



International Journal of Current Research and Academic Review

ISSN: 2347-3215 Volume 3 Number 11 (November-2015) pp. 66-72

www.ijcrar.com



Research Review on Rare Earth (RE) Activated Silicate Phosphor for LED Application

Chaudhari Dilip Bhagvat¹, O. Hmahajan² and Sadique Shaikh^{3*}

¹Department of Physics, Arts and Science College, Bhalod, M.S, India

²Department of Pysics, M.J.College, Jalgaon, M.S, India

³Department of Computer, Arts and Science College, Bhalod, M.S, India

*Corresponding author

KEYWORDS

Rare earth materials,
Photo luminance,
Intrinsic photo
luminance,
Extrinsic photo
luminance,
Sensitized
Photoluminescence,
LED
applications

A B S T R A C T

Since the birth of the incandescent lamps more than a century ago, several new lamps have been developed. Many of them are discharge lamps with far higher efficacies (lumen per watt) than the incandescent lamps. Different lamps have different possibility with regard to wattage, efficacy size, performance and color temperature. The word “Phosphor” was invented in the early 17th century with the discovery of the “Bolognian stone” in Italy. This sintered stone was observed emitting red light in the dark after exposure of sun light. Similar finding were reported from many places in Europe and these light emitting stones were named phosphors, means, “light bearer” in Greek. The word Phosphorescence was derived from the word phosphor, which means light emission from a substance after the exciting radiation, has ceased. This paper is the research review on rare earth with silicon phosphors for novelty LED application.

Introduction

In the recent years, much attention has been focused on oxide-based luminescent materials due to their commercial applications in color television, fluorescent tube(1,2), X-rayphosphors, and scintillators. Recently various phosphor materials have been actively investigated to improve their luminescent properties and to meet the development of different display and

luminescence devices. Inorganic compounds doped with rare earth ions form an important class of phosphors as they possess a few interesting characteristics such as excellent chemical stability, high luminescence efficiency, and flexible emission colors with different activators(3,4). There is growing interest in the development of new full color emitting phosphor materials that combine

thermal and chemical stability in air with high emission quantum yield at room temperature. The search for blue phosphors is of particular importance because of the limited number of stable blue luminescent materials available. Danielson et al. have reported a novel blue luminescent material Sr₂CeO₄ prepared by combinatorial material synthesis technique, which exhibits the emission peak at 485 nm. Subsequently, several studies of this luminescent materials were conducted, and some synthetic routes have been developed to prepare the Sr₂CeO₄ powders and films, including traditional solid-state reaction, chemical coprecipitations, Echini's method, microwave annealing, ultrasonic spray pyrolysis, and pulsed laser depositions. Sr₂CeO₄ consists of infinite edge-sharing CeO₆ octahedra chains separated by Sr atoms. The luminescence originates from a ligand-to-metal Ce⁴⁺ charge transfer (CT). In CT transitions an electron is transferred from a ligand to 4fⁿ shell of a rare earth (RE) ion (5,6). Some states that arise as a result of such transition are stable and can relax to the groundstate with a photon emission. This phosphor exhibits blue-white luminescence efficiently under excitation with UV light, cathode ray or X-ray. Sr₂CeO₄ also acts as a sensitizer to transfer the absorbed energy to the dopants (activators) such as rare earth ions. The broad emission band is suitable for the doping of rare earth ions in pursuing new luminescent materials and some research work has been carried out by traditional solid-state reaction, namely the metal oxides are used as precursors and the reaction reagents have to be calcinate at very high temperature for a long time. Sr₂CeO₄ phosphor has been widely studied because of its importance in the realization of a new generation of optoelectronic and displaying devices(7). Furthermore, luminescent properties were found to greatly depend on particle size, size distribution and particle

morphology. This relationship is of current interest, and may lead to new fabrication processes to yield high-quality luminescent materials. Therefore, it is interesting to develop a synthetic route to yield Sr₂CeO₄ particles with smaller size and uniform morphology, since they have higher packing density and larger percentage of the active sites than bulk material(8). In light of the foregoing, the purpose of this thesis was drawn. Thus the main aim of the present study is the synthesis, characterization and photoluminescence properties of pure and rare earths (Dy, La and Eu) doped Sr₂CeO₄ phosphors of 0.01, 0.1, 0.2, 0.5 and 1.0% molar concentrations(9).

Luminescence

Light can be classified in two ways, one is incandescence and the other is luminescence.

Incandescence is the light glow by the heating of the materials and a bright light is produced. Luminescence is a collective term for different phenomena where a substance emits light without being strongly heated. This definition is also reflected by the term "cold light". The word luminescence was first used by a German physicist, in 1888, Eilhardt Wiedemann. In Latin 'Lumen' means 'light'(10). The materials exhibiting this phenomenon are known as 'Luminescent materials' or 'Phosphors' meaning 'lightbearer' in Greek. The term phosphor was coined in 17th century by an Italian alchemist named Vincentinus Casciarolo of Bologna. The phenomenon of luminescence can be classified into various categories depending on the mode of excitation(12).

- 1) Photoluminescence, when the excitation is by electromagnetic radiation/photons.

- 2) Cathodoluminescence, when the excitation is by energetic electrons or cathode rays.
- 3) Electroluminescence is light emission triggered by electric influences.
- 4) Radioluminescence, when the excitation is by high-energy X-rays or γ rays.
- 5) Sonoluminescence, when the excitation is by ultrasonic waves.
- 6) Triboluminescence can occur when a material is mechanically treated.
- 7) Chemiluminescence is light emitted during chemical reactions.
- 8) Bioluminescence is the form of chemiluminescence from living organisms.
- 9) Thermoluminescence, also known as thermally stimulated luminescence, is the luminescence activated thermally after initial irradiation by other means such as UV or X-rays. It is not to be confused with thermal radiation: the thermal excitation only triggers the release of stored energy.

Photoluminescence

Photoluminescence (PL) refers to the luminescence stimulated by the excitation of solid material (phosphor) by light of another wavelength, typically ultraviolet (UV), visible or infrared light. PL analysis is non-destructive and the technique requires very little sample manipulation or environmental control. The fundamental limitation of PL analysis is its reliance on radiative events (13).

The materials with poor radiative efficiencies, such as low quality indirect semiconductors, are difficult to study via ordinary PL. Similarly, the identification of impurity and defect states depends on their optical activity. The most prevalent use of photoluminescent phosphors is in fluorescent lamps and it is divided into two

major types, namely intrinsic photoluminescence and extrinsic photoluminescence. Intrinsic photoluminescence is displayed by materials, which contain no impurity atoms. Extrinsic photoluminescence results from intentionally incorporated impurities, in most cases metallic impurities or intrinsic defects (14).

Intrinsic Photoluminescence

There are three kinds of intrinsic photoluminescence, namely band-to-band, excitons and cross-luminescence. Band-to-band results from the recombination of an electron in the conduction band with a hole in the valence band and can only be observed in a very pure crystal at relatively high temperatures. An exciton is a composite particle resulting from the coupling of an electron and a hole; it then travels in a crystal and produces luminescence by releasing its energy at luminescent centers. Cross-luminescence is produced by the recombination of an electron in the valence band with a hole in the outermost core band. It can only take place when the energy difference between the top of the valence band and that of the outermost core band is smaller than the band-gap energy; otherwise, an Auger process occurs.

Extrinsic Photoluminescence

Most of the observed types of luminescence that have practical applications belong to this category. Extrinsic luminescence is classified into two types, namely localized and delocalized luminescence. In a delocalized luminescence the excited electrons and holes of the host lattice participate in the luminescence process, while in a case of the localized luminescence the excitation and emission processes are confined in a localized luminescence center, the host lattice does

not contribute to luminescence process. By definition, sensitized photoluminescence refers to a process whereby an impurity species (activator or acceptor) having no appreciable light absorption ability in a given spectral domain, is made to emit radiation upon excitation as a result of absorption by and transfer from another impurity species (sensitizer, or donor).

Phosphor Research Past and Present

Research and Technology in phosphors requires a unique combination of interdisciplinary methods and techniques. Synthesis and preparation of inorganic phosphors are based on physical and inorganic chemistry. Luminescence mechanism are interpreted and elucidated on the basis of solid state physics. The research and development of major applications of phosphors belongs to the field of illuminating engineering, electronics and image engineering. Research on phosphors has a long history. A Prototype phosphor the Zn S-type phosphor for TV tube was first prepared by Theodore Sidot a young French chemist in 1886. This marked the beginning of scientific research and synthesis of phosphors. In early 20th century Leonard and coworkers in Germany performed active and extensive research on the phosphors(15,16).

They prepared various kinds of phosphors based on alkaline earth chalcogenides and investigated their luminescence properties. Early lamp phosphors were natural fluorescing minerals, e.g. Willemite, Mn-activated Zinc orthosilicate, that were grinded to a powder and empirically blended together so as to obtain an approximately white field from fluorescent lamp (17,18). P.W. Pohl and co-workers in Germany investigated Ti²⁺-activated alkali halide phosphors in details in the late 1920s and 1930s. A major turning point follows the

development in 1940s with synthesis of Sb-Mn co-activated halophosphate phosphors. In a single material blue emission from the Sb³⁺ activator and the orange emission from Mn²⁺ co-activator can be adjusted such that they can produce white field corresponding to wide range of color temperature. Homboltz and co-worker at Radio Corporation of America (RCA) also investigated many phosphors for application in TV tubes. Their achievements are compiled in Leverenz's book. Data on the emission spectra in the book remains useful even today. After World War II, the advances in the optical spectroscopy of solids, especially those of transition metal ions help to evolve research on phosphor and solid state luminescence. In 1960 efficient rare earth activated phosphors were developed for use in color TV (Tb³⁺- green, Eu³⁺- red and Dy³⁺ - yellow). In 1970 tricolor lamp was introduced(19,20).

Blue emission from Eu²⁺, red emission from Eu³⁺ and green emission from Ce³⁺ - Tb³⁺ pair was used in tricolor lamp. At present a combination of halophosphate and troposphere blend is used in many lamps as a compromise between performance, phosphor cost and the lamp making cost(24,25).

In phosphor area today top priority is the replacement of the high performance, but very expensive rare earth activated phosphors with cheaper materials. This essentially means replacing the rare earth ions with transition metal ions or post transition ions. The advent of trichromatic fluorescent lamps is the corner stone in the lighting industry. The introduction of rare-earth phosphor systems for lamp applications has revolutionized the industry for it addressed the major issues concerning the lamp performance viz; higher lumen output (90-100 lumens/W)(21,22,23).

Higher wall load factor and 17 better color rendition index (Ra=90), in particular the high wall load –factor enabled this phosphor system to be applied in compact fluorescent lamps where stability against high-load of UV is the stringent requirement for the successful lamp performance(26,27). Interestingly, the triband phosphor system performing near the physical limit leaves noscope for further improvement in the luminous efficiency. That's why new ways in the research are being focused on the design of in-expensive phosphor system without compromising the performance and effectively harnessing the influence of impurities to achieve the ultimate efficiency. The search does not seem to be elusive. Equally important are alternate discharge mechanism (e.g. Xe – discharge) paving way for higher lumen and more importantly, the concept of quantum – cutters underlying generating more than one visible photon for one UV(28,29).

Energy transfer and sensitization of luminescence

The energy transfer processes are often used in practical phosphors in order to enhance the emission efficiency. The process is called as sensitization of luminescence. The donor is called as sensitizer. The emission intensity in Mn^{2+} activated silicate, phosphate and sulfide phosphor for sulfide phosphors for example is sensitized by Pb^{2+} and Ce^{3+} (30,31). In halo phosphate phosphors $3Ca_3(PO_4)_2Ca(FCL)_2: Sb^{3+}, Mn^{3+}$, the Sb^{3+} plays a role of a sensitizer as well as activator. Ce^{3+} sensitizes the green emission of Tb^{3+} in many oxides, Phosphates and van dates(32,33,34). The energy transfer is the process of the excited state energy from donor to an activator. This transfer occurs without appearance of a photon and is the primary result of the multipole interactions between donor and

activator(35). This process is occur, when the energy difference between the ground state and the excited state of a sensitizer and an activator are equal and suitable electrostatic or magnetic origin interaction exist between them. In addition, the emission spectrum of the sensitizer ion and the absorption spectrum of an activator ion have to show spectral overlap for the energy conservation reasons (36,37).

Conclusion

Double activation of phosphors is a promising technique for improving luminescent properties of materials. The double activation of material like $CaWO_4$ with Tb^{3+} and Eu^{3+} , in the presence of alkaline salts as flux, gives the possibility to synthesize phosphors with variable chromatic emissions. Variable luminescence colors could be obtained when calcium tungstate phosphors containing 0-5 mole % activator ions were exposed to relatively low excitation energies, such as 365 or 254 nm ultraviolet radiations. Under high energy excitation such as VUV (147 nm) radiation or electron beam, white light could be observed. Due to very good chromatic variability, $CaWO_4: Eu, Tb$ or other rare earth materials powders are potentially utilizable in the manufacture of fluorescent lamps for advertising signs, or other color rendering devices like LED etc.

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