Journal of the European Ceramic Society xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

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

Original Article

Stable and efficient all-inorganic color converter based on phosphor in tellurite glass for next-generation laser-excited white lighting

Yang Peng[a,b], Yun Mou[a], Hao Wang[c], Yong Zhuo[d], Hong Li[d], Mingxiang Chen[a,*], Xiaobing Luo[b,*]

[a] School of Mechanical Science and Engineering, Huazhong University of Science and Technology, Wuhan 430074, China
[b] State Key Laboratory of Coal Combustion and Thermal Packaging Laboratory, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan, 430074, China
[c] Wuhan National Laboratory for Optoelectronics, Huazhong University of Science and Technology, Wuhan 430074, China
[d] State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan 430070, China

ARTICLE INFO

Keywords:
Phosphor-in-glass (PiG)
Tellurite glass matrix
Luminescence
White laser diodes (LDs)

ABSTRACT

Laser lighting is considered as a next-generation high-power lighting due to its high-brightness, directional emission, and quasi-point source. However, thermally stable color converter is an essential requirement for white laser diodes (LDs). Herein, we proposed a stable and efficient phosphor-in-glass (PiG) in which YAG:Ce^{3+} and MFG:Mn^{4+} phosphors were embedded into tellurite glass matrixes. The glass matrixes with low-melting temperature and high refractive index were prepared by designing their composition. The luminescence of YAG:Ce^{3+} PiGs was adjusted by controlling phosphor thickness. Aiming to compensate for red emission, multi-color PiGs were realized by stacking MFG:Mn^{4+} layers on YAG:Ce^{3+} layer. The phosphor crystals are chemically stable and maintain intact in the glass matrix. Furthermore, white LDs were fabricated by combining the PiGs with blue LDs. As the phosphor thickness increases, the chromaticity of white LDs shifts from cool to warm white, and the white LDs exhibit excellent thermal stability under different excitation powers.

1. Introduction

Solid-state lighting (SSL) has been drawn extensive applications in general illumination, display backlighting, and vehicles lighting because of its long lifetime, low energy consumption, and environmental protection [1–4]. Currently, the commercial SSL source is white light-emitting diodes (LEDs), which are produced by LED chip combined with phosphors or multi-color LED chips [5–7]. Notably, white LEDs still present incredible challenges, such as efficiency droop and large divergence angle [8,9]. To solve these issues, laser diodes (LDs) provide a promising alternative to achieve white lighting due to their high-brightness, directional light emission, and quasi-point source [10–12]. The high-brightness lase-excited white lighting can be realized by combining blue LDs with a down-converting color converter [13,14]. However, the traditional color converter of phosphor embedded with organic resin is prone to aging and carbonization under high-density laser excitation owing to its poor heat resistance and low thermal conductivity [15–17]. The thermal degradation leads to light efficiency reduction, chromaticity shift, and reliability decrease. Thus, the color converter with high thermal stability is an essential requirement for high-power laser-excited white lighting.

Phosphor-in-glass (PiG) composite, which is prepared by a low-temperature (< 800 °C) sintering of glass matrix and phosphor particles, has been developed as a feasible color converter for high-power lighting because of its robustness, high thermal stability, and low thermal expansion coefficient [18–21]. Initially, $Y_3Al_5O_{12}$:Ce^{3+} (YAG:Ce^{3+}) PiG has been employed for high-power lighting, which is a certain number of YAG:Ce^{3+} phosphor particles dispersed in a glass matrix [22–24]. In addition, some red and green phosphors have been added to achieve multi-color PiGs for the enhancement of light quality [25–27]. It is worth noting that the luminescent performances of PiG converter are limited by two key factors. The one is the thermal degradation and chemical reaction of phosphors by melting glass matrix, resulting in the reduction of their original emissive properties [28]. The other is the refractive index difference between glass matrix and phosphors, which leads to the scattering loss on the phosphor particles and then affects the transmittance of PiG [29]. Based on these considerations, the precursor glass matrix should be carefully designed to gain a low melting temperature for the maintaining of phosphor properties and a high refractive index for the index-matching of phosphor. Currently, the lead-free tellurite (TeO_2-based) glass is regarded as the ideal glass matrix for the PiG preparation [30–32]. However, most

---

[*] Corresponding authors.
E-mail addresses: chimish@163.com (M. Chen), luoxb@hust.edu.cn (X. Luo).

https://doi.org/10.1016/j.jeurceramsoc.2018.08.014
Received 20 June 2018; Received in revised form 9 August 2018; Accepted 10 August 2018
0955-2219/ © 2018 Published by Elsevier Ltd.

Please cite this article as: Peng, Y., Journal of the European Ceramic Society (2018), https://doi.org/10.1016/j.jeurceramsoc.2018.08.014

of the prepared PiG still requires sintering temperature higher than 550 °C, and commercial nitride red phosphors are hard to be embedded into the tellurite glass due to the bad chemical reaction between nitride and melting glass [33]. Furthermore, it is impossible to realize the index-matching of glass matrix and two phosphors for the multi-color PiG under mixed-sintering process.

Herein, a stable and efficient all-inorganic color converter based on PiG was proposed for laser-excited white lighting. Precursor tellurite (TeO_2-ZnO-Na_2O-B_2O_3) glass matrixes with different refractive indexes were prepared by adjusting their stoichiometric composition. YAG:Ce^{3+} PiGs were prepared by introducing YAG:Ce^{3+} phosphor into the glass matrix through screen-printing and sintering. In order to compensate for red emission, Mn^{4+}-doped magnesium fluorogermanate ($3.5MgO{\cdot}0.5MgF_2{\cdot}GeO_2$:$Mn^{4+}$, MFG:$Mn^{4+}$) phosphor was added into the glass matrix for the preparation of multi-color PiGs. The microstructures and luminescence of PiGs were studied. The YAG:Ce^{3+} and multi-color PiGs were used to package blue LDs for the fabrication of white LDs, and their optical performances and thermal stability were investigated.

2. Experimental details

2.1. Preparation of precursor glass matrix and PiG converter

The precursor glass matrixes with a composition of TeO_2–ZnO–Na_2O–B_2O_3 were prepared by a melting-quenching method. The stoichiometric ratio of glass matrixes was designed to adjust their refractive index. The reaction mixture was melted in a platinum crucible at 850 °C for 40 min and then poured in a pre-heated steel plate, subsequently annealed at 300 °C for 90 min to relieve internal stress, and finally cooled to room temperature. The obtained glass bulk was milled to glass powders by using a ball grinder. In order to realize the index-matching of glass matrix and two phosphors, the prepared glass powders with different refractive indexes were used for the PiG preparation.

The PiG converter was prepared by screen-printing and sintering process, as presented in Fig. 1(a). The printing paste was obtained by adequately mixing the glass powders, phosphor particles, and organic solvent, and then printed on a borosilicate glass plate. This glass substrate has excellent heat resistance, high transmittance, and similar thermal expansion coefficient with the glass matrix. For the YAG:Ce^{3+} PiG, the content of YAG:Ce^{3+} phosphor (YAG-05, Intematix, USA) was designed at 40 wt% and the thickness of phosphor layer was controlled by altering the printing number. The effects of sintering temperature on the luminescence of YAG:Ce^{3+} PiG was evaluated under temperature ranging from 450 to 600 °C. In addition, a red MFG:Mn^{4+} phosphor was added into the glass matrix to enhance light quality, which possesses high thermal and chemical stability for the preparation of PiG [34,35]. The multi-color PiG was prepared by printing 20 wt% MFG:Mn^{4+} phosphor (T66-015, Jiangmen Kanhoo Industry Co., Ltd, China) layer on the 40 wt% YAG:Ce^{3+} phosphor layer, and the thickness was adjusted to achieve chromaticity-tunable PiG. In order to examine the thermal stability of PiG, phosphor-in-silicone (PiS) samples were prepared and compared.

Table 1
Stoichiometric composition of precursor glass matrix and the corresponding refractive index.

Glass samples	Stoichiometric composition (mol%)				Refractive index
	TeO_2	ZnO	Na_2O	B_2O_3	
Glass 1	75	20	5	0	2.03
Glass 2	65	25	10	0	1.95
Glass 3	55	30	15	0	1.86
Glass 4	45	30	10	15	1.79
Glass 5	35	30	15	20	1.72
Glass 6	25	30	10	35	1.66

2.2. Fabrication of PiG-based white LDs

The PiG-based white LDs were fabricated by combining the prepared PiGs and blue LDs, which includes two packaging types, trans-missive white LDs and reflective white LDs, as shown in Fig. 1(b) and (c), respectively. For the trans-missive white LDs, a commercial blue LD (L450P1600MM, Thorlabs) with a peak wavelength of 450 nm was focused on the PiG by using an aspheric lens (A110TM, Thorlabs), which can realize the white lighting source with a small form factor. Thus, the trans-missive type was used to evaluate the optical performances of PiG-based white LDs in this work.

2.3. Characterizations

The crystalline phases of glass matrixes and PiGs were analyzed by an X-ray diffraction system (XRD, X'Pert PRO MRD, PANalytical) with a nickel-filtered CuKα radiation in the range of 10–70° (2θ). The refractive indexes of glass matrixes were measured by a spectroscopic ellipsometry (M-2000 V, J. A. Woollam, USA). The photoluminescence excitation (PLE) and PL emission spectra of phosphors and PiGs were recorded on a fluorescence spectrophotometer (FP-6500, Jasco, Japan). The microstructures of PiGs were characterized by a scanning electron

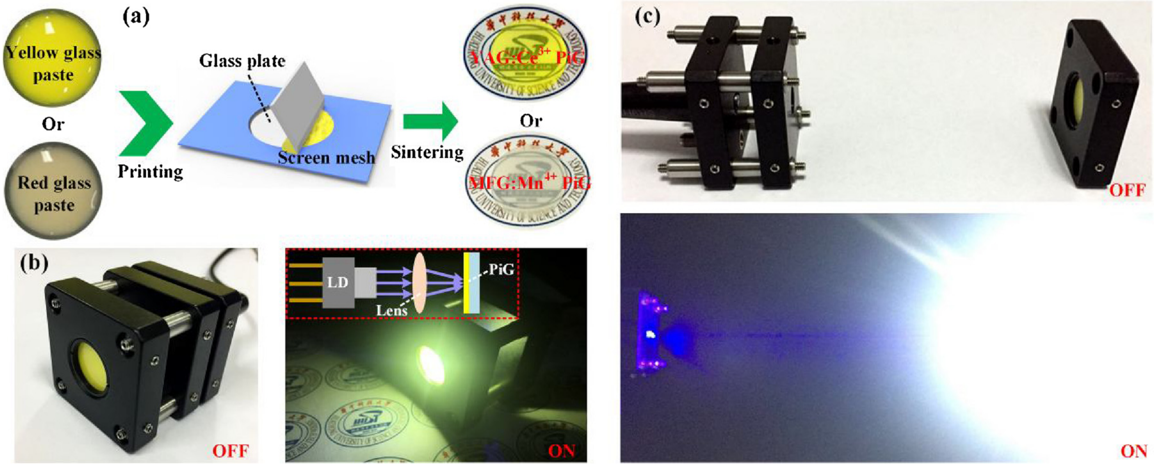

Fig. 1. (a) Preparation process of PiG converter by screen-printing and sintering. Photographs of (b) trans-missive PiG-based white LD and (c) reflective PiG-based white LD out operation and in operation.