

The Electroluminescence Brightness of Rare-Earth-Doped ZnS Phosphors

Surendra Prasad Tamrakar

Department of Physics, Govt. P.G. College, Maihar, INDIA- 485771

Abstract:

Zinc sulfide (ZnS) is an important II–VI semiconductor phosphor that has been extensively investigated for electroluminescent (EL) displays because of its wide band gap, chemical stability, and ability to accommodate different luminescent activator ions. Incorporation of rare-earth ions such as Tb^{3+} , Sm^{3+} , Eu^{3+} , Ce^{3+} and Tm^{3+} into ZnS provides characteristic emission bands and enables the development of multicolor electroluminescent devices. The electroluminescence brightness of these materials depends strongly on rare-earth concentration, crystal structure, defect chemistry, host–dopant interactions, film crystallinity, excitation voltage and frequency, and the presence of suitable codopants. Among the rare-earth-doped ZnS systems, ZnS:Tb has demonstrated particularly strong green electroluminescence and has been investigated extensively for thin-film electroluminescent displays. Published studies have demonstrated that suitable oxygen or fluorine codoping can substantially improve the brightness of ZnS:Tb-based devices. For example, ZnS:Tb,F thin films with optimized oxygen incorporation have demonstrated luminance of 82 cd m^{-2} , while optimized sputtered ZnS:Tb,F thin-film devices have been reported with brightness as high as 830 cd m^{-2} . More recently, ZnS:Tb electroluminescent devices fabricated by ultrasonic spray pyrolysis have achieved approximately 41 cd m^{-2} at 76.9 V. This paper reviews the relationship between rare-earth doping and EL brightness in ZnS phosphors, discusses the mechanisms responsible for light generation, and identifies the principal parameters controlling device performance.

Keywords: Zinc sulfide, ZnS phosphor, rare-earth ions, electroluminescence, brightness, luminance, Tb^{3+} , Eu^{3+} , Sm^{3+} , thin-film electroluminescence.

1. Introduction:

Electroluminescence is the emission of light from a material as a consequence of electrical excitation. Zinc sulfide is one of the most extensively investigated semiconductor hosts for electroluminescent phosphors because its wide band gap and suitable electronic structure permit efficient interaction between energetic charge carriers and luminescent centers. The optical properties of ZnS can be modified substantially by incorporating transition-metal or rare-earth activator ions. A recent review of ZnS phosphors emphasizes that dopant selection, concentration, host structure and device architecture strongly influence the photoluminescence and electroluminescence behavior of ZnS-based materials.

Rare-earth ions are particularly attractive activators because their partially filled 4f electronic shells produce relatively sharp and characteristic emission lines. Rare-earth-doped ZnS has consequently been investigated for multicolor electroluminescent displays. Important systems include ZnS:Tb for green emission, ZnS:Sm for red emission, and ZnS:Tm and other rare-earth-containing materials for additional spectral regions.

The brightness of an EL phosphor is not determined solely by the concentration of the activator. It is the result of several interacting processes, including carrier injection, carrier acceleration, energy transfer to the luminescent center, radiative recombination, non-radiative relaxation, trapping and detrapping, and the microstructure of the phosphor layer. Therefore, optimization of rare-earth-doped ZnS requires simultaneous control of composition, crystallinity, defects and electrical excitation.

2. Structure and Optical Properties of ZnS:

ZnS occurs primarily in two crystal structures: cubic sphalerite and hexagonal wurtzite. The crystal structure affects the electronic states, defect population and optical properties of the material. ZnS has a wide band gap of approximately 3.6 eV, making it suitable as a host for luminescent centers and electroluminescent devices.

The introduction of rare-earth ions into ZnS modifies the optical behavior through localized electronic states. In rare-earth ions, transitions involving 4f states are relatively shielded by outer electronic shells, which helps produce characteristic narrow emission bands. The observed emission can therefore provide information about the oxidation state and local environment of the activator.

For example, ZnS:Tb produces characteristic green emission associated with Tb³⁺ transitions, particularly the ⁵D₄ → ⁷F_J transitions. Recent ZnS:Tb EL devices have shown a principal emission near 542 nm.

3. Electroluminescence Mechanism:

In an AC thin-film electroluminescent device, the phosphor layer is generally placed between insulating layers and electrodes. A simplified device can be represented as

Electrode / Insulator / ZnS:RE / Insulator / Electrode, where RE represents the rare-earth activator.

When an AC voltage is applied, electrons are accelerated by the electric field. These energetic electrons interact with the ZnS host and luminescent centers. Energy transfer to a rare-earth ion excites it to a higher electronic state. The ion subsequently returns toward its ground state through radiative transitions, producing visible light. The overall process can be represented schematically as:

Electrical excitation → carrier acceleration → excitation of rare-earth center → radiative relaxation → visible emission

The brightness therefore depends on both the number of carriers participating in excitation and the probability that the excited activator undergoes radiative rather than non-radiative relaxation.

Early investigations of rare-earth-doped ZnS identified the importance of accelerated-carrier and collision-related excitation mechanisms in electroluminescence. In Tb-doped ZnS, the emission spectrum contains the characteristic sharp-line transitions of Tb³⁺.

4. Effect of Rare-Earth Dopants on Electroluminescence:

4.1 Terbium-doped ZnS:

Among rare-earth-doped ZnS phosphors, ZnS:Tb is one of the most extensively studied green-emitting systems. Tb³⁺ produces strong green emission, making it attractive for display applications. The brightness is strongly dependent on the chemical environment of the Tb activator. Fluorine and oxygen codoping have been particularly important approaches for improving ZnS:Tb EL performance. An investigation of ZnS:Tb,F thin films found that oxygen codoping produced a maximum brightness of 82 cd m⁻² at 60 Hz at approximately 3.6 at.% oxygen. Reducing the oxygen concentration to 2.2 at.% gave 56 cd m⁻², while increasing it to 8.1 at.% reduced the brightness to 42 cd m⁻². This demonstrates that oxygen concentration has an optimum rather than a simple monotonic effect on EL brightness.

The improvement at moderate oxygen concentration was attributed mainly to increased conduction charge, whereas excessive oxygen reduced excitation and radiative efficiencies. This illustrates the importance of defect and trap engineering in rare-earth-doped ZnS. Film crystallinity is another important parameter. Optimized RF-sputtered ZnS:Tb,F films have been reported to produce green EL devices with brightness of approximately 830 cd m⁻² and luminous efficiency of 0.8 lm W⁻¹ under 1 kHz sinusoidal excitation. More recent work using ultrasonic spray pyrolysis fabricated ZnS:Tb MISIM electroluminescent devices and obtained luminance up to approximately 41 cd m⁻² at 76.9 V, with a threshold voltage of about 46 V RMS.

These results demonstrate that brightness depends not only on the chemical composition of the phosphor but also strongly on deposition method and device architecture.

4.2 Samarium-doped ZnS:

Sm³⁺ is particularly interesting for red emission. ZnS:Sm can exhibit characteristic Sm³⁺ transitions near 570, 606 and 653 nm. Experimental studies have shown that the atmosphere used during phosphor preparation can strongly influence Sm³⁺ emission. Reductive firing conditions promoted characteristic Sm³⁺ luminescence, whereas samples prepared under inert conditions primarily exhibited host-related emission.

The incorporation of Sm³⁺ is more complicated than that of a divalent ion because of the difference in valence and ionic radius between Sm³⁺ and Zn²⁺. Consequently, defects, charge compensation and synthesis atmosphere can play major roles in determining the luminescence efficiency.

4.3 Europium-doped ZnS:

Europium is another important rare-earth activator for red emission. ZnS:Eu³⁺ phosphors have been synthesized with different Eu concentrations and have demonstrated intense red photoluminescence. Studies have investigated concentration-dependent emission together with structural and Judd–Ofelt parameters.

For EL applications, however, photoluminescence intensity alone is not sufficient to predict brightness. Efficient electrical excitation of Eu centers requires appropriate carrier transport and energy-transfer

pathways. Consequently, future investigations should correlate PL intensity, EL luminance, excitation voltage and carrier behavior rather than using PL intensity as the sole measure of phosphor performance.

4.4 Other Rare-Earth Activators:

Ce³⁺ and Tm³⁺ have also been investigated as activators in ZnS and related phosphor systems. Rare-earth-doped ZnS materials can provide tunable emission through changes in activator concentration, host structure and defect chemistry. A recent review specifically identifies Ce³⁺, Eu³⁺ and Tb³⁺ among the rare-earth ions investigated in ZnS nanophosphors and highlights their potential for optical-display applications.

5. Factors Controlling Electroluminescence Brightness:

The EL brightness of rare-earth-doped ZnS is governed by several parameters.

5.1 Activator concentration:

At low concentration, increasing the rare-earth concentration generally increases the number of luminescent centers. Beyond an optimum concentration, concentration quenching can occur because energy can migrate between neighboring activators and eventually reach non-radiative sites.

Therefore, the relationship between dopant concentration and brightness is generally expected to show an optimum concentration rather than unlimited improvement.

5.2 Crystal structure and crystallinity:

The phase and crystallinity of ZnS affect carrier transport, defect density and the local environment of the activator. Improved crystallinity can reduce undesirable non-radiative pathways and improve EL performance. Studies of ZnS:Tb,F films have directly correlated deposition conditions and crystallinity with high-brightness EL performance.

5.3 Oxygen and fluorine codoping:

Codoping provides a means of controlling charge compensation and trap states. In ZnS:Tb,F, optimized oxygen incorporation can increase brightness considerably, while excessive oxygen can create detrimental deep traps and reduce luminescence.

5.4 Applied voltage:

Increasing the applied voltage generally increases the electric field experienced by the phosphor layer and can increase the energy acquired by carriers. Consequently, EL intensity commonly increases after the threshold field is reached.

In ZnS:Tb devices fabricated using ultrasonic spray pyrolysis, increasing the applied voltage increased EL intensity and shifted the CIE coordinates toward a purer green color.

5.5 Frequency:

AC EL devices are sensitive to excitation frequency because the frequency influences charge injection, trapping and detrapping processes. Thus, optimum brightness is associated with a combination of voltage, frequency and device structure rather than voltage alone.

5.6 Phosphor-layer thickness:

The thickness of the ZnS:RE layer affects carrier transport, electric-field distribution and the volume of material participating in light generation. Excessive thickness can increase absorption or reduce the effective electric field, whereas an insufficient thickness may reduce the number of active luminescent centers.

5.7 Particle size and morphology:

In nanophosphors, particle size and morphology influence surface defects, quantum confinement and the spatial distribution of dopant ions. Rare-earth-doped ZnS nanomaterials therefore require careful control of synthesis conditions. Recent reviews emphasize the relationship between morphology and luminescence properties in rare-earth-doped phosphors. R. Royal Society of Chemistry Publications

6. Experimental Methodology for Investigating EL Brightness:

A systematic experimental study can be designed using ZnS doped with selected rare-earth ions such as Tb^{3+} , Eu^{3+} and Sm^{3+} .

6.1 Preparation of phosphors:

ZnS phosphors can be synthesized using solid-state reaction, chemical precipitation, hydrothermal synthesis, sol-gel methods or thin-film deposition techniques. The rare-earth precursor should be mixed with ZnS in controlled concentrations, for example:

0.1 mol%

0.5 mol%

1 mol%

2 mol%

3 mol%

5 mol%

The optimum range should ultimately be established experimentally rather than assumed.

6.2 Structural characterization:

X-ray diffraction (XRD) should be used to determine:

Crystal phase, Lattice parameters, Crystallite size, Degree of crystallinity & Possible secondary phases

Scanning electron microscopy (SEM) or transmission electron microscopy (TEM) can be used to investigate morphology and particle size. Energy-dispersive X-ray spectroscopy (EDS) can verify elemental composition.

6.3 Optical characterization:

Photoluminescence excitation and emission spectra should be measured to identify the characteristic transitions of each rare-earth activator.

For example, Tb^{3+} emission is expected predominantly in the green region, while Sm^{3+} and Eu^{3+} can provide red-region emission.

6.4 Electroluminescent device fabrication:

For thin-film measurements, a typical structure is:

Glass / transparent electrode / dielectric / ZnS:RE / dielectric / metal electrode

The device should be driven using a controlled AC voltage source.

6.5 Brightness measurement:

EL luminance should be measured using a calibrated luminance meter or spectroradiometric system. The following parameters should be recorded:

Luminance (cd m^{-2}), Applied voltage, Threshold voltage, Frequency, EL emission spectrum, CIE chromaticity coordinates, Luminous efficiency & Power consumption.

The brightness-voltage relationship can then be plotted as:

$$L = f(V)$$

where L is luminance and V is the applied voltage.

7. Discussion:

The literature demonstrates that the brightness of rare-earth-doped ZnS is controlled by a complex interaction between the activator ion, host lattice and device structure. Simply increasing rare-earth concentration does not necessarily produce higher brightness. Instead, an optimum concentration is expected because excessive dopant concentration can introduce concentration quenching and non-radiative energy-transfer pathways.

ZnS:Tb provides a particularly clear example. Its strong green emission and compatibility with thin-film EL structures have made it one of the most successful rare-earth-doped ZnS systems. Historical work established ZnS:Tb as an important green EL material, while subsequent studies demonstrated that oxygen and fluorine incorporation, improved crystallinity and optimized deposition conditions can significantly affect brightness.

The reported brightness values also show why results from different studies should not be compared without considering device architecture. For example, reported luminance values range from tens of cd m^{-2} in some nanocrystal or spray-pyrolysis devices to hundreds of cd m^{-2} in optimized sputtered thin-film structures.

Consequently, a meaningful comparison should include at least the phosphor composition, dopant concentration, film thickness, deposition technique, dielectric structure, applied voltage and frequency.

8. Conclusion:

Rare-earth-doped ZnS phosphors are promising electroluminescent materials because the ZnS host provides a suitable wide-band-gap semiconductor matrix while rare-earth ions introduce characteristic luminescent centers. The electroluminescence brightness depends on activator concentration, crystal structure, defect states, codoping, film morphology, phosphor thickness, applied voltage and excitation frequency.

Among the systems investigated, ZnS:Tb is particularly important because of its intense green emission and demonstrated high-brightness thin-film EL performance. Oxygen and fluorine codoping can improve the brightness by modifying charge transport and luminescent-center excitation, although excessive codoping can introduce non-radiative losses. ZnS:Sm and ZnS:Eu provide promising red-emitting systems, but their electrical excitation and stability require further optimization.

Overall, achieving high brightness requires simultaneous optimization of host crystal quality, rare-earth concentration, defect chemistry and EL device architecture. Future research combining nanostructure engineering, controlled codoping and improved thin-film deposition could lead to more efficient, low-voltage and high-brightness ZnS-based electroluminescent devices.

REFERENCES:

1. Lahariya, V. N., & Dhoble, S. J. (2022). Development and advancement of undoped and doped zinc sulfide for phosphor application. *Displays*, 74, 102186. DOI: 10.1016/j.displa.2022.102186.
2. Ronda, C. R., et al. (1998). Rare earths in electroluminescent and field emission display phosphors. *Journal of Alloys and Compounds*, 275–277, 702–708. DOI: 10.1016/S0925-8388(98)00421-6.
3. Archana, L. S., & Rajendran, D. N. (2021). Luminescence of rare earth doped ZnS nanophosphors for the applications in optical displays. *Materials Today: Proceedings*, 41, 461–467. DOI: 10.1016/j.matpr.2020.05.227.
4. Hsu, C. T., Lin, Y. J., Su, Y. K., & Yokoyama, M. Crystallinity of ZnS:Tb,F thin films and characteristics of green-color thin-film electroluminescent devices prepared by RF-magnetron sputtering.
5. Oxygen codoping of ZnS:Tb,F electroluminescent thin film. *Journal of Luminescence*, 109, 75–83 (2004). DOI: 10.1016/j.jlumin.2003.12.054.
6. Fabrication and characterization of green ZnS:Tb AC-electroluminescent devices by ultrasonic spray pyrolysis. *Optical Materials*, 146, 114520 (2023). DOI: 10.1016/j.optmat.2023.114520.
7. Influence of rare earth substitution on structure, photoluminescence emission properties and Judd–Ofelt analysis of ZnS:Eu³⁺ red phosphors. *Journal of Luminescence*, 243, 118679 (2022). DOI: 10.1016/j.jlumin.2021.118679.
8. Photoluminescence of ZnS:Sm phosphor prepared in a reductive atmosphere. *Ceramics International*, 26, 153–158 (2000). DOI: 10.1016/S0272-8842(99)00034-6.