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Rare Earth ions- doped Luminescent Glasses For white light emission Applications—A Review

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Abstract

These days, white light-emitting luminescents (WLELs) have garnered a lot of interest for use in displays, general lighting, and various electronic devices because of their superior mechanical durability, extended lifespan, and exceptional efficiency when compared to conventional incandescent and fluorescent lights. Nevertheless, there are a few significant flaws that are mostly related to phosphor and resin, including poor colour rendering capabilities, inhomogeneous spectrum distribution, and deterioration with heat and moisture. As a result, the development of phosphor-embedded glass-ceramics has emerged as a viable method for producing robust solid-state lighting fixtures. However, there is a higher chance of interactions happening between the glass host and the phosphor substance in these procedures. As a new generation of phosphor and/or epoxy-free white light sources, rare earth ion-doped luminescent glasses have attracted a lot of attention thus far because of their advantageous qualities, which include high thermal and chemical stability, high transparency, and a simple manufacturing process.Through down-shifting and up-conversion emissions, this review article seeks to provide a thorough summary of current developments in singly, doubly, and triply doped glasses with Rare Earth ions for solid-state lighting applications. Theoretical background is provided in depth, covering radiative and colorimetric characteristics, glass manufacturing techniques, and energy transmission processes. In order to improve the white light emission of luminescent glasses and expand their application areas, a number of efficient strategies are finally highlighted that minimise the significant challenges related to rare earths providing energy transfer from quantum dots or nanoparticles to lanthanides and doping lanthanides in low phonon energy glass.

Introduction

In addition to causing disputes between nations over energy supply, the world's population growth and technological advancements have resulted in a sharp increase in energy consumption, which is also causing serious environmental issues including greenhouse gas emissions. Over 20% of the world's power is used for lighting technologies, and 7% of CO2 emissions come from these sources [1-3]. To this end, tremendous efforts are made to create lighting sources that are both energy-efficient and ecologically friendly.

Because of their excellent thermal and chemical stability, outstanding lanthanide solubility, high transparency, homogenous emission, and simple manufacturing procedure, rare earth ion-doped glasses have special benefits in the development of white light-emitting luminous materials [4–7].

The synthesis routes, glass crystallisation technology, materials design principles, and optimisation strategies for phosphor embedded glass-ceramic (GC) based white light-emitting luminescent and/or LED colour converters have all been thoroughly described in a number of review articles that have been published to date [8–10]. To the best of our knowledge, however, in contrast to earlier GC phosphor studies, the current study is the first thorough and methodical literature review examining the production of white light through glasses doped with one or more Rare Earth ions, as well as highlighting the current advancements and scientific challenges associated with this field.

In this article, we highlight current advancements and trends in the production of white light using single, dual, and triple glasses doped with rare earth ions that rely on upconversion and downshifting processes.

2. Energy transfer mechanisms in Rare Earth ions- doped- doped

When exposed to the right kind of light, trivalent rare earth ions may produce a broad spectrum of emissions, ranging from UV to NIR and even far infrared. Figure 1 illustrates the three primary photoluminescence (PL) processes that occur in rare earth ion-doped luminous materials: upconversion (UC), downshifting (DS), and down-conversion (also known as quantum cutting, QC). The UC process is regarded as an anti-Stokes process as, in contrast to the other two processes, it does not follow Stokes law. To create white light-emitting luminous glasses and achieve the required colorimetric characteristics, one must understand the energy transfer mechanisms between acceptor and donor ions inside the glass matrix. Consequently, the PL mechanisms are the exclusive focus of this section.

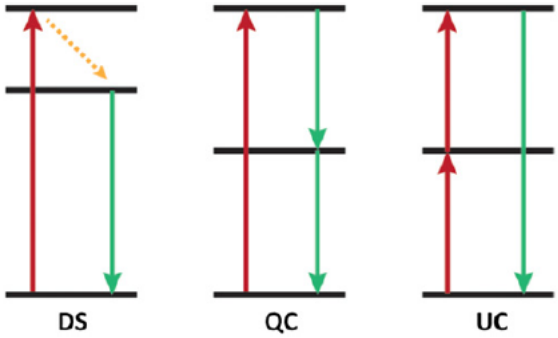

Figure 1 Three energy transfer mechanisms—DS, QC, and UC—shown schematically from left to right. The photon excitation and radiative emission are depicted by the upward red and descending green arrows, respectively. A process of non-radiative energy transfer is shown by the dashed line.

2.1.1. Down-shifting (DS) and quantum cutting (QC) processes.

In the Stokes process of DS luminescence of Ln3+, a single high-energy photon is absorbed by the luminescent material and transformed into a low-energy photon. The process known as quantum conversion (QC) produces quantum values bigger than unity if the absorbed photon is split into two or more lower-energy photons [11, 12]. Dexter initially presented the idea of producing quantum yields greater than 100% in 1957 by splitting a single photon into two lower-energy photons [13], which demonstrated that a single UV photon of Pr3+ is transformed into two visible photons. In a related study, Pr3+ activated phosphorus material quantum yield values larger than unity were obtained by Piper et al. [14]. Generally, QC is employed to boost solar cell efficiency. Though it is outside the purview of this paper, readers who are interested in learning more might consult [15] for a thorough analysis of the topic.Most crucially, strong white light emission from single (e.g., Dy3+) or multiple (e.g., Ce3+/Sm3+ or Eu3+/Tb3+/Tm3+) Rare Earth ion-doped glasses may be obtained by UV light stimulation with the aid of the DS method; this will be covered in section 3 of this study.

2.1.2. Up-conversion (UC) process.

The non-linear anti-Stokes process of UC luminescence of Ln3+ involves the absorption of one or more low energy photons by luminescent centres, which then transform them into a higher energy photon. This process was first discovered by Auzel in the 1960s, and it has attracted the attention of researchers in the field because, in addition to being advantageous in that it lessens host degradation brought on by short wavelengths of UV excitation in the DS process, it is also feasible to obtain a variety of photons in the visible region of the electromagnetic spectrum using a low-cost, commercially available 980 nm NIR diode laser [15]. Prior to 1966, Dexter's study believed that all energy transfers occurred from the first ion's excited state to the second ion's ground state [17].However, Auzel first proposed that energy transfer between ions may occur between two ions that are both in an excited state and that not only absolute energy but also energy differences can be exchanged among ions by observing the UC in a Yb3+–Er3+ doped system [18-19]. The UC process for lanthanide-based systems may be broadly classified into five types, as seen in figure 2: cooperative energy transfer (CET), photon

avalanche (PA), excited state absorption (ESA), energy transfer up-conversion (ETU), and energy migration-mediated up-conversion (EMU).

ESA is a single-ion process in which an ion with many stable intermediate energy levels successively absorbs two excitation photons. The absorption of the second photon raises the ion to a higher excited energy level if the first absorbed photon remains in the intermediate level for a sufficient amount of time. Eventually, as a result of de-excitation, an upconverted photon will be released (see figure 2(a)). This procedure is also known as two-step absorption as two photons are sequentially absorbed. To achieve ESA, dopants with a wide absorption cross-section, low doping concentration, and high power density are required. This is due to the possibility that high doping concentration-related non-radiative crossrelaxations might reduce the emission intensity.

The most prevalent process in Ln3+ doped systems is called ETU (short for Addition de Photons par Transfert d'Energie), a French abbreviation that was officially adopted. ETU is the most effective process among the five methods shown in Figure 2 and typically occurs in a system with an activator (Ho3+, Er3+, Tm3+, etc.) and a sensitizer (often Yb3+ owing to its wide absorption cross section). In ETU, after excitation, sensitizer ions use a dipole-dipole resonant interaction to non-radiatively transmit their energy to activator ions, which pumps the activator ions to their excited states (see figure 2(b)). It is important to note that the energy transfer from the sensitizer fills both the intermediate and emission levels of activators [20].

The activator's high absorbance at the sensitizer's emission wavelength may cause ETUs with greater efficiency, such as those stimulated at 980 nm by the pair of activators and sensitizer, Yb3+ and Er3+. Phonon aided energy transfer is the technique of using the host's phonons to compensate for a small energy mismatch between the activator's emission wavelength and the sensitizer's absorption wavelength, as in the case of Yb3+–Tm3+ or Yb3+–Ho3+ couples [21].

The energy of the excitation photon is not the same as the energy of the ground and intermediate states of the ion in the PA process (see figure 2(c)). As a result, the ion goes through an ESA process and populates a highly excited state (hyper excited), while some electrons are promoted to an intermediate state. A cross relaxation process then occupies the intermediate levels of the ion and a nearby ion. As long as there is less hyper excited ion depletion than ground state ion depletion, this process will continue [16]. An ETU process and a CET procedure are comparable. Nevertheless, the activators in this process don't actually have any intermediate energy levels.

As a result, the energy is concurrently transmitted to the activator and two sensitizers are pushed to a virtually excited state (see figure 2(d)). Numerous studies have been conducted on this phenomenon in bulk materials, glasses, polymers, and nanomaterials [22-23]. In an effort to improve the efficiency of UC emissions in cases where the proper intermediate amounts of activators are absent, Wang et al. suggested the EMU technique in 2011. Four luminous centers the sensitizer, accumulator, migrator, and activator are integrated into distinct layers throughout this process. First, the ETU populates the accumulator's higher energy levels.

Energy from the accumulator's excited state is then transmitted to the migrator, and energy from the core's migrators is transferred to those positioned in the shell. The energy is eventually absorbed by the activator, and radiative emission is seen when the accumulator and activator transition from their excited states to their ground states (refer to figure 2(e) [24].

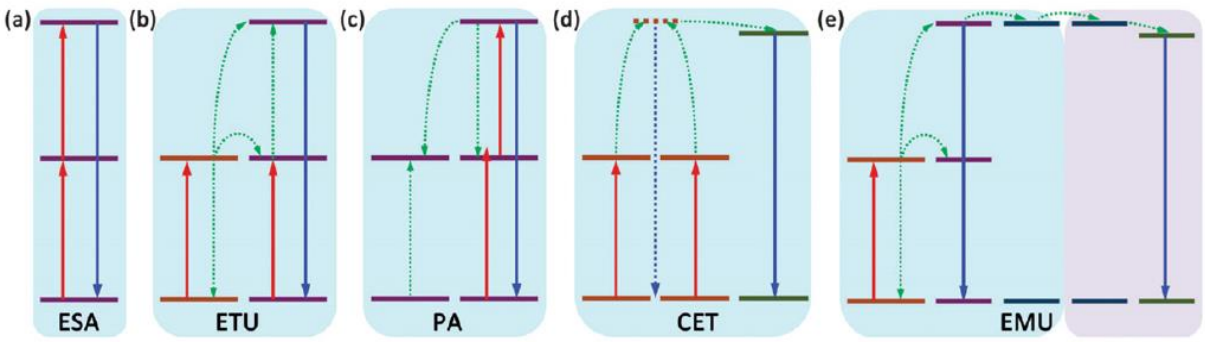

Figure 2. Diagrams that show how the procedures for (a) ESA, (b) ETU, (c) PA, (d) CET, and (e) EMU are represented in UC. Full arrows on the graphs denoting radiative emission processes and upward (blue) and downward (red) excitation processes, respectively. Processes of energy transmission are shown by dashed (green) arrows. Please take note that for clarity, non-radiative relaxations are not provided here. distinct regions are

emphasised with distinct backdrop colours, and different types of luminous centres are displayed with varying coloured energy levels. Reproduced with authorization [20].

3. White light emission

3.1. Glasses with Dy3+ singly doped

Of all the lanthanide ions that can directly emit white light, trivalent Dy3+ with a 4f9 electron configuration is the most suitable dopant because it exhibits two strong emission peaks in the blue (470–500 nm) and yellow–orange (570–600 nm) regions, which correspond to the 4F9/2→6H15/2 and 4F9/2→6H13/2 transitions, respectively.

3.2. Glasses with single-doped Eu2+

Because of its adjustable broad band emission in the visible range, crystalline phosphors coupled with Eu2+ ions were identified as potential luminous materials for WLEL[25]. Because of this, scientists have been looking at Eu2+ doped glasses as potent substitutes for their crystalline counterparts [26, 27]. While glasses lacking long-range structural order offer plenty and continuously discernible sites available for luminescent activators, crystalline phosphors have limited cation sites with discernible crystalline environments, making it difficult to obtain adjustable excitation and emission from Eu2+ ions in these materials [27].

3.3. Co-doped glasses Dy3+–Ln (where Ln = Eu, Tm, Ce)

While Dy3+ singly-doped glasses may effectively produce white light, co-doping with an alternative Ln3+ ion is advised and being studied by several researchers in order to produce high-quality white light. Much work has recently gone into creating co-doped glasses for Dy3+/Eu3+, Dy3+/Tm3+, and Dy3+/Ce3+ that can create white light using the ET mechanism by transferring donor (sensitizer) ions to acceptor (activator) ions.

Conclusions

The production of white light in a single host doped with rare earth ions has garnered significant interest in the domains of chemistry, physics, and material research.Because glasses have so many benefits over other host materials, including excellent transparency and long-term stability, they are becoming increasingly used for the purpose of emitting white light. Based on this pattern, a thorough overview of the most recent developments in the production of white light in rare earth ion-doped luminescent glasses based on down-shifting and UC processes is given in this article. Furthermore, a few successful methods for resolving the issues with lanthanide ions related to their low luminescence efficiency and tiny absorption cross section are compiled.

Enhancing white light emission and achieving tunable colour emission in Rare Earth ion-doped glasses excited by a single light source is a growing need in this field in order to broaden the range of applications in fields like optical temperature sensing devices, 3D volumetric displays, and anti-counterfeiting applications, among others.In conclusion, future research on the use of rare earth ion-doped glasses with high quantum efficiency and tunable emission colour under a single light excitation source for white light emission will not only support the glasses' widespread use in commercial WLEL applications but will also open up new avenues for application.

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