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High-aluminum phosphate glasses for single-mode waveguide-typed red light source

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ABSTRACT

High-aluminum phosphate (HAP) glasses with excellent chemical durability have been fabricated and investigated for thermal ion-exchanged optical waveguide. With the content adjustment, the glass constituents turn into high-aluminum area and the glass stability has been appropriately improved with more Al^{3+} ions cross-linked with phosphate chains, resulting in a restriction of ion-exchange rate. Consequently, stable single-mode slab waveguide operating in visible region was fabricated on Pr^{3+} doped HAP glass substrates by K^+–Na^+ ion-exchange. For Pr^{3+} doped HAP glasses, Judd–Ofelt intensity parameter Ω_2 is solved to be 8.04×10^{-20} cm^2, implying a strong asymmetrical and covalent environment around Pr^{3+} in the optical glasses. Using the Ω_t values, spontaneous transition probability (A_{rad}) and branching ratio (β) of $^1D_2 \rightarrow {}^3H_4$ emission are calculated to be 824.3 s^{-1} and 13.54%, respectively, indicating that the transition emission is dominant in visible region. The radiative lifetime (τ_{rad}) and the quantum efficiency (η_q) of $^1D_2$ level are identified to be 164.3 μs and 87.7%, respectively, and the quantum yield (QY) of $^1D_2 \rightarrow {}^3H_4$ transition emission is derived to be 2.3%. These results demonstrate that Pr^{3+} doped HAP glasses are a promising substrate in developing high-density waveguide-typed red light source, which contains attractive potential applications in medical treatment and illumination.

1. Introduction

Optical waveguides have drawn much attention as they are the most indispensable and fundamental part of integrated optics circuits [1–5]. Among all the substrates used in fabricating optical devices, glasses based integrated optical devices possess several obvious merits over others such as an excellent coupling efficiency with glass fiber and no intrinsic material birefringence compared to crystallized semiconductors [6–9]. The trivalent rare-earth ions incorporated phosphate glasses are a promising candidate to develop optical devices because of their significant properties, i.e., high thermal expansion coefficient, ultraviolet transmission, suitable refractive index, less dispersion and low melting temperature. Moreover, phosphate glasses represent high rare-earth ions solubility, good chemical stability and excellent ion exchangeability, which allow high concentration doping without significant non-radiative relaxation and are attractive to fabricate high efficiency waveguides that can meet the demand of high-power and compact laser cavity [10–19]. With the addition of Al_2O_3, the thermal and chemical stability of phosphate glasses will be largely improved [20–25] for stable requirements in wet chemical etching and ion-exchange process during waveguide fabrication.

Ion-exchange technique has been widely used in fabricating high-quality glass waveguide due to various benefits, i.e., low surface scattering losses, symmetric refractive index profiles, and easy fabrication of single mode waveguide, excellent mode matching to single-mode fiber and low birefringence across a broad range of waveguide widths [26–38]. K^+–Na^+ ion-exchange is one of the most frequently-used techniques to fabricate low-loss optical device that can be effectively coupled with single-mode fibers, which is mainly attributed to the facts that the refractive index selectively raised with the K^+ ions exchanged into the glass substrate when the glass substrate is submerged in pure molten KNO_3, and during K^+–Na^+ ion exchange process no concentration control of the melt is required and no subsequent metallic ion clusters are formed [39–47]. In the previous work, an attempt was made at fabricating waveguide devices in NMAP (Na_2O–MgO–Al_2O_3–P_2O_5) glass substrates incorporating with trivalent rare-earth ions by K^+–Na^+ ion exchange, and after ion exchange NMAP glass substrate appears appropriate single-mode in near-infrared (NIR) region [48].

In this work, ion-exchangeable high-aluminum phosphate (HAP) glasses are designed for the purpose of making single-mode optical waveguide operating in visible region and Pr^{3+} is introduced in the glasses in order to obtain the effective red emission. With the addition

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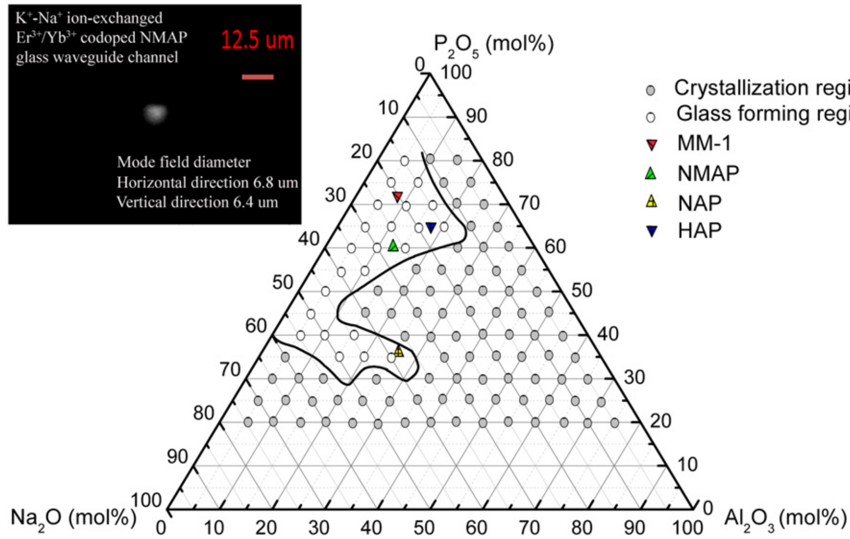

Fig. 1. Ternary phase diagram of Na_2O–Al_2O_3–P_2O_5 glass system. Inserted photo: Near-field mode pattern at the output facet recorded by a video camera when 1.53 μm laser was coupled into the channel waveguide.

of the Al_2O_3 content as well as the decrease of Na_2O content, glass stability has been enhanced to control the ion-exchange rate and single-mode red-lighting source waveguide was fabricated by K^+–Na^+ ion exchange method. Large value of the Ω_2 intensity parameter (8.04×10^{-20} cm^2) reveals a strong asymmetrical and covalent environment around Pr^{3+} in the optical glasses and quantum efficiency (η_q) for $^1D_2$ level is obtained to be 87.7%. The intense red fluorescence attributed to $^1D_2 \rightarrow {}^3H_4$ transition has been quantitatively investigated under the excitation of commercial blue light emitting diode (LED) by using an integrating sphere for absolute measurements including spectral power distribution, photon distribution and quantum yield (QY). The controllable ion-exchange process to form stable single-mode waveguide demonstrates that HAP glasses possess great potential in developing optical waveguide devices especially operating in visible region.

2. Experimental

According to the molar composition 17.0Na_2O–2.0MgO–17.0Al_2O_3–64.0P_2O_5 (HAP), Pr^{3+} doped HAP glasses were prepared from high-purity $NaPO_3$, $Mg(PO_3)_2$, Al_2O_3 and $Al(PO_3)_3$ powders. Additional 0.2 wt.% Pr_6O_{11} was introduced into HAP glass composition based on the host weight. After being well mixed, the mixtures were first preheated in a platinum crucible at 230 °C for 6 h, then melted at 1350 °C for 1 h using an electric furnace in air atmosphere, and finally quenched on a preheated aluminum mold. The obtained glasses were annealed at 510 °C for 3 h, and cooled down slowly to room temperature. In preparing K^+–Na^+ ion-exchanged, the annealed glasses were sliced and optically polished into pieces, then Pr^{3+} doped HAP glass substrates were merged in a molten KNO_3 at 390 °C for 2 h to fabricate slab waveguides.

For 0.2 wt.% Pr_6O_{11} doped HAP glasses, the density was obtained to be 2.613 $g \cdot cm^{-3}$ by Archimedes method, and the number density of Pr^{3+} ions was calculated to be 1.845×10^{19} cm^{-3}. Using a Metricon 2010 prism coupler, the refractive indices were identified to be 1.5174 at 632.8 nm and 1.5037 at 1536 nm, respectively. At other wavelengths, the refractive indices can be derived by the Cauchy equation $n = A + B/\lambda^2$ with $A = 1.5009$ and $B = 6607.4$ nm^2, and curves of reflected light intensity versus index value have been recorded for ion-exchanged HAP slab glass waveguide. Absorption spectrum of Pr^{3+} doped HAP glasses was detected by a Perkin-Elmer UV–vis–NIR Lambda 19 double-beam spectrophotometer. Fluorescence and excitation spectra were determined by a Jobin Yvon Fluorolog-3 spectrophotometer with a R928 photomultiplier (PMT) tube as detector and a CW Xe-lamp as pump source. Fluorescence decay curve was obtained under the same setup together with a flash Xe-lamp. Differential thermal analysis (DTA) scan of the Pr^{3+} doped HAP glasses was carried out by a WCR-2D differential thermal analyzer at the rate of 10 °C/min from room temperature to 1000 °C. The spectral power distributions of glass samples were measured using an integrating sphere of 30 cm diameter, which was connected to a CCD detector (Ocean Optics, USB4000) with a 400 μm-core optical fiber. The luminescence pictures were taken using a Sony α200 digital camera.

3. Results and discussion

Metaphosphates such as $NaPO_3$, $Mg(PO_3)_2$ and $Al(PO_3)_3$ possess low moisture and excellent glass forming ability so they are selected as raw materials. An indispensable content of Na_2O must be introduced into the glass host to achieve an effective K^+–Na^+ ion exchange and a reasonable melt temperature. Na_2O acts as a glass modifier in glass system but too high concentration of Na_2O will lead to an inferior chemical durability [49]. Generally, in order to complete the ion-exchange process in molten KNO_3 for hours the glass host must be able to sustain a good surface quality. Therefore, good chemical durability is a significant requirement for the glass host to manufacture waveguide. Richard et al. reported that the chemical durability of Na_2O–Al_2O_3–P_2O_5 glass system will be improved with the addition of Al_2O_3 content as well as the decrease of Na_2O content and Al^{3+} ions can strengthen the glass network and enhance the glass stability by cross-linking phosphate chains

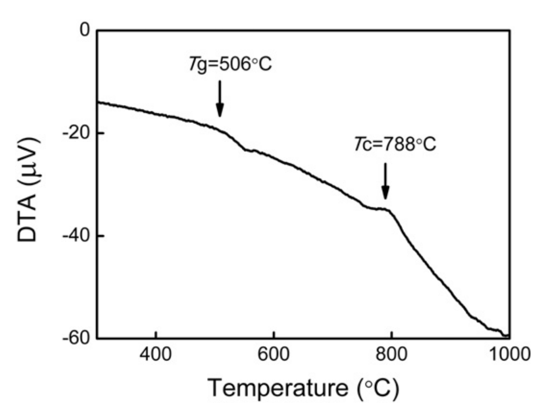

Fig. 2. DTA curve of 0.2 wt.% Pr_6O_{11} doped HAP glasses.