Journal of Luminescence
Volume 242, February 2022, 118586

Broadening the excitation spectrum of $BaMgAl_{10}O_{17}:Cr^{3+}$ using Eu^{2+} as a codopant

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https://doi.org/10.1016/j.jlumin.2021.118586
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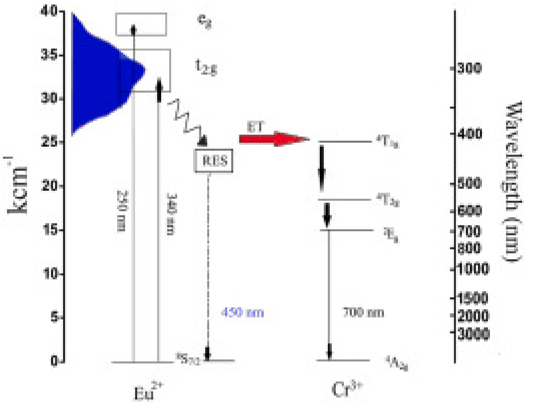
Highlights

- Combustion synthesis of $BaMgAl_{10}O_{17}:Eu^{2+},Cr^{3+}$ phosphors reported.
- Luminescence of Eu^{2+} and Cr^{3+} observed in as-combusted powders.
- Eu^{2+} .→ Cr^{3+} energy transfer was observed with 40.2% efficiency
- Excitation spectrum for Cr^{3+} broadens after Eu^{2+} codoping.

Abstract

BAM:Eu is a very well known, commercial phosphor that is used for tricolor fluorescent lamps and plasma display panels. In recent years, Cr^{3+} doped BAM had been suggested as a phosphor for LED lamps for plant growth. However, excitation spectrum of Cr^{3+} is narrow. To overcome this problem, we have attempted co-doping by Eu^{2+}. $Eu^{2+} \rightarrow Cr^{3+}$ energy transfer was observed in $BaMgAl_{10}O_{17}:Eu^{2+},Cr^{3+}$ phosphor. The energy transfer was established by photoluminescence emission, excitation and lifetime measurements. Efficiency of the energy transfer is 40.2%. By virtue of this energy transfer, the excitation spectrum corresponding to Cr^{3+} emission covers a broad spectral region 340–430 nm. These phosphors were prepared by facile combustion synthesis which is a fast method. It is suggested that this phosphor will be useful for preparing LED lamps based on near ultraviolet, violet and blue chips.

Graphical abstract



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Introduction

Luminescent materials receive attention of the scientists due to the variety of applications [[1], [2], [3]]. About a half century back, Verstegen and Steven explored various aluminates derived from beta alumina [4] and studied luminescence of Eu^{2+} activators. Later, Verstegen [5] prepared $Ba_{0.86}Eu_{0.14}Mg_2Al_{16}O_{27}$ phosphors with an emission peaking at 450 nm and found it suitable as a blue component of tricolor fluorescent lamp. Later, it was found that the correct formula was not $BaMg_2Al_{16}O_{27}$ but $BaMgAl_{10}O_{17}$ [6]. Since then, $BaMgAl_{10}O_{17}$ is abbreviated as BAM. Use of BAM:Eu for lamps and related applications have been reviewed extensively, long back [7].

Work on BAM received impetus due to application in tri-colour fluorescent lighting, and rather surprisingly, even after nearly 50 years, the interest and investigations on BAM related phosphors are continuing [[8], [9], [10]]. Apart from Eu^{2+} [11,12], luminescence of several other activators like lanthanides Sm^{2+} [13], Gd^{3+} [14], Ce^{3+}, Tb^{3+} [15], and 3d transition metal ions like Cr^{3+} [16,17], Mn^{2+} [[18], [19], [20]], Mn^{4+} [21] has also been investigated. Er^{3+} and Nd^{3+} have also been used as dopants, or rather co-dopants in BAM:Eu. However, characteristic emission was not studied, instead the focus was on enhancement of Eu^{2+} emission intensity [22], especially for vacuum ultraviolet (VUV) excitation [23]. BAM has been exploited as a host for studying energy transfers between various sensitizer-activator pairs. Among these, Eu^{2+}-Mn^{2+} pair had been studied very extensively [[24], [25], [26], [27]]. It enables green emission of Mn^{2+}; emission of Eu^{2+} being blue. Other notable pair exhibiting energy transfer is Eu^{2+}-Yb^{3+} which yields near infrared (NIR) emission with nUV excitation that can be useful for modification of the solar spectrum for enhancing performance of c-Si solar cell [28]. Apart from sensitizer-activator pairs, an interesting energy transfer is from host itself. BAM has absorption in VUV region. Energy transfer from the host enables VUV excited luminescence of Eu^{2+} [29]. This makes BAM:Eu^{2+} phosphor suitable for applications like plasma display panel (PDP) [30,31], scintillator [32] and Mercury free fluorescent lamps [33]. VUV excitation required for this application could be enhanced by various codopants such as Mg^{2+} at Al^{3+} site [34].

BAM based phosphors have been used not only for fluorescent lighting and PDP, but variety of other applications have been envisaged. BAM:Eu^{2+} is a phosphor for thermography: remote temperature measurement [35]. Lifzig et al. [36] suggested Gas-phase thermometry using BAM:Eu^{2+} while Ojo et al. [37] used it for thermographic laser Doppler velocimetry. Excitation spectrum for BAM:Eu^{2+} is spread over wide range from UV to nUV and thus it can be used as a blue component for LED lamps based on nUV emitting chips [38]. The phosphor works at high excitation densities as well and thus can be used for laser-driven solid state lighting [39]. BAM can accommodate 3d transition metal codopants also at Al sites. BAM:Eu^{2+} containing such codopants can be used as blue fluorescent pigment [40,41]. NIR emission of Cr^{3+} leads to design of LED lamps for plant growth [17].

BAM based phosphors are conventionally prepared using solid state reaction. The reaction is typically carried out at the temperatures ranging between 1300 and 1600C [4]. Over the period of long history of these phosphors, a variety of methods aiming at simpler procedures have been employed. These include use of precursors which decompose and react at lower tempertures [42], decomposition of metal complex [43], citrate complex method [44], nano-coating method [45], sputtering [46], radio frequency sputtering [47], aerosol flame deposition [48], polymeric gel deflagration [49], Aerosol Pyrolysis [50], spray pyrolysis [51], flux-assisted spray pyrolysis [52], flame spray pyrolysis [53], atomic layer deposition (ALD) [54], Microwave synthesis [55], microwave irradiation technique [56], hydrothermal synthesis [57]. Ingenious tricks have been used for simplifying the synthesis. e.g. in combustion method, exothermic reaction between urea and metal nitrates drives the reaction [58,59].

In recent years, Cr^{3+} activated BAM has been studied as a phosphor for horticulture lighting [17]. However, excitation spectrum of Cr^{3+} is rather narrow. For a phosphor to work as LED lamp phosphor, broad excitation spectrum is desired. Modification of the excitation spectrum and/or enhancement of intensity can be achieved through sensitization. BAM:Eu is an already proven phosphor which has withstood test of industry over a long period. There are no reports on $Eu^{2+} \rightarrow Cr^{3+}$ energy transfer in BAM. In this paper we report results on such energy transfer which results in broader excitation spectrum.

Section snippets

Experimental

BAM:Eu, BAM:Cr and BAM:Eu,Cr phosphors were prepared by combustion synthesis. A detailed description is presented in our earlier work [60]. Salient points are as follows. “Aluminium nitrate has exothermic reaction with urea. Reagent grade (Indian Rare Earths, Ltd.) Europium/Chromium oxides were converted to the corresponding nitrates by dissolving in minimum amount of nitric acid. The nitrates were dried by prolonged, gentle warming. Stoichiometric amounts of hydrated nitrates of barium,…

Results and discussion

The formation of $BaMgAl_{10}O_{17}$ was ascertained with the help of XRD. Obtained patterns match with ICDD 26–0163. These results are well known and hence not presented here. $BaMgAl_{10}O_{17}$ is structurally related to hexagonal beta -alumina $NaAl_{11}O_{17}$ [63]. Beta - alumina is built out of spinel blocks separated by an intermediate layer, which accommodates two large ions Na^+ and O^{2-} per spinel blocks. In this structure when all Na^+ions are replaced by Ba^{2+} and Al^{3+} ions are replaced by Mg^{2+} in the spinel …

Conclusions

$Eu^{2+} \rightarrow Cr^{3+}$ energy transfer is observed in BAM:Eu,Cr. The efficiency of transfer is estimated as 40.2% using lifetime measurements. The energy transfer results in the broadening of the excitation spectrum of Cr^{3+}. The broadened spectrum extends into nUV region. Thus, Cr^{3+} emission can be excited by any wavelength between 340 and

450nm. As efficient LEDs are available for this range, BAM:Eu,Cr can become useful for obtaining LED based lamps for plant growth. $Eu^{2+} \rightarrow Cr^{3+}$ energy transfer becomes…

Credit author statement

S.G.Revankar – Synthesis, Manuscript writing, K.A.Gedekar- Synthesis and Editing, S.P.Puppulwar-Editing of manuscript, S.P.Wankhede- Synthesis and Editing, P.D. Belsare – Characterization, S. V. Moharil – Basic concept and Editing.…

Declaration of competing interest

Authors declare no conflict of interest.…

Acknowledgements

Facilities for recording luminescence decay and XPS were kindly provided by Dr.K.P.Adhi, Savitribai Phule Pune University. We are thankful to Prof. S.B.Kondwar, RTM Nagpur University for his help in scanning electron microscopy.…

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Ionoluminescence from Europium-doped BaMgAl<inf>10</inf>O<inf>17</inf> nanophosphors under different doping concentrations
2024, Journal of Alloys and Compounds

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Efficient blue-luminescence in boracite Zn<inf>3</inf>B<inf>7</inf>O<inf>13</inf>Cl and its further enhancement via anion substitution and post-annealing treatment

2023, Journal of Luminescence

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Synthesis, structure and photoluminescence properties of NIR phosphor LiAlSi<inf>2</inf>O<inf>6</inf>:Cr³⁺

2022, Optical Materials

> *Citation Excerpt :*
>
> ...To our surprise, there is a peak of Cr in LiAlSi2O6. Since chromium is inevitably contained in Al2O3, which has been proposed in other literatures [23], it is normal to detect Cr in LiAlSi2O6. The solid-state method can make Cr into LiAlSi2O6 lattice successfully....

Show abstract

Luminescence characteristics of Bi³⁺, Cr³⁺ and Bi³⁺/Cr³⁺ activated Sr<inf>3</inf>Y<inf>2</inf>Ge<inf>3</inf>O<inf>12</inf> phosphors

2022, Journal of Luminescence

> *Citation Excerpt :*
>
> ...Nonetheless, the parity-forbidden 3d transition of Cr3+ results in the low absorption and excitation efficiencies. Fortunately, it has been found that some ions benefit to the enhancement of Cr3+ emission via energy transfer while they are codoped into the host, such as Ce3+ [3], Eu2+ [12], Mn2+ [13] and Bi3+ [14]. Currently, Y3Al5O12:Ce3+ is one of the most widely used phosphors in pc-WLEDs....

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