Er^{3+}/Yb^{3+} Codoped Phosphate Glass Planar Waveguides by Ag^{+}-Li^{+} Ion Exchange*

ZHAO Shi-long[1], XU Shi-qing[1], WANG Bao-ling[1], HU Li-li[2]

(1 *College of Materials Science and Engineering*, *China Jiliang University*, *Hangzhou* 310018, *China*)
(2 *Shanghai Institute of Optics and Fine Mechanics*, *Chinese Academy of Sciences*, *Shanghai* 210018, *China*)

Abstract: A chemically stable Er^{3+}/Yb^{3+} codoped phosphate glass is prepared and used in fabrication of planar waveguides for optical amplifiers and lasers. The weight loss rate of this phophate glass is 4.7×10^{-5} g • cm^{-2} • hr^{-1}, which is smaller than that of Kiger′s commercial phosphate glass QX/Er. Planar optical waveguides are formed by Ag^{+}-Li^{+} ion exchange and the effective refractive indices are determined by m-lines at 632.8nm. Diffusion parameters such as ion exchange depth, surface refractive indices, variation of refractive index and diffusion coefficient are calculated based on refractive index profiles obtained by Inverse WKB method.

Key words: Ag^{+}-Li^{+} ion exchange; Planar waveguide; Phosphate glass

CLCN: TN252 **Document Code**: A **Article ID**: 1004-4213(2008)04-0818-4

0 Introduction

Optical communication system operating at around 1.55 μm wavelength region requires efficient optical amplifiers. Erbium-doped fiber amplifier (EDFA) provides the active medium for light generation and amplification, and the successes in EDFA stimulate the development of integrated optics amplifier that can provide a high gain within a short length. Recently, Er^{3+}-doped waveguide amplifier (EDWA) has received great attention because of its reducing cost and size of the optical amplifiers[1]. Typically, the Er^{3+} concentration in EDWA is ten times than that of EDFA. Among the different glass hosts for rare earth ions[2~6], silica-based glass has been frequently used because of its superior chemical resistance and compatibility with optical fiber. However, the dopant concentration of Er^{3+} ions is limited due to the cooperative upconversion and the ion clustering effects. Phosphate glass is known as an excellent rare earth host material because of its good spectroscopic and laser properties and the weak concentration quenching, so 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 glasses.

Among different optical waveguide fabrication techniques, ions exchange in glass is one of the most promising fabrication techniques [7-9]. Compared to Ag^{+}-Na^{+} ion exchange process, there were few reports about Ag^{+}-Li^{+} ion exchange process used for waveguide device fabrication. Recently, WONG S F et al.[10] demonstrated an Er^{3+}/Yb^{3+} codoped phosphate glass waveguide amplifier by Ag^{+}-Li^{+} ion exchange and obtained a net gain ~3.3dB/cm. Through optimizing melting conditions and glass compositions, a new chemically stable Er^{3+}/Yb^{3+} codoped Li-based phosphate glass (named WMLi) was developed and ion exchange properties of this glass was investigated.

1 Experiment

WMLi glass sample with composition of P_2O_5-Li_2O-SrO-Al_2O_3-Yb_2O_3-Er_2O_3 was prepared with high purity chemical materials. It was firstly melted in a high quality quartz crucible and then proceeded the refining and stirring in a platinum crucible at an appropriate temperature to get homogenous glass. Glass without bubble and striate was chosen for the following experiments. Six surfaces of the glass sample with a dimension of 30 × 15 × 2 mm^3 were polished to high optical quality. The chemical durability of glass sample was evaluated by testing the weight loss of glass sample in boiling water.

Mixed molten salt KNO_3 + $AgNO_3$ was utilized for ion exchange experiments. Planar waveguides were formed by immersing precleared and preheated glass samples into the mixed molten salt. Three different molten salt compositions were used in ion exchange process. Salt bath temperature was controlled at 340℃ ~ 360℃, and

---

* Supported by Zhejiang Provincial Education Department Foundation(20050394)

Tel: 0571 - 86835781 Email: shilong_zhao@hotmail.com

Received date: 2006-10-15

ion exchange time changed from 120 to 240 min. The input prism coupling method in conjunction with a He-Ne laser was used to determine the effective refractive indices of the planar waveguides for transverse electric (TE) modes, and the experimental apparatus is shown in Fig. 1.

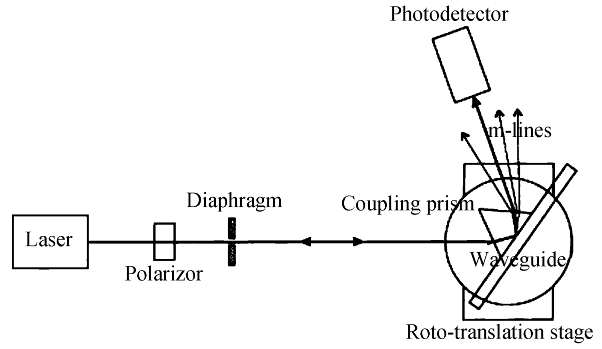

Fig. 1　The m-lines experimental apparatus

The mode effective refractive indices of waveguides were determined by the formula

$$n_{\mathrm{eff}} = \sin\theta\cos\delta + (n_{\mathrm{p}}^{2} - \sin^{2}\theta)^{1/2}\sin\delta \qquad (1)$$

Where δ is the prism angle, n_{p} is the refractive index of the prism, and θ is the synchronous angle of the m order mode.

2　Results and dscussions

The basic properties of WMLi glass are listed in Table 1. The weight loss rate of WMLi glass is 4.7×10^{-5} g · cm^{-2} · hr^{-1}, which is smaller than that of Kiger's commercial phosphate glass QX/Er (5.2×10^{-5} g · cm^{-2} · hr^{-1})[11]. This indicates that WMLi glass has good chemical durability and is suitable for ion exchange process. Furthermore, the glass transformation temperature (528℃) is high enough to allow ion exchange to carry out at high temperature.

Tab. 1　Basic properties of WMLi glass

Density	2.67g · cm^{-3}
n_{d}	1.5323
Glass transformation temperature	528℃
Glass softening temperature	570℃
Thermal expansion coefficient (20℃～300℃)	82×10^{-7} ℃$^{-1}$
Chemical durability	4.7×10^{-5}g · cm^{-2} · hr^{-1}

The calculated effective refractive indices of Ag^{+}-Li^{+} ion exchange optical waveguides based on formula (1) were listed in Table 2.

Tab. 2　Effective refractive indices of Ag^{+}-Li^{+} ion exchange optical waveguides

Sample	Molten salt/(mol%)	Temp/℃	Time/min	Effective refractive indices
1	1%$AgNO_3$ 99%KNO_3	340	120	1.5433, 1.5401, 1.5372, 1.5352, 1.5337
2	1%$AgNO_3$ 99%KNO_3	340	180	1.5429, 1.5402, 1.5379, 1.5363, 1.5348, 1.5335
3	1%$AgNO_3$ 99%KNO_3	340	240	1.5442, 1.5415, 1.5395, 1.5378, 1.5363, 1.5350, 1.5340, 1.5330
4	1%$AgNO_3$ 99%KNO_3	350	120	1.5422, 1.5395, 1.5374, 1.5353, 1.5340, 1.5329
5	1%$AgNO_3$ 99%KNO_3	360	120	1.5398, 1.5379, 1.5363, 1.5349, 1.5337, 1.5329
6	5%$AgNO_3$ 95%KNO_3	340	120	1.5561, 1.5510, 1.5474, 1.5441, 1.5411, 1.5383, 1.5361, 1.5341, 1.5325
7	10%$AgNO_3$ 90%KNO_3	340	120	1.5646, 1.5584, 1.5539, 1.5499, 1.5465, 1.5432, 1.5403, 1.5379, 1.5357, 1.5341, 1.5327

Alike with the process in Ag^{+}-Na^{+} ion exchange optical waveguides[12], the refractive index profiles of Ag^{+}-Li^{+} ion exchange optical waveguides were obtained through numerical solution for a graded index waveguide by Inverse WKB method. The diffusion parameters such as ion exchange effective depth (d), surface refractive index (n_0), variation of refractive index (Δn) and diffusion coefficient (D) are following calculated and listed in Table 3.

Tab. 3　Diffusion constant of Ag^{+}-Li^{+} ion exchange optical waveguides

Sample	n_0	Δn	d/μm	$D/(\mathrm{m^2 s^{-1}}\times10^{-15})$
1	1.5468	0.0145	10.19	3.065
2	1.5461	0.0138	12.98	2.925
3	1.5479	0.0156	15.54	2.795
4	1.5464	0.0141	11.82	4.851
5	1.5422	0.0099	14.22	7.021
6	1.5634	0.0311	11.14	4.309
7	1.5733	0.0410	11.81	4.843

Based on these obtained data, the characteristic of Ag^{+}-Li^{+} ion exchange optical waveguides was analyzed to link the process and the device parameters. Fig. 2 shows the relationship between the effective diffusion depth d and the square root of the diffusion time for samples ion exchanged at 340℃ and indicates that the longer the ion exchange time, the deeper the waveguide. A linear relationship was obtained. It is known that effective diffusion depth d can be expressed by $d = 2\sqrt{Dt}$, where D is the effective depth coefficient and t is diffusion time. From the slope of the fitting line in Fig. 2, the estimated effective diffusion coefficient D at 340℃ is found to 2.81×10^{-15} m^2/s, which much larger than that of Ag^{+}-Na^{+} ion exchange[12]. Thus it maybe obtain a desired waveguide depth in a short time.

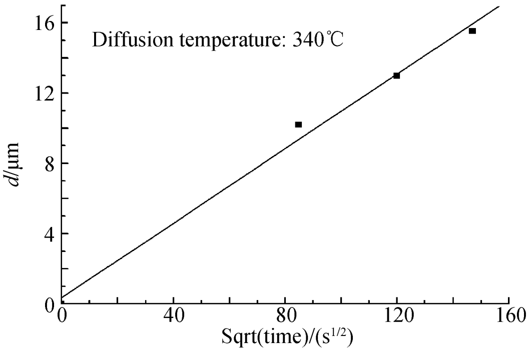

Fig. 2 Variation of effective depth versus the square of diffusion time

The equilibrium at the melt-substrate interface was investigated in order to obtain an experimental relationship between the maximum refractive index change and the silver concentration in the molten salt. Fig. 3 shows the relationship of refractive index variation against the molar concentration of $AgNO_3$. As expected, variation of refractive index is consistent with increase of $AgNO_3$ molar concentration, but there is no linear dependence. Due to the ion radius of Li^+ ion is smaller than that of Na^+ ion, the re-diffusion velocity of Li^+ ion is quicker than that of Na^+ ion during the physical cooling and decrease the surface refractive index of ion exchange optical waveguide, these factors result in that there is no linear dependence between refractive index change and the molar concentration of $AgNO_3$.

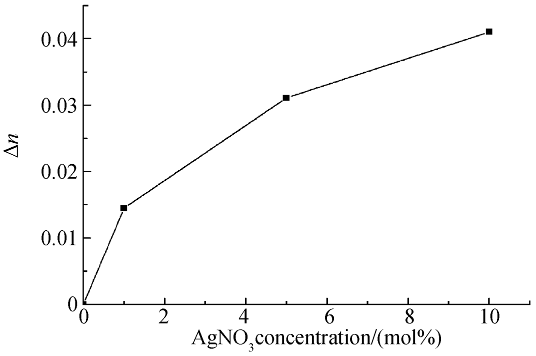

Fig. 3 Refractive index change against the molar concentration of $AgNO_3$

In order to estimate the variation of the diffusion coefficient D with temperature T, three batches of ion exchanged waveguides were fabricated at 340℃, 350℃ and 360℃. The diffusion coefficients at different temperature were estimated using the calculated effective depth. The variation of D with T is given by an Arhenius type relation $D(T) = D_0 e^{-\Delta H/RT}$, where ΔH is activation energy, D_0 is a pre-exponential factor, and R is the gas constant(8.314J · K^{-1} · mol^{-1}). In Fig. 4, we obtained $D_0 = 6.29$ (10^{-4} m^{2}s^{-1} and $\Delta H = 1.32$ (10^5Jmol^{-1} which is smaller than that of Na-based phosphate glass[12]. Due to the exponential relationship between D and T, it is important exactly control the temperature in the ion exchange process.

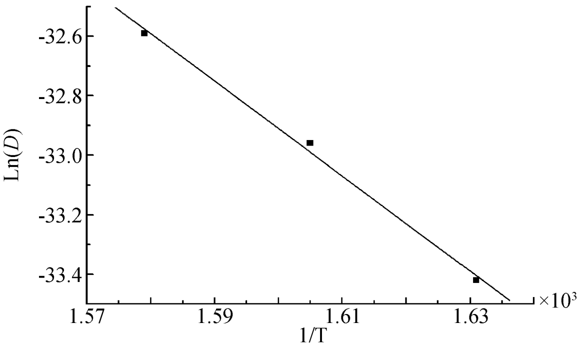

Fig. 4 The relationship between Ln(D) and the inverse temperature 1/T

3 Conclusions

A new Er^{3+}/Yb^{3+} codoped Li-based Er^{3+}/Yb^{3+} codoped phosphate glass was fabricated which exhibits good physical chemical properties and the weight loss rate of the phophate glass was 4.7×10^{-5} g · cm^{-2} · hr^{-1}. Planar optical waveguides made by Ag^+-Li^+ ion exchange were characterized by m-lines. With the help of numerical solution for a graded index waveguide, a series of waveguide parameters were estimated. The calculated effective diffusion coefficient (D_0) at 340℃ and activation energy(ΔH) are 2.81×10^{-15} m^2/s and 1.32×10^5J · mol^{-1}, respectively. These results were very useful for further fabrication of erbium-doped waveguide lasers and amplifiers by ion exchange technique.

References

[1] HEMPSTEAD M, Ion-exchanged glass waveguide lasers and amplifiers[C]. *SPIE*, 1997, **2996**: 94-102.

[2] WINICK K A. Rare-earth-doped waveguide lasers in glass and $LiNbO_3$: a review[C]. *SPIE*, 1998, **3280**: 88-104.

[3] LI Wei-nan, ZOU Kuai-sheng, ZHAO Wei, *et al*. Luminescence of Er^{3+}-doped ions in EDWA glasses[J]. *Acta Photonica Sinica*, 2004, **33**(7): 846-849.

[4] LI Wei-nan, ZOU Kuai-sheng, Shen Hua, *et al*. Investigation on spectrum characteristic of basic glass applied to EDWA[J]. *Acta Photonica Sinica*, 2004, **33**(6): 693-696.

[5] ZHAO Shi-long, CHEN Bao-yu, HU Li-li. Er^{3+}-doped tungsten-tellurite glass and planar waveguides[J]. *J Inorg Mater*, 2005, **20**(4): 831-836.

[6] FAVRE A, LEE E, APOSTOLOPOULOS V, *et al*. Fabrication and characterization of planar and channel waveguides in bismuth-based oxide glasses[C]. *SPIE*, 2003, **4990**: 103-110.

[7] ZHOU Z, The buried channel optical waveguides on glass by high electric field technique[C], *SPIE*, 2006, **6351**: 635138-635141.

[8] BRIAN R W, SEPPO H. Advanced modeling and design of ion-exchanged glass waveguides and devices[C]. *SPIE*, 2004, **5451**: 402-413.

[9] SCHRÖFEL J, ŠPIRKOVÁ J, HÜTTEL I, *et al*. Low-loss optical waveguides fabricated by Li^{+} for Na^{+} ion exchange in Na_2O rich glass substrate[C]. *SPIE*, 2001, **4277**: 359-366.

[10] WONG S F, PUN E Y B and CHUNG P S. Er^{3+}-Yb^{3+} codoped phosphate glass waveguide amplifier using Ag^{+}-Li^{+} ion exchange[J]. *IEEE Photo Tech Lett*, 2002, **14**(1): 80-82.

[11] JIANG S, MYERS M and PEYGHAMBARIAN N. Er^{3+} doped phosphate glasses and lasers[J]. *J Non-Cryst Solids*, 1998, **239**(1&3):143-148.

[12] ZHAO S, CHEN B, HU J, *et al*. Planar waveguides formed in a new chemically stable Er^{3+}/Yb^{3+} co-doped phosphate glass[J]. *Chin Opt Lett*, 2005, **3**(2):101-102.

Ag^{+}-Li^{+}离子交换制作Er^{3+}/Yb^{3+}共掺磷酸盐玻璃平面光波导

赵士龙[1]，徐时清[1]，王宝玲[1]，胡丽丽[2]

(1 中国计量学院 材料科学与工程学院，杭州 310018)

(2 中国科学院上海光学精密机械研究所，上海 210018)

收稿日期：2006-10-15

摘　要：制备了化学稳定的Er^{3+}/Yb^{3+}共掺的磷酸盐玻璃，并在其中制作了用于光放大器和激光器的平面光波导．这种磷酸盐玻璃的失重速率为$4.7\times10^{-5}\,g\cdot cm^{-2}\cdot hr^{-1}$，小于Kigre公司商业化的磷酸盐玻璃QX/Er的失重速率．采用Ag^{+}-Li^{+}交换技术制作了平面光波导并用m-线光谱在632.8 nm测量了平面光波导的有效折射率．根据反WKB法得到折射率形貌，计算了离子交换参数如：离子交换深度、表面折射率，折射率改变和扩散系数等．

关键词：Ag^{+}-Li^{+}离子交换；平面光波导；磷酸盐玻璃

ZHAO Shi-long was born in 1975. He received his Doctorial degree from Shanghai Institute of Optics and Fine Mechanics, CAS in 2005. His research interests focus on fabrication of planar waveguide materials and devices for optical communication systems.