The effects of B/(B+Al) ratio on glass formation regions and properties of phosphate edge-cladding glasses

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The glass-forming region of P_2O_5-Al_2O_3-B_2O_3-ZnO-Na_2O-CuCl system with different Al_2O_3 and B_2O_3 contents was studied. The dependence of glasses properties on B/(B+Al) ratio was investigated. The absorption coefficient of copper ion in a specific glass was measured. These results are very helpful to the designing of a cladding glass for large size neodymium phosphate glass.

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Phosphate glasses generally have relatively large thermal expansion coefficient, low optical dispersion and low glass transition temperature, making them candidates for technologically important materials, e.g., glass-to metal seals, laser hosts, and bio-compactable materials[1]. Understanding their structure is important to design glasses with specific properties for above applications. Because the range of glass-forming compositions is quite large and P has a formal charge of +5, phosphate glasses also offer an important opportunity to the fundamental structural investigation. The addition of Al_2O_3 to phosphate glass has significant effects on physical and chemical properties, including raising the glass transition temperature, decreasing the thermal expansion coefficient, and improving the chemical durability[2]. And the addition of B_2O_3 has long been known to improve the durability of phosphate glasses[3]. Alumino-phosphate glasses have mixed network structures of aluminate and phosphate. Borosilicate glasses have mixed network structure of borate and silicate. Such glasses often possess desirable combinations of properties that are difficult to obtain from compositions with only one network former. The glass properties can be controlled not only by varying the relative proportion of network formers, but also by controlling the coordination number of a particular cation.

In large aperture neodymium phosphate disc laser systems, great care should be taken to suppress parasitic oscillation phenomena that can reduce laser gain efficiency[4,5]. A general method of edge-cladding includes mixing a low fusion temperature glass powder, which contains copper ions to absorb 1053-nm laser, with a dispersing agent to form a slurry, coating the slurry on the edge of the disc laser glass, and heat-treating the coated glass below the temperature at which the disc glass is softened and deformed, thereby melt-bond is formed between the low fusion temperature glass and the edge of neodymium phosphate disc glass. Usually there are strict requirements on the highly agreements of refractive index and thermal properties of cladding and disc glasses. Montagne *et al.*[6] reported P_2O_5-ZnO-Na_2O system, which showed very low T_g (272 °C), but the chemical durability was poor. Toratani *et al.*[7] studied P_2O_5-ZnO-Na_2O-Al_2O_3-B_2O_3-CuO system, but the relationship between structure and properties was not discussed.

In this report, P_2O_5-ZnO-Na_2O-Al_2O_3-B_2O_3-CuCl glass was chosen as the candidate for edging cladding. In order to find a cladding glass which is compatible to our neodymium phosphate laser glass, the glass-forming regions of P_2O_5-ZnO-Na_2O-Al_2O_3-B_2O_3-CuCl system with different contents of Al_2O_3 and B_2O_3 were explored, the glasses properties dependent on B/(B+Al) ratio were investigated, and the absorption coefficient of copper ion in a specific glass was measured.

Phosphate edge-cladding glasses were prepared from mixtures of reagent grade P_2O_5, NaH_2PO_4, Na_2CO_3,

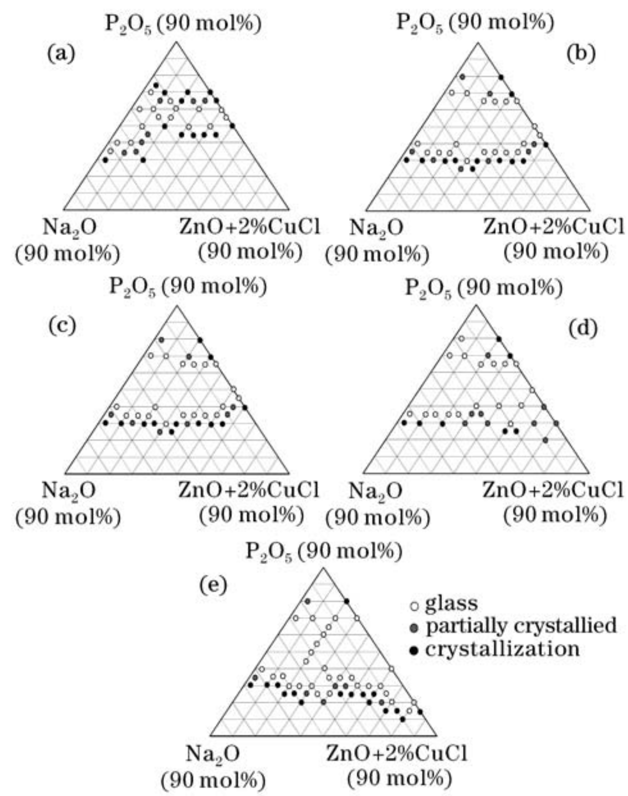

Fig. 1. Glass-forming regions of P_2O_5-ZnO(2% CuCl)-Na_2O system. (a) 10 mol% Al_2O_3; (b) 7 mol% Al_2O_3 + 3 mol% B_2O_3; (c) 5 mol% Al_2O_3+5 mol% B_2O_3; (d) 3 mol% Al_2O_3+7 mol% B_2O_3; (e) 10 mol% B_2O_3.

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Table 1. Nominal and Experimental Compositions (in mol%) of Edge-Cladding Phosphate Glasses

Sample	P_2O_5	Al_2O_3	B_2O_3[a]	CuCl[b]	Na_2O	ZnO	B/(B+Al) (%)
B-0	54	10	0	2	18	16	0
B-$0_{(ICP)}$	57.24	9.56	0.19	1.85	16.48	14.68	
B-30	54	7	3	2	18	16	30
B-$30_{(ICP)}$	57.47	6.60	2.30	1.91	17.23	14.49	
B-50	54	5	5	2	18	16	50
B-$50_{(ICP)}$	58.92	5.00	2.50	1.94	16.26	15.36	
B-70	54	3	7	2	18	16	70
B-$70_{(ICP)}$	59.34	3.04	4.24	1.92	16.93	14.52	
B-100	54	0	10	2	18	16	100
B-$100_{(ICP)}$	59.09	0.33	5.97	1.90	17.50	15.20	

a: the content of B_2O_3 is only for reference, for the large volatilization during sample preparation;
b: the ICP result is CuO instead of CuCl.

$Al(H_2PO_4)_3$, H_3BO_3, $Zn(H_2PO_4)_2$, and CuCl. First the glass-forming regions were investigated. They were shown in Fig. 1. For the glass formation region experiments, about 10-g mixtures were thoroughly dry mixed. After that, the batch was placed in an alumina crucible, and melted at 900—1250 °C for about 20 min. The melt was then cast into a preheated stainless steel plate and annealed at proper temperatures.

Several glasses were chosen to study the properties. Their nominal and experimental compositions are listed in Table 1. And about 50-g mixtures were thoroughly dry mixied. After that, the batch was placed in an alumina crucible, initially heated at 300 °C for about 1 h in order to evaporate water in the batch. 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 the glass transition temperature. After that, the glasses were stored in a desiccator for testing.

The experimental compositions were determined by an ICP-AES from American IRIS Intrepid.

The thermal expansion coefficient (α), glass transition temperature (T_g) and dilatometer softening temperatures (T_f) were determined by a horizontal dilatometry (NETZSCH DIL 402EP), using a heating rate of 5 °C/min. The size is $5 \times 5 \times 36$ (mm).

The relative chemical durability was determined by measuring the weight loss of polished glass samples after immersion into deionized water at 70 °C for 24 h. The dissolution rate was defined as the weight loss per unit surface area and unit time (day) (mg·cm^{-2}·d^{-1}).

Refractive indices of all glass samples were measured with the V-prism method. The refractive index at 1.053 μm is obtained according to the values of n_d, n_c, n_f using Cauchy equation[8].

Transmission spectrum was recorded with Perkin-Elmer Lambda 900UV/VIS/NIR spectrophotometer over a range of 300—1500 nm. For this measurement, the sample was polished and its size is $20 \times 10 \times 1$ (mm).

Figure 1 shows the dependence of glass-forming regions on the contents of Al_2O_3 and B_2O_3. Due to the severe evaporating, the glass-forming regions were not given when P_2O_5 mole percent exceeded 72 mol%.

With the addition of Al_2O_3, the glass-forming regions become narrower. The composition with 10 mol% Al_2O_3 has the smallest glass-forming regions, as shown in Fig. 1(a). With the addition of B_2O_3, the glass-forming regions become wider. The composition with 10 mol% B_2O_3 has the widest glass-forming regions, as shown in Fig. 1(e).

In the compositions studied, the coordination of B^{3+} is mainly tetrahedral, B(4) units are a “glass former”. Therefore the incorporation of B(4) units into the chain-like phosphate glass structure results in the enhancement of dimensionality of the structural network from one dimension to three dimension. Such a cross-linking of structural network gives wider glass-forming regions with an increasing content of B_2O_3. It is consistent with the result of Ref. [9] that in phosphate-rich borophosphate glasses, B(4) units are preferred than B(3) units.

In aluminophosphate glasses, the coordination of Al^{3+} will be either tetrahedral or hexahedral. Al(4) is often considered as a “glass former”, whereas Al(6) is considered as a “glass modifier”. So in the compositions studied, the coordination of Al^{3+} must be mainly hexahedral, and aluminum has the similar role with sodium as modifier. Because Al-O bonds are stronger and shorter than Na-O bond, and Al has more electrons than Na, the glass-forming regions become narrow with the increase of Al_2O_3. It is consistent with the result of Ref. [2] that Al(6) dominates the glass structure when up to $\sim$ 15 mol% Al_2O_3 is added to $NaPO_3$, and Al(4) forms

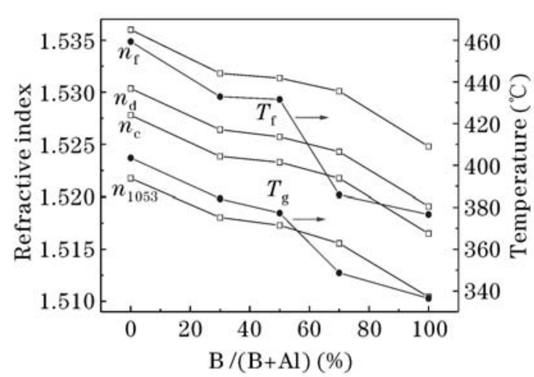

Fig. 2. Dependence of the refractive index, T_g, and T_f on the B/(B+Al) ratio.

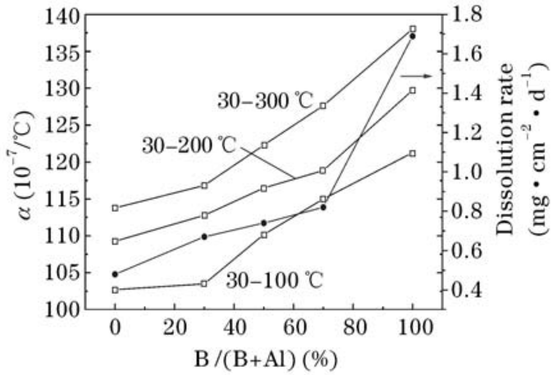

Fig. 3. Dependence of relative chemical durability and thermal expansion coefficient α on the B/(B+Al) ratio.

only at higher Al_2O_3 contents.

Figures 2 and 3 show the dependence of the glass refractive indices, T_g, T_f, relative chemical durability, and thermal expansion coefficients on B/(B+Al) ratio.

It can be seen from Fig. 2 that there is a linear decrease of the refractive indices due to the increase of B/(B+Al) ratio. The refractive index is proportional to the molar refractivity and inversely proportional to the molar volume. With increasing ionic radius, the refractivity and molar volume are all raised[10]. The changes of refractive index on the ratio of B/(B+Al) indicate that the refractivity increases more rapidly than the molar volume with the increase of Al_2O_3.

There is an obvious decreases of T_g and T_f with the increase of B/(B+Al) ratio. Both Al_2O_3 and B_2O_3 have the effects on raising the glass transition temperature and dilatometer softening temperatures[11,12]. Figure 2 indicates that the Al_2O_3 has more obvious effort on the increase of T_g and T_f than B_2O_3. The changes of T_g, T_f on the ratio of B/(B+Al) show that Al is the dominate factor.

Because Al_2O_3 contributes more than B_2O_3 and greatly improves the chemical durability of phosphate glass, and there is a monotonic increase of thermal expansion coefficient. With the increase of B/(B+Al) ratio, the relative chemical durability of the compositions becomes poor, as shown in Fig. 3. It indicates that Al_2O_3 and B_2O_3 have different effects on the thermal expansion coefficient of phosphate glass.

Figure 4 is the transmission spectrum of sample B-50 which contains copper ions. There is a strong band in the range of 700—1400 nm, which is assigned to the absorption of Cu^{2+}. In the original batch, the reductive state of copper is +1, but in the melting process, the Cu^+ is oxidized into Cu^{2+}, and Cu^+ itself has no absorption in this range.

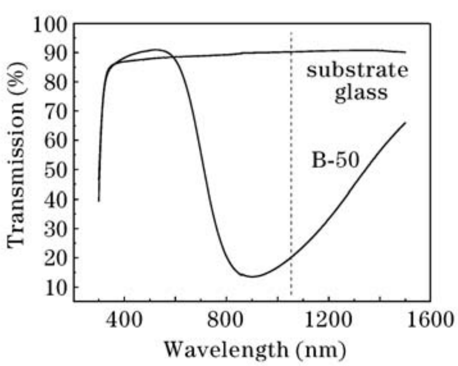

Fig. 4. Transmission spectrum of sample B-50.

The absorption coefficient of sample B-50 is calculated from[13]

$$\alpha = \ln(T_0/T)/L, \tag{1}$$

where L is the thickness of the sample (cm), T_0 the transmission percentage of B50-0 at 1.053 μm, and T the transmission percentage of B-50 at 1.053 μm. From the calculating, the absorption coefficient of sample B-50 is 15.05 cm^{-1}.

The edge-cladding glass for neodymium phosphate laser glass has been investigated based on P_2O_5-ZnO-Na_2O-B_2O_3-Al_2O_3-CuCl system. The effects of Al_2O_3 and B_2O_3 on glass formation region, chemical durability, refractive index, glass transition, and dilatometer softening temperatures, and thermal expansion coefficient were studied. In P_2O_5-ZnO-Na_2O-B_2O_3-Al_2O_3-CuCl system, when the total mole percent of Al_2O_3 and B_2O_3 is 10 mol%, the glass-forming region becomes narrower with the increase of Al_2O_3. The glass-forming region becomes wider with the increase of B_2O_3. The increase of B_2O_3 is detrimental to chemical durability of glass. The refractive index, glass transition, and dilatometer softening temperatures decrease with the increase of B_2O_3. While thermal expansion coefficient increases with the increase of B_2O_3. The absorption coefficient of the P_2O_5-ZnO-Na_2O-B_2O_3-Al_2O_3-CuCl with 2 mol% CuCl is 15.05 cm^{-1}. Comparing with N_{31} laser glass, the T_g of the edge-cladding glasses is a little higher, and the refractive index is still a little lower. The further researching work is in process.

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