Materials Research Bulletin 105 (2018) 277–285

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Mn^{4+}/Zn^{2+}:YAG glass ceramic for light emitting devices

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ARTICLE INFO

Keywords:
Mn^{4+}
Red-emitting phosphor
Luminescent
Glass ceramic

ABSTRACT

The rare-earth-free Mn^{4+}-activated oxide red phosphors draw great attention for their potential applications in the field of light-emitting diodes (LEDs). In this work, the red-emitting Mn^{4+}/Zn^{2+}:$Y_3Al_5O_{12}$ phosphor, showing strong red emission peaked at ~ 672 nm as a result of the spin-forbidden $^2E_{2g} \rightarrow {}^4A_{2g}$ electron transition of Mn^{4+} ions under 478 nm excitation, was synthesized by a traditional solid-state reaction route in air. The microstructure and luminescent performance of this red-emission phosphor was investigated in detail. From the experimentally measured spectroscopic data, the crystal field strength (Dq) and the Racah parameters *B* and *C* were calculated, respectively. In addition, Zn^{2+} dopant was found to be beneficial for enhancing Mn^{4+} luminescence. Subsequently, Mn^{4+}/Zn^{2+}:YAG glass ceramic was successfully prepared via using Mn^{4+}/Zn^{2+}:YAG phosphors incorporated into tellurate glass. A tunable lighting device was successfully achieved by coupling the red-emitting Mn^{4+}/Zn^{2+}:YAG GC with the commercial blue chips and Ce^{3+}:$Lu_3Al_5O_{12}$ GC.

1. Introduction

In recent years, white light-emitting diodes (WLEDs), which are regarded as the next-generation solid-state lighting devices, have obtained widespread attention because of their superior properties in many aspects such as energy-saving, long operational lifetime, small size, short response time and environment-friendly distinctions [1–6]. Nowadays, the current leading commercial WLEDs are mostly fabricated by combining a blue InGaN chip and yellow-emitting phosphors dispersed in an organic resin or silicone [7–11]. $Y_3Al_5O_{12}$:Ce^{3+} (YAG:Ce^{3+}) is an excellent yellow-emitting phosphor for InGaN chip excitation with high photoluminescence (PL) quantum yield (QY) and good thermal stability [12–16]. Unfortunately, the current WLEDs still have two vital shortcomings. On the one hand, polymer resins in the high-power WLEDs are likely to readily age and become yellow bringing out serious decline of LED performance, which is of main concern because it is a limiting factor to improve the high power solid state lighting devices [17–20]. On the other hand, the short of red components in luminescence spectra of commercial WLEDs lead to low color rendering index (CRI) and high correlated color temperature (CCT), which is hard to obtain a natural and vivid WLED. Hence, a desirable inorganic color converter with high thermal stability and mixing a red phosphor that can absorb blue light with YAG:Ce^{3+} are greatly desired to generate a high-quality and durable warm white light.

State of the art, in order to conquer the drawback of polymer binders, phosphor-in-glass (PiG) inorganic color converter, a type of glass-based encapsulants, has been demonstrated as a promising encapsulant to substitute phosphor in silicone (PiS) due to the superior thermal conductivity of glass, low sintering temperature and facile process. In addition, a series of rare-earth-doped red phosphors are synthesized, such as the nitrides (e.g., Eu^{2+}:$CaAlSiN_3$, Eu^{2+}:$Sr_2Si_5N_8$) [21,22], sulfides (e.g., Eu^{2+}:CaS) [23], which are most commercialized owing to their excellent properties. However, these red phosphors still have several defects. For instance, most of the rare earth ions are very expensive, and some rare-earth chlorides and citrates are toxic and harmful [24,25]. Therefore, numerous scholars have devoted to explore new red phosphors activated by transition metal ions. As an alternative, Mn^{4+} doped red phosphors with broad band excitation and deep-red narrow band emission have received much attention [26–29].

Mn^{4+} belongs to transition metal ion with outer $3d^3$ electron configuration. An excellent spectral feature of Mn^{4+} is that it provides broad band excitation and narrow band emission for its unique electronic structure. Moreover, the optical properties of Mn^{4+} doped materials are strongly influenced by local crystal field environments. They usually exhibit broad and strong absorption between 250 and 550 nm and emit light from 600 to 750 nm. These distinct optical properties meet the spectral demands for a perfect red-emitting phosphor, in addition with the abundance of raw material sources, and thus enable Mn^{4+}-doped compounds to be promising candidate red-emitting

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https://doi.org/10.1016/j.materresbull.2018.05.003
Received 18 December 2017; Received in revised form 25 March 2018; Accepted 2 May 2018

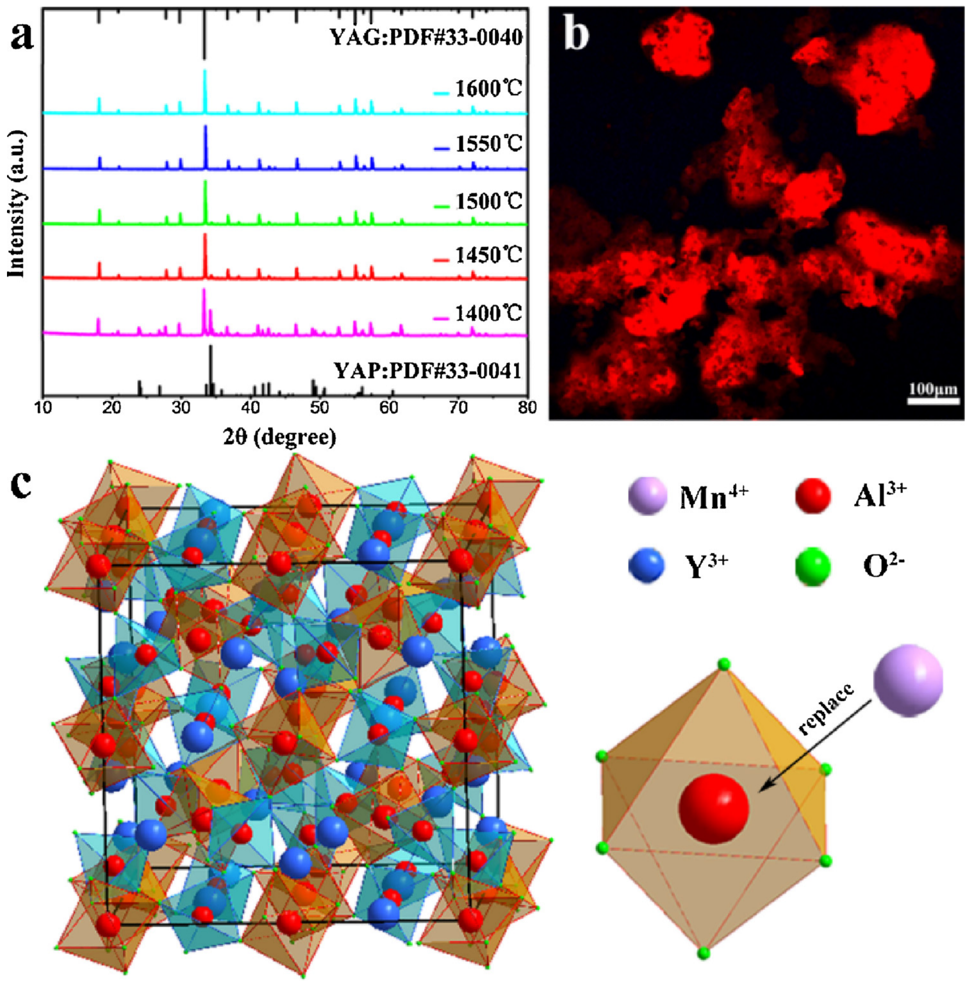

Fig. 1. (a) XRD patterns of Mn^{4+}:YAG phosphor sintered at 1400 ℃–1600 ℃; bars represent standard $YAlO_3$ (PDF#33-0040) and $Y_3Al_5O_{12}$(PDF#33-0040) crystal date. (b) Fluorescent microscopic image of Mn^{4+}(0.1 mol%):YAG excited by blue light at 460 nm. (c) Cell structure of YAG: red spheres represent Al^{3+} on tetrahedral and octahedral sites, whereas purple spheres represent substitution of Mn^{4+} ions for Al^{3+} at $[AlO_6]$ octahedral sites (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

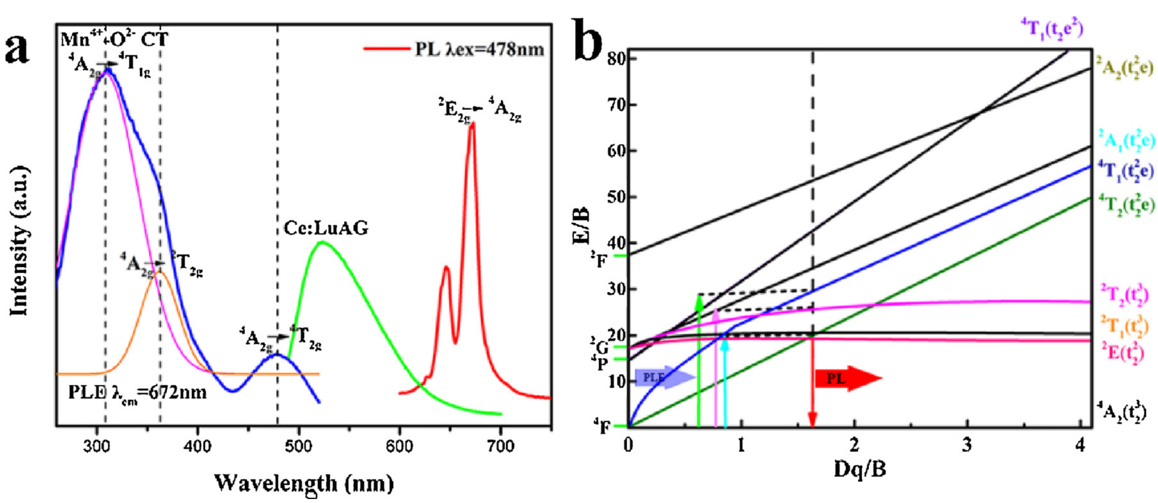

Fig. 2. (a) Room temperature PLE (λ_{em} = 672 nm) and PL (λ_{ex} = 478 nm) spectra of Mn^{4+}(0.1 mol%):YAG sample, where the solid pink and orange lines represent date fit using Gaussian function. The green line represents the referenced emission of commercial Ce:LuAG phosphor under 460 nm excitation. (b) Tanabe-Sugano energy level diagram of Mn^{4+} in an octahedral crystal field (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).