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A Study of Solid-State Lighting for Rare Earth Ions Experiments

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Abstract - The aim of this study is to the best of one's knowledge, this is the first time that blue light emitting flexible AC powder electroluminescence (ACPEL) devices have been fabricated with undoped and Europium incorporated ZnGa2O4 as well as undoped CaWO4 phosphors and their characteristics were tested. The materials that are directly or indirectly used to advance the existing technology or to develop new technologies are technologically important. It can be achieved by improving performance, improving activity or changing the overall performance of the device in terms of accuracy, cost, handling and safety etc. In the last few years a major progress in the phosphorus sector has been explored through the introduction in different host matrices of phosphorus for solid state lighting applications of transitional metal ions and trivalent rare earth ions (lanthanides), the use of luminescent centers (dopants). Usually, most phosphors consist of a host material that is composed of a family of sulphides, phosphates, aluminats, oxides, molybdates, tungsten sulphides, silicates etc (transition metal ions and lanthanides). The host grating is usually a wide-band semi-conductor or insulator and it is suitable for accommodating doping ions. The host compound also controls little of the luminescent phosphorus' physical and chemical behavior, such as emission intensity and life-long properties. In most cases, the concentration levels of dopant ions or activator ions range from a few ppm to 1 to 5 ppm in host trees. Soft-chemical pathways are a technique for low-temperature synthesis which permits better reaction compositional homogeneity. However, it is important to ensure that certain compounds such as transitional metals and rare earth based oxides have their synthesis, chemical and thermal stability. In order to obtain these technologically significant materials, a careful choice of preparation techniques and the fine tuning of process parameters are necessary.

Keywords - Solid-State Lighting, Rare Earth Ions, AC powder electroluminescence, Soft-chemical pathways, low-temperature synthesis

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INTRODUCTION

There are many ways to think about energy, and it's a big part of our daily lives. As the world's economy grows so does our way of life, the environment in which we live, and our health. Global yearly primary energy consumption has increased by more than tenfold in the twenty-first century based on modest economic and population development. Due to an increasing need for energy, rising oil costs, uncertainty about energy supplies and the dread of global warming, energy research has become increasingly important in recent decades. Renewable energy is widely acknowledged as a cost-effective and ecologically friendly alternative. Reduce global energy consumption for lighting by half while reducing emissions of greenhouse gases, for example, using renewable energy sources such as solar and wind energies in power sources for most efficient use and long-life illumination source. Nanotechnology is a rapidly expanding field of study that encompasses a wide range of disciplines. It has the potential to transform the methods used to make materials and products, as well as the types and extents to which they can be used in various applications. Solid-state lighting devices, sensors, photonics, drug delivery, proteomics, and bio-molecular electronics are all based on nanomaterials, which are the building blocks of these new technologies. Additionally, energy conservation and environmental concerns are of paramount importance around the world. Efforts are made to produce energy-efficient appliances. Solid-state and other energy-efficient lighting systems have grown in popularity as a result of an increased need for energy-saving and environmentally friendly lighting technologies [2-4].

Miniaturization requests and progress in nanofabrication are prompting worldwide interest in Nano phosphors as white-emission mercury-free lighting sources. By comparison with their bulk counterparts, Nano phosphors exhibit reduced concentration quenching effects and a great potential to enhance luminescence efficiency and

tunability. In this paper, the physics of the nanophoshors is overviewed with a focus on the impact of spatial confinement and surface-to-volume ratio on the luminescence issue, as well as rare earth-activated multicolor emission for white light (WL) output. In this respect, the prominently practiced strategies to achieve WL emission are single nanophosphors directly yielding WL by means of co-doping and superposition of the individual red, green, and blue emissions from different nanophosphors. Recently, a new class of efficient broadband WL emitting nanophosphors has been proposed, i.e., nominally un-doped rare earth frees oxide (yttrium oxide, Y2O3) nanopowders and Cr transition metal-doped garnet nanocrystals. In regard to this unconventional WL emission, the main points are: it is strictly a nanoscale phenomenon, the presence of an emitting center may favor WL emission without being necessary for observing it, and, its inherent origin is still unknown. A comparison between such an unconventional WL emission and the existing literature is presented to point out its novelty and superior lighting performances.

Solid-state lighting based on light emitting diodes (LEDs) is a rapidly growing market that is progressively replacing the old lighting lamp technologies (incandescent light bulbs, compact fluorescence lamps, and high-intensity discharge lamps). The underlying reason is that, while the efficiency performances of conventional white light (WL) sources (lamps) seem to have reached an upper limit, solid-state WL-emitting LEDs are a generation of lighting sources with mature technology and are particularly interesting for achieving mercury-freedom, better power output, and small volumes in integrated electronics. In particular, in the field of indoor and outdoor lighting, most efforts are being focused on artificial sources with high efficiency, low power consumption, durability, thermal and chromatic stability, fast switching, small size, high color rendering, price competitiveness, environmental friendliness, and, very importantly, sunlight-like WL emission (which is the most comfortable to the human eye). The breakthrough in the emergence and development of LED-based WL sources dates to the development of red LEDs and the invention of bright-blue LEDs by Nakamura et al. in the mid-1990s [4], when efficient WL production was demonstrated by mixed blue-yellow emission resulting from a blue emitting (λ ≈ 440−460 nm) InGaN LED chip exciting a yellow-emitting down-converting Ce-doped yttrium aluminum garnet (Y3Al5O12) crystal. Ce3+-activated Y3Al5O12 features broadband yellow emission, efficient absorption for blue light (420−480 nm), quantum efficiencies larger than 90%, high thermal quenching temperatures (~700 K), and fast decay rates (~63 ns). The intentional addition of Mg2+ and Si4+ ions enables a shift of the emission maximum of Ce3+-activated Y3Al5O12 to around 600 nm, which leads to a warm WL emission under pumping with a blue emitting LED. Actually, most high-brightness white LED sources use a (blue near-ultraviolet or ultraviolet (UV)) diode that pumps a single or a combination of luminescent materials termed phosphors. Such phosphor-converted LEDs have gained tremendous achievements into various applications and promise to further expand their application fields. As a general remark, fundamental and applicative research efforts to improve performances of WL LED sources are currently mainly devoted to nanophosphors (i.e., nano-sized phosphors) due to changes of several properties related to scaled-down size and opportunities of engineered functionalities for the desired application. For instance, an increasing trend to miniaturization favored by the progress in nanotechnology and the development of nano-medicine have prompted interest in Nano phosphors as luminescent markers for imaging in medical diagnosis and therapy as well as multiplexed biological labeling. Such applications take advantage from up-conversion luminescence, large anti-Stokes shifts (up to 500 nm), excellent photo-stability, high luminescence quantum efficiency, long luminescence lifetime, narrow emission lines, high color purity, and removal of UV excitation-induced photo-damage to biological samples, quantum cutting, and absence of photo-bleaching and photo-blinking in Nano phosphors.

PHOSPHORS AND PHOSPHOR-CONVERTED SOLID-STATE LIGHTING SOURCES:

1. Phosphors and Luminescence Mechanisms

Inorganic phosphors are solid-state efficient luminescence materials that can be involved in conventional down-conversion processes (i.e., emission of photons with lower energy than the exciting photons) as well as up-conversion processes (i.e., emission of photons with energy exceeding the exciting photon energy by 10–100 kBT).

Figure 1.1 shows a schematics of a down-conversion process (Figure 1.1a) and an up-conversion process (Figure 1.1b) following energy absorption (“abs” label) between the ground state and the excited states (referred to as A* and A**) of an element A. Decay channels of the absorbed energy can be radiative (“r” label) through down-conversion and up-conversion emission or non-radiative (“nr” label), typically heat transfer, which compete with luminescence and deteriorate the luminescence yield and efficiency (number of photons emitted divided by the number of photons absorbed). Phosphors can have different composition according to the following main classification:

- Thermally and chemically stable crystalline materials that inherently contain luminescent centers,
- Optically inactive materials (termed host crystals) doped with optimized concentrations and kind of luminescent ions (activators, sensitizers, activator–sensitizer pairs), and

- Defect-related luminescent materials that emit under proper concentration of the defect and/or reaction conditions.

The host material of a phosphor is usually a wide band-gap material (e.g., oxides, nitrides, and sulfides) that fulfills a stringent requirement such as low lattice phonon frequencies to improve the emission efficiency and reduce non-Radiative losses. On the other hand, the host crystal plays a role in determining dopant-ligand coordination and spatial distance as well as site-symmetry, which is an important issue depending on the dopant nature and bulk versus nanoscale regime. As it will be detailed, the host material may affect luminescence properties such as emission color, quantum conversion efficiency, and thermal quenching of optical transitions involving d electronic orbitals. Notably, as the lanthanide-ligand bonds are more ionic than the transition metal-ligand bonds, more coordination situations are possible in the case of RE elements and this corresponds to more symmetries.

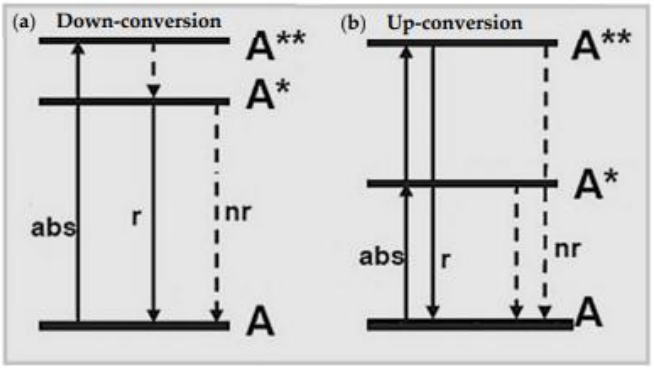

Figure 1: Schematics of (a) down-conversion emission and (b) up-conversion emission resulting from energy absorption (abs) by an element A with excited states A* and A. Labels "r" and "nr" refer to radiative and non-radiative decay-channels, respectively**

Radiative emission of phosphors can result from two main classes of processes, which are, sensitization by the host lattice or transitions due to dopants termed "activator" (A) if acting as emitting centers and "sensitizer" (S) if their energy levels let transfer energy to the emitting activator ions [24]. In the former situation (Figure 1.2a), band-to-band excitation by effective photon absorption generates electron–hole pairs (typically excitons under UV excitation) and then conduction excited electrons relax to donor levels ("D" label) and holes transfer to acceptor states ("A" label) rather than recombining radiatively. Hence, fluorescence by sensitization by the host lattice stems from levels of the donor–acceptor pair. In the case of luminescence between discrete energy levels of emitting centers without the participation of the host material, the simplest situation occurs when an activator dopant element (A) gets excited to a state A* following energy absorption and emits radiatively through down-conversion processes (Figure 1.2b). Fluorescence with tunable color output of an activator element can be induced indirectly by energy transfer from a directly excited sensitizer to the excited state of a nearby radiatively emitting activator (Figure 1.2c).

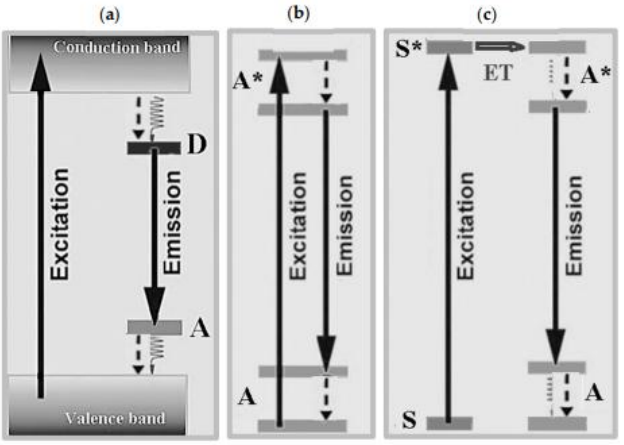

Figure 2: (a) Sensitization of the host lattice. (b) An activator element (A) gets excited to a state A* following energy absorption and emits radiatively through down-conversion. (c) The energy absorbed by a sensitizer S having an excited state S* is transferred to an excited state of a nearby activator dopant (A*) that emits radiatively. Dashed lines refer to non-radiative

An efficient sensitizer is required to have strong and broad absorption/emission favoring energy transfer towards the distribution of the absorption lines of the acceptor ion. Among available sensitizers and activators, the Er3+-Yb3+ pair is particularly suitable under excitation at 980 nm [25]. Fluorides usually exhibit low phonon energy of (350 cm−1) and, for instance, hexagonal NaYF4 crystal co-doped with Yb3+-Er3+ pairs is an efficient up-conversion phosphor under excitation at 980 nm [26]. The above considerations shed light on the important role played by the energy transfer processes, which can be classified into resonant, semi–resonant, and double resonant energy transfer. In the former case, energy transfer occurs from donor to acceptor with slightly lower-lying energy levels in such a way to make unlikely backward energy transfer from acceptor to donor. Semi–resonant and double resonant energy transfer are examples of non-resonant energy transfer. For semi–resonant processes, also termed phonon-assisted energy transfer, several phonons bridge the small energy mismatch between the donor and acceptor ions, and luminescence quenching may result due to the phonon-related radiative losses.

2. Dopant Emitting Centers

The above general overview points out that luminescence at a designed color output requires that both the absorbed energy could be channeled to discrete states of emitting centers and effective interplay of luminescence processes occurs. The dopant commonly used in phosphor materials are RE and TM elements, which can be classified

according to their absorption electronic transitions, as dictated by their electronic configuration. Actually, most phosphors incorporate RE elements that include, as the periodic table of elements in Figure 3 shows, scandium (Sc), yttrium (Y), lanthanum (La) and the 14 lanthanide elements (cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu) with atomic number Z ranging.

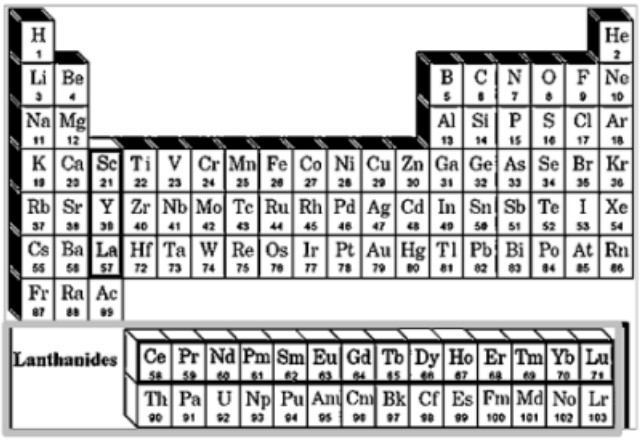

Figure 3: Periodic table of elements.

A peculiarity of RE ions is their characteristic sharp emission energies related to their electronic configuration [Xe]4fN, where N refers to the number of electrons in the f-shell. Trivalent lanthanide ions have an outer electronic configuration 5s25p64fN where N ranges from 1 (Ce ion) to 13 (Yb ion) and the valence electrons 4fN are shielded from interactions with the chemical environment (host crystal lattice and ligands) by means of the 5s25p6 outer less-bounded configuration.

3. Phosphor-Converted White-Light Emitting Diodes (LEDs)

Since a LED is inherently a single-color emitter, WL emission from LED-based devices requires strategies that overlap/mix in a balanced way either two complementary colors or three primary colors (red (R), green (G), and blue (B)). For this purpose, the richness of color outputs and transition processes of RE elements make them key components of phosphors. Technically, LED WL-sources can consist of multiple LED chips (the so-called multiple LED approach), a (near-)UV emitting LED combined with RGB phosphors (Figure 1.4, left panel), and a blue-emitting LED plus a yellow phosphor (Figure 1.4, right panel) that can be replaced by a mixture of green and red phosphors with similar emission profiles. Despite the advantages of using only LEDs (without phosphors) due to the relatively narrow emission bands, practical disadvantages of the multiple LED approach are more complex electronics, current- and temperature-dependent color shifts, high production costs, and the request of combining at least four LEDs. For these reasons as well as more flexible design opportunities, currently, most of the commercially available LED-based WL sources rely on phosphor-converted LEDs, i.e., on combining a single LED light source with one or more phosphors. In phosphor-converted LED devices using a blue emitting LED, the phosphor converter is directly packed on the blue LED in such a way that the absorption of blue light by the phosphor yields yellow emission that, combined with the transmitted blue light, leads to WL luminescence (Figure 4, right panel).

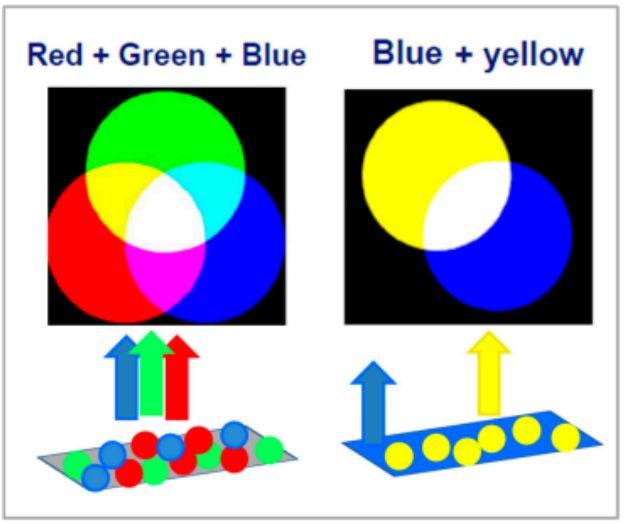

Figure 4: Most common principles used in white light emitting LEDs: (left panel) a (near-) ultraviolet (UV) emitting LED combined with RGB emitting phosphors and (right panel) a blue-emitting LED irradiating a yellow phosphor.

AN OVERVIEW OF SOLID STATE LIGHTING DEVICES

In the absence of sunlight, lighting technology is a vital alternative. In the context of lighting, history can be seen as a progression of more efficient methods for producing visible light in the chosen spectrum. The classic technologies that have been created thus far are incandescence and fluorescence. In the last 200 years, these technologies have seen substantial progress, but it appears that they have reached a saturation point at efficiency of 1–25%. Compared to CFLs, which have an efficiency of 20-25 percent, incandescent bulbs have 5 percent efficiency. These challenges, which include energy usage, environmental effect, and health of persons, have spurred research into white LED light sources [6]. An energy-efficient lighting system is being researched by the scientific community. SSL devices have shown to be one of the most environmentally friendly and energy efficient lighting technologies. Since solid-state lighting (SSL) is a freshly developed technology, it has the potential to significantly reduce lighting energy consumption and contribute considerably to our nation's efforts to combat climate change. LEDs, electroluminescence devices (EL), organic light emitting diodes (OLEDs), polymer light emitting diodes, quantum dot (Q-LEDs)

and carbon dot light emitting diodes (C-LEDs) are all examples of solid-state lighting systems. Using solid-state lighting instead of incandescent lighting could lower the amount of energy needed to provide lighting, which is related with a light output of less than 20 lumens per watt for incandescent lighting. On the order of 160 lumens per watt, light-emitting diodes are highly efficient. The equivalent of 230 typical 500 MW coal plants might be replaced by LED light sources, resulting in a reduction in greenhouse gas emissions of roughly 200 million tonnes [6]. SSL technology, which would use highly luminous semiconducting nanoparticles, could be a viable option in the present age of sensible energy storage. In view of its peculiar structural, optical, and electronic features and efforts to manufacture lighting sources and technology, in home and non-commercial or industrial illumination applications, [12], it has garnered considerable attention around the world. The discovery of an efficient light conversion nanophosphor is critical in the development of a solid state lighting system. Materials that absorb energy and then emit it as light are referred to as luminescent nanophosphors, which are literally "light bearing materials" (ultraviolet, visible or Infrared). Many obstacles must be overcome along the road in order to produce light from semiconductor materials with band-gaps that cover the entire visible spectrum. Mercury-free affordable nanophosphors are being developed that convert longer wavelength UltraViolet (UV) to blue light and eventually into white-light with better luminous efficacy, energy savings and low power consumption features.

Characteristics of Solid-State Lighting

Solid-state lighting is increasingly used in a variety of lighting applications because it offers many benefits such as:

- Long life LEDs can provide 50,000 hours or more of life, which can reduce maintenance costs. In comparison, an incandescent light bulb lasts approximately1,000 hours.
- Energy savings The best commercial LED lighting systems to provide three or more times the luminous efficacy (expressed in lumens per watt) of incandescent lighting. Colored LEDs are especially advantageous for colored lighting applications because filters are not needed.
- Intrinsically safe LED systems generally operate at low voltages and are cool to the touch.
- Better quality and light output LEDs have minimum ultraviolet and infrared radiation and can be tuned to emit color.
- Smaller and flexible light fixtures The small size of LEDs makes them useful for lighting tight spaces. New generation OLEDs are flat and flexible, thus suitable for unique applications.
- Durability LEDs offer high durability as they have no filament to break and can withstand vibrations.

CONCLUSION

The main focus of this thesis is on the synthesis and characterisation of inorganic luminous nanomaterials based on Gallates (Ga2O3, ZnGa2O4) and Tungstates (CaWO4, Ca3WO6). Before and after doping with rare earth ions, these nanomaterials' structural and luminescent properties are examined using XRD, SEM, TEM, FT-IR, Raman, UV/VIS absorption, Photoluminescence (PL) and Electroluminescence (EL) techniques, as well as X-ray diffraction, Scanning Electron Microscope (SEM), and Transmission Electron Microscope (TEM). Following the hydrolysis of Zn2+ and Ga3+ in ethylene glycol medium at 140°C, the ZnGa2O4 phosphors were produced by heating them at 900°C for an hour. Similar experimental conditions were used to produce binary oxides such as ZnO and Ga2O3 phosphors. Phosphors using ZnO, Ga2O3, and ZnGa2O4 had hexagonal, monoclinic, and cubic XRD patterns. This nanophosphor ZnGa2O4 (with a particle size of less than 100nm) is made up of aggregated, irregularly-shaped round particles, as can be seen by scanning electron microscopy (SEM). Near-band edge emissions (NBE) at 385nm, as well as broad emission (490nm) at deep levels (DL) in ZnO'sbandgap due to intrinsic point defects and surface defects, were observed from the luminescence observations. Emissions from gallium oxides were concentrated in the 440nm to 470nm range due to an electronic transition involving Ga-O bonds in the GaO6 octahedron. In the ZnGa2O4 host, the 440 nm emission peak is due to self-activated centres arising from the hexagonal Ga–O structural units, which is typical of ZnGa2O4 hosts. Recombination of charge carriers from oxygen vacancies in the lattice is primarily responsible for the broad bluish green emission band about 496nm. Based on the structural and luminescence properties, both the Ga2O3 and ZnGa2O4 phosphors are viable options for visible light emitting luminous host materials. Extensive consideration is given to the development of both undoped and rare earth ions doped nanophosphors.

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