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Luminescence Spectroscopic Investigation of Eu^{3+} Doped Oxides: Review

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Abstract

Given their potential utility in a variety of fields, including solid-state lighting, flat-panel displays, solar energy converters, optical amplifiers, and more, phosphors and glasses driven by Rare Earth (RE) ions and emitting multiple colors have attracted a lot of interest. Full-spectrum lighting, high-efficiency near-infrared emission, and wide colour gamut display are the primary difficulties for these emerging RE doped phosphors, which are dependent on the emission characteristics of the phosphors utilized. The various methods of synthesis for Eu^{3+} activated red emitting phosphors are discussed, with an emphasis on the aspects that contribute to improved luminous performance. This luminescence analysis is used in investing the Crystal structure and defects in metal oxides from which it provides information on the chemical and mechanical behavior of metal oxides during mining and processing operations. In this description, we outline the research findings and talk about the luminescence theory of the Eu^{3+} doped glasses and oxides for the red emission.

Keywords: Europium, Metal Oxides, Photoluminescence, WLED

1.0 Introduction

When electromagnetic radiation is made to traverse to a solid or gas, the molecules are excited, and the material lights. The process, known as luminescence, involves the emission of light during the de-excitation of electrons from the excited state to the ground state. Different types of luminescence have been classified according on the sort of excitation they use. Chemiluminescence is the term used to describe luminescence in which the energy released during a chemical reaction serves as the excitation source. Lighting's growth can be understood as an effort to create ever-more-efficient means of producing light within the visible spectrum while eliminating the generation of unnecessary radiation outside of it. Incandescence, Fluorescence, and High Intensity Discharges (HID) are the three classic technologies. These three time-tested methods have come a long way in the last two centuries, achieving efficiency anywhere from 1% to 25%. Fourthly, there is a new technique called solid-state lighting, which operates on the idea that photons are created when the electrons and holes in semiconductors are recombined under a forward bias and the resulting photons are detected at the chip level. White light is made by combining a variety of colored phosphors. In order to achieve high efficiency and high luminescence equivalence, rare-earth element-based phosphors are used to confine emissions to the visible range through line-type f-f transitions[1].

Doped europium in either the divalent (Eu^{2+}) or trivalent (Eu^{3+}) state produces strong red-light emission from the host material. The possibility of using Eu^{3+}

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to detect X-rays has also been explored. Eu^{3+} ions typically reside in the spots of the host crystals that lack inversion symmetry. The electric dipole transition from $^5D_0 \rightarrow ^7F_2$ is responsible for the prominent red emission, the line observed between 610 and 630 nm. The magnetic dipole transition from $^5D_0 \rightarrow ^7F_1$ causes the emission line at around 600 nm, the need for a suitable red phosphor for use in colour TV led to the development of Eu^{3+} in 1964[3]. For increased screening efficiency and recycling stability, $Y_2O_2S:Eu^{3+}$ eventually replaced this in Cathode Ray Tube (CRT) manufacturing. Field Emission Displays (FED) and High-quality Color-Rendering lamps (HCR) have both made use of $Y_2O_3:Eu^{3+}$[2,19].

The phosphors of small particle size can be created using liquid phase reaction techniques, such as sol-gel, co-precipitation, microwave, and combustion synthesis. These liquid phase synthesis techniques allow for the precise control and uniform distribution of each constituent (particularly the activator ions) throughout the synthesis of phosphor materials. Surfactants and capping agents like glycerol, etc., can aid in fine-tuning a chemical process and, by extension, the morphology of phosphor particles. While usable, the colour given by a halo-phosphate lamp falls short of expectations, making it imperative to generate CRIs of 80 or greater. This idea has not been marketed because of the poor dependability and maintenance qualities of the phosphors with a colour temperature of 4200K. The luminescence spectroscopy studies of Eu^{3+}-doped oxides are the focus of this article. The use of materials with rare earth ions has become increasingly popular in recent years. Phosphor materials doped with rare earth dopant are typically excited by an ultraviolet source, resulting in emission in the visible spectrum. White light can be generated in glass hosts by down-shifting and up-conversion phenomena, and this article will provide a broad overview of both processes, whether the glass has been doped with a single Eu^{3+} ion or many ions. Following this, we discuss the difficulties of using Eu^{3+}-doped glasses and briefly review the methods currently in use to improve white light production. The results regarding glasses that generate white light is stressed[7,8].

The luminescence spectroscopy studies of Eu^{3+}-doped oxides are the focus of this article. Since many minerals exhibit unique luminescence spectra, geologist make use of this data to identify the composition of rock samples and depending on the impurities, crystal defects and minerals association, the data help in mining industries to assess for the economic viability of a particular deposit. Since the use of metal oxides with rare earth ions has become increasingly popular in recent years, the mining industries focus on sustainable and ecofriendly practices. In this regard luminescence studies provide information on release of metal oxides into the environment and their potential impact on ecosystems.

2.0 Motivation for the Present Study

All compounds show various intense Eu^{3+} excitation peaks around 362 nm ($^7F_0 \rightarrow ^5D_4$); 394 nm ($^7F_0 \rightarrow ^5L_6$); 415 nm ($^7F_0 \rightarrow ^5D_3$); 464 nm ($^7F_0 \rightarrow ^5D_2$); 526 nm ($^7F_0 \rightarrow ^5D_1$); 534 nm ($^7F_1 \rightarrow ^5D_1$). And also a charge transfer (CT) band due to O→Eu transition below 300 nm is detected. Further the peaks above 570 nm are mainly assigned to emission bands originating from Eu^{3+}, $^5D_0$ excited state. In Eu^{3+} doped luminescence materials, Downshifting (DS), down-conversion, and Up-conversion (UC) are the three-primary Photoluminescence (PL) mechanisms. The UC process is regarded as anti-Stokes because, unlike the preceding two processes, it does not adhere to the Stokes law. One needs to be aware of the mechanisms involved in the energy transfer between donor and acceptor ions inside the glass matrix in order to create white light-generating luminescent glasses and to achieve desirable colorimetric features. As a result, the PL mechanisms are the only topic covered in this section[9,10].

3.0 Experimental Section

The normalized RT excitation spectra of 1% Eu^{3+} doped Ca_2LnSbO_6 (Ln=Lu, Y, Gd, and La) and Ca_2EuSbO_6. The spectra have been normalized to the intensity maximum of the $^7F_0 \rightarrow ^5L_6$ transition Pubs.acs.org (2021)[8]. In ESA, an ion with numerous stable intermediate energy levels absorbs two excitation photons in sequence. Absorption of second photon promotes the ion to a more excited energy level, and absorption of third photon causes the ion to de-excite, leading to the emission of an up-converted photon if the first photon is held at the intermediate level for a long enough time. Since it requires the sequential

absorption of the two photons, this method is also known as "two-step absorption". To put ESA into Practice, one need a high-power density, dopants with a wide absorption cross section, and a low doping concentration. This is because the emission intensity may be weakened at high doping concentrations due to cross-relaxations that do not involve radiation.

As the most effective of the six mechanisms, ETU (Energy Transfer Up-conversion) takes place in a system with a sensitizer and an activator. ETU employs a non-radiative energy transfer mechanism in which the sensitizer ions transfer energy to the activator ions via dipole-dipole resonant interaction after the excitation. Keeping in mind that the intermediate levels of activators are also populated by the sensitizer's energy transfer, not just the emitting levels. The host's phonons can bridge the energy gap between the activator's absorption and the sensitizer's emission[8,12].

In the PA process, the energy of the excitation photon is distinct from the energies of the ion's ground and intermediate states. As a result of electrons being shifted to a higher energy level, the ion goes through an ESA process and becomes populated by its more excited form (super excited). The next step is for the ion and an adjacent ion to engage in a cross-relaxation process within their respective intermediate levels. This trend will persist so long as hyper-excited ions are depleted at a slower rate than ground-state ions. Either a CET or an ETU process will yield the same results. However, in this procedure, activators do not have true intermediate energy levels. Hence, two sensitizers are pushed to an effectively excited state while energy is being given to the activator simultaneously. The procedure has been investigated extensively in a wide variety of materials, including glass, polymer, bulk, and nanoscale materials. In 2011, researchers attempted to address the insufficiency of intermediate amounts of activators in UC emissions by using the EMU approach. A sensitizer, accumulator, migrant, and activator are four types of luminous centers used in this procedure. To start, ETU is used to populate the accumulator's upper energy levels. After that, the accumulator's excited state is transmitted to the migrator, and the point is moved from the core's migrators to the shell's migrators. As the activator takes in the energy, the accumulator and activator return to their ground states via radiative emission from their excited states[10,12].

4.0 Phase Formation and Structural Analysis

The reaction occurred at a standard high temperature in a solid-state setting, with the $LaBMO_6$ host lattice doped with $Eu^{3+}$is discussed by the researcher. The crystal structure of phosphor $LaBMO_6$ [M =W/Mo] is shown in Figure 1. The XRD patterns at room temperature of the sample are shown in Figure 2. The researcher reported

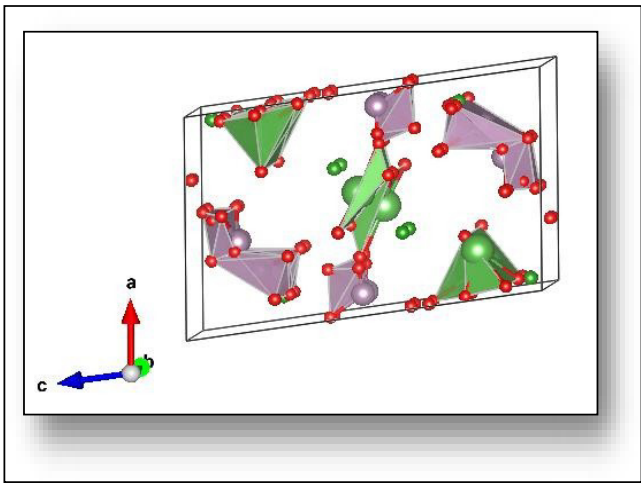

Figure 1. The crystal structure LaBMO6 [M = W/Mo].

that on comparison of the XRD peaks with the JCPDS card number 35-0261, the alignment and quality of all the reflected images were found excellent. Also reported that XRD analysis showed a close agreement with JCPDS card No. 37-1100 for $LaBWO_6$ compositions. It was reported that the addition of the dopant Eu^{3+} ion has no effect on the structure of the produced molecule due to similarity in the ionic radii[13].

5.0 Photoluminescence Spectroscopy (PI)

Luminescence spectra of Eu^{3+} ion excited $LaBMO_6$ [M = W/Mo] at (393/465 nm) are shown in Figure 3. The emission spectra associated show the three prominent emissions featured at 596, 615, and 650 nm, provide information that the Eu^{3+} occupied site of inverse symmetry which is caused by a shift in the electric dipole at a wavelength of 615 nm. The $^5D_0 \rightarrow {}^7F_1$ transition is responsible for the mixed orangish red emission at about

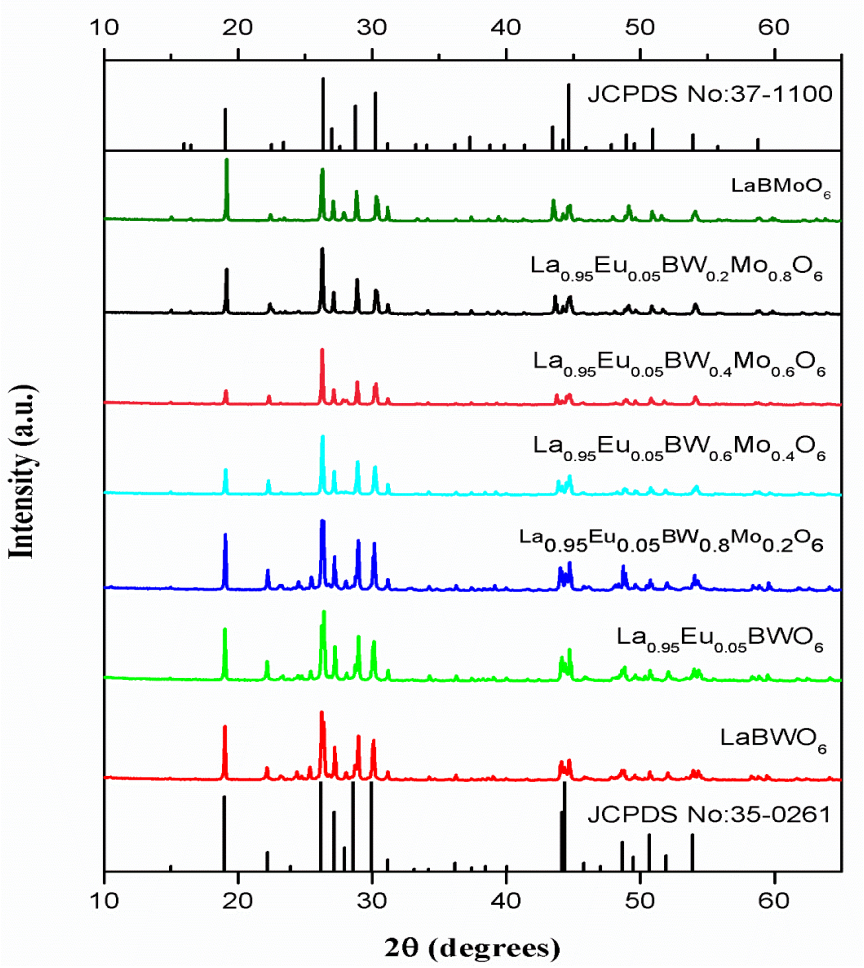

Figure 2. XRD patterns of LaBWO6, La0.95BW$_{(1-x)}$MoxO6:0.05Eu^{3+} phosphors..

596 nm. The strength of the emission is determined by how well the host lattice absorbs light. The broad CT band absorbed from UV as a result of O-W or O-Mo charge transfer is used to synthesize phosphor, which satisfies

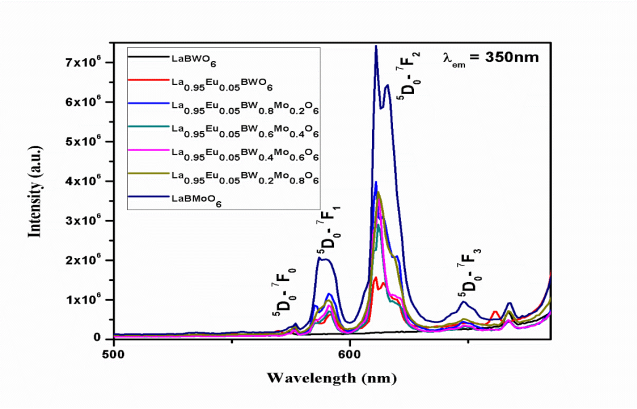

Figure 3. Emission characteristics of La0.95BW(1–x) MoxO6:0.05Eu^{3+}phosphors (λ_{ex} = 350 nm).

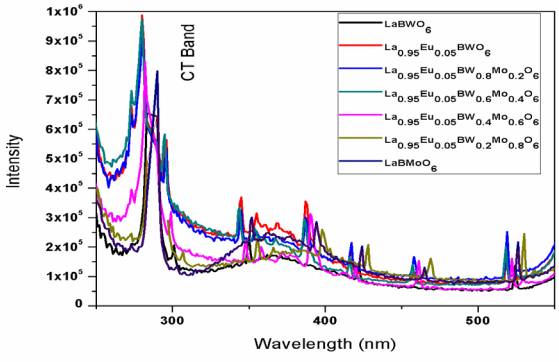

Figure 4. Excitation characteristics of La0.95BW(1–x) MoxO6:0.05Eu^{3+}.

the host's crisp line-like emission over a wide wavelength range (250–400 nm). There is a line-like emission at 615 nm because all the energy is transferred to the center metal ion, Eu^{3+}[14,15].

6.0 Synthesis Methods of Lanthanide-Doped Glass Systems

Glasses can be made using number of different fusion and non-fusion processes. Where fusion methods include melt quenchers and non-fusion methods includes production of glass directly from gaseous or solid state also from solgel process. This section will focus on the standard melt-quenching methodology, one of the oldest and most used fusion-based glass-making methods. Melt-quenching is a method for making glass by melting the raw materials after they have been well combined, and then quickly cooling them to room temperature. This technique is often used to produce oxide glasses in scientific research. Starting materials are weighed carefully after the glass system and dopants are being selected, and the resulting glass batch is then mixed thoroughly in a container to ensure uniformity. Then the material is transferred to a crucible and heated in a furnace. Crucibles made of platinum, platinum-gold, or platinum-rhodium reduce contamination. Those working with platinum crucibles should be aware that Cl and NO_3 can cause reactions. Bottom-loading furnaces are preferable since the user is protected from direct contact with the furnaces heat source. However, when the elevator mechanism moves down, the glass encasing the crucible can cool rapidly, requiring more intricate movements as the glass is poured. For annealing the glass, second furnace is used, after the mixtures are poured in to a stainless steel or graphite mould. Spectroscopic and optical tests require scratch-free, plane-parallel surfaces on the glass samples. Ceramographic processes are used to grind the models harshly and smoothly and then polish them to a high gloss for this purpose. The 120, 240, 320, 400, 600, and 800 grit abrasive papers are used for rough grinding, while the 1200 and 2500 grit abrasive papers are used for smooth grinding. Samples should be thoroughly cleaned with alcohol and ultrasonic cleanser between each stage. A final polish can be accomplished with a polishing pad by either alumina, cerium oxide, or diamond paste. Everything is done while spinning on a wheel[15,16].

7.0 Non-Fusion Based Glass Making Techniques

There are many methods for creating glass, not just the fusion-based one. High shearing forces caused by shockwaves can instantly transform a solid into glass. Dialectic glasses are what you need to have a meaningful conversation. It is possible that the glassy lunar samples were created by meteoroid impacts and represent an example of dialectic glasses. High-energy subatomic particle irradiation can also result in the formation of glasses (metamict solids). High-energy alpha particles from irradiation can permanently rearrange the atomic structure by displacing atoms from their usual orbits. Another method that does not involve fusing ingredients together is called "deposition" and it can be used to create both nonreactive and reactive glasses. Evaporated elements (such as Si, Ge, and Se) gets deposited as non-crystalline thin films on a cold substrate in the nonreactive process. Once the necessary measurements have been taken, the framework can be sintered into permanent slabs. Sol-gel glassmaking is another option to the nearly 30-year-old fusion-based glassmaking technologies. Typically, metal alkoxides or salts or oxides are hydrolyzed to produce a sol and then used as a precursor in the glass-making process. After a certain time period has passed, a gel is created by the polymerization of the colloidal particles in the soil. After that, the gel is either heated or left to rest (aged) at room temperature for a certain period in order to eliminate the interstitial by-products present in the gel (like alcohols and water). After sintering the gel for the required amount of time and temperature, the glass structure is achieved. Examples include Kajihara *et al.,* who used the co-solvent-free sol-gel method to effectively synthesize monolithic glass, which is devoid of additives such alcohols, organic solvents, polymers, and surfactants. The processing time is long, the raw materials are expensive, and it is difficult to get crack-free monolithic samples because of stresses that develop during the drying phase when using the sol-gel method[17,18].

8.0 Discussion

Absorption spectra can be used to estimate the electronic transitions and radiative characteristics of Eu^{3+} ions in a glass host. The strength of the ion oscillations in the ground state determines the energy of the absorption bands. Both the theoretical oscillator strength (f_{theor}) and the experimental oscillator strength (f_{exp}) can be determined with the use of formulae (focal). In addition, an equation can be used to calculate the root-mean-square deviation (rms). According to the text and focus values, the absorption peak at the $^6H_{15/2}$ to $^6F_{11/2}$ transition is the strongest of all of them. This peak is especially sensitive to changes in the local structure around these ions, confirming that even small modifications can have a significant effect on the peak's strength. Examining the local structure and emission features around the Eu^{3+} ions in a glass host material J-O intensity parameters are calculated using a conventional least-squares fitting f_{exp} and f_{cal}. The Ω_2 value for oxide glasses indicate the asymmetry of the local environment around Eu^{3+} ions. Where, the Ω_2 value for fluoride glasses indicate the covalence nature between Eu^{3+} ions and ligand anions. For example, Rao *et al.*, described that the higher values of Ω_2 parameter is related to the higher asymmetry of ion sites owing to high polarizability[20]. Kıbrıslı *et al.,* showed that Ω_2 values exhibit an increment with increasing concentration of Dy_2O_3, due to higher asymmetry around the ions. The other J–O parameters, Ω_4 and Ω_6, correspond to bulk properties of the rigidity and viscosity of the host materials[8,11,13].

The emission at 575 nm ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) displays a sequence of narrow excitation lines associated to the f-f transitions, and this wavelength is used to study the Photoluminescence Emission (PLE) spectra of different glass systems. The primary goal of PLE measurements is to identify the wavelength band of strong excitation from which the material shows the strong emission. It has also been observed that the highest intensity occurs around 350 nm during the transition from $^6H_{15/2}\rightarrow{}^6P_{7/2}$ in a small number of glass systems, including zinc-fluorophosphate, zinc-phosphate, and lead-fluorosilicate. The maximum output of PLE bands varies because of the different absorption edge values for different glass systems. A noticeable shift in the absorption edge has been seen in glass systems with a high concentration of heavy metals, with longer wavelengths becoming the new sweet spot[8,17,19].

The PL emission spectra are recorded using an excitation wavelength chosen from among the most intense bands. 450-700 nm PL spectra of lithium-tungsten-tellurite glasses with x mol% dopant (x = 0-3% mol%) and lead-telluro-borate glasses with 1mol% dopant[11].

9.0 Conclusion

The emission from the $La_{0.95}Eu_{0.05}BW_{1-x}Mo_xO{=}6$ host lattice, doped with Eu_{3+} changes with the varied amount of Mo (10). With CIE chromaticity coordinate values, x=0.6647 and y=0.3349, of $La_{0.95}Eu_{0.05}BW_{0.8}Mo_{0.2}O_6$ shows near to the NTSC standard for red emission, which indicate that the right amount of W and Mo is required to get Eu^{3+} red emission. The spectral analyses show that these Lanthanide doped glasses may be useful in the yellow- and red-based WLED. In Addition, alternative mixed metal oxide systems should be investigated to produce red emission by Eu activation, with concentration variations to produce high emission intensity. Some glass systems have color coordinate values close to the standard white light coordinates (x=0.33, y=0.33), which proves that EU^{3+} doped oxides are ideal for producing white light. In addition, the Y/B intensity ratio varies noticeably depending on the host glass chemical make-up. Doped glasses are excellent candidates for a wide range of uses, since their CCT values are typically greater than fluorescent tubes, and most of them display neutral and cool-white light. Zero denotes the colorlessness of pure white light. This indicates that the white light is emitted by the most color-impure samples, where the percentage of each color is as close to zero as feasible[11,13,18,19]. Luminescence studies of metal oxides also assist in identifying the areas with high metal oxide concentration, where the emissions from these provide valuable data for exploring and prospecting new minerals. They help mining professionals in decision making and improve the processes.

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