New chemically stable Er^{3+}-Yb^{3+} co-doped phosphate glass for optical waveguide lasers and amplifiers

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A set of phosphate glasses with different amounts of Al_2O_3, Na_2O, La_2O_3 and AlF_3 contents were prepared to search for a phosphate glass which is suitable for ion-exchange process. Based on chemical durability test results and spectroscopic properties, a glass with excellent chemical durability and good spectroscopic properties is developed for ion-exchange process. The emission cross section of Er^{3+} in this glass is calculated to be 0.72×10^{-20} cm^2 by McCumber theory. The planar waveguide with three modes at 632.8 nm and one mode at 1540 nm can be realized by 335 °C 3 hours ion-exchange in 5%$AgNO_3$+95%KNO_3 molten salt.

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The rapid development of optical networks has stimulated great demands on passive and active integrated waveguide devices. Different technologies, such as ion-exchange[1], glass-on-silicon[2] and radio frequency (RF) sputtering[3] have been employed to fabricate integrated optical devices. Among these, ion-exchange process is the most commonly used technique because of its simplicity and low cost. Phosphate glass is known as an excellent rare-earth host material because of its good spectral and laser properties, and the weak concentration quenching[4]. High rare earth ion doping is possible in phosphate glass matrix. It is possible to achieve a high gain within relatively short length in waveguide device made from phosphate glass. However, most commonly available phosphate glasses exhibit poor chemical durability due to their weak network structure[5]. On the other hand, glass should be soaked in molten nitrate salt at elevated temperatures for several hours during the ion-exchange process. In order to obtain good surface quality after ion exchange process, good chemical durability is very important. In addition, the spectroscopic properties should also be considered.

Glass samples were prepared with high purity chemical materials containing less than 5 ppm of iron and copper. The mixed batches were melted with high quality quartz crucible at about 1300 °C. The glass was cast on a pre-heated iron mould and transferred to an annealing furnace. Several glasses with different amounts of Al_2O_3, Na_2O, La_2O_3 and AlF_3 contents were melted to investigate the influence of glass compositions on chemical durability and spectral properties. Table 1 lists partial components of some experimental glass samples. Since sodium ions exchange well with silver ions for waveguide fabrication, a certain amount of Na_2O is needed in the glass[1] to achieve the efficient ion-exchange. Because the chemical and physical properties of La^{3+} are similar to those of Er^{3+} or Yb^{3+} ions, La_2O_3 was introduced in the glass to compensate the variation of glass properties caused by the change of species and amounts of rare-earth ions doped in these glasses. Small amount of AlF_3 was added to help remove hydroxyl groups in glass melt.

The chemical durability of glass samples was evaluated by testing the weight-loss of glass samples after an hour immersion in boiling distilled water. The glass samples were placed in a beaker filled with distilled water. After boiling for an hour, samples were rinsed, dried, and weighed. Then the weight-loss per surface area was calculated. Table 2 lists weight-loss rate of glass samples in boiling water. It is found that the chemical durability of WM-1 glass with the highest Al_2O_3 content (9.8 wt.-%) is the best. The weight-loss of this glass (1.45×10^{-5} g·cm^{-2}) is comparable to that of Q-246 silicate glass and Kigre's commercial glass. In phosphate glass, the PO_4 tetrahedron is the basic structural unit. Because of the pentavalency of phosphorus, only three corners of PO_4 tetrahedron are connected, which results in a weak network structure of phosphate glasses compared to that of silicate glasses. With the addition of Al_2O_3 in phosphate glasses, the combination of trivalent Al and pentavalent P in tetrahedral coordination allows for a cross linked network structure resembling that of SiO_2[5]. Therefore, the weak structure of phosphate glasses was fortified

Table 1. Partial Components of Glass Samples

Sample	Composition (wt.-%)			
	Al_2O_3	Na_2O	La_2O_3	AlF_3
WM1	9.8	6.9	4.1	
WM2	5.0	7.5		
WM3	4.8	7.2	11.9	
WM4	5.0	7.5		0.32
WM5	4.8	7.2	11.8	0.31

Table 2. Weight-Loss Rate of Glass Samples in Boiling Water

Sample	WM1	WM2	WM3	WM4	WM5
Δu (g·cm^{-2}·hr^{-1})	1.45×10^{-5}	2.54×10^{-5}	2.93×10^{-5}	3.62×10^{-5}	3.55×10^{-5}

Table 3. Basic Properties of WM-1 Phosphate Glass

Density	2.83 g/cm^3
n_d	1.535
Knoop Hardness	430 kg/mm^2
$n_{1.54\ \mu m}$	1.525
v_d	66.97
Glass Transformation Temperature	530 °C
Glass Softening Temperature	573 °C
Thermal Expansion Coefficient (20 − 300 °C)	94 × 10^{-7} °C^{-1}

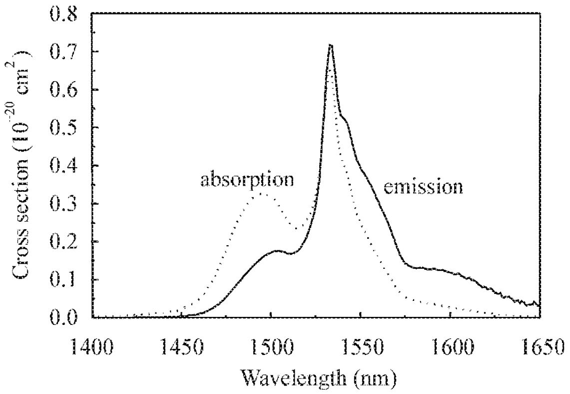

Fig. 1. Absorption and emission spectra of Er^{3+} ion in the WM-1 glass.

by introducing Al_2O_3 into glass. Glass containing 9.8 wt.-% Al_2O_3 has the highest Knoop hardness (468 kg·mm^{-2}), higher glass transition temperature and lower thermal expansion coefficient among all glasses. The amount of Na_2O has also a strong influence on chemical durability. It is well known that glasses containing large amount of alkali oxide usually exhibit poor chemical durability. However, more than 6 wt.-% Na_2O is required for efficient ion-exchange process. Thus, glass composition should be optimized on the basis of extensive chemical durability test experiments as well as spectroscopic properties investigations. One glass designated WM-1, which combines excellent chemical durability and good spectroscopic properties, was developed. The basic properties of this glass are listed in Table 3.

The spectroscopic properties of WM-1 glass co-doped with Er^{3+} and Yb^{3+} were investigated by measuring absorption and emission spectra as well as fluorescence lifetime. The glass contains 2.0 × 10^{20} ions/cm^3 Er^{3+} and 4.0 × 10^{20} ions/cm^3 Yb^{3+}. The absorption cross section was determined from the absorption spectrum. The peak absorption cross section was 0.65 × 10^{-20} cm^2 at 1.533 μm. To avoid the effect of re-absorption, $^4I_{13/2}$ to $^4I_{15/2}$ emission spectrum of WM-1 glass is calculated from absorption spectrum with McCumber theory[6]. Figure 1 illustrates the absorption and emission cross sections of Er^{3+} ion in the WM-1 sample. The peak emission cross section was found to be 0.72 × 10^{-20} cm^2 at 1.533 μm. It is higher than that reported for IOG-1 phosphate glass[7]. The full-width at half-maximum (FWHM) is 42 nm. Judd-Ofelt theory was used to evaluate the spectroscopic properties of WM-1 based on eight measured absorption bands from

Table 4. Effective Mode Indices of Some Ion-Exchanged WM-1 Glasses

Temperature (°C)	Time (min)	Number of Modes	Effective Mode Indices
335	120	2	1.5409, 1.5483
335	180	3	1.5390, 1.5425, 1.5493
345	120	3	1.5389, 1.5424, 1.5491
355	120	3	1.5407, 1.5448, 1.5510

300 to 700 nm. The Judd-Ofelt intensity parameters Ω_t (t = 2, 4, 6) are calculated to be $\Omega_2 = 6.45 \times 10^{-20}$ cm^2, $\Omega_4 = 1.56 \times 10^{-20}$ cm^2, and $\Omega_6 = 0.89 \times 10^{-20}$ cm^2. They are similar to the values reported in Ref. [8], using Ω_t data, the spontaneous emission probability A, the emission branching ratios β and the radiative lifetime τ_{rad} can be evaluated. At the $^4I_{13/2}$ metastable level, A, β, and τ_{rad} are 109 s^{-1}, 1, and 9.1 ms, respectively. The radiative quantum efficiency of the $|(S,L)J\rangle$ manifold is defined as $\eta = \tau_{meas}/\tau_{rad}$, where τ_{meas} and τ_{rad} are the measured fluorescence and calculated radiative lifetimes, respectively. τ_{rad} for the $^4I_{13/2}$ to $^4I_{15/2}$ transition is calculated to be 9.1 ms, and τ_{meas} is measured to be 7.9 ms. Thus, the radiative quantum efficiency for the $^4I_{13/2}$ to $^4I_{15/2}$ transition is estimated to be about 87%. It indicates that there is no significant quenching due to the high Er^{3+} ion concentration and no obvious non-radiative de-excitation caused by the hydroxyl group (OH^-) in glass.

Ion exchange was performed by immersing glass sample in a molten salt bath. Both larger surfaces of the glass sample were mirror-polished before ion exchange. A variety of molten salt bathes containing different amounts of $AgNO_3$ and KNO_3 were used for the ion exchange process. Salt bath temperatures varied from 335 to 355 °C, and the ion exchange times changed from 120 to 180 mins. The WM-1 glass was stable during the ion-exchange process without visible deterioration after ion exchange. Partial representative experimental results are listed in Table 4. The used molten salt compositions were 5% $AgNO_3$ and 95% KNO_3 in weight percent. A planar waveguide with one mode at 1.54 μm and three modes at 632.3 nm was demonstrated in the WM-1 glass after ion-exchange for 120 min at 345 to 355 °C.

In conclusion, a new Er^{3+}-Yb^{3+} co-doped phosphate glass, which combines good spectroscopic properties and excellent chemical durability for ion-exchange process, was developed in this work. One mode at 1540 nm and three modes at 632.8 nm can be achieved after ion exchange at 335 °C for 3 hours in 5%$AgNO_3$+95%KNO_3 molten salt. Our preliminary ion-exchange experimental results indicate this glass is a promising material for active waveguide applications.

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