pressure in order to cause the solution to penetrate the cavities within the photonic inverse opals and remove excess water.

[0059] When the inverse opals appeared dry, the inverse opals were transferred to a ceramic crucible. The inverse opals were then annealed in air with the following heating program:

The temperature was ramped to 120° C. at 10°/min and held for 1 hour.

The temperature was ramped to 450° C. at 10°/min and held for 1 hour.

The temperature was ramped to 500° C. at 10°/min and held for 1 hour.

FIG. 9 shows the PL of the P1 inverse opal and P1 inverse opal coated with hafnium as in Example 2. FIG. 5 shows the emission spectra of the hafnium-containing solid composite phosphor filled with CCl₄ upon 330 and 390 nm excitation.

Example 3

[0060] P1-Photonic Inverse opals with two coats of Hf were prepared as follows. SiO₂ inverse opals were coated with hafnium oxide using the PAD method of coating. 211 mg of the solution from example B was diluted with 109 mg of deionized (18 MΩ) H₂O. The solution was then dropped onto 31 mg of P1 photonic inverse opals in a 20-mL scintillation vial. The vial was rotated to ensure total coverage of the inverse opals by the coating solution. The coated inverse opals were then rotovapped under negative pressure in order to cause the solution to penetrate the cavities within the photonic inverse opals and remove excess water.

[0061] When the inverse opals appeared dry, the inverse opals were transferred to a ceramic crucible. The inverse opals were then annealed in air with the following heating program:

The temperature was ramped to 120° C. at 10°/min and held for 1 hour.

The temperature was ramped to 450° C. at 10°/min and held for 1 hour.

The temperature was ramped to 500° C. at 10°/min and held for 1 hour.

[0062] The inverse opals were removed from the crucible and placed in a scintillation vial. Another solution of 213 mg Hf solution plus 115 mg H₂O was dropped onto the P1 inverse

opals with 1 coat of Hf. The vial was rotated to ensure total coverage of the inverse opals by the coating solution. The coated inverse opals were then rotovapped under negative pressure in order to cause the solution to penetrate the cavities within the photonic inverse opals and remove excess water.

[0063] When the inverse opals appeared dry, the inverse opals were transferred to a ceramic crucible. The inverse opals were then annealed in air with the following heating program:

The temperature was ramped to 120° C. at 10°/min and held for 1 hour.

The temperature was ramped to 450° C. at 10°/min and held for 1 hour.

The temperature was ramped to 500° C. at 10°/min and held for 1 hour.

Example 4

[0064] P3-Photonic Inverse opals with one coat of Hf were prepared as follows. SiO₂ inverse opals were coated with hafnium oxide using the PAD method of coating. Two hundred mg of the solution from example B was diluted with 100 mg of deionized (18 MΩ) H₂O. The solution was then dropped onto 32 mg of P3 photonic inverse opals in a 20-mL scintillation vial. The vial was rotated to ensure total coverage of the inverse opals by the coating solution. The coated inverse opals were then rotovapped under negative pressure in order to cause the solution to penetrate the cavities within the photonic inverse opals and remove excess water.

[0065] When the inverse opals appeared dry, the inverse opals were transferred to a ceramic crucible. The inverse opals were then annealed in air with the following heating program:

The temperature was ramped to 120° C. at 10°/min and held for 1 hour.

The temperature was ramped to 450° C. at 10°/min and held for 1 hour.

The temperature was ramped to 500° C. at 10°/min and held for 1 hour.

[0066] The inverse opals were removed from the crucible and placed in an NMR tube to investigate emissions of the coated inverse opals. FIG. 4 shows the emission spectra of the hafnium-containing solid composite phosphor filled with CCl₄ upon 330 and 390 nm excitation.

Example 5

[0067] P3—Photonic Inverse opals with two coats of Hf were prepared as follows. SiO₂ inverse opals were coated with hafnium oxide using the PAD method of coating. 211 mg of the solution from example B was diluted with 109 mg of deionized (18 MΩ) H₂O. The solution was then dropped onto 34 mg of P3 photonic inverse opals in a 20-mL scintillation vial. The vial was rotated to ensure total coverage of the inverse opals by the coating solution. The coated inverse opals were then rotovapped under negative pressure in order to cause the solution to penetrate the cavities within the photonic inverse opals and remove excess water.

[0068] When the inverse opals appeared dry, the inverse opals were transferred to a ceramic crucible. The inverse opals were then annealed in air with the following heating program:

The temperature was ramped to 120° C. at 10°/min and held for 1 hour.

The temperature was ramped to 450° C. at 10°/min and held for 1 hour.

The temperature was ramped to 500° C. at 10°/min and held for 1 hour.

[0069] The inverse opals were removed from the crucible and placed in a scintillation vial. Another solution of 213 mg Hf solution plus 115 mg H₂O was dropped onto the P1 inverse opals with 1 coat of Hf. The vial was rotated to ensure total coverage of the inverse opals by the coating solution. The coated inverse opals were then rotovapped under negative pressure in order to cause the solution to penetrate the cavities within the photonic inverse opals and remove excess water.

[0070] When the inverse opals appeared dry, the inverse opals were transferred to a ceramic crucible. The inverse opals were then annealed in air with the following heating program:

The temperature was ramped to 120° C. at 10°/min and held for 1 hour.

The temperature was ramped to 450° C. at 10°/min and held for 1 hour.

The temperature was ramped to 500° C. at 10°/min and held for 1 hour.

FIG. 1 shows the emission spectra of the hafnium-containing solid composite phosphor upon 350 and 420 nm excitation. FIG. 2 shows the emission spectrum when the pores are filled with CCl₄.

Example 6

[0071] P3—Photonic Inverse opals with three coats of Hf were prepared as follows. SiO₂ inverse opals were coated with hafnium oxide using the PAD method of coating. 219 mg of the solution from example B was diluted with 112 mg of deionized (18 MΩ) H₂O. The solution was then dropped onto 36 mg of P3 photonic inverse opals in a 20-mL scintillation vial. The vial was rotated to ensure total coverage of the inverse opals by the coating solution. The coated inverse opals were then rotovapped under negative pressure in order to cause the solution to penetrate the cavities within the photonic inverse opals and remove excess water.

[0072] When the inverse opals appeared dry, the inverse opals were transferred to a ceramic crucible. The inverse opals were then annealed in air with the following heating program:

The temperature was ramped to 120° C. at 10°/min and held for 1 hour.

The temperature was ramped to 450° C. at 10°/min and held for 1 hour.

The temperature was ramped to 500° C. at 10°/min and held for 1 hour.

[0073] The inverse opals were removed from the crucible and placed in a scintillation vial. Another solution of 206 mg Hf solution plus 109 mg H₂O was dropped onto the P3 inverse opals with 1 coat of Hf. The vial was rotated to ensure total coverage of the inverse opals by the coating solution. The coated inverse opals were then rotovapped under negative pressure in order to cause the solution to penetrate the cavities within the photonic inverse opals and remove excess water.

[0074] When the inverse opals appeared dry, the inverse opals were transferred to a ceramic crucible. The inverse opals were then annealed in air with the following heating program:

The temperature was ramped to 120° C. at 10°/min and held for 1 hour.

The temperature was ramped to 450° C. at 10°/min and held for 1 hour.

The temperature was ramped to 500° C. at 10°/min and held for 1 hour.

[0075] The inverse opals were removed from the crucible and placed in a scintillation vial. Another solution of 220 mg Hf solution plus 115 mg H₂O was dropped onto the P3 inverse opals with 2 coats of Hf. The vial was rotated to ensure total coverage of the inverse opals by the coating solution. The coated inverse opals were then rotovapped under negative pressure in order to cause the solution to penetrate the cavities within the photonic inverse opals and remove excess water.

[0076] When the inverse opals appeared dry, the inverse opals were transferred to a ceramic crucible. The inverse opals were then annealed in air with the following heating program:

The temperature was ramped to 120° C. at 10°/min and held for 1 hour.

The temperature was ramped to 450° C. at 10°/min and held for 1 hour.

The temperature was ramped to 500° C. at 10°/min and held for 1 hour.

Example 7

[0077] P1—Photonic Inverse opals with one coat of Zn were prepared as follows. SiO₂ inverse opals were coated with zinc oxide using the PAD method of coating. 200 μL of the solution from Example C was diluted with 100 μL of deionized (18 MΩ) H₂O. The solution was then dropped onto 31 mg of P1 photonic inverse opals in a 20-mL scintillation vial. The vial was rotated to ensure total coverage of the inverse opals by the coating solution. The coated inverse opals were then rotovapped under negative pressure in order to cause the solution to penetrate the cavities within the photonic inverse opals and remove excess water.

[0078] When the inverse opals appeared dry, the inverse opals were transferred to a ceramic crucible. The inverse opals were then annealed in air with the following heating program:

The temperature was ramped to 120° C. at 10°/min and held for 1 hour.

The temperature was ramped to 450° C. at 10°/min and held for 1 hour.

The temperature was ramped to 500° C. at 10°/min and held for 1 hour.

[0079] FIG. 3 shows the emission spectra of the zinc-containing solid composite phosphor filled with CCl₄ upon 330 nm excitation.

Example 8

[0080] P3—Photonic Inverse opals with two coats of Zn were prepared as follows. SiO₂ inverse opals were coated with zinc oxide using the PAD method of coating. 200 μL of the solution from example C was diluted with 100 μL of deionized (18 MΩ) H₂O. The solution was then dropped onto 31 mg of P3 photonic inverse opals in a 20-mL scintillation vial. The vial was rotated to ensure total coverage of the inverse opals by the coating solution. The coated inverse opals were then rotovapped under negative pressure in order to cause the solution to penetrate the cavities within the photonic inverse opals and remove excess water.

[0081] When the inverse opals appeared dry, the inverse opals were transferred to a ceramic crucible. The inverse opals were then annealed in air with the following heating program:

The temperature was ramped to 120° C. at 10°/min and held for 1 hour.

The temperature was ramped to 450° C. at 10°/min and held for 1 hour.

The temperature was ramped to 500° C. at 10°/min and held for 1 hour.

[0082] The inverse opals were removed from the crucible and placed in a scintillation vial. Another solution of 200 μ L Zn solution plus 100 μ L H₂O was dropped onto the P3 inverse opals with 1 coat of Zn. The vial was rotated to ensure total coverage of the inverse opals by the coating solution. The coated inverse opals were then rotovapped under negative pressure in order to cause the solution to penetrate the cavities within the photonic inverse opals and remove excess water.

[0083] When the inverse opals appeared dry, the inverse opals were transferred to a ceramic crucible. The inverse opals were then annealed in air with the following heating program:

The temperature was ramped to 120° C. at 10°/min and held for 1 hour.

The temperature was ramped to 450° C. at 10°/min and held for 1 hour.

The temperature was ramped to 500° C. at 10°/min and held for 1 hour.

Example 9

[0084] P1—Photonic Inverse opals with one coat of Zr were prepared as follows. SiO₂ inverse opals were coated with zirconium oxide using the PAD method of coating. 192 mg of the solution from example D was diluted with 107 mg of deionized (18 M Ω) H₂O. The solution was then dropped onto 32 mg of P1 photonic inverse opals in a 20-mL scintillation vial. The vial was rotated to ensure total coverage of the inverse opals by the coating solution. The coated inverse opals were then rotovapped under negative pressure in order to cause the solution to penetrate the cavities within the photonic inverse opals and remove excess water.

[0085] When the inverse opals appeared dry, the inverse opals were transferred to a ceramic crucible. The inverse opals were then annealed in air with the following heating program:

[0086] The temperature was ramped to 120° C. at 10°/min and held for 1 hour.

The temperature was ramped to 450° C. at 10°/min and held for 1 hour.

The temperature was ramped to 500° C. at 10°/min and held for 1 hour.

Example 10

[0087] P3—Photonic Inverse opals with two coats of Zr were prepared as follows SiO₂ inverse opals were coated with zirconium oxide using the PAD method of coating. 238 mg of the solution from example D was diluted with 135 mg of deionized (18 M Ω) H₂O. The solution was then dropped onto 30 mg of P3 photonic inverse opals in a 20-mL scintillation vial. The vial was rotated to ensure total coverage of the inverse opals by the coating solution. The coated inverse opals were then rotovapped under negative pressure in order

to cause the solution to penetrate the cavities within the photonic inverse opals and remove excess water.

[0088] When the inverse opals appeared dry, the inverse opals were transferred to a ceramic crucible. The inverse opals were then annealed in air with the following heating program:

The temperature was ramped to 120° C. at 10°/min and held for 1 hour.

The temperature was ramped to 450° C. at 10°/min and held for 1 hour.

The temperature was ramped to 500° C. at 10°/min and held for 1 hour.

[0089] The inverse opals were removed from the crucible and placed in a scintillation vial. Another solution of 238 mg Zr solution plus 135 mg H₂O was dropped onto the P3 inverse opals with 1 coat of Zr. The vial was rotated to ensure total coverage of the inverse opals by the coating solution. The coated inverse opals were then rotovapped under negative pressure in order to cause the solution to penetrate the cavities within the photonic inverse opals and remove excess water.

[0090] When the inverse opals appeared dry, the inverse opals were transferred to a ceramic crucible. The inverse opals were then annealed in air with the following heating program:

The temperature was ramped to 120° C. at 10°/min and held for 1 hour.

The temperature was ramped to 450° C. at 10°/min and held for 1 hour.

The temperature was ramped to 500° C. at 10°/min and held for 1 hour.

Example 11

[0091] P3—Photonic Inverse opals with one coat of Zr were prepared as follows. SiO₂ inverse opals were coated with zirconium oxide using the PAD method of coating. 192 mg of the solution from example D was diluted with 107 mg of deionized (18 M Ω) H₂O. The solution was then dropped onto 32 mg of P3 photonic inverse opals in a 20-mL scintillation vial. The vial was rotated to ensure total coverage of the inverse opals by the coating solution. The coated inverse opals were then rotovapped under negative pressure in order to cause the solution to penetrate the cavities within the photonic inverse opals and remove excess water.

[0092] When the inverse opals appeared dry, the inverse opals were transferred to a ceramic crucible. The inverse opals were then annealed in air with the following heating program:

The temperature was ramped to 120° C. at 10°/min and held for 1 hour.

The temperature was ramped to 450° C. at 10°/min and held for 1 hour.

The temperature was ramped to 500° C. at 10°/min and held for 1 hour.

Example 12

[0093] P1—Photonic inverse opals with one coat of a mixed Zn:Hf coating 1:1 ratio were prepared as follows. SiO₂ inverse opals were coated with tungsten oxide using the PAD method of coating. A solution of a 1:1 molar ratio of Zn:Hf was prepared by combining the solutions from example B and example C in the appropriate ratios. The solution was then dropped onto 32 mg of P1 photonic inverse opals in a 20-mL scintillation vial. The vial was rotated to ensure total coverage

of the inverse opals by the coating solution. The coated inverse opals were then rotovapped under negative pressure in order to cause the solution to penetrate the cavities within the photonic inverse opals and remove excess water.

[0094] When the inverse opals appeared dry, the inverse opals were transferred to a ceramic crucible. The inverse opals were then annealed in air with the following heating program:

The temperature was ramped to 120° C. at 10°/min and held for 1 hour.

The temperature was ramped to 450° C. at 10°/min and held for 1 hour.

The temperature was ramped to 500° C. at 10°/min and held for 1 hour.

FIG. 7 shows the emission spectra of a hafnium-containing solid composite phosphor upon 365 nm excitation. FIG. 8 shows the emission spectra of the hafnium-zinc-containing solid composite phosphor filled with CCl₄ upon 390 nm excitation.

Example 13

[0095] The zirconium-coated mesoporous silica was prepared by taking 192 mg of the zirconium solution and diluting with 100 mg of deionized (18 MΩ) H₂O. The solution was then dropped onto 32 mg of the silica photonic crystals in a 20-mL scintillation vial. The vial was rotated to ensure total coverage of the crystals by the coating solution. The coated crystals were then rotovapped under negative pressure in order to cause the solution to penetrate the cavities within the photonic crystals and remove excess water. When the crystals appeared dry, the crystals were transferred to a ceramic crucible. The crystals were then annealed in air with the following heating program: The temperature was ramped to 120° C. at 10°/min and held for 1 hour. The temperature was ramped to 450° C. at 10°/min and held for 1 hour. The temperature was ramped to 500° C. at 10°/min and held for 1 hour. The resulting zirconium-coated mesoporous silica was very bright under UV light.

Example 14

[0096] The hafnium coated mesoporous silica was prepared by taking 200 mg of the hafnium solution and diluting with 100 mg of deionized (18 MΩ) H₂O. The solution was then dropped onto 32 mg of the titanium oxide photonic crystals in a 20-mL scintillation vial. The vial was rotated to ensure total coverage of the crystals by the coating solution. The coated crystals were then rotovapped under negative pressure in order to cause the solution to penetrate the cavities within the photonic crystals and remove excess water. When the crystals appeared dry, the crystals were transferred to a ceramic crucible. The crystals were then annealed in air with the following heating program: The temperature was ramped to 120° C. at 10°/min and held for 1 hour. The temperature was ramped to 450° C. at 10°/min and held for 1 hour. The temperature was ramped to 500° C. at 10°/min and held for 1 hour.

[0097] The foregoing description of the invention has been presented for purposes of illustration and description and is not intended to be exhaustive or to limit the invention to the precise form disclosed, and obviously many modifications and variations are possible in light of the above teaching. The embodiments were chosen and described in order to best explain the principles of the invention and its practical appli-

cation to thereby enable others skilled in the art to best utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto.

What is claimed is:

1. A composite comprising: a phosphor material of at least one of among hafnium oxide, niobium oxide, tantalum oxide or zirconium oxide as a conformal coating on a porous substrate, the composite characterized as exhibiting photoluminescence at room temperature.

2. The composite of claim 1 wherein the porous substrate is of silica.

3. The composite of claim 2 wherein the porous silica substrate is an inverse opal structure.

4. The composite of claim 2 wherein the porous silica substrate is a zeolite.

5. The composite of claim 1 wherein the composite is further characterized as having a broad emission spectrum having a width at ½ maximum greater than 80 nm.

6. The structure of claim 1 further including a material with a pre-selected index of refraction within pores of said porous substrate adapted to minimize light scattering from said structure.

7. The composite of claim 6 wherein said material with a pre-selected index of refraction is a liquid, gel or solid.

8. The composite of claim 6 wherein said index of refraction is either greater than 1.0 or is approximately equal to the index of refraction of the porous substrate.

9. A composite comprising: a phosphor material of at least one of among hafnium oxide, niobium oxide, tantalum oxide, zinc oxide or zirconium oxide as a conformal coating on a porous substrate, the composite characterized as exhibiting photoluminescence at room temperature and as having a broad emission spectrum having a width at ½ maximum greater than 80 nm.

10. The composite of claim 9 wherein the porous substrate is of silica.

11. The composite of claim 10 wherein the porous silica substrate is an inverse opal structure.

12. The composite of claim 10 wherein the porous silica substrate is a zeolite.

13. The composite of claim 9 further including a material with a pre-selected index of refraction within pores of said porous substrate adapted to minimize light scattering from said structure.

14. The composite of claim 13 wherein said material with a pre-selected index of refraction is a liquid, gel or solid.

15. The composite of claim 13 wherein said index of refraction is either greater than 1.0 or is approximately equal to the index of refraction of the porous substrate.

16. A light-emitting device comprising:

a mesoporous silicon or silica support structure having pores, an interior surface, and an exterior surface, and a conformal metal-oxide-containing film that coats said interior surface and exterior surface of said mesoporous silicon or silica support structure without substantially blocking the pores of said mesoporous silicon support structure.

17. The light-emitting device of claim 16, wherein the pores of said mesoporous silicon or silica support structure have sizes in a range of from 1 to 20 nm.

18. The light-emitting device of claim **16**, wherein said mesoporous silicon or silica support structure comprises an inverse opal or a photonic crystal.

19. The light-emitting device of claim **16**, wherein said metal oxide-containing film that coats the interior and exterior surfaces of said mesoporous silicon or silica support structure comprises a transition metal oxide or a lanthanide oxide.

20. The light-emitting device of claim **16**, wherein said metal oxide-containing film that coats the interior and exterior surfaces of said mesoporous silicon or silica support structure comprises a group-4 transition metal or a group-5 transition metal.

21. The light-emitting device of claim **16**, wherein said metal oxide-containing film that coats the interior and exte-

rior surfaces of said mesoporous silicon or silica support structure includes titanium, zirconium, hafnium, or zinc.

22. The light-emitting device of claim **16**, wherein the pores of said mesoporous silicon or silica support structure are filled with an index matching material.

23. A radiation detector comprising:

a light-emitting device that comprises a mesoporous silicon or silica support structure having pores, an interior surface, and an exterior surface, and a conformal metal-oxide-containing film that coats said interior surface and exterior surface of said mesoporous silicon or silica support structure without substantially blocking the pores of said mesoporous silicon support structure.

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