Effects of SiO₂ on Properties and Structures of

Li₂O-MgO-Al₂O₃-P₂O₅ Glasses

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ABSTRACT

Effects of substitutions of SiO₂ for Al₂O₃ and P₂O₅ in a single baseline phosphate glass, Nd³⁺ : Li₂O-MgO-Al₂O₃-P₂O₅, on glass structure and properties are investigated. For glasses with Al₂O₃ replaced by SiO₂, coordination number of Al becomes larger, and P=O bond and Si with six oxygens coordinated emerge. For glasses with P₂O₅ replaced, coordination number of Al becomes smaller, P(Q²) changes to P(Q¹) and all Si units are four coordinated. The reason for coordination number of Al and Si change may come from the variation of terminal oxygen quantity. The relationship between glass structure and physical (ρ , T_g , CTE), mechanical (E), and optical properties (n_D , σ_{em} , $\Delta\lambda_{em}$) are builded.

1. Introduction

In recent years, silicophosphate glasses have been investigated for its unique properties such as good mechanical properties, chemical stability and photosensitivity [1-4]. Silicophosphate glasses can be applied in many aspects such as fuel cell, optical fibers, biomaterials and optical amplifiers [5-8].

Studies of network structures of the silicophosphate glasses have recently gained a considerable attention [9-11], which remains active because of complexity of the glass network involving mixed glass formers, P₂O₅ and SiO₂, plus Al₂O₃ and other

variations of modifiers of alkalis and alkaline earth oxides. Larsen, et. al. [12] performed a Raman spectroscopic study of $\text{SiO}_2\text{-P}_2\text{O}_5\text{-Al}_2\text{O}_3\text{-MgO}$ glass system and reported some degree of changes for position and intensity of the bands near 605 cm^{-1} , 723 cm^{-1} , 1305 cm^{-1} , etc., as a function of SiO_2 concentration while other oxides changed simultaneously. Without using NMR (nuclear magnetic resonance) technique to aid structure analysis, it was not possible to gain more accurate structural information for local environments of Al-O, Si-O, and P-O although both four-fold and six-fold aluminum species were proposed to exist in the glasses with O/P ratio from 3.27 to 4.05. Besides, coordination of silicon in the glass was not studied[12]. For $\text{SiO}_2\text{-P}_2\text{O}_5\text{-Na}_2\text{O}$ glass system, on the other hand, changes in both phosphate network and coordination of Si-O were reported[13].

Raman and infrared (IR) spectroscopy are powerful tools for characterization of glass structures, combining with curve-fitting method to elucidate network structure evolution as functions of glass compositions [14-16]. Magic angle spinning nuclear magnetic resonance technique (MAS NMR) enables quantitatively probing glass network structures in depth[17-19]. In our study reported here, a baseline glass, $\text{SiO}_2\text{-P}_2\text{O}_5\text{-Al}_2\text{O}_3\text{-Li}_2\text{O-MgO}$ glass, was chosen to systematically investigate effects of SiO_2 substitution for Al_2O_3 and P_2O_5 on properties relevant to laser glass applications without changing concentrations of Li_2O and MgO . Also included in the study were detail structure characterizations by using Raman and ^{29}Si , ^{27}Al , and ^{31}P MAS NMR techniques.

2. Experimental

Two series of phosphate based glasses were designed from a single baseline (BL, $x=0$) in our study: A-series, $x\text{SiO}_2\text{-}65\text{P}_2\text{O}_5\text{-(}15\text{-}x\text{) Al}_2\text{O}_3\text{-}10\text{Li}_2\text{O-}10\text{MgO}$ ($x = 3, 6, 9, 12, 14.5\text{ mol\%}$), and P-series, $x\text{SiO}_2\text{-(}65\text{-}x\text{) P}_2\text{O}_5\text{-}15\text{Al}_2\text{O}_3\text{-}10\text{Li}_2\text{O-}10\text{MgO}$ ($x = 4, 8, 12, 16\text{mol\%}$). For both series, 1wt% Nd_2O_3 and 0.5wt% Sb_2O_3 were added. Table 1 details their target glass compositions. Batches of the glasses composed of analytical grade chemicals of SiO_2 , Al(OH)_3 , $\text{Al(H}_2\text{PO}_4)_3$, LiHPO_4 , $\text{Mg(H}_2\text{PO}_4)_2$, Nd_2O_3 , and Sb_2O_3 . Each batch mixture was thoroughly mixed and melted in a quartz crucible at 1400°C for 2 hour. To minimize hydroxyl concentration in the glass, dry CCl_4 was

used as bubbling gas during glass melting. After fining, each melt was casted into a stainless steel mold and the mold was transported to a preheated muffle furnace to anneal the glass block at 550°C for 150 min; the furnace was subsequently cooled to room temperature at a rate of 10°C/h. The annealed samples were cut, ground, and polished for various property and Raman measurements, whereas the NMR measurements used pulverized glass samples.

Table. 1 Composition of the Li₂O-MgO-Al₂O₃-P₂O₅-SiO₂ glasses (mol%)

Sample	P ₂ O ₅	SiO ₂	Al ₂ O ₃	Li ₂ O	MgO	O/P	Doping
BL	65.0	0.0	15.0	10.0	10.0	3.00	1.0 wt% Nd ₂ O ₃ , 0.5wt% Sb ₂ O ₃
A1	65.0	3.0	12.0	10.0	10.0	2.98	
A2	65.0	6.0	9.0	10.0	10.0	2.95	
A3	65.0	9.0	6.0	10.0	10.0	2.93	
A4	65.0	12.0	3.0	10.0	10.0	2.91	
A5	65.0	14.5	0.5	10.0	10.0	2.89	
P1	61.0	4.0	15.0	10.0	10.0	3.10	
P2	57.0	8.0	15.0	10.0	10.0	3.21	
P3	53.0	12.0	15.0	10.0	10.0	3.34	
P4	49.0	16.0	15.0	10.0	10.0	3.49	

The refractive index (n_D) and density (ρ) of the glass samples were measured using the prism minimum deviation method and Archimedes method, for which distilled water was used as immersion liquid), respectively. An in-situ nano-mechanical tester (TriboIndenter, Hysitron, America) was used to measure glass Young's modulus (E). Fracture toughness measurement (K_{IC}) of the glasses was determined by using a universal material test machine (INSTRON—5566, America). Glass transition temperature (T_g) was determined from the method measuring glass linear thermal expansion using a dilatometer (NETZSCH DIL 402EP, Germany). Thermal conductivity of the glasses was measured by using a rapid thermal equipment (QTM-500, KEM, Japan). The emission spectra of the glasses were recorded using

FLS 920 spectrofluorometer excited by 808nm laser diode (Edinburgh Analytical Instruments, Edinburgh, UK). Based on the emission spectra, neodymium (Nd^{3+}) emission cross section (σ_{em}) and emission bandwidth ($\Delta\lambda_{\text{em}}$) of the glasses were calculated using the same method as shown in reference [20]

Raman spectra of the glasses were acquired using Renishaw Invia microRaman spectrophotometer using the 488 nm excitation line. IR absorption spectra were acquired using a Nexus FTIR spectrometer. MAS NMR spectra were acquired using a Bruker Advance III HD 500M spectrometer at the magnetic field strength of 11.7 T with a 4 mm rotor. ^{29}Si MAS NMR spectra were recorded at the spinning rate of 8 kHz, using pulse length of 6.2 μs and relaxation time of 30 s. ^{27}Al MAS NMR were recorded at the spinning rate of 12 kHz, using pulse length of 0.83 μs and relaxation time of 0.5s. ^{31}P MAS NMR were recorded at the spinning rate of 12 kHz, using pulse length of 4.7 μs and relaxation time of 60s. All measurements were performed at room temperature.

3. Results

3.1 Glass properties

Fig.1 shows glass density, refractive index, and Young's modulus of the A- and P-series. Both ρ and E decrease with the substitution of SiO_2 for Al_2O_3 and P_2O_5 . The same trend holds for n_D of the P-series, while the A-series changes little. The most significant change is seen on E when SiO_2 substitute for Al_2O_3 , implying Al_2O_3 affects Young's modulus more than P_2O_5 and SiO_2 reduces Young's modulus the most among the three oxides.

Fig.1 Effects of SiO₂ substitution for Al₂O₃ (A-series) and P₂O₅ (P-series) on (a) glass density, ρ , (b) refractive index, n_D , and (c) Young's modulus, E .

Fig. 2 shows glass transition temperature, coefficient of thermal expansion, emission coefficient cross section, and emission bandwidth of the A-series and P-series. In general glasses of the P-series exhibit more or less monotonic property changes, similar to the changes of ρ , n_D , and E as SiO₂ gradually substitutes for P₂O₅. The A-series, however, shows more complex, nonlinear responses of T_g , CTE, σ_{em} , and $\Delta\lambda_{em}$ to the SiO₂ substitution for Al₂O₃.

Fig. 2 Effects of SiO₂ substitution for Al₂O₃ (A-series) and P₂O₅ (P-series) on glass transition temperature, T_g (a), coefficient of thermal expansion, CTE (b), emission cross section, σ_{em} (c), and emission bandwidth, $\Delta\lambda_{em}$ (d).

3.2 Characterizations of glass structures

3.2.1 Raman spectroscopic investigation

Fig. 3 shows the measured, Raman spectra of the BL glass and glasses of the A- and P-series, covering the frequency range between 100 cm⁻¹ and 1500 cm⁻¹. The spectra were normalized by their maximum intensity and vertically shifted for clarity. There are two characteristic frequency regions, 500 cm⁻¹ - 900 cm⁻¹ and 900 cm⁻¹ - 1400 cm⁻¹, over which glass structural information can be deduced.

Fig.3 (a) Raman spectra of glasses with Al₂O₃ replaced by SiO₂; (b) Raman spectra of glasses with P₂O₅ replaced by SiO₂

Overall, the bands over the frequency range of 500 cm⁻¹ - 900 cm⁻¹ are related to

vibrational modes of the bridging oxygen atoms (*BOs*) of the phosphate network and the bands over the frequency range of 900 cm^{-1} - 1400 cm^{-1} represent a mixture of vibrational modes that are associated with Q^1 (or $(\text{PO}_4)^{2-}$ with 1*BO*), Q^2 (or $(\text{PO}_4)^-$ with 2*BOs*), and Q^3 (or (PO_4) with 3*BOs* and one terminal double bond oxygen ($\text{P}=\text{O}$) structural units [21-23]. The overall characteristic changes of the bands can be qualitatively summarized as follows.

For the A-series shown in Fig. 3(a), relative to the BL glass, four noticeable changes are: intensity increase of the 625 cm^{-1} band, position shift to higher wavenumber of the 705 cm^{-1} band, position shift to lower wavenumber of the 1210 cm^{-1} band, and intensity increase of the 1350 cm^{-1} band as SiO_2 is gradually introduced into the BL glass, replacing Al_2O_3 . For the P-series shown in Fig. 3(b), similar changes of these bands are noted; however, the band near 1350 cm^{-1} seems to be stable with little change as SiO_2 is gradually introduced into the BL glass, replacing P_2O_5 . Also noted is that the 625 cm^{-1} band is more or less symmetric for the P-series, whereas it becomes more asymmetric at higher SiO_2 and lower Al_2O_3 for the A-series. As will be shown later by ^{29}Si MAS NMR analysis (cf. Fig.5) that SiO_2 in the A-series contains both six-fold (SiO_6 or $\text{Si}(\text{PO})_6$) and four-fold (SiO_4 or $\text{Si}(\text{PO})_4$) coordinated silicon units, while only SiO_4 or $\text{Si}(\text{PO})_4$ tetrahedral units are found in the P-series.

Besides, vibrational modes of Si-O-Si (or T^n) should be expected to exist over the region of 900 cm^{-1} - 1220 cm^{-1} , where T^n represents the silica structural units with the *n*-number of *BOs*. However, identification of the silicate species from the spectra is not possible due to line broadening and overlapping of many vibrational modes from the multiple structural units. An improved spectrum analysis will be discussed later using Raman difference spectrum (RDS) analysis in conjunction with band assignments reported from the literature, plus chemical information from ^{29}Si MAS NMR measurements to be discussed later.

3.2.2 Nuclear magnetic resonance spectroscopic investigation

Fig.4 ^{31}P NMR spectra of glasses with Al_2O_3 or P_2O_5 replaced by SiO_2

Fig. 4 shows ^{31}P MAS NMR spectra of the same sets of the glasses. A dominant resonance band of the glasses with an iso-chemical shift (δ_{iso}) centered around -30 ppm was evident; the band is more or less symmetric and broad, covering the chemical shift from -10 ppm to -60 ppm. Also existed are spinning sidebands from chemical anisotropy of the phosphate species responsible for each respective central resonance due to magic angle spinning [24]. In literature, Q^1 , Q^2 , and Q^3 groups of the phosphate units are reported to have δ_{iso} values around (+6 ppm, -6 ppm), (-14 ppm, -32 ppm), and (-36 ppm, -55 ppm), respectively. Because of the symmetric band shape with δ_{iso} near -30 ppm, plus a small tail on each side, one may postulate that predominant structural units in the A-series, including the BL glass, are of Q^2 . The assumption is consistent with their overall metaphosphate network structure as defined by the O/P ratio (2.89 to 3.00).

For the P-series, the resonance band center line shifts from -30 ppm to near -25 ppm at higher SiO_2 , or lower P_2O_5 , which implies possible increase in Q^1 units at the expense of Q^2 units; the speciation reaction is not unexpected based on the increase of the O/P ratio from 3.00 to nearly 3.50, i.e., the metaphosphate-like network structure of the BL glass gradually transforms to the pyrophosphate-like network structure [21, 24]. For both series, there exists a small amount of Q^3 units containing $\text{P}=\text{O}$, which is consistent with the Raman analysis showing the presence of the 1350 cm^{-1} band [16, 21]

Fig.5 ^{27}Al NMR spectra of glasses with Al_2O_3 or P_2O_5 replaced by SiO_2

Fig. 5 shows ^{27}Al MAS NMR spectra of the same two sets of glasses. There are three distinctive resonance bands with δ_{iso} values centered near -19 ppm, 5 ppm, and 35 ppm, respectively and they can be assigned to six-fold (AlO_6 or Al(PO)_6), five-fold (AlO_5 or Al(PO)_5), and four-fold (AlO_4 or Al(PO)_4) coordinated aluminum, respectively [19, 25]. In the following discussions, both structural expressions are used interchangeably.

Brow [19, 25] reported that all of aluminum were six-fold, AlO_6 , in configuration for metaphosphate glass compositions of $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-P}_2\text{O}_5$. For the compositions under our investigation, the A-series with predominantly metaphosphate network, AlO_6 units are dominant; small proportions of AlO_5 and AlO_4 units, however, also exist, both of which decrease with SiO_2 substitution for Al_2O_3 (cf. Fig. 5(a)). For the P-series, on the other hand, all three types of AlO_x ($x = 6, 5, 4$) coexist independent of SiO_2 , while Al_2O_3 is kept constant. The SiO_2 substitution for P_2O_5 , however, affects the proportions of each AlO_n units, specifically increase in SiO_2 results in reduction in AlO_6 units and increase in both AlO_5 and AlO_4 units (cf. Fig. 5(b)).

Fig.6 ^{29}Si NMR spectra of glasses with Al_2O_3 or P_2O_5 replaced by SiO_2

Fig.6 illustrates ^{29}Si MAS NMR spectra of some of the SiO_2 -containing glasses from the A- and P-series. The replacement of Al_2O_3 by SiO_2 , illustrated in Fig. 6(a), results in formation of both four-fold SiO_4 or $\text{Si}(\text{PO})_4$ and six-fold SiO_6 or $\text{Si}(\text{PO})_6$ in the glasses which have metaphosphate network structure based on their O/P ratios being close to 3.0. The coordination of silicon assignments are based on their resonance bands with δ_{iso} centered at -115 ppm and -213 ppm, respectively[17, 26]. For the cases of P_2O_5 replacement by SiO_2 , however, only one resonance band with δ_{iso} centered at -119 ppm is found; implying only SiO_4 tetrahedron units stable independent of the level of SiO_2 substitution as the metaphosphate network are transformed to the pyrophosphate network according to their O/P ratios.

4. Discussion

4.1 Glass structure

Network of the phosphate glass can be characterized by their perspective O/P ratio [21]. Metaphosphate glass has the O/P ratio of 3.0; its network is primarily composed of Q^2 units. For the A-series, a slight decrease in the O/P ratio from 3.0 to 2.89, as more Al_2O_3 replaced by SiO_2 , favors the generation of Q^1 and Q^3 units at the expense of Q^2 units. The expected speciation reaction is qualitatively supported by the Raman spectroscopic study, i.e., the Raman band intensity near 1350 cm^{-1} , which is associated with $\text{P}=\text{O}$ in the Q^3 units [16] and the band near 1210 cm^{-1} , representing a symmetric stretching mode of Q^2 units, $\nu_s(\text{PO}_2)$ of Q^2 , shifted to lower frequency (cf. Fig.4 (a)). The low-frequency shift suggests the increase in the contribution of symmetric stretching mode from Q^1 units, $\nu_s(\text{PO}_2)$ of Q^1 units. However, overall the O/P ratio change is not significant; it can be seen that the chemical shift of the dominant resonance band in the ^{31}P MAS NMR spectra changes little, implying that the glasses in the A-series are of metaphosphate network structure.

For the P-series, with SiO_2 substitution for P_2O_5 , the O/P ratio changes significantly from 3.00 to 3.49, implying that the network structure ought to transform

from metaphosphate to pyrophosphate, generating more Q^1 at the expense of Q^2 units. Raman spectra of the P-series exhibits more significant shift of the 1210 cm^{-1} band to lower frequency as well as the increase in the band intensity. On the other hand, there is little change in Q^3 units as represented by the band near 1350 cm^{-1} . In addition, δ_{iso} of the dominant ^{31}P MAS NMR band also exhibits more significant, positive shift, implying more Q^1 units formed.

The network structure evolution seen in the A- and P-series can be further examined by using Raman difference spectrum analysis (RDS) as follows. Fig. 7 shows the RDS spectra for both sets of the glasses, which are created by subtracting the BL glass spectrum from each spectrum of the modified glasses. The RDS bands with peak positions from 615 cm^{-1} to 665 cm^{-1} represent symmetric stretching mode of *BOs*, i.e., $\nu_s(\text{P-O-P})$. Its intensity change for the A-series is more pronounced than that for the P-series. The RDS band near 700 cm^{-1} represents $\nu_s(\text{P-O-P})$ of Q^2 units. Clearly, Its intensity decreases continuously for the P-series, implying reduction of Q^2 units as a result of SiO_2 substitution for P_2O_5 . In terms of *NBOs* vibration mode, $\nu_s(\text{PO}_2)$ of Q^2 units near 1220 cm^{-1} also suggests that the RDS band is fluctuated about zero for the A-series, but decreases monotonically for the P-series. For the A-series, $\nu_s(\text{P=O})$ of Q^3 units shows significant increase, whereas little change for the P-series. The findings suggest that increase in SiO_2 at the expense of Al_2O_3 favors the speciation reaction as $2Q^2 \rightarrow Q^1 + Q^3$, resulting in increase in P=O bond in the glass from new Q^3 units formed. Although significant changes in the RDS band between 1160 cm^{-1} and 1190 cm^{-1} are evident (cf. Fig. 7), it is impossible to separate vibration modes of Si-O-Si in terms of T^n species ($n=2, 3, 4$ from low to high frequency) from the vibrational modes of the related phosphate units. It is, however, expected that the band shift and intensity increase are related to incorporation of SiO_2 in the phosphate network for both series, which is more significant for the P-series, in which P_2O_5 is replaced by SiO_2 .

Fig. 7 Raman difference spectrum of the glasses with Al_2O_3 or P_2O_5 replaced by SiO_2

In our study, ^{27}Al MAS NMR results show that there are three types of aluminum coordination in the $\text{Li}_2\text{O-MgO-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses with and without SiO_2 , which are AlO_4 , AlO_5 , and AlO_6 . For the A-series with predominantly metaphosphate network structure, AlO_6 unit is a major species and AlO_4 and AlO_5 units are minor. For the P-series, its network moving from metaphosphate to pyrophosphate, all of AlO_4 , AlO_5 , and AlO_6 coexist with significant proportions of each at constant Al_2O_3 . The results are in agreement with findings from $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses as well as $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses, i.e., the average Al-O coordination number depends on the O/P ratio, starting with AlO_6 at the O/P ratio 3.0 and decreasing as the O/P ratio becomes higher from 3.0 to 4.0 [19]. For $\text{ZnO-Al}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses, the three types of aluminum species, $\text{AlO}_{4,5,6}$, also coexist over a wide range of O/P ratio from 2.99 to 3.80.

Although the coordination numbers are different for the these two glasses with

similar ratio O/P, a trend can be deduced that the coordination number of Al increases as content of TOs (terminal oxygens) available to coordinate Al enhancing. Hopper has shown that when TOs available to coordinate network modifier ion was greater than the coordination number, then those cation polyhedra could be incorporated into phosphate structure without needing to share TOs with other metal cation polyhedra[27]. When number of TOs was less than coordination number, some of the cation polyhedra must share TO. If one assumes that these Li and Mg do not share TOs with each other or with any Al-polyhedra and all Si is 4-coordinated, the number of TOs remaining per Al can be calculated from the molar fractions of the glass compositions according to:

$$\frac{TO}{Al} = \frac{6[Al_2O_3] + 2[P_2O_5] - 2[MgO] - 3[Li_2O]}{2[Al_2O_3]} \quad (0.1)$$

The Nd_2O_3 and Sb_2O_3 is not considered in this equation due to their low concentration and coordination number of Mg and Li are 4 and 5 respectively[28]. The calculated value of TO/Al is 4 for P1 glass with O/P nearly 3. This is different number with the detected Al coordination condition with 6-coordinated Al-polyhedra dominated. This maybe come from Mg/Li sharing non-bridging oxide with each other or Al. But this calculated value gives a variation trend of number of TOs coordinated to Al. With Al_2O_3 replaced by SiO_2 , the value changes from 4.25(A1) to 33(A5), meaning that the available TOs coordinated to Al increase. So proportion of 4,5-coordinated Al decreases and nearly all Al polyhedra are six-coordinated in A5 glass. There is a very different trend for the series of glasses with P_2O_5 replaced by SiO_2 , due to decrease of the number of TOs coordinated to Al from 4(BL) to 2.93(P4). For BL glass with no SiO_2 included, the 4, 5 and 6 coordinated Al indicates $Al(OP)_4$, $Al(OP)_5$ and $Al(OP)_6$ units, respectively[26]. Although intensities of Peaks of ^{27}Al NMR spectra changes with SiO_2 content variation, peak positions do not change, meaning that second neighbour ion does not change and no $Al(OSi)_4$, $Al(OSi)_5$ and $Al(OSi)_6$ groups generated.

In literature, bending modes of SiO_4 and SiO_6 units, $\delta(^{[4]}Si-O-^{[4]}Si)$ and $\delta(^{[4]}Si-O-^{[6,5]}Si)$, were proposed over 500 cm^{-1} - 600 cm^{-1} range, stretching of SiO_6 , $\nu(^{[6]}Si-O-^{[6]}Si)$ near 740 cm^{-1} , and asymmetric stretching, $\nu_{as}(^{[4]}Si-O-^{[6,5]}Si)$, over 940

- 990 cm^{-1} [29, 30]. Over the above cited frequency ranges, Raman spectra of the glasses cannot provide clear information about their existence because of overlapping of multiple vibration modes of the related structures. However, from the RDS spectra, clearly shown is a significant increase of the relative scattering intensity, plus band shift from 665 cm^{-1} to 600 cm^{-1} , for the A-series and similar, but modest changes for the P-series. Combining both ^{29}Si MAS NMR and RDS spectroscopic results, it is plausible to consider the Raman bands near 600 cm^{-1} contain contributions from SiO_4 or Si(PO)_4 and SiO_6 or Si(PO)_6 units.

Based on literature [31], we tentatively assigned the resonance band near -213 ppm as six-fold silicon bonded with PO_4 as Si(OP)_6 because $^{[6]}\text{Si-O-}^{[6]}\text{Si}$ or Si(OSi)_6 should have a more positive δ_{iso} value [32]. Miyabe et al. [33] and Hermansen et. al. [34] proposed that SiO_6 units are created by forming bonding with two Q^2 units of phosphate network and one SiO_4 unit, resulting an octahedral structure sharing only the corners with the adjacent PO_4 tetrahedral units, while additional nominal charges of the SiO_6 units are compensated by nearby modifier ions. However, the previous work cannot explain necessary conditions governing formation of SiO_6 or it cannot explain the effects of SiO_2 substitutions for Al_2O_3 and P_2O_5 on formation of SiO_6 as seen in our study. With Al_2O_3 replaced by SiO_2 , Si(OP)_6 units are detected by ^{29}Si NMR, but these units can not form in the P series. As discussed for Al coordination, terminal oxygen in the glass plays a crucial role in the cation coordination transfer [35]. Because the microscopic optical basicity difference between P-O-Al(4) and P-O-Al(6) is smaller than that between P-O-Si(4) and P-O-Si(6), transfer from Al(OP)_4 to Al(OP)_6 happen first when terminal oxygen is abundant [36]. As shown in Fig.5 and Fig.6, Si(OP)_6 units emerge only when all Al atoms in glass are 6-coordinated. That may be the same reason for the result that 6-coordinated Si disappears when Al_2O_3 replacing P_2O_5 by R. Dupree [26].

As discussed previously, the O/P ratio affects phosphate network structure; as the network evolves from metaphosphate to pyrophosphate, distributions of both AlO_x ($x = 4, 5, 6$) and SiO_x ($x = 4, 6$) change significantly. It can be seen that SiO_6 units form only in the A-series that contain predominantly AlO_6 units, whereas disappearance of

SiO₆ units in the P-series that contain appreciable amounts of AlO₄ and AlO₅ besides AlO₆. It follows that there is a possibility that the stability of SiO₆ units in the phosphate glass is influenced by available AlO₆ units in the glass.

4.2 Relationships between properties and structure

The decrease in density with replacement of Al₂O₃/P₂O₅ by SiO₂ is mainly due to the glass structure variation. In the P series, the replacement of Al(OP)₆ with more open Al(OP)₄ structures induces a more open glass structure and lower glass density. In the Al series, some P(Q²) units change to P(Q³) units with a P=O double bond, and the total Al(OP)₆ content decreases. Huidan Zeng et al. has shown that as six-coordinated Si can make a tight network in Na₂O-SiO₂-P₂O₅ glasses[9]. But as discussed above, the SiO₆ emerges only when glass has not enough Al to connect with the redundant terminal oxygens. And in consideration of the hardness of coordination number change of Si atom, the content of 6-coordinated Si formed to neutralize terminal oxygen is lower than that of Al atom. So replacement of Al₂O₃ by SiO₂ also makes a more open network structure and a low glass density.

As shown in Fig.1, glass refractive index in present study decreases as SiO₂ addition. But variation extent of refractive index in Al series is much smaller than that of P series. Given that the extent of density variation in these two series is nearly the same, average polarizability of units in glass has a greater impact on refractive index in the Al series. As Al₂O₃ replaced by SiO₂, average coordination number increases and some Si atoms present as six-coordinated. This variation induces a larger molar refraction due to the higher average polarizability of oxygen ion. When P₂O₅ replaced by SiO₂, all Si atoms are four-coordinated and average coordination number of Al atom decreases, resulting in more bridging oxygen, lower average polarizability of oxygen ion and smaller molar refraction of this kind of glass.

In terms of the responses of glass T_g and CTE, substitution of SiO₂ for either Al₂O₃ or P₂O₅ appears to either decrease or increase degree of phosphate network polymerization, which may be explained on the basis of the phosphate structure changes based on Raman and NMR spectroscopy findings. Specifically, for the A-series, CTE continuously increases and T_g decreases with SiO₂ in an S-shape, which could be related to amount of SiO₆ or Si(PO)₆

units generated at different stages as shown by ^{29}Si MAS NMR study (cf. Fig. 5(a)), where as AlO_6 or Al(PO)_6 units are dominant structure units (Fig. 4(a)). As discussed above, the total number of six coordinated Al and Si decreases and Q^3 with P=O bond decrease the network polymerization. For the P-series, the P unit Q^2 changes to Q^1 and coordination number decreases, which decreases the degree of network polymerization and lower T_g . It should be noted the CTE decrease as P_2O_5 replaced by SiO_2 , and this may be related to the bond nature of the glass network. The elastic moduli reflect a mean volume density of energy while T_g is related to a mean atomic bonding energy regardless of the packing density[37]. So in present study, glasses with high SiO_2 content show a low Young's modulus value.

Nd^{3+} -emission properties (σ_{em} and $\Delta\lambda_{\text{em}}$) of the glasses can be related to the structure of the glasses. For the A-series, there is continuous decrease in $\Delta\lambda_{\text{em}}$, suggesting that local bonding environment of Nd^{3+} ions becomes very similar, especially at higher SiO_2 . There is an initial decrease in σ_{em} before it increases at higher SiO_2 , substituting for Al_2O_3 , which could be related to amount of SiO_6 or Si(PO)_6 units generated at different stages as discussed above. Compared to the A-series, σ_{em} and $\Delta\lambda_{\text{em}}$ of the P-series are nearly the same as the corresponding values of the BL samples. In the A-series, total number of six coordinated Al and Si, which can 'tighten' the phosphate chain, decreases, inducing a larger asymmetry of ligand field surrounding Nd^{3+} ion and larger σ_{em} [38]. For the P-series, although number of six coordinated Al decreases, the chain-like glass structure mainly formed by P-O-P is partly replaced by tightened SiO_4 structure, So rigidity of the glass structure changes to a lesser extent inducing a smaller emission properties variation.

Summary

Effects of substitutions of SiO_2 for Al_2O_3 and P_2O_5 in a single baseline phosphate glass, $\text{Nd}^{3+} : \text{Li}_2\text{O-MgO-Al}_2\text{O}_3\text{-P}_2\text{O}_5$, on physical (ρ , T_g , CTE), mechanical (E), and optical properties (n_D , σ_{em} , $\Delta\lambda_{\text{em}}$) were systematically investigated in relationship to structure evolution of the glasses. Characterizations of the glass structures were performed by using Raman and NMR spectroscopic techniques; the latter covered ^{31}P , ^{27}Al , and ^{29}Si MAS NMR measurements. The property responses to each type of oxide substitutions were detailed by using structural information derived from the

spectroscopic studies. In general, as SiO_2 substitutes for Al_2O_3 , nonlinear property responses often result, which is attributed to formation of six-fold silicate units, SiO_6 or Si(PO)_6 . At the same, six-fold aluminate units, AlO_6 or Al(PO)_6 , dominate in the glass. Without the octahedral silica units, but tetrahedral silica (SiO_4) units found in the case of SiO_2 substitution for P_2O_5 , the properties respond to composition change are more or less in a linear fashion. By analyzing the number of terminal oxygens available to coordinate Al, it can be concluded that six coordinated Si emerges only when all Al atoms in glass are 6-coordinated.

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