Effect of MAE on the properties of phosphate edge-cladding glasses

Fenggang Zhao (赵凤刚)[1,2], Guonian Wang (汪国年)[1], and Lili Hu (胡丽丽)[1]

[1]*Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800*

[2]*Graduate School of the Chinese Academy of Sciences, Beijing 100039*

Received February 13, 2007

Edge-cladding is a key factor in improving saturated small signal gain coefficient β_s of large laser disc glass. In this paper, the glasses were melted with traditional method. The influences of mixed alkali effect (MAE) on refractive index, thermal expansion coefficient α, glass transition temperature T_g, dilatometer softening temperature T_d, and relative chemical durability of phosphate edge-cladding glasses were studied. The results reveal that when $Li/(Na + Li) = 0.5$, T_g, T_d, and dissolution rate (DR) reach a minimal value. These results are preferred in phosphate edge-cladding glasses.

OCIS codes: 160.4760, 160.4670, 160.2750, 140.4480, 140.3380.

Inertial confinement fusion (ICF) and X-ray laser (XRL) are the basic project for national defense. Large aperture neodymium phosphate disc laser is the key component of high power solid state laser. In order to achieve high gain efficiency of main amplifier, great care should be taken to suppress parasitic oscillation. This phenomenon was first noted by Swain *et al.*[1] who reported a significant increase in gain by using an edge-cladding to absorb some of the amplified fluorescences.

Toratani *et al.*[2] introduced a general method of edge-cladding: making a slurry with a low melting temperature glass powder, which contains copper ions to absorb 1053-nm laser, and a dispersing agent: coating the slurry on the edge of the disc laser glass, and the coated glass is heated below the temperature at which the glass disc is softened and deformed, thereby melt-bond layer is formed between the low melting temperature glass and the edge of neodymium phosphate glass disc. In order to obtain high gain efficiency, the edge-cladding glasses must meet the following requirements[3,4]: the ability to absorb the light at 1053 nm, low welding temperature, good chemical durability and good thermal stability, and suitable refractive index and thermal expansion coefficient.

In our previous work[5], the effect of B/(B+Al) molar ratio on P_2O_5-ZnO-Na_2O-CuCl edge-cladding glass was discussed. The thermal expansion coefficient α is suitable, but glass transition temperature T_g is a little high and the refractive index is a little low. Mixed alkali effect (MAE) has long been used to adjust the properties of glasses, including T_g, α, chemical durability, density ρ, molar volume V_m[6,7].

In this paper, we study the effect of Li-Na MAE on the properties of P_2O_5-ZnO-Na_2O-Al_2O_3-B_2O_3-CuCl edge-cladding glass, explore a way to reduce T_g and dilatometer softening temperature T_d and to adjust the refractive index. Some properties of N_{31} neodymium phosphate laser glass are listed in Table 1[8].

Phosphate edge-cladding glasses were prepared from mixtures of reagent grade P_2O_5, NaH_2PO_4, Na_2CO_3, $Al(H_2PO_4)_3$, H_3BO_3, $Zn(H_2PO_4)_2$, CuCl, Li_2CO_3, and LiH_2PO_4. The compositions are listed in Table 2. About 30-g mixture was thoroughly dry mixing. After that, the batch was placed in an alumina crucible, initially heated at 300 °C for 1 h in order to evaporate water, then melted in air for 1 h at 1100—1150 °C. The melts were then cast into a preheated stainless steel plate and annealed at about 10 °C above T_g. After that, the glasses were stored in a desiccator for testing.

The parameters α, T_g, and T_d were determined by dilatometry (NETZSCH DIL 402EP), using a heating rate of 5 °C/min. The samples were 5 × 5 × 36 (mm). The chemical durability was determined by measuring the mass loss of polished glass samples after immersion into deionized water at 70 °C for 24 h. The dissolution rate (DR) was defined as the mass loss per unit surface area and unit time ($mg \cdot cm^{-2} \cdot h^{-1}$). Refractive indices of all glass samples were measured with the V-prism method. The refractive index at 1053 nm is obtained according to the values of n_d, n_c, n_f using Cauchy equation[9].

Figure 1 shows the dependence of refractive index on Li/(Li+Na) molar ratio, increasing with the addition of Li. The refractive index is proportional to the molar refractivity and inversely proportional to the molar

Table 1. Some Properties of N_{31} Glass

T_g (°C)	α (10^{-7} K^{-1})	n_{1053}	Shape	Size (mm)
430	128	1.53	Rectangle	600 × 300 × 40

Table 2. Batch Compositions (mol%) of Phosphate Edge-Cladding Glass

Sample	P_2O_5	Al_2O_3	B_2O_3	CuCl	Na_2O	Li_2O	ZnO
JXY-1	60	5	2	5	17		11
JXY-2	60	5	2	5	12.75	4.25	11
JXY-3	60	5	2	5	8.5	8.5	11
JXY-4	60	5	2	5	4.25	12.75	11
JXY-5	60	5	2	5		17	11

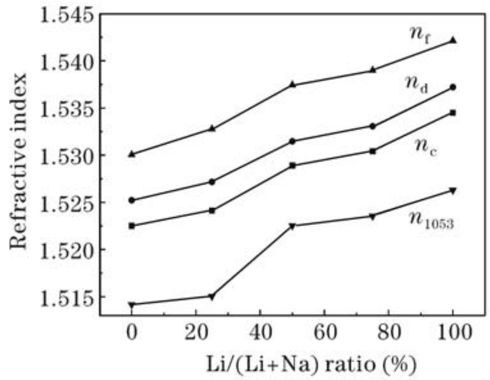

Fig. 1. Dependence of refractive index on Li/(Li+Na) molar ratio.

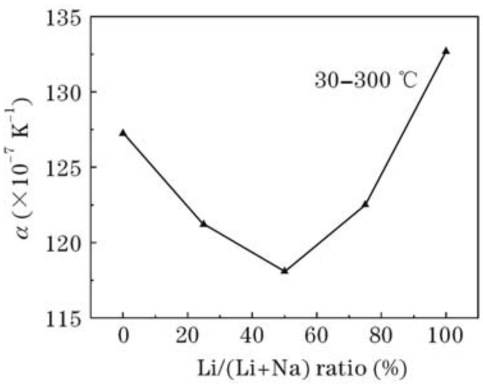

Fig. 2. Dependence of α on Li/(Li+Na) ratio.

volume. With increasing ionic radius, the refractivity and molar volume are also increased[10]. For large ions, the refractivity is the main factor, but for little ions, the molar volume is the main factor. Because Na^+ and Li^+ are small ions and $Li^+ < Na^+$, the refractivity increases linearly with the increase of Li/(Li+Na) ratio.

Figures 2 shows the dependence of α on Li/(Li+Na) molar ratio. α decreases with the addition of Li, and when Li/(Li + Na) = 0.5, it reaches a minimal value, about 7.2% deviation from linearity.

Figure 3 shows the dependences of T_g and T_d on Li/(Li+Na) molar ratio. T_g and T_d decrease with the addition of Li, and when Li/(Li + Na) = 0.5, they reach

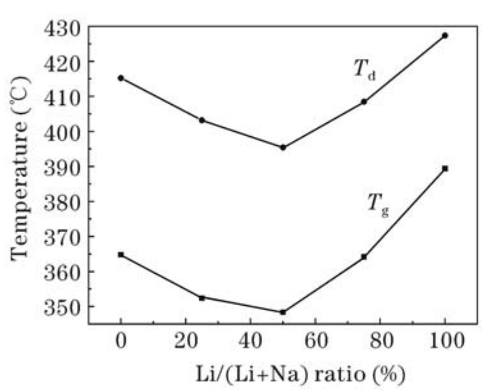

Fig. 3. Dependences of T_g and T_d on Li/(Li+Na) ratio.

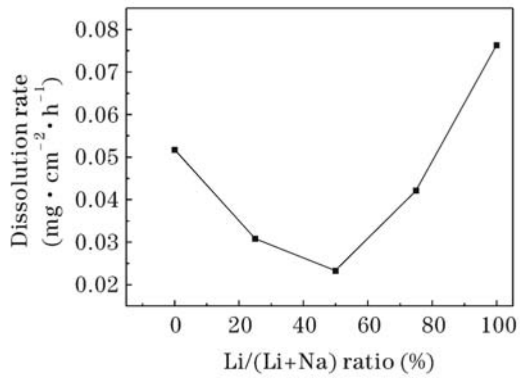

Fig. 4. Dependence of DR on Li/(Li+Na) ratio.

a minimal value, about 4.5% deviation for T_g and 4.8% deviation for T_d from linearity.

Figure 4 shows the dependence of DR on Li/(Li+Na) molar ratio. DR decreases with the addition of Li, and when Li/(Li + Na) = 0.5, it reaches a minimal value, about 54.8% deviation from linearity.

MAE is a phenomenon observed in many oxide glasses in which several ionic transport-related properties change as a function of composition in a highly non-additive fashion when one alkali oxide is replaced by another. The assumption made in the "random ion distribution model"[11] shows that two types of alkali ions in a mixed alkali glass have distinctly different conduction pathways, which means that A ions block the pathways for the B ions, and *vice versa*. Since the local structural environments of Na and Li ions are distinctly different, there is a large energy mismatch for Na jump to Li sites, and *vice versa*[12]. This fact in combination with the low dimensionality of the pathways of the nonstatistic distribution[13] of the cations causes the strong blocking effect in the mixed alkali glasses. Furthermore, there are all sizes of holes in the phosphate glasses, with the addition of a second alkali, the structure is more compact. The block effect and more compact structure are the reason for lower α, T_g, T_d, and higher chemical durability.

In conclusion, we investigated the effect of MAE on phosphate edge-cladding glasses. The results reveal that when Li/(Na+Li) = 0.5, T_g, T_d, and DR reach a minimal value, T_g has a 4.5% deviation, DR has a 54.8 deviation, for n_d, it has a 0.41% positive deviation compared with Li/(Na+Li) = 0. These results are preferred in phosphate edge-cladding glasses.

This work was supported by the National Natural Science Foundation of China under Grant No. 60607014. F. Zhao's e-mail address is zhao_fg@126.com.

References

1. J. E. Swain, R. E. Kidder, K. Pettipiece, F. Rainer, E. D. Baird, and B. Loth, J. Appl. Phys. **40,** 3973 (1969).
2. H. Toratani and Hidakamachi, "Edge-cladding glass of disc laser glass" US Patent 4217382 (Aug. 12, 1980).
3. Y. Asahara, Kawasaki, T. Izumitani, and Hino, "Sealing glass for laser glass" US Patent 3885974 (May 27, 1975).
4. Y. Asahara, T. Izumitani, and K. Nakagawa, "Sealing method for laser glass" US Patent 3966448 (June 29, 1976).

5. F. Zhao, Q. Dong, and L. Hu, Chin. Opt. Lett. **5,** 41 (2007).
6. X. Fang, C. S. Ray, and D. E. Day, J. Non-Cryst. Solids **319,** 314 (2003).
7. F. Muñoz, F. Agulló-Rueda, L. Montagne, R. Marchand, A. Durán, and L. Pascual, J. Non-Cryst. Solids **347,** 153 (2004).
8. C. Zhu, *Study of Edge-Cladding Technics in Suppressing Parasitic Oscillation of Phosphate Glasses* (in Chinese) (Shanghai Institute of Optics and Fine Mechanics, Shanghai, 1998).
9. G. Cao, H. Hu, and F. Gan, Acta Opt. Sin. (in Chinese) **25,** 72 (2005).
10. F. Gan, *Optical and Spectroscopic Properties of Glass* (Shanghai Scientific and Technical Publishers, Shanghai, 1992).
11. J. Swenson, A. Matic, C. Karlsson, L. Börjesson, C. Meneghini, and W. S. Howells, Phys. Rev. B **63,** 132202 (2001).
12. S. Balasubramanian and K. J. Rao, J. Non-Cryst. Solids **181,** 157 (1995).
13. J. Swenson and S. Adams, Phys. Rev. Lett. **90,** 155507 (2003).