

$\text{Na}_2\text{O}-\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5$ 玻璃的结构与性能的分子动力学模拟

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摘 要: 磷硅酸盐玻璃因有着良好的生物活性和光学性能, 已广泛用于生物材料、光纤等领域。运用分子动力学模拟方法研究 Li_2O 含量对 $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5$ 玻璃的微观结构以及扩散性能影响, 着重讨论了其微观结构与维氏硬度, 扩散系数之间的关系。结果表明: 玻璃的磷网络聚合度(Q^p)随着 Li_2O 逐渐替代 Na_2O 而增加, 硬度随着 Q^p 的增加而增大。体系中 Li^+ 的自扩散系数比 Na^+ 大, 即 Li^+ 比 Na^+ 更易扩散。 Li^+ 的势垒随着 Li_2O 增加而逐渐变小, Li_2O 对 Na_2O 取代有益于 Li^+ 扩散。

关键词: 磷硅酸盐玻璃; 分子动力学; 模拟; 结构性质; 扩散行为; 网络聚合度

中图分类号: TQ171 文献标志码: A 文章编号: 0454-5648(2022)02-0378-10

网络出版时间: 2022-01-20



Structure and Properties of $\text{Na}_2\text{O}-\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5$ Glasses via Molecular Dynamics Simulations

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Abstract: Phosphosilicate glasses are widely used in optical fiber, biological materials and other fields because of their excellent optical properties and biological activity. The influence of Li_2O content on the microstructure and diffusion properties of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5$ glass was investigated via molecular dynamics simulation, and the relationship among the microstructure, Vickers hardness and diffusion coefficient was analyzed. The results show that the degree of phosphorus network polymerization (Q^p) increases with the substitution of Li_2O for Na_2O , and the hardness increases with the increase of Q^p . The self-diffusion of Li^+ ions is greater than that of Na^+ ions, indicating that Li^+ ions are easier to diffuse rather than Na^+ ions. The potential barrier of Li^+ ions decreases with the increase of Li_2O . Li_2O is beneficial to the substitution of Na_2O for the diffusion of Li^+ ions.

Keywords: phosphosilicate glass; molecular dynamics; simulation; structure properties; diffusion behavior; network polymerization

1 Introduction

Aluminosilicate glass is an important system in industrial glass with high strength and surface hardness, high chemical stability and impact resistance, and has been widely used in fields such as touch screens, mobile memory matrix materials and solar cells^[1-2]. In addition, aluminosilicate glass is also commonly used as a glass matrix material for ion exchange, which is of wide interest to scientists because of its low plastic deformation, high surface compressibility and relatively low thermal expansion

and contraction effects during ion exchange^[3-5].

Since $[\text{AlO}_4]$ tetrahedral voids are larger than those of $[\text{SiO}_4]$, the introduction of Al_2O_3 in silicate glasses can promote ion exchange and improve the surface hardness and damage resistance of the glass^[6]. However, the addition of Al_2O_3 will increase the melting temperature of the glass, which will increase the difficulty of glass production and the manufacturing cost. $\text{Li}_2\text{O}/\text{Na}_2\text{O}$ introducing into the aluminosilicate glass can achieve rapid ion exchange at a relatively low temperature while reducing the glass transition temperature. The introduction of P_2O_5

收稿日期: 2021-06-16。 修订日期: 2021-06-30。

基金项目: 国家自然科学基金项目(51872092, 52072122)。

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Received date: 2021-06-16. Revised date: 2021-06-30.

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into aluminosilicate glass can further open the glass network framework, promote the ion exchange process, and improve the damage resistance and mechanical strength^[7]. Although chemical strengthening technology has been known for decades, the atomic mechanism that ultimately leads to ion exchange has not been well understood. Studying the self-diffusion and inter-diffusion behavior of alkali ions is of great significance to clarify the chemical strengthening mechanism and further improve the mechanical properties of these glasses^[8-10].

During the ion exchange process, the diffusion of alkali metal ions is affected by the structure, temperature, and molten salt composition of the glass. The density of the glass structure is one of the main factors affecting ion diffusion. Molecular dynamics (MD) simulation can overcome difficulties, such as high temperature experiments, complex structure testing, and expensive costs. It can accurately characterize the structure of melts at high temperatures, explain the mechanism of performance changes caused by structural changes in the ion exchange process from a microscopic point of view, and calculate high melting points and the thermodynamics, structure and transport properties of high vapor pressure materials^[10-13]. MD simulation can provide different insights for exchanging the properties of reinforced glass. The relationship between microstructure and hardness was investigated by introducing an appropriate amount of Li_2O into $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$ glasses to investigate the mechanism of Li_2O introduction on the mechanical properties of phosphosilicate glasses, so as to establish the link between Li_2O content and the properties of phosphosilicate glasses, and provide a theoretical guide for the composition preference of chemically strengthened glasses.

2 Experimental

2.1 Starting materials

Samples were prepared by a traditional melting-quenching procedure. Chemical compositions are $(23.75-x) \text{Na}_2\text{O}-x\text{Li}_2\text{O}-16\text{Al}_2\text{O}_3-55.25\text{SiO}_2-5\text{P}_2\text{O}_5$ ($x=0, 5\%, 10\%, 15\%, 20\%$, mole fraction). The names of the glasses are given by L0, L5, L10, L15 and L20. After mixing uniformly, the raw materials were put

into a high temperature silicon-molybdenum electrical furnace fully pre-firing uniformly at $800\text{ }^\circ\text{C}$ for 30 min, then heated at $1\ 650\text{ }^\circ\text{C}$ for 3 h. The samples were taken out and quenched in a preheated copper plate and annealed at $600\text{ }^\circ\text{C}$ for 5 h. Densities were measured with the Archimedes law using deionized water as the immersion liquid.

2.2 Vickers hardness (H_V)

The glass samples were subjected to a microhardness tester (HXD-1000TMC/LCD, Shanghai Taiming Optical Instrument Co. Ltd., Shanghai, China) with a load of $0.980\ 7\ \text{N}$ (100 GF). The surface of the sample was continuously loaded for 10 s, and then the diagonal length of indentation was measured. Each glass sample was tested at 5 parallel test points and averaged to obtain micro-Vickers hardness values.

2.3 Network connectivity (n_c)

Network connectivity (n_c) is defined as the average number of bridging oxygens in each glass forming body atom, its value is 4 in pure SiO_2 glass with a complete three-dimensional network structure, and $n_c=2$ represents a chain structure^[14].

2.4 Simulation detail

The structure model of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$ glass was obtained by molecular dynamics method. Table 1 shows the total number of atoms in each model and the size of the box. The simulated force field^[12] included the short-range Buckingham potential^[15] and the long-range Coulomb potential. The Coulomb force was summed up by Ewald method^[16]. The accuracy was set to 10^{-5} , the cutoff distance of the van der Waals force was set to 1 nm, a random initial configuration and periodic boundary conditions were used, and the integration step was set to 1 fs. The initial configuration was fully melted at a high temperature of 4 000 K, and the process runs for 100 ps under the NVT canonical ensemble. Subsequently, the system is gradually cooled to room temperature through 4 000, 3 500, 3 000, 2 500, 2 000, 1 500, 1 000, 300 K at a cooling rate of 5 K/ps under the NPT ensemble. At each temperature, after the system runs for 100 ps in the NPT ensemble, it then switches to the NVE ensemble for 60 ps, where the first 20 ps is used for balance and the next 40 ps is used to calculate the diffusion coefficient. The potential parameters used in the simulation are shown in Table 2.

Table 1 Number of atoms in different styles, cubic box size and glass density

Sample No.	Number of atom							Length/nm	Density/(g·cm ⁻³)
	Li	Na	Al	Si	P	O	Total		
L0	0	1 330	896	1 547	280	5 803	9 856	5.150	2.427
L5	280	1 050	896	1 547	280	5 803	9 856	5.112	2.427
L10	560	770	896	1 547	280	5 803	9 856	5.079	2.417
L15	840	490	896	1 547	280	5 803	9 856	5.039	2.417
L20	1 120	210	896	1 547	280	5 803	9 856	5.005	2.407

The Buckingham short-range force includes exponential repulsion term and power attraction term, representing dispersion force, in the form:

$$V'_{ij}(r) = A_{ij} \cdot \exp\left(-\frac{r}{\rho_{ij}}\right) - C_{ij} / r^6 \quad (1)$$

Where A , ρ and C represent the parameters, respectively, while r represents the distance between atoms. The parameters are shown in Table 2.

Table 2 Parameter value of Buckingham potential function

Bond	A_{ij}/eV	ρ_{ij}/nm	$C_{ij} \times 10^6/(\text{eV} \cdot \text{nm}^6)$
$\text{Si}^{2.4}\text{-O}^{-1.2}$	13 702.91	0.019 4	54.681
$\text{Al}^{1.8}\text{-O}^{-1.2}$	12 201.42	0.019 6	31.997
$\text{P}^{3.0}\text{-O}^{-1.2}$	26 655.47	0.018 2	86.856
$\text{Na}^{1.2}\text{-O}^{-1.2}$	4 383.76	0.024 4	30.700
$\text{Li}^{1.2}\text{-O}^{-1.2}$	41 051.94	0.015 1	0
$\text{O}^{-1.2}\text{-O}^{-1.2}$	2 029.22	0.034 3	192.580

3 Results

3.1 Vickers hardness and density

The density and hardness changes with the Li_2O content are shown in Fig. 1. It can be seen that as the content of Li_2O increases, the density of the glass decreases sequentially, while the Vickers hardness of the glass gradually increases from 5.0 to 5.7 GPa with the increase of the content of Li_2O ^[1].

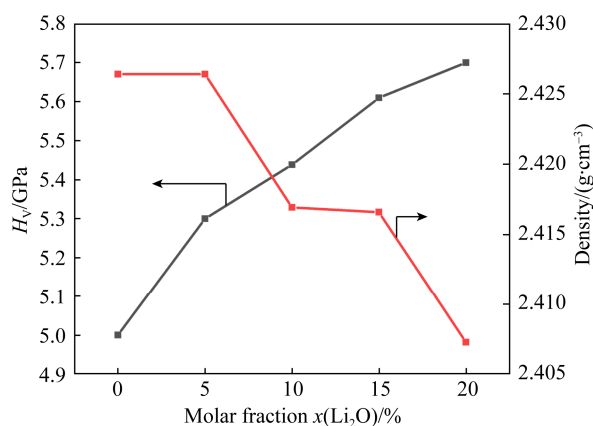


Fig. 1 Density and Vickers hardness of $(23.75-x)\text{Na}_2\text{O}-x\text{Li}_2\text{O}-16\text{Al}_2\text{O}_3-55.25\text{SiO}_2-5\text{P}_2\text{O}_5$ glasses

3.2 General structural features of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$ glasses

Fig. 2 shows the simulated glass density and experimental glass density. It can be found that the deviation is less than 0.055 g/cm^3 , and their variation trend is consistent with the Li_2O content, thus confirming that the potential parameters selected in this paper have a good accuracy in simulating the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5-\text{SiO}_2$ glass structure.

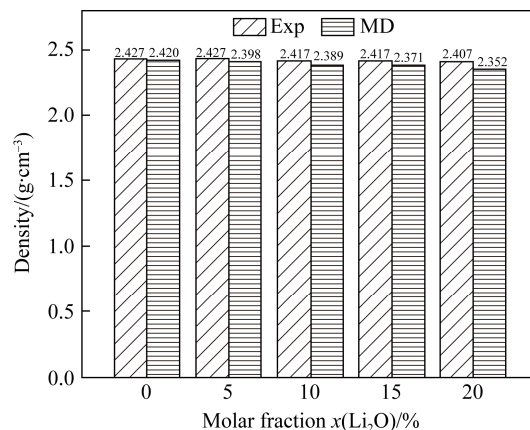


Fig. 2 Glass density changes with Li_2O contents by experiments and MD

3.2.1 Radial distribution functions (RDF) and coordination numbers (N_c)

RDFs ($g(r)$) represents the average number of atoms of the atomic species j which located at the distance r of the studied atom i and is defined as follows^[2]:

$$g_{ij}(r) = \frac{V}{N_i N_j} \sum_k \frac{n_{kj}(r - \frac{\Delta r}{2}, r + \frac{\Delta r}{2})}{4\pi r^2 \Delta r} \quad (2)$$

where N_i , N_j is the total number of i and j atoms in the system. n_{kj} is the number of k atoms included in the thickness of the spherical shell Δr is located at a distance r . V is the volume of the system. Further analysis of RDFs can get basic structural information such as average bond length. With the integration of RDF, N_c can be obtained as Eq. 3^[19–20]:

$$N_{ij}(r) = \frac{4\pi r N_j}{V} \int_0^r r^2 g_{ij}(r) dr \quad (3)$$

Fig. 3 shows the partial radial distribution function between different atoms and oxygen atoms. From Fig. 3, it can be analyzed that the bond lengths of Si–O, Al–O, P–O, O–O, Na–O and Li–O are 0.160, 0.177, 0.150, 0.262, 0.246, 0.189 nm, respectively, which are consistent with the previous report data^[21], confirming the reliability of the simulation.

As shown in Fig. 4, the N_c (coordination number) differences of Si, Al and P are not significant. The coordination number of Si–O, Al–O and P–O is 4.00, 4.01, and 4.00, respectively, N_c do not change significantly with the change of composition. It can also be seen that Si–O and P–O coordination curves have a wide and flat platform, while Al–O coordination curve has a narrow platform. However, the Na/Li–O–O coordination curve does not have any platform.

Based on the above calculation and analysis results, the data obtained by molecular dynamics simulation are relatively consistent with those obtained by other researchers^[15,18–20]. The bond lengths and coordination numbers between the atomic pairs are very close. This

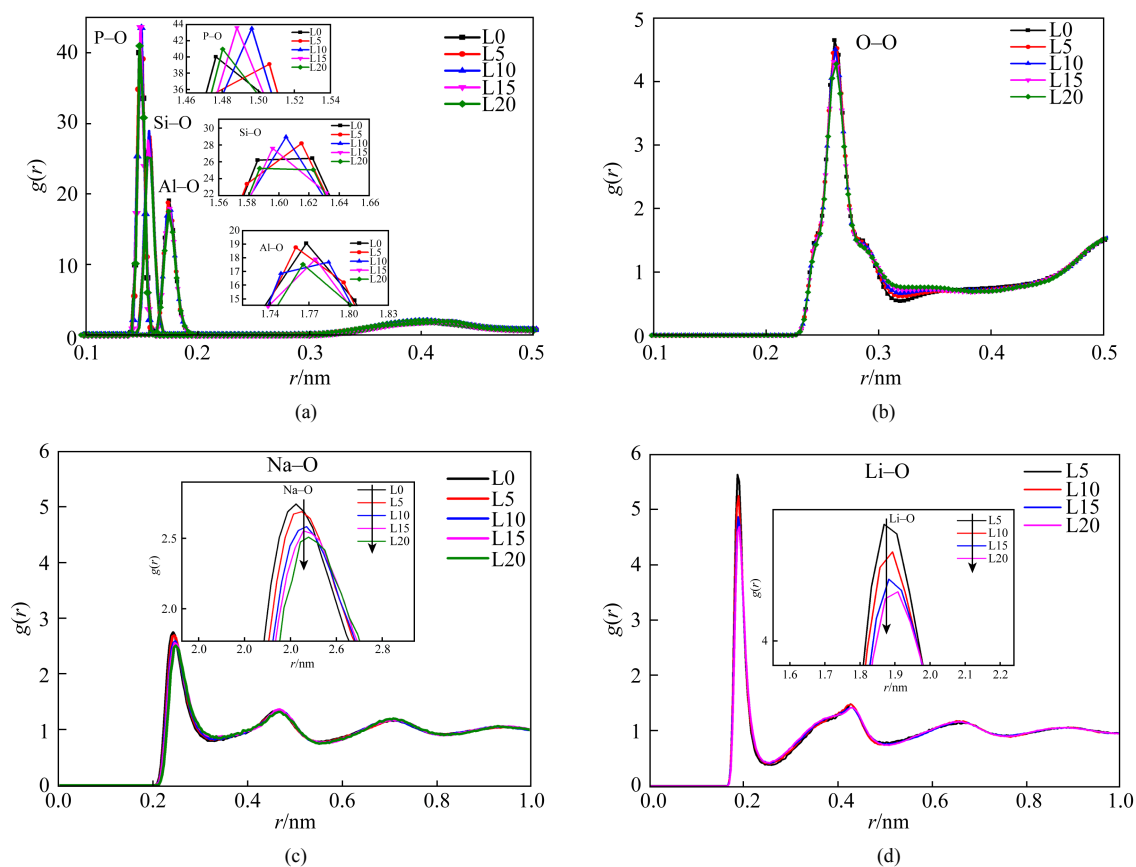
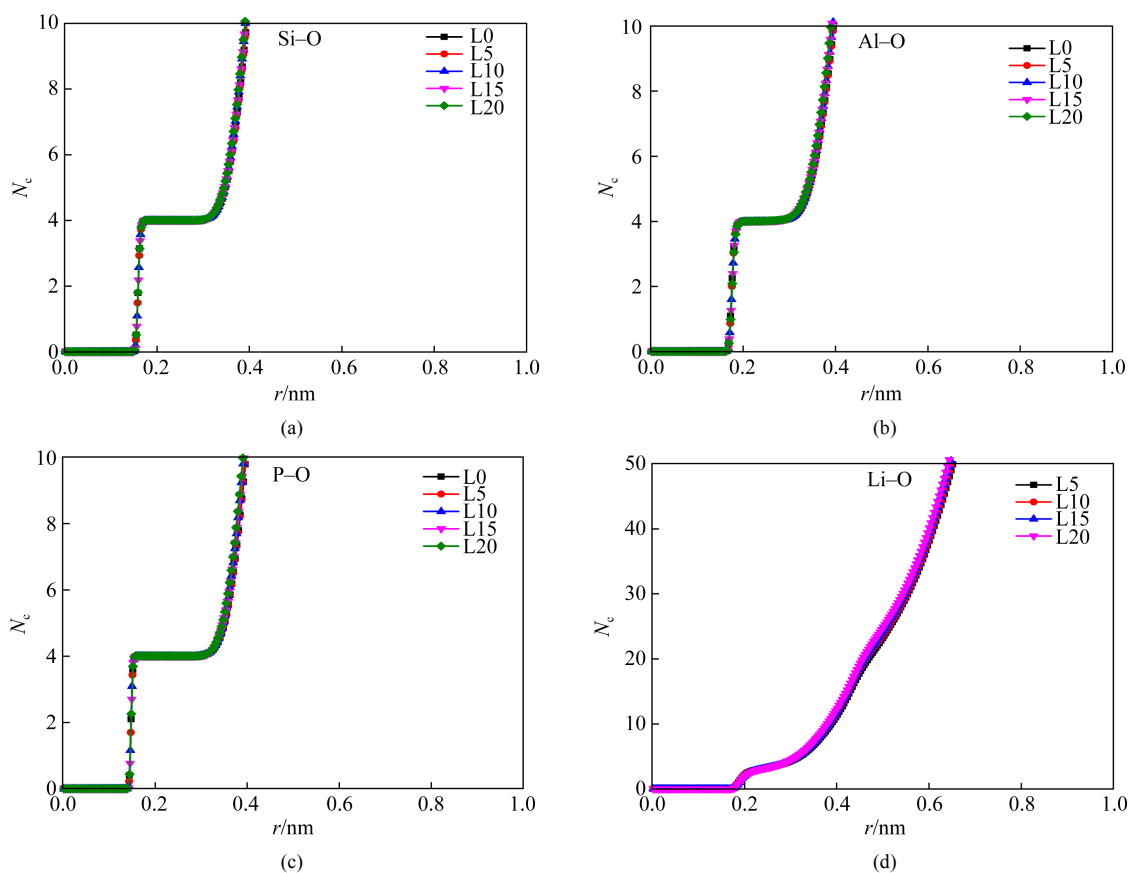


Fig. 3 Diagram of partial radial distribution function between different atoms and oxygen atoms

Fig. 4 Diagram of coordination number (N_c) between different atoms and oxygen atoms

further verifies the rationality and accuracy of the potential function selected in this article.

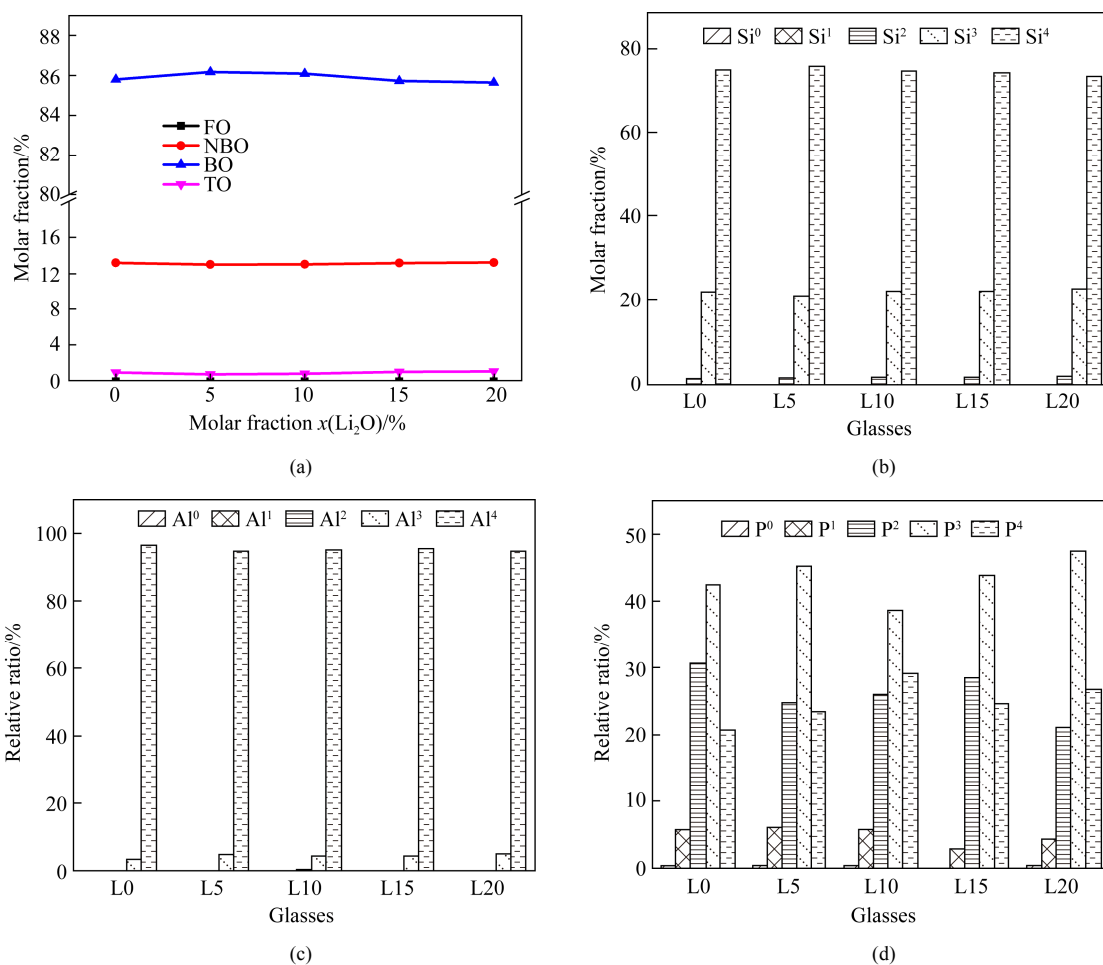
3.2.2 Distribution of oxygen types and Q^n units

The calculation of oxygen types were carried out in I.S.A.A.C.S software^[22]. Fig. 5 shows the changes of different kinds of oxygen atoms with the content of Li_2O . In simulation statistics, there are four types of oxygen, including free oxygen (FO) and three-bonded oxygen (TBO), which link to three network formers.

This is consistent with the molecular dynamics simulation results of other oxide glasses. In addition, with the increase of Li_2O content, the content of bridging oxygen (BO) firstly increases and then decreases, while the content of non-bridging oxygen

(NBO) and TBO have an opposite trend, and the content of free oxygen and triple bond oxygen in the system is relatively low.

The degree of polymerization of glass networks can be described as Q^n . Customized code was used to calculate the number of BO and TBO connected to the tetrahedron by MATLAB. Fig. 5 shows the Q^n distribution of $[\text{SiO}_4]$, $[\text{AlO}_4]$ and $[\text{PO}_4]$, respectively. It can be revealing that $[\text{SiO}_4]$ and $[\text{AlO}_4]$ tetrahedra mainly exist as Q^4 structural units, while P is more inclined to form as P^3 structural units, followed by P^2 and P^4 structural units. With the increase of Li_2O content, Q^n distribution in Si and Al networks did not change significantly.



Note: Contents of Si^0 , Si^1 , Al^0 , Al^1 , Al^2 and P^0 are very low, cannot be shown in this Figure.

Fig. 5 Oxygen types and Q^n distribution of the network formers

3.3 Diffusion behaviors of Li^+/Na^+

Through the statistical analysis of the particle trajectory by means of MD simulation, the function of the mean square displacement (δ_{MSD}) about time would be generated.

$$\delta_{\text{MSD}} = \langle \Delta r^2(t) \rangle = \frac{1}{N} \left\langle \sum |r_{i(t)} - r_{i(0)}|^2 \right\rangle \quad (4)$$

where $r_{i(t)}$ presents the location of atom i at the time of t and the bracket expresses an ensemble average

taken over many origin times.

δ_{MSD} is an important physical quantity to quantify the diffusion behavior. Fig. 6(a) and Fig. 6(b) were the mean square displacement of Li^+ and Na^+ in L10 glass at different temperatures. The δ_{MSD} decreases with increasing temperature.

Combined with statistical mechanics and statistical thermodynamics, the transport properties such as the self-diffusion coefficient (D) of the melt were studied.

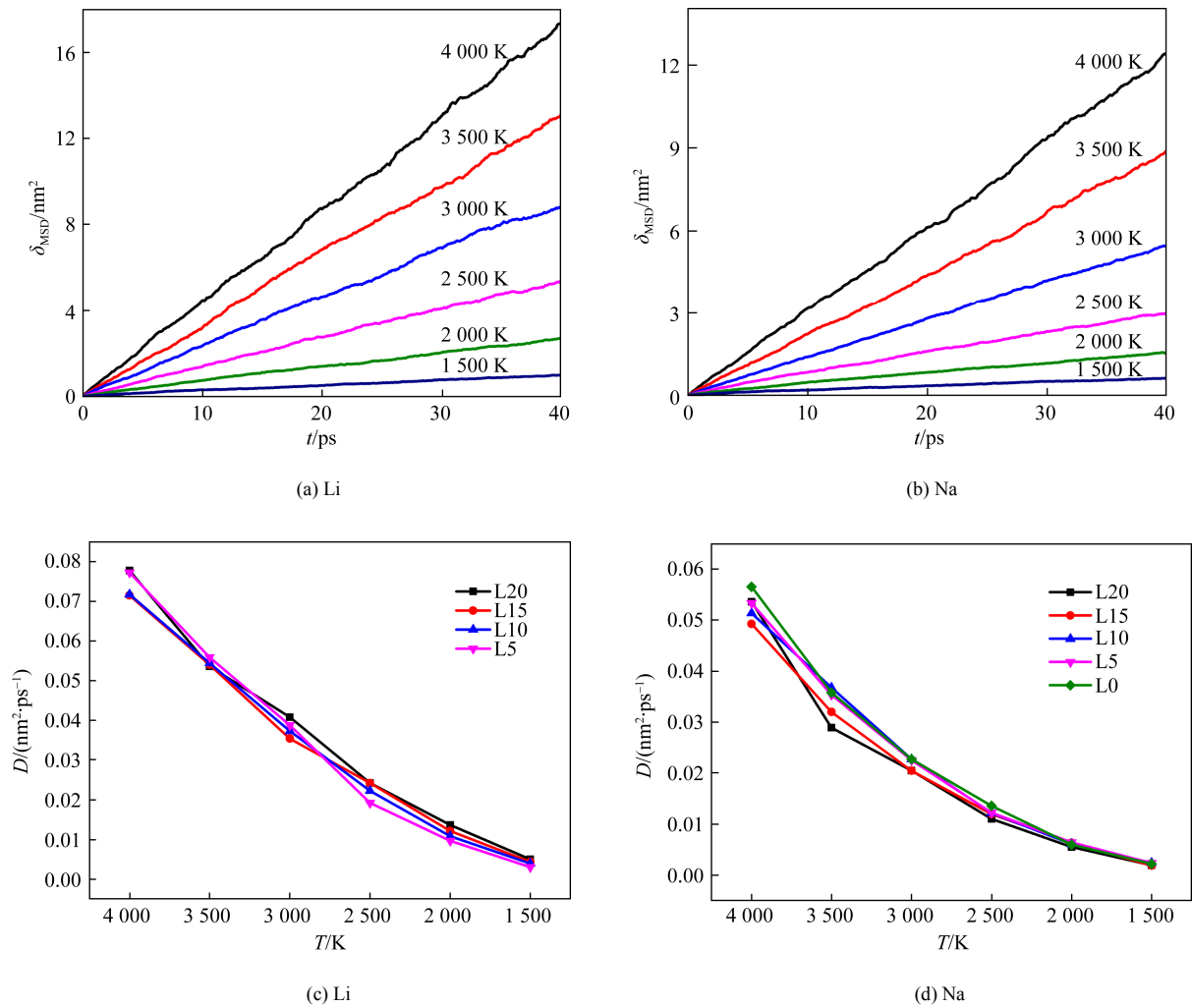


Fig. 6 Mean square displacement (a, b) and diffusion coefficient D with temperature of Li^+ (c) and Na^+ (d)

The D is calculated based on the δ_{MSD} curve of the particles. The relationship between the D and δ_{MSD} curve is shown in the Eq. 5^[19, 23] below:

$$D = \lim_{t \rightarrow \infty} \frac{1}{6} \frac{d[\Delta \bar{r}^2(t)]}{dt} \quad (5)$$

Variation of the diffusion coefficient of Li^+ and Na^+ with temperature is shown in Fig. 6(c) and Fig. 6(d). The diffusion coefficients of Li^+ and Na^+ decrease significantly as the temperature decreases. The diffusion capacity of Li^+ , Na^+ ions would not change with Li_2O content, especially in the low temperature range. In addition, the curve of diffusion coefficient with temperature is in good agreement with Arrhenius's equation. As the temperature drops, the slope of the curve becomes smaller and smaller.

4 Discussion

4.1 Structural and transport properties

The average bond lengths of the corresponding atoms Si-O, Al-O, P-O, O-O, Na-O and Li-O is 0.161, 0.177, 0.150, 0.262, 0.246, 0.189 nm,

respectively. The size of the bond length from short to long is P-O, Si-O, Al-O, Li-O, Na-O, O-O. The average distance of Si-O is smaller than the average distance of Al-O and greater than the average distance of P-O, which indicates that the bonding ability of Si-O is stronger than that of Al-O and weaker than that of P-O. The network stability from high to low is P-O, Si-O, Al-O, Li-O, Na-O. In addition to the first peak of the Si-O network, the RDF of P-O, Si-O, Al-O, Li-O and Na-O also has a gentler second peak, indicating that long-range ordered structure appeared with increasing distance between two atoms.

The equilibrium mechanism of attractive and repulsive forces between particles can be understood by calculating the N_c of atoms^[24]. The coordination numbers of Si-O, Al-O, and P-O are 4.005, 4.010 and 4.000, respectively. This indicates that almost all Si exist as $[\text{SiO}_4]$ structural units, and in addition to $[\text{AlO}_4]$ structural units, there are also some Al atoms with higher coordination, as shown in Fig. 4. The P atom exists as a $[\text{PO}_4]$ structural unit. It can also be seen that the Si-O and P-O coordination curves have a

wide and flat platform, while the Al–O coordination curve has a narrow platform. It shows that the stability of $[\text{SiO}_4]$ and $[\text{PO}_4]$ tetrahedral structure is better than $[\text{AlO}_4]$ tetrahedral structure. The substitution of Li_2O for Na_2O has no significant effect on the bond length between Si–O, Al–O, P–O, and O–O and the coordination number. The bond lengths of Na–O and Li–O increase with the increase of Li_2O content.

Fig. 5(a) shows the variation of oxygen type with the content of Li_2O , the content of BO exceeds 80%, and the content of NBO ranges from 10% to 20%. Na^+ and Li^+ in the glass are acted as the network modifier to destroyed the T–O–T (T=Al, Si, P) bond to form NBO. On the other hand, they are used as charge compensation to stabilize the tetrahedral structure $[\text{AlO}_4]$. As Li_2O substituted to the Na_2O gradually, the relative proportion between the glass modifier and glass network former remains constant. And the oxygen atoms in the system fluctuate less.

Further analysis of the oxygen type shows that there is positive correlation between the NBO and FO, TO. The results are shown in Fig. 7(a). Sen and Youngman^[25] inferred from their experimental results

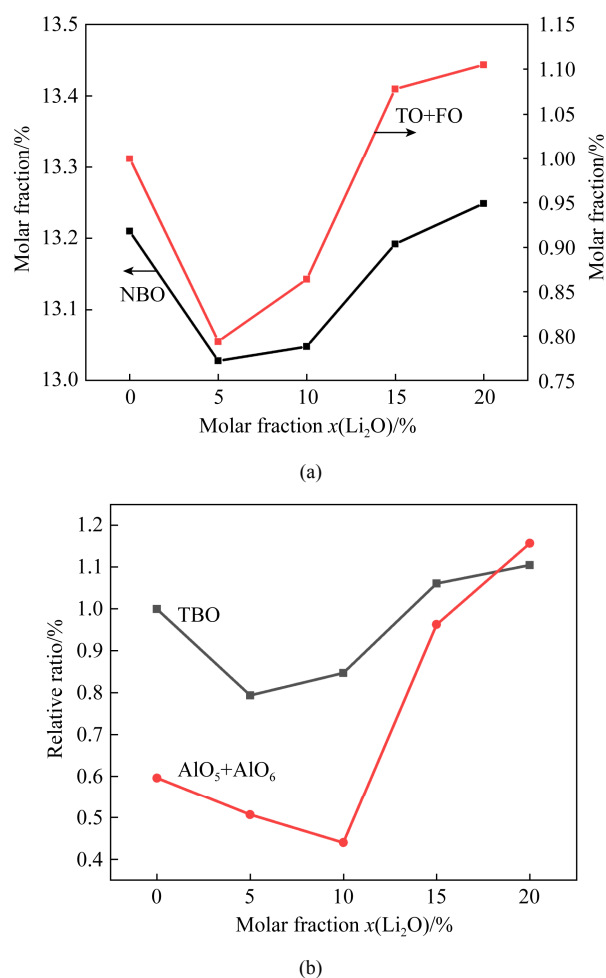


Fig. 7 Evolution with Li_2O content of the percentage of (a) NBO with TO+FO, (b) triclusters and $\text{AlO}_5+\text{AlO}_6$ with respect to the total amount of them

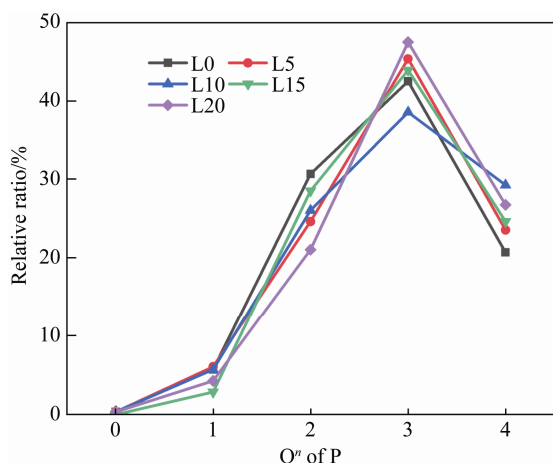
in the glass state that TBO achieved charge balance at very low concentration (1%, mass fraction) with AlO_5 and AlO_6 . The results in good agreement with this hypothesis, and Fig. 7(b) shows that TBO formation is still the main mechanism of charge compensation for AlO_5 and AlO_6 components.

Fig. 5 shows the Q^n distribution of Si/Al/P formers. With the increase of Li_2O content, the Q^n distribution in the Si and Al network does not change significantly. Their network is mainly composed of Q^4 and Q^3 structural units with a high degree of aggregation. Li^+ and Na^+ are similar in chemical properties and bonding. Although the ion radius of Na^+ is approximately larger than that of Li^+ , sodium ions have a lower field strength than lithium ions. Therefore, in the influence on the Q^n distribution, chemical similarity is in a dominant position.

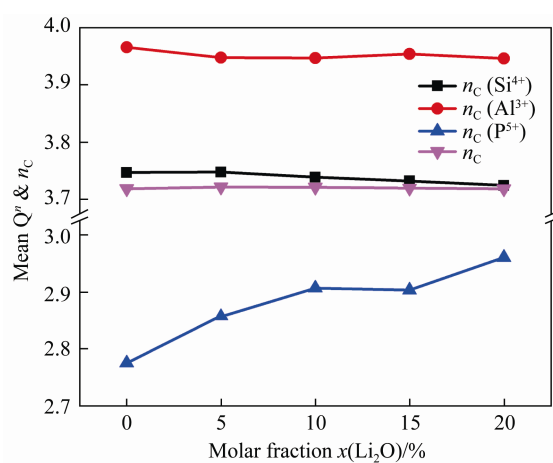
While Q^n in P network is mainly P^3 structural unit, followed by P^2 and P^4 structural unit (Fig. 8(a)). With the increase of Li_2O content, P^2 structural units are gradually transformed into P^3 and P^4 structural units. In other words, the introduction of Li^+ has an accumulation effect on P network structure, while it has a depolymerization effect on Si and Al networks. As Li^+ partially replaces Na^+ , the glass network will depolymerization. The $\text{P}=\text{O}$ will be broken and enhance the densification of the glass network structure. The effects will mutually offset so that the connectivity of the glass system will change little while the degree of polymerization of the P network will increase.

The n_c values of the glasses fluctuated around 3.72 with increasing Li_2O content (Fig. 8(b)), which may be due to the fact that the total content of alkali metal atoms in the system was fixed in this study, while the contents of BO and NBO were relatively stable. The increase in Q^n with increasing Li_2O content suggests that in this series of glasses, the polymerization of the P network by Li^+ promotes the connection of the P network. Similar aggregation of P was also found in 45S5 bioglass^[21]. The change of Li_2O content has little influence on silicon network and aluminum network, which is consistent with the change of Q^n distribution. In general, the contribution of silicon and aluminum to the degree of network connectivity is the main, while the network connectivity of phosphorus is significantly lower than that of the whole network.

As can be seen from Fig. 6 that the displacement of Li^+ is larger than Na^+ at the same temperature, which due to the radius of Li^+ is smaller than Na^+ , and the binding of the glass network to Li^+ is smaller. In the initial stage of diffusion, the motion trajectory of ions is spherical, and δ_{MSD} is proportional to the square of time. After a period of time, the transition to the diffusion stage can be clearly seen in the Fig. 9. At this point, the diffusion of ions is controlled by Einstein's random walk. δ_{MSD} curve is a inclined line, and the slope of the line can reflect the diffusion ability of ions.



(a)



(b)

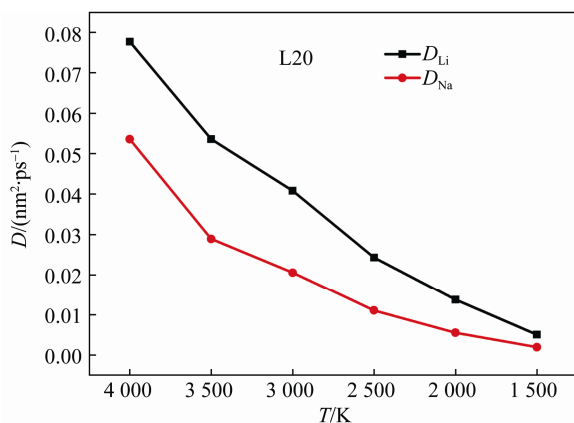
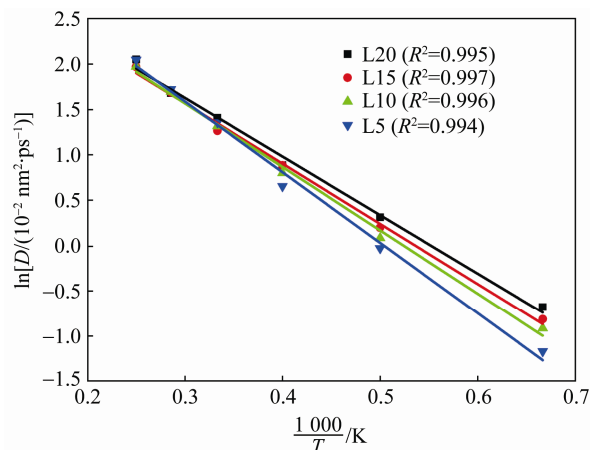
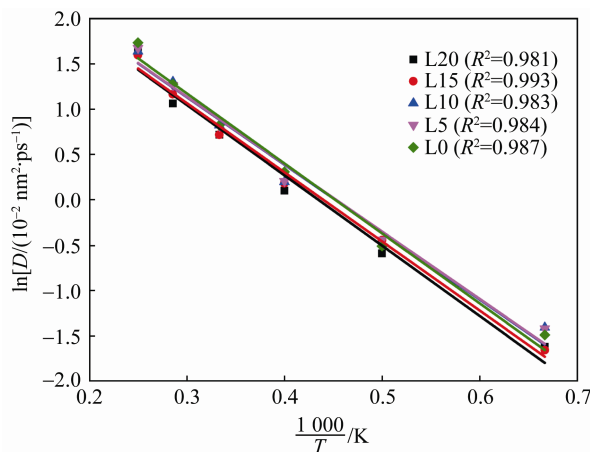
Fig. 8 Network connectivity n_c of the network formersFig. 9 Diffusion coefficient with temperature of Li^+ and Na^+

Fig. 10 shows the variation of the diffusion coefficients of Li^+ and Na^+ with the reciprocal of temperature. The linear regressivity of the relationship between the diffusion coefficients D and $1/T$ for Li^+ and Na^+ is well matched. (R^2 is 0.98–0.99), which is consistent with the ideal Arrhenius curve. It can more intuitively react the Arrhenius behavior of the

diffusion coefficient. The diffusion barrier of ions can be calculated based on the Arrhenius equation.



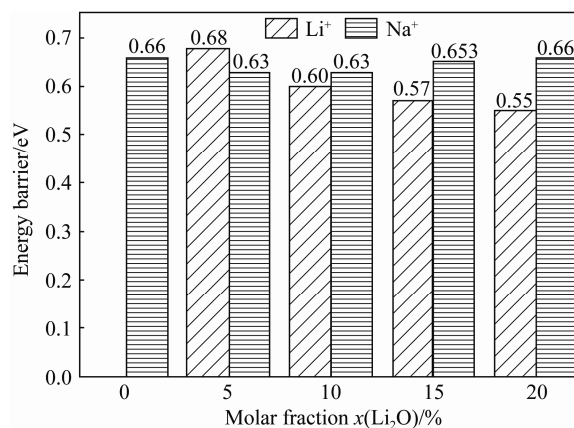
(a)



(b)

Fig. 10 $\ln D$ with temperature of Li^+ (a) and Na^+ (b)

The influence of $\text{Li}_2\text{O}/\text{Na}_2\text{O}$ substitution on the diffusion barrier is shown in Fig. 11. The potential barrier of Li ions gradually decreases with decreasing temperature, and its value decreases from 0.66 eV to 0.55 eV, which indicates that $\text{Li}_2\text{O}/\text{Na}_2\text{O}$ substitution is

Fig. 11 Diffusion barrier changes with Li_2O content

beneficial to Li^+ diffusion. The $\text{Li}_2\text{O}/\text{Na}_2\text{O}$ substitution would change potential barrier of Na^+ from 0.63 to 0.66. Pedone *et al.*^[26] found that diffusion barrier of Na^+ is 0.56 eV for sodium silicate glass, and for calcium carbonate glass with SiO_2 content of 70%–75% (mole fraction) through MD simulation, the diffusion barrier of Na^+ is 0.74 eV. Also in agreement with experiment of Frischat^[27], which the diffusion barrier of Na^+ is 0.6–0.8 eV in the sodium silicate glass melt.

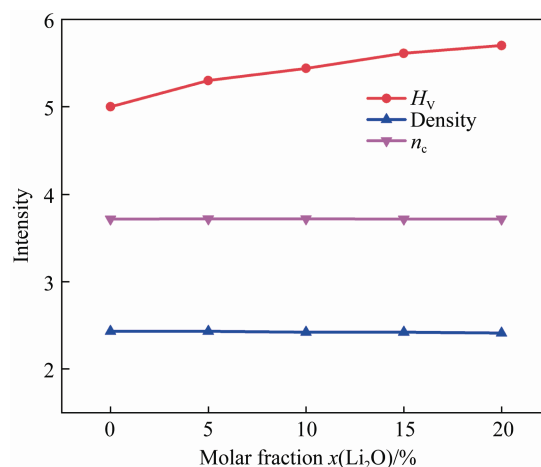
4.2 Relationship between mechanical properties and n_c

The introduction of Li^+ makes the glass network depolymerize and open the $\text{P}=\text{O}$ bond at the same time, which enhances the density of the glass network structure, and the magnitude of the two effects exactly cancel each other and make the connectivity of the glass network without explicit changes, while the decrease of density is caused by the gradual decrease of the atomic mass of the glass when Li_2O replaces Na_2O . In addition, the density of glass is related to the density of atoms and the coordination number. The addition of Li^+ will replace Na^+ to fill the gaps in the network and make the network structure looser, so the density of the glass will decrease. In terms of polyhedral coordination, $[\text{AlO}_6]$ and $[\text{AlO}_5]$, as the outer body of the network, fills in the gap of the structural network, so the density of glass increases. The content of $[\text{AlO}_6]$ and $[\text{AlO}_5]$ is very little, which contributes little to the network gap tightness. The Vickers hardness of the glass increases gradually with Li_2O and is about 5.0–5.7 GPa. As the content of Li_2O increases, the density of the glass network increases, resulting in an increase in the hardness of the glass.

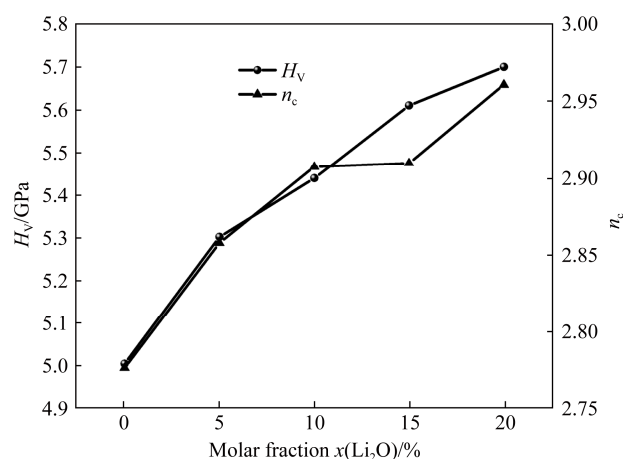
5 Conclusion

Molecular dynamics simulation method was applied to investigate the influence of Li_2O content on the microstructure and diffusion properties of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{P}_2\text{O}_5$ glass, and the relationship between the microstructure, Vickers hardness and diffusion coefficient were emphatically discussed. The bond length of $\text{Na}-\text{O}$ is increasing with Li_2O gradually substituted Na_2O . Bridging oxygen content is increasing and then decrease with the increasing content of Li_2O . The increasing content of Li_2O can increase the degree of polymerization of P and could strengthen the Vickers hardness, and the network connectivity of glass has no obvious change when the formers content is constant. In addition, Li^+ is easier to diffuse than Na^+ and the substitution of sodium oxide by lithium oxide is conducive to the diffusion of Li^+ . Degree of polymerization of P was utilized to explain the improved mechanical properties in order to

provide good insight for accelerating the design of high-performance glassy materials.



(a)



(b)

Fig. 12 n_c , H_V (V_m) and density of $(23.75-x)\text{Na}_2\text{O}-x\text{Li}_2\text{O}-16\text{Al}_2\text{O}_3-55.25\text{SiO}_2-5\text{P}_2\text{O}_5$ glasses

Acknowledgements

We would like to thank Dr. Jiacheng Li (Shanghai Institute of Optics and Fine Mechanics, the Chinese Academy of Sciences) and Dr. Xvsheng Qiao (Zhejiang University) for helpful suggestions.

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