Defect Powered Zinc Gallo Germanates for Tunable Light Emitting Diodes

▪ Rare Earth Free Phosphors

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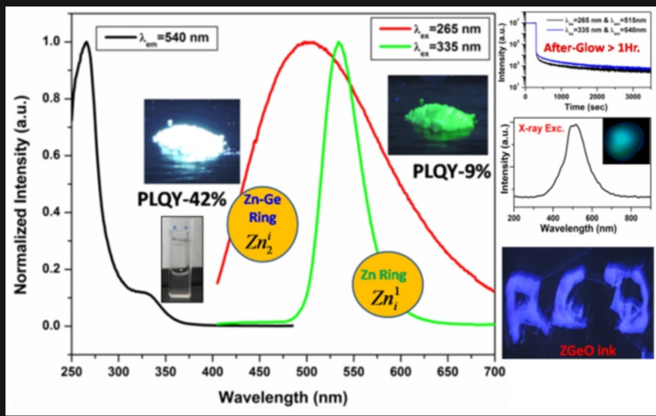
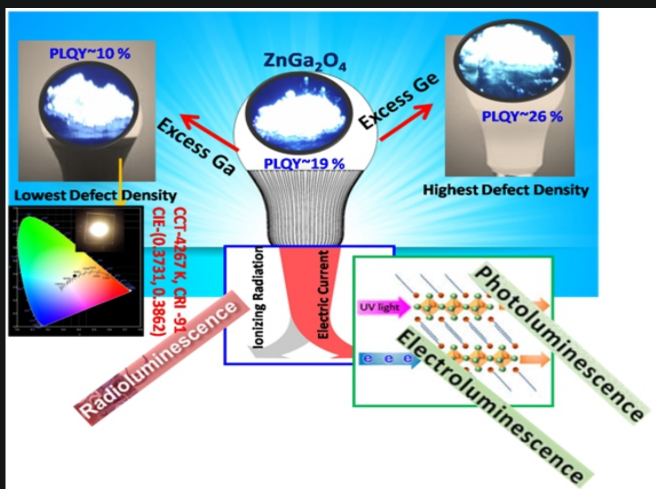
The entire world is going through a severe energy crunch owing to increased industrialization, ever increasing population and depleting fossil fuel resources. It is believed the maximum damage is triggered by electricity sector as of the total global power consumption around 15% is required for electric lighting and replacing the existing light source with phosphor converted light emitting diodes (pc-LEDs) can be a game changer in resolving this issue. However, light-emitting diodes (LED) and other advanced lighting technologies can reduce lighting power consumption by half due to their high efficiency. This can potentially reduce CO_2 emissions by 800 million tons per year, which is equivalent to 684 coal-fired power plants. But most of the existing pc-LEDs are driven by rare earth which is neither benign from safety aspects nor conducive from cost of production.

To reduce the burden of solid state lighting and phosphor converted light emitting diode (pc-LEDs) technologies on rare earths (RE) and avoid their potential supply risks we have developed RE free Zn_2GeO_4 (ZGeO) [Gupta et al. *ACS Appl. Electron. Mater*. 2023, 5, 12862] and $ZnGa_2O_4$ (ZGeO) phosphor. ZGeO demonstrated color tunable emission from bluish white to green on changing the excitation wavelength from 265 to 335 nm linked to zinc interstitials in zinc (Zn_i^2) and zinc-germanium rings (Zn_i^1) respectively with photoluminescence quantum yield (PLQY) of 42 and 9 % respectively. We have further synthesized, defect-induced long and brightly emitting rare-earth free $ZnGa_2O_4$ (ZGaO) with PLQY~19%. Defects generated in large numbers via high temperature annealing along with antisites boosted the generation of trapping centres leading long persistent luminescence in both the samples.

The defect was further engineered in $ZnGa_2O_4$ by reacting it with different percentages of Ga_2O_3/GeO_2 yielding stoichiometric $Zn3Ga_2GeO_8$ (S-ZGG), gallium excess $Zn_3Ga_4GeO_{11}$ (Ga-ZGG) and germanium excess $Zn_3Ga_2Ge_2O_{10}$ (Ge-ZGG) of zinc gallo germanate samples [Gupta et al. *Chem. Eng. Journal*, 2023, 74, 145595]. The defect density follows the trend Ge-ZZG>S-ZGG>ZGaO>Ga-ZGG which is directly culminated in achieving a high PLQY of ~ 26% in Ge-ZGG. But a lower defect in Ga-ZGG aided in achieving the finest white light emission with correlated color temperature (CCT) of 4267 K, color rendering index (CRI) of 91, and CIE of (0.3731, 0.3862). We have further proposed a flexible and rare pathway to engineer such defects that tuned the broadband emission from cold white to the energy efficient warm white lighting. We believe this work is an excellent contribution to resolve the issues of expensive RE doping, doping induced strain, complex organic synthesis, safety concern, and serve as a strategic pathway to design thermally stable and cost effective on demand rare earth free tunable LED with suitable CCT and high CRI.



▲ Scheme 1: Excitation Tunable emission, afterglow decay, radioluminescence and anticounterfeting application of Zn_2GeO_4.



▲ Scheme 2: All inorganic high PLQY (~19%) and persistent bluish-white light emitting $ZnGa_2O_4$ exhibiting radio and electroluminescence and designing rare earth free compositionally modulated defect powered Zinc gallo germanate Tunable LEDs.

Dr. Santosh K. Gupta, is currently working as a Scientific Officer/F at Radiochemistry Division, BARC, Mumbai. His research area focuses on designing light emitting materials for health, energy and environment etc. Dr. Gupta is the recipient of several awards notable among them are Fulbright and JSPS Fellowship, DAE and Scientific India Young Scientist award, IANCAS Tarun Datta Medal, SMC Bronze and CRS silver medal. He has also been bestowed with membership of Indian National Young Academy of Sciences (INSA-INYAS) & National Academy of Sciences (NASc) and young associate of Maharashtra Academy of Sciences (MASc). Dr. Gupta has more than 225 peer reviewed international journal articles to his credit.