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Highly thermally stable single-component warm-white-emitting ZANP glass: Synthesis, luminescence, energy transfer, and color tunability

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ABSTRACT

Luminescent glass demonstrates potential for applications as color converters in white-light-emitting diodes (W-LEDs). In this study, solution combustion synthesis combined with low-temperature melt quenching was employed as a novel route for preparing new white-light fluorescent glasses (rare-earth-doped ZnO–Al₂O₃–Na₂O–P₂O₅, ZANP). The developed solution combustion synthesis can considerably decrease the reaction temperature and time, with several advantages such as energy and time savings. X-ray diffraction and photoluminescence spectroscopy, as well as decay curves, CRI, and CCT, as well as the Commission Internationale de l'Éclairage (CIE) 1931 chromaticity coordinates, were assessed to examine the microstructure and photoluminescence properties of Tm³⁺/Dy³⁺ co-doped and Tm³⁺/Dy³⁺/Eu³⁺ tri-doped ZANP glasses for use in W-LEDs. Experimental results revealed that ZANP glass co-doped with Tm³⁺ and Dy³⁺ exhibits blue- and yellow-light emissions based on the energy transfer of dipole-dipole interaction between Tm³⁺ and Dy³⁺, which can realize the adjustment of color in a wide range. The emitting color coordinate (0.343, 0.344) of ZANP: 1.0Tm³⁺, 0.75Dy³⁺ approach ideal white light. Also, by the introduction of additional Eu³⁺ doping, ZANP:1.0Tm³⁺, 0.75Dy³⁺, 0.1%Eu³⁺ glass emit warm-white light (CCT = 3198 K) under an excitation of 361 nm. Moreover, the tri-doped ZANP glasses exhibit good thermal stability, where the luminous intensity at 498 K remains exceeding 50% of that at room temperature, and the color coordinate offset is only 2.87×10^{-2} relative to room temperature.

1. Introduction

In recent years, as a new generation of lighting sources, white-light-emitting diodes (W-LEDs) have attracted immense research interest in terms of their low energy consumption, small volume, rapid response, and long service life. W-LEDs have been regarded as candidates that can replace traditional incandescent fluorescent lamps [1–5]. Typically, commercial W-LEDs are obtained by the coating of yellow-emitting Y₃Al₅O₁₂:Ce³⁺ (YAG:Ce) phosphor on a blue InGaN chip surface [6]. However, the W-LEDs exhibit some drawbacks of poor white-light emission and even the deviation of the emission wavelength due to the aging of packaging resin. To overcome these drawbacks and to achieve bright white-light emission, rare-earth (RE)-ion-doped glasses are highly desired for W-LEDs because of advantages such as homogeneous light luminescence, better thermal and mechanical stabilities, and lower fabrication cost [7,8].

It is crucial to select suitable glass host materials for the doping of RE ions. White-light emission has been explored in silicate, borate,

tellurite, and fluoride glass matrices [9–13]. Compared with the above-mentioned glass formers, phosphate-based glasses [14,15] exhibit considerable advantages such as low melting temperature, high thermal expansion coefficient, low viscosity, and especially high-ultraviolet (UV) transmission [16].

However, pure phosphate glasses exhibit some drawbacks of high hygroscopicity and low chemical durability, thereby limiting their practical utility. These drawbacks can be improved by the addition of small amounts of one or more oxides such as ZnO, Al₂O₃, PbO, SnO, and Fe₂O₃ [17]. Lanthanide-ion-doped zinc phosphate glasses exhibit low phonon energy, high transparency in the UV–Vis range, and excellent photoluminescence performance. Even with high RE ion concentrations, these glasses can serve as good hosts with homogeneously distributed RE ions. The presence of Al₂O₃ in phosphate glasses converts a part of the PO₄ tetrahedral linkages to the AlO₄ tetrahedral linkages, which can improve thermal and chemical durability. In addition, the replacement of zinc by sodium has been reported to decrease the density and increase the molar volume of the glasses, whereas with

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increasing sodium content, the glass transition temperature and chemical durability decrease. According to our previously reported study [18], ZnO–Al₂O₃–Na₂O–P₂O₅ (ZANP) glass is possibly attractive as an excellent host for tunable color-light-emitting phosphors.

Moreover, a majority of the glasses, including phosphor glasses, are typically prepared by a conventional melt-quenching technique, which often requires a high operating temperature of ~1100 °C; this temperature is not feasible with respect to both cost and energy saving. In this paper, a novel two-step method, was proposed to first produce a phosphor powder by solution combustion synthesis [19–22], followed by low-temperature melt-quenching to prepare phosphor glasses. In addition, luminescence properties as well as energy transfer processes, thermal-quenching characteristics and fluorescence quantum efficiencies of Tm³⁺/Dy³⁺ co-doped or Tm³⁺/Dy³⁺/Eu³⁺ tri-doped ZANP glasses were all investigated.

2. Experimental section

2.1. Sample preparation

Glasses with different chemical compositions of (49.5–x)P₂O₅–15Na₂O–30ZnO–5Al₂O₃–0.5Tm₂O₃–xDy₂O₃ (x = 0, 0.125, 0.25, 0.375, and 0.5 mol%) and (49.125–y)P₂O₅–15Na₂O–30ZnO–5Al₂O₃–0.5Tm₂O₃–0.375Dy₂O₃–yEu₂O₃ (y = 0, 0.025, 0.05, 0.075, and 0.1 mol%) were prepared by a two-step method in which phosphor powders were first prepared by solution combustion synthesis, followed by low-temperature melt quenching to obtain phosphor glasses. Table 1 summarizes the compositions of the aforementioned ZANP glasses. Starting materials included NaNO₃ (A.R.), Zn(NO₃)₂·6H₂O (A.R.), Al(NO₃)₃·9H₂O (A.R.), CO(NH₂)₂ (A.R.), H₃PO₄ (68%), Tm₂O₃(A.R.), Dy₂O₃ (A.R.), and Eu₂O₃ (A.R.). The details of the preparation method are as follows. First, the starting materials were weighed according to the desired stoichiometry for further use. Tm₂O₃ and Dy₂O₃ (and Eu₂O₃) were dissolved in deionized water with appropriate amounts of dilute nitric acid to obtain RE nitrate solution, followed by adding NaNO₃, Zn(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, H₃PO₄, and CO(NH₂)₂ and subsequent stirring. Next, the as-obtained transparent solutions were placed into a porcelain crucible to initiate combustion at 400 °C for 30 min, affording a porous mass. The raw fine powder (phosphor powder) was then prepared by grinding.

Subsequently, a certain amount of phosphor powder was weighed and placed in a corundum crucible at 700 °C for 20 min. The molten glass liquid was poured into a stainless-steel mold which had been preheated at 350 °C, and was quenched in air to form glass. Finally, the as-prepared glass was annealed at 350 °C for 2 h and was cooled to room temperature to release the thermal stress generated during molding. The glass samples were obtained by cutting and surface polishing.

Table 1
Chemical composition of ZANP glasses.

Glass Number	Matrix glass component (mol%)				RE component (mol%)		
	Na ₂ O	ZnO	Al ₂ O ₃	P ₂ O ₅	Tm ₂ O ₃	Dy ₂ O ₃	Eu ₂ O ₃
A	15	30	5	50	0.5	–	–
B	15	30	5	50	–	0.5	–
D	15	30	5	50	0.5	0.125	–
E	15	30	5	50	0.5	0.25	–
F	15	30	5	50	0.5	0.375	–
G	15	30	5	50	0.5	0.5	–
H	15	30	5	50	0.5	0.375	0.025
I	15	30	5	50	0.5	0.375	0.05
J	15	30	5	50	0.5	0.375	0.075
K	15	30	5	50	0.5	0.375	0.1

2.2. Instrumental methods

X-ray diffraction (XRD) patterns were recorded on an XRD system (Rigaku D/max 2500, Tokyo, Japan) using CuK_α (λ = 1.54178 Å) radiation (200 mA, 40 kV) with a step size of 0.02° and a scanning rate of 6°/min over a 2θ range of 10–70°. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 380 FTIR spectrometer with a spectral resolution of 0.5 cm⁻¹. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra were recorded on an FLS980 spectrofluorometer (Edinburgh Instruments) equipped with a 450-W Xe lamp as the excitation source. Fluorescence decay curves were measured on the FLS980 spectrofluorometer (Edinburgh Instruments) equipped with a 100-W adjustable microsecond flash light. High-temperature PL experiments were carried out on the FLS980 spectrofluorometer (Edinburgh Instruments). CRI and CCT, as well as the Commission Internationale de l'Éclairage (CIE) 1931 chromaticity coordinates, were assessed using a photoelectric test system (V2.00 LED spec system).

3. Results and discussion

3.1. Synthesis

3.1.1. Selection of fuel types

During solution combustion synthesis, different fuels considerably affect the reaction products. Taking the 15Na₂O–30ZnO–5Al₂O₃–50P₂O₅ glass component as an example, the raw materials and three fuels were subjected to low-temperature combustion according to the above-mentioned preparation. Fig. S1 shows the appearance of the products: The products obtained by different fuels vary widely. Black powders are prepared using glycine as the fuel. However, black flakes are observed using citric acid. Transparent flake-like glasses are obtained only when using urea. Therefore, urea is selected as the fuel for solution combustion.

3.1.2. Determination of combustion temperature

In addition to the fuel type, the combustion temperature is also a crucial factor. Using urea as the reaction fuel, experiments were performed at 250 °C, 300 °C, 350 °C, 400 °C, 450 °C, and 500 °C, respectively. Fig. S2 shows the appearances of the products. At the combustion temperatures of less than 350 °C, non-transparent solids are observed. At the combustion temperatures of larger than 350 °C, transparent flaky solids are obtained.

Furthermore, the samples prepared at different combustion temperatures are stripped and ground to powders. Fig. 1 shows the XRD diffraction patterns. At the combustion temperatures of larger than 350 °C, dispersive peaks are observed in the XRD diffraction patterns, indicative of amorphous products. At the combustion temperatures of less than 350 °C, some XRD diffraction peaks corresponding to crystals are observed, except for an amorphous diffraction band. At a low

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