

Intelligent Material Solutions, Covert Tagging and Serialization Systems

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Abstract

We propose an innovative covert tagging system based on five specific and unique rare earth crystalline compositions capable of converting wavelengths of light up or down the electromagnetic spectrum. By incorporating precise ratios of rare earth ions in unique host lattices and synthesizing them under exact conditions we can achieve excellent control and tunability of their optical properties through highly complex energy transfer mechanisms. The optical emissions of the upconverting rare earth crystals can be tuned for various parameters such as lifetime, emission spectra, and relative ratio between a phosphor with multiple emission peaks spectra. Additionally, a handheld detection platform will be developed that will be capable of identifying all of the unique optical signatures within a single composition and also differentiate from other compositions. The detection platform will provide a cost-effective and secure platform for identification of the various covert markers.

Introduction

There are vast numbers of covert marking technologies currently being employed at all levels of industry and government; each with a specific feature meant to be detected and recognized only by authorized individuals. However, due to the advancement of various chemical and microscopic analytical techniques such as (XRF, ICP-Mass Spectrometry, FTIR, Raman, etc) it has been increasingly difficult to develop covert taggants with sufficient complexity to prevent reverse engineering of the taggant. The increased ability of the groups or organizations to utilize these analytical techniques to decipher covert marks has resulted in the demand for advanced materials capable of providing optical or electronic signatures that cannot be decoded or identified to belong to a particular chemical composition.

Intelligent Material Solutions, Inc. (herein referred to as IntMatSol) specializes in the design and synthesis of inorganic crystalline materials and nano-materials with high degrees of tunability over various parameters such as; particle size, morphology, emission, absorption, and lifetime. Through decades of experience in the advanced optical materials field, our company can design limitless types of materials with unique optical properties that are virtually indistinguishable from each other through elemental or electron microscopic techniques. While each specific material composition will have it's own spectrally different signature, elemental analysis or any other analytical techniques cannot correlate specific composition to spectral feature. This is achieved through our unique understanding of the optical properties of the rare earths and the ability to tune those properties by minor adjustments in the activators that are present in low concentrations not distinguishable from other trace impurities (<1%) that may be in the crystal structure. Through trade secret processing

technologies and a vast understanding of the photophysical properties of the upconverting energy transfer mechanisms we can develop highly complex systems for authentication that can be integrated into almost any medium or platform. As mentioned, the IntMatSol core technology is based on complex inorganic compositions of metals and rare earth dopants which produce unique optical signatures that can be tailored to absorb or emit in any region of the XRay to Mid-IR spectrum. Figure 1 and 2 are examples of various rare earth visible (Fig. 1) and infrared (Fig. 2) emitting phosphors. As depicted in the figure, each dopant possess a unique spectral signature with little to no overlap from other dopants. Additionally, the lifetimes of each emission wavelength can be tuned from (a few microseconds to milliseconds at any wavelength). The primary energy transfer mechanisms for these materials are summarized below.

Upconversion

Up-conversion (UC) occurs when a material is photoexcited at a longer wavelengths resulting in photoemission at a shorter wavelength. UC is also referred to as anti- Stokes emission since Stokes law states that the wavelength of the emitted light should be greater than the wavelength of the exciting radiation. In terms of the particle nature of light, UC implies that absorption of two or more low energy photons may result in the emission of a higher energy photon. Figure 1 below depicts the ytterbium absorber utilized for infrared (980nm) to visible upconversion emission.

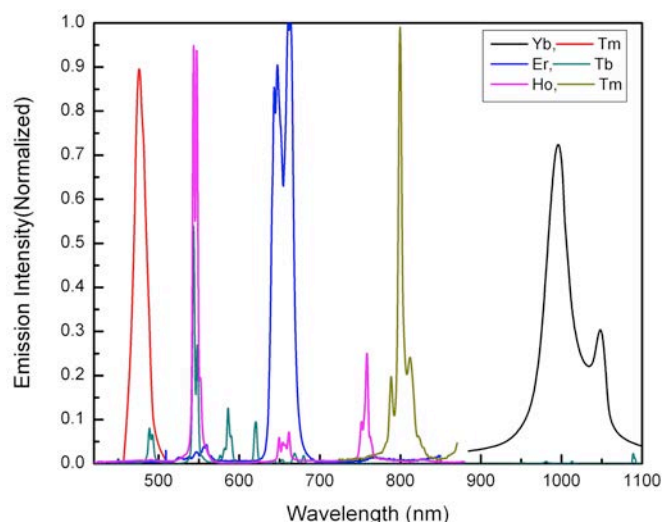


Figure 1. Visible Emission/Absorption (black line) Spectra for various rare earth upconverting phosphors.

Downconversion

Down-conversion occurs when a material is photoexcited at a shorter wavelength resulting in multiple photoemission at longer wavelengths. Essentially, two or more low energy photons may be emitted for each high-energy photon absorbed. As a result, such a structure could have quantum efficiency equal to or exceeding 200% for a given excitation wavelength.

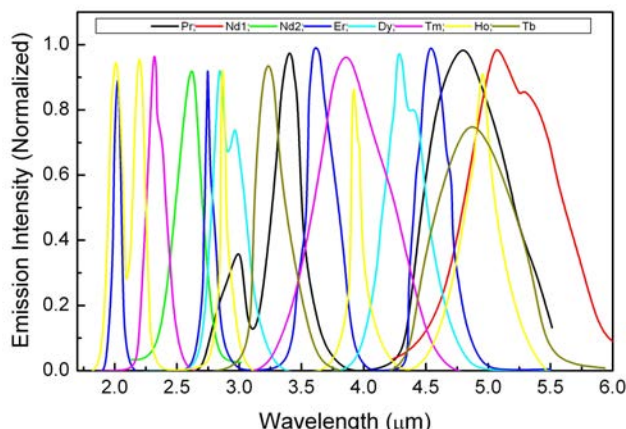


Figure 2. Overlay Mid-IR emission spectra for various rare earth dopants.

Complex Optical Signatures

The key advantage of the rare earth phosphors is the high degree of tunability for each parameter of the energy conversion mechanism from one wavelength to another. The features of the phosphors which can be readily controlled and remain unique to specific crystalline compositions and structures are described below:

Discrete Absorption/Emission Spectral Signatures -

By combining specific ratios of rare earth activators in high temperature crystalline processes, highly ordered crystal lattices are created giving way to complex energy transfer pathways between rare earth pairs. Depending on the rare earth dopants and the crystal host one can achieve tunable absorption and emission spectra.

Emission Spectra Peak Ratios – Within a given rare earth dopant pair, for instance, Ytterbium, Erbium, the spectra signature of the erbium possesses multiple emission peaks which can also be tuned relative to one another. By changing the rare earth dopant ratio and/or host lattice composition the relative peak ratios can be altered and is easily reproducible batch to batch. Figure 3 depicts the rare earth emission of two different ratios of Ytterbium/Holmium. Slight variations in the dopant pair will increase or decrease the relative intensity of the 540 and 660nm peaks.

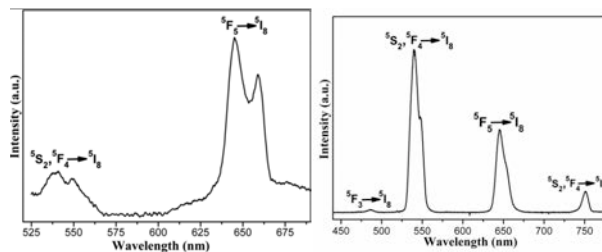


Figure 3. Emission spectra of two Yb, Ho phosphors with only slight change in dopant concentration providing excellent tunability of relative peak ratios.

Triple Ion Doping- IntMatSol has developed a comprehensive library of crystal structures and optimum rare earth compositions yielding highly complex energy transfer mechanisms with only slight changes in chemical composition. The figure below depicts the emission spectra of Yb, Tm phosphors (left panel) and Yb, Tm, Nd (right panel) triply doped phosphors. Incorporating small amounts of particular absorbers can cause electrons to populate energy levels giving a change in overall spectra profile. In this instance, the addition of Neodymium, causes a decrease in the 800-nm emission subsequently, the available energy populates the blue (480nm) and red (660nm) energy levels. The 800nm emission seen in the Yb, Tm dopant pair is significantly suppressed with Neodymium in the crystal lattice. Additionally, the dopant/activator concentrations in these materials are <0.5%.

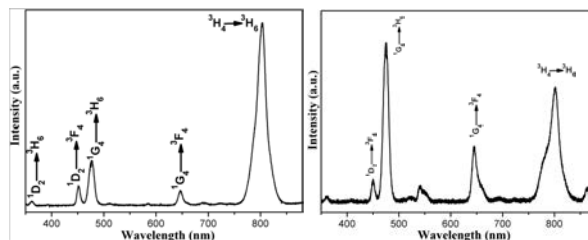


Figure 4. Emission spectra of Yb, Tm doped crystals (left panel) and the change in spectral signature with the addition of Neodymium (right panel)

Lifetime

In addition to the characteristic absorption and emission spectra that can be obtained the rise and decay times of each material can also be tuned. The rise time is measured from the moment the first excitation photon is absorbed to when the first emission photon is observed. The decay time is measured by the slope of the emission decay, or the time it takes for the phosphor to stop emitting once the excitation source is turned off. This is also described as the time it takes for depletion of electrons from the excited energy levels. Figure 5 depicts the rise and decay time tunability of a Y2O3:Yb,Er doped phosphor excited at 1540nm. By changing the dopant ratio the rise and decay times can be reliably altered.

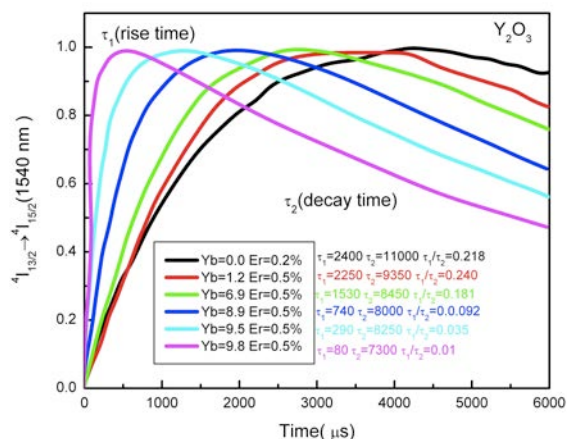


Figure 5. Rise/Decay Times of Yttrium Oxide upconverting phosphor of varying Ytterbium/Erbium ratios.

Multiplexed Detection of Taggants

Another major objective of this proposal is to determine the feasibility of producing a low-cost handheld reader, or phosphorimeter, which can simultaneously detect and discriminate several different up-converting phosphor signals and their uniquely characteristic emission properties, the parameters of which can be multiplexed and combinatorially analyzed in real-time to generate variable optical sequence codes for authenticity monitoring. Due to their advantageous photophysical and emissive properties the particles can be compositionally tuned in a variety of ways to enable this capability but difficult to reproduce by a counterfeiter given their chemical complexities. For this proposal, we will concentrate on developing a device for silicon based detection of the visible- and NIR-emitting upconverters (anti-Stokes NIR excitation \rightarrow VIS/NIR emission), but the same principles can eventually be applied for the analysis of the down-converting particles as well as for detection in the mid-IR regime using InGaAs based detectors. Operationally, the ultimate goal is to provide fast and 100%-accurate read-out authenticity verification of the satellite electronic parts by (1) applying completely counterfeit-proof and tailorable optically encoded signatures, and (in the context of) (2) an optical reader and its multi-parameter data processing which itself additionally serves as a technically challenging deterrent.

A key technology that will be exploited is its specialization in the 980 nm vertical cavity surface emitting laser (VCSEL), a semiconductor laser diode typically used for fiber optic data communications but which offers in this proposal several advantages when used as a spectrophotometric excitation source and which can be mass-produced at extremely low cost. In this proposal, an experimental proof-of-concept experimental prototype will be developed which will consist of both designed and off-the-shelf optical and electronic components. Of most importance will be demonstrating feasibility of scalability to further miniaturized, commercializable designs particularly with respect to size, power consumption, cost and performance.

The bench-top prototype will be used to demonstrate feasibility of multiplexing of the various emission parameters of the

particles, namely the luminescence intensities and lifetimes for each individual emission wavelength. For example, for five wavelengths (i.e. 5 particles) this will yield over a trillion sequence combinations available as codes for the anti-counterfeiting application. To our knowledge, neither a portable bench-top nor field-deployable handheld device has been reported or commercialized which constitutes this multiplexing capability. Key to this approach is the use of spectrally separated lifetime measurements which will enable the ability to not only easily distinguish the various well separated optical signatures but also between two or more compositions differing by only a few fraction of a percent such as by adding impurities to help prevent a given signature from being known by compositional analysis alone. The longer term goal is to commercialize a low-cost handheld device with the controlling and processing microelectronics on a chip to enable built-in user interface and which will predominantly consist of designed and manufactured optoelectronic components difficult to reproduce by device counterfeiters. Figure 6 is the results of a feasibility study performed confirming the ability for multiplexed detection of visible emissions from the upconverting phosphors.

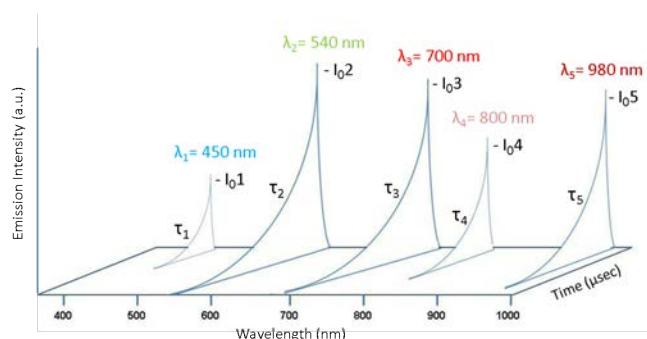


Figure 6. Multiplexed Detection of five unique upconverting phosphors utilizing 1.5-micron excitation. This was performed utilizing a benchtop prototype detector.

Technical Plan/Approach

The up-converting phosphors are ideally suited for the proposed application because of their relatively long phosphorescence lifetime decays attributed to the trivalent rare earth (or lanthanide) metals. Phosphorescence is emission of luminescence which involves an internal conversion process called intersystem crossing for populating triplet states from the lowest excited singlet state and returning to ground state yielding slow emissions decay rates (microseconds to milliseconds) compared to the fluorescence of organic fluorophores which emit photons returning to the ground state from an excited singlet state with rapid lifetime decays in the nanosecond time scale. We will use "pulse" or "time-domain" lifetime measurements (as opposed to frequency-domain (or phase modulation)). Following a brief excitation pulse, for decay times longer than about 20 ns, sophisticated and expensive photon counting techniques such as TCSPC typically used for fluorescence measurements are not necessary but rather simple, relatively inexpensive time-gating approaches can be used instead for measurements of either steady-state luminescence or intensity decays (lifetimes) on timescales, in the case of phosphorescence, which conform to the microsecond speeds of

most current image detector arrays such as CMOS and CCD linear or area sensor arrays as well as photodiode arrays, all of which also offer the potential benefit of being used to spectrally discriminate multiple single exponential decays differing according to their emission wavelengths. In this proposal, we plan to exploit this advantage to enable a “multiplexing” capability whereby a mixture of phosphor particles differing in emission wavelengths (under single 980 nm excitation), as well as differing in pre-determined values for their emission intensities and average lifetimes are used to develop a capacity for a very large number of anti-counterfeiting coding sequence combinations.

The Principle

Briefly, typically an excited state population decays exponentially after turning off the excitation pulse by first-order kinetics, following the decay law, $I(t) = I_0 \exp(-t/\tau)$, whereby for a single exponential decay $I(t)$ = time dependent intensity, I_0 = the intensity at time 0 (or amplitude), and τ = the average time a phosphor (or fluorophor) remains in the excited state (or $\langle \tau \rangle$) and is equal to the lifetime. (The lifetime τ is the inverse of the total decay rate, $\tau = (T + k_{nr})^{-1}$, where at time t following excitation, T is the emissive rate and k_{nr} is the non-radiative decay rate). In general, the inverse of the lifetime is the sum of the rates which depopulate the excited state. The luminescence lifetime can be simply determined from the slope of a plot of $\ln I(t)$ versus t (equal to $1/\tau$). It can also be the time needed for the intensity to decrease to $1/e$ of its original value (time 0). Thus, for any given known emission wavelength a number of parameters fitting the exponential decay law can be monitored for their use in developing anti-counterfeiting codes. As mentioned above, in this proposal we will concentrate on combining known emission wavelengths, intensity amplitudes and lifetimes in this regard. Using the experimental prototype, for this proposal we will produce 3D histograms graphically demonstrating this proof-of-principle, such as the one depicted and described in Figure 1 below. Thus, and most importantly, using only the 3 parameters of wavelength(λ), I_0 , and τ per 5 up-converted wavelengths analyzed (namely 980 nm, 800 nm, 700 nm, 540 nm and 450 nm) under single 980 nm excitation it will be possible to generate $15!$ (factorial) sequence combinations if involving the use of all of these parameters, or approximately 1.3×10^{12} , over a TRILLION sequences available for authenticity monitoring in this scenario. [Note that just adding one more parameter, such as rise time for example, would yield 2.4×10^{18} sequences]. It is important to note that these particular anti-Stokes emission bands are purely resolvable without spectral overlap, thus simplifying the optics by not requiring the need for any band-pass filters for their discrimination when using a polychromator (spectrograph) coupled with a linear sensor array detector. There are many combinatorial scenarios to generate novel signatures that can envisioned, which includes creating new mixed Tau values without wavelength discrimination. The large number of unique signature coding choices should encompass utility for a vast number of components, products and product brands which could be varied periodically at will without reiteration.

Verification of Authenticity

Because the method is based on the use of known amounts of well spectrally resolved phosphors and their combined relative

amplitudes $I(t,0)$ as well as their known single exponential lifetime decays, software development for verification of authenticity using known combinatorial sequences will be fairly straight forward. Because of this and the fact that there is no need to recover lifetimes from samples of unknown composition the use of data processing techniques such TRES (Time-Resolved Emission Spectra), DAS (Decay Associated Spectra) or Global Analysis will not be needed. Instead the multi-wavelength decays ($I(\tau, \lambda)$) can be recorded and compared with a pre-loaded data set or an internal standard, either of which provides $I_s(t, \lambda)$. Then one can simply compare $I(t, \lambda)$ with $I_s(t, \lambda)$ with appropriate statistical considerations to describe an authenticity.

Alternative Approaches

Most time-domain (TD) measurements are performed using time-correlated single-photon counting (TCSPC), but usually for fluorescence when rapid measurements are needed in the nanosecond time scale. In principle the method can be used for phosphorescence but it is generally considered overkill and besides requires different and expensive electronic modules and components such as high repetitive rate mode-locked picosecond laser light sources, time-to-amplitude converter and constant fraction discriminator. For these reasons, it is not our intent to test the TCSPC method. The other main method of measuring decay time is the frequency-domain (FD) or phase-modulation method, in which case excitation light is intensity modulated and at variable high frequencies and the emission responds at the same modulation frequency causing the lifetime to be delayed relative the excitation. The delay is measured as a phase shift. We may investigate this method for the purpose of discriminating the phosphorescence “rise times”, which are difficult to do in the time-domain in the μsec timescale. The rise times displayed by the phosphors provides a unique spectral feature that is not found for the vast majority of luminescent species. For most species the emission occurs from the initially excited state and begins to decay immediately. For the phosphors there is a time delay while the emission state is being populated causing the rise time. This rise time can result in a unique frequency domain observation, a phase angle over 90 degrees. If the rise times of the phosphors do not depend significantly on excitation intensity then the rise times can be used in the same way as the decay times. Typically there is lower parameter correlation when a rise time is present. With the exception of rise times, both TD and FD measurements yield essentially the same information, but FD is better suited for studying multi-exponential intensity decays, which per phosphor is not a concern here.

Technical Risk

We expect the technical risk to be low given that we are proposing to integrate already described and proven principles, methods and systems in the field of phosphorimetry. The novelty proposed here is the eventual development of a low-cost handheld device which can perform multiplexed phosphorimetry (λ, I_0, τ) which to our knowledge have neither been reported nor deployed in the field. A problem we might encounter relates to the sampled intensity levels measured for lifetime analysis on the μsec timescale. If the signals are too low, particularly in a longer standoff detection, a higher power laser diode excitation source

may be needed which could increase the cost of the system, but not by a dramatic amount, we expect, especially at higher volume sales. Another potential concern might be background interferences by both back-scattered laser light and ambient light. However, these pose a low level risk since they can be easily corrected for, and the fact the measurements are correlated to the specific wavelengths and lifetimes of the phosphors.

Author Biographies

Josh Collins and Howard Bell are partners in Intelligent Material Solutions Inc. Howard has been working with phosphors for over 25 years. He has designed materials for the US Treasury and Fortune 500 companies. Josh is the crystallographer growing the materials. Josh is the Chief Technical Officer at IMS and runs the San Diego branch. Josh is a guest researcher at NIH and has been published in PNAS, Nature and other peer review journals.