

Temperature-induced structural changes and mechanical degradation in phosphoric acid- based geopolymers

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Research Article

Keywords: Phosphate acid-based geopolymer (PABG), molecular dynamics (MD) simulation, temperature dependence, structural evolution, mechanical response

Posted Date: August 24th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10603842/v1>

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Additional Declarations: No competing interests reported.

Abstract

Understanding the high-temperature behavior of geopolymers is essential for their potential applications in refractory materials, thermal insulation, and fire-resistant structural systems. Here, atomistic simulations were conducted to investigate the temperature-dependent structural evolution and mechanical response of phosphate acid-based polymers (PABGs) over a temperature range of 300–1173 K. Results indicate that the local Si–O, P–O, and Al–O units remain largely intact, while the nanoscale network gradually becomes disordered with increasing temperature. This evolution is reflected by the attenuation of higher-order radial distribution function peaks, the reduction of P-related bridging bonds, the redistribution of Al coordination states, the enhanced mobility of P atoms, and the increase in porosity. In particular, Si–O–P and Al–O–P linkages are more temperature-sensitive than Si–O–Al bonds. The porosity increases from 35.32% to 47.44%, while the bulk density decreases from 1.885 g/cm^{−3} to 1.390 g/cm^{−3}, indicating progressive structural loosening under thermal exposure. Tensile simulations further show a marked decrease in Young's modulus from 42.5 GPa at 300 K to 25.5 GPa at 1173 K, corresponding to an overall reduction of 40.0%. This mechanical degradation is closely associated with bond weakening, coordination rearrangement, increased atomic mobility, and pore growth. All these factors collectively reduce network connectivity and stress transfer efficiency.

1. Introduction

Geopolymers are inorganic polymeric binders formed by the chemical activation of aluminosilicate precursors and are widely regarded as promising alternatives to ordinary Portland cement because of their low-temperature synthesis, high mechanical strength, chemical durability, and good fire resistance[1–3]. In contrast to conventional cement systems, geopolymer technology offers a route to reduce reliance on clinker-based binders while enabling the use of industrial by-products and naturally occurring aluminosilicate resources[4, 5]. Within the broad geopolymer family, phosphoric acid-based geopolymers (PABGs), also referred to as phosphate-activated or silico-aluminophosphate geopolymers, constitute a distinctive acid-activated class in which phosphate species participate directly in the formation of the network structure[6, 7].

Compared with alkali-activated aluminosilicate geopolymers, PABGs exhibit several unique features[8–10]. Previous studies have shown that they can harden rapidly under relatively mild conditions, display strong adhesion to mineral substrates, and maintain good stability at elevated temperature[11]. These characteristics make them attractive for applications such as refractory binders, thermal protection materials, rapid repair systems, and waste immobilization matrices[12, 13]. Structurally, PABGs differ from conventional alkali-activated geopolymers because their framework contains phosphate-related linkages, typically involving Si–O–P and Al–O–P connections in addition to aluminosilicate bonding motifs[14, 15]. As a result, their temperature-dependent behavior is expected to be governed not only by the stability of Si–O and Al–O units, but also by the integrity of P-centered structural segments.

The thermal response of PABGs has received increasing attention in recent years. Experimental studies have shown that heating can induce dehydration, pore redistribution, network rearrangement, and, at sufficiently high temperature, phase transformation and crystallization in phosphate-based geopolymer systems[16, 17]. For example, Guo et al.[18] showed that acid-based geopolymers prepared from metakaolin undergo distinct microstructural evolution during thermal exposure, which is closely related to their thermal stability and residual properties. More recently, Yang et al.[19] demonstrated that the fire performance of phosphoric acid-activated metakaolin geopolymers is strongly affected by structural features such as density and porosity, further highlighting the importance of thermal-induced network changes in these materials. In addition, the thermal stability of phosphate-based geopolymer systems has been shown to depend strongly on precursor characteristics and processing conditions, since different metakaolin raw materials can lead to substantial differences in water resistance and fire resistance after phosphoric acid activation.[20, 21] Although these studies have substantially improved the experimental understanding of PABGs, the atomistic origin of their temperature-dependent degradation remains insufficiently resolved.

Molecular dynamics (MD) simulation provides an effective way to address this issue, particularly for amorphous binder systems whose local structure is difficult to characterize unambiguously by experiment alone. In cementitious materials, numerical and atomistic approaches have already proved valuable for understanding self-healing behavior, nanoscale bonding, elasticity, porosity effects, and interfacial phenomena[22, 23]. First-principles studies have clarified the bonding and elastic characteristics of tobermorite and C–S–H, while molecular simulations have shown how porosity influences the stiffness and stability of C–S–H at the nanoscale[24, 25]. Other atomistic studies have examined interfacial bond strengthening, ductility enhancement by carbon nanotubes, and wetting behavior in cement-based systems[26]. In addition, the mechanical origin of alite has been analyzed from an atomistic perspective[27], and thermal and acoustic transport has been investigated in nanoporous geopolymer nanocomposites[28]. These studies collectively demonstrate that atomistic modeling is capable of establishing direct links between local structure and macroscopic performance in complex binder materials.

For geopolymer systems, molecular dynamics (MD) simulations have been increasingly used to probe the effects of molecular water, network polymerization, and reactive structural evolution[29–31]. Sadat et al.[32] showed that molecular water significantly affects both the structure and mechanics of amorphous geopolymer binders. Zhang et al.[33] used reactive MD to model the polymerization process of geopolymer gels, while Li et al.[34] employed reactive MD to analyze the structure, reactivity, and mechanical behavior of sustainable geopolymer materials. However, most of these studies have focused on alkali-activated aluminosilicate systems[28, 35]. By comparison, atomistic simulations dedicated specifically to PABGs remain very limited. Huang et al.[36] reported the first MD model of phosphoric acid-based geopolymer and showed that the simulated density, bond lengths, RDFs, and elastic properties were in reasonable agreement with available data. Hu et al.[37] subsequently investigated water adsorption and diffusion in PABGs using molecular modeling. Nevertheless, these studies mainly

addressed static structural characteristics or transport behavior, and a systematic analysis of temperature-dependent structural evolution and its connection to mechanical degradation is still lacking.

In this work, the temperature-dependent structural evolution and mechanical response of phosphoric acid-based geopolymers are investigated by reactive molecular dynamics simulations. A phosphate–aluminosilicate model containing Si, Al, P, O, and H was constructed to represent the essential network structure of the material. Simulations were performed over the temperature range of 300–1173 K in order to capture ambient conditions, low-temperature activation, intermediate structural relaxation, and severe thermal exposure. The structural response was analyzed in terms of radial distribution functions, bond populations, aluminum coordination states, mean-squared displacement of P atoms, and porosity evolution. The mechanical behavior was then evaluated through uniaxial tensile simulations and the corresponding Young’s modulus. The objective of this study is to clarify the atomistic origin of the temperature-dependent structural degradation and to establish the relationship between network evolution and mechanical performance in phosphoric acid-based geopolymers.

2. Model building and simulation details

2.1 Modeling phosphoric acid-based geopolymer

The phosphoric acid-based geopolymer (PABG) system in this study was constructed based on its established formation mechanism[38]. The model consists of five elemental species, namely phosphorus (P), silicon (Si), aluminum (Al), oxygen (O), and hydrogen (H), forming a phosphate–aluminosilicate network (Fig. 1). Hydrogen atoms were incorporated as structural hydroxyl groups or charge-balancing species to ensure overall electroneutrality. The basic information of PABG is shown in Table 1.

The fundamental building blocks of the geopolymer network include three types of tetrahedral units, i.e., $[\text{PO}_4]$, $[\text{SiO}_4]$, and $[\text{AlO}_4]$, which represent the primary reactive species generated during the acid activation of aluminosilicate precursors (e.g., metakaolin) with phosphoric acid. Specifically, $[\text{PO}_4]$ units originate from partially dissociated phosphoric acid species (e.g., H_2PO_4^- , HPO_4^{2-}), which readily undergo condensation reactions under elevated temperatures, forming bridging linkages such as P–O–P and P–O–(Si/Al). Meanwhile, $[\text{SiO}_4]$ and $[\text{AlO}_4]$ tetrahedra are derived from depolymerized aluminosilicate species under acidic conditions and participate in subsequent polycondensation reactions.

During the geopolymerization process, these tetrahedral units are interconnected via shared oxygen atoms, leading to the formation of a three-dimensional amorphous network dominated by –Si–O–P–, –Al–O–P–, and –Si–O–Al– linkages. This structural feature distinguishes phosphoric acid-based geopolymers from conventional alkali-activated systems, which are primarily composed of Si–O–Si and Si–O–Al bonds.

Based on previous studies, the atomic composition was determined using a Si/P ratio of 3 and an Al/P ratio of 1[39]. The initial atomic configuration was generated by randomly distributing all atoms within a

cubic periodic simulation box, with an initial density close to experimentally measured values. After structural relaxation, the model reaches an equilibrium density of about 2.0 g/cm³. This value is consistent with the typical experimental range reported for PABG systems (1.9–2.2 g/cm³)[11], supporting the reliability of the constructed structure.

Table 1
Basic information of the constructed PABG simulation model.

Parameter	Value
Simulation box size	51.98 Å × 51.55 Å × 51.78 Å
Total number of atoms	12300
Elemental composition	Si: 1200; Al: 400; P: 400; O: 6100; H: 4200
Atomic ratio	Si/P = 3.0; Al/P = 1.0
Framework oxide composition (wt%)	SiO ₂ : 59.64; Al ₂ O ₃ : 16.87; P ₂ O ₅ : 23.49

2.2 Simulation details

All simulations were carried out using reactive molecular dynamics (MD). Periodic boundary conditions were applied in all three spatial directions. Prior to dynamic simulations, the system was subjected to energy minimization using the conjugate gradient algorithm to eliminate unfavorable atomic overlaps and high-energy configurations. The convergence criteria were set to 10⁻⁴ kcal/mol for total energy and 10⁻⁶ kcal/mol/Å for atomic forces. Following minimization, an initial equilibration was performed in the canonical (NVT) ensemble at 300 K for 100 ps to relieve residual stresses and stabilize the short-range structure.

To obtain a fully reacted and structurally relaxed amorphous geopolymer network, a melt–quench procedure was employed. The system was heated from 300 K to 1200 K over 100 ps under the NVT ensemble, followed by isothermal annealing at 1200 K for 300 ps to facilitate structural rearrangement and promote condensation reactions. Subsequently, the system was cooled from 1200 K back to 300 K over 300 ps under the NVT ensemble. After cooling, a long equilibration was conducted in the isothermal–isobaric (NPT) ensemble at 300 K and 1 atm for 1000 ps to stabilize the system density and pressure, yielding a well-relaxed amorphous reference structure.

The equilibrated configuration at 300 K was then used as the starting point for the temperature-dependent simulations. To evaluate the thermal response of the phosphoric acid-based geopolymer over a representative range of service and degradation conditions, independent simulations were performed at 300 K, 373 K, 573 K, 873 K, and 1173 K. These temperatures were selected to represent different thermal states of the system, namely ambient conditions (300 K), low-temperature activation (373 K), dehydration and early structural relaxation (573 K), intermediate high-temperature exposure (873 K), and severe thermal conditions (1173 K). For each target temperature, the system was gradually heated from 300 K to the desired temperature over 300 ps in the NVT ensemble, followed by 300 ps of isothermal

equilibration. A subsequent 1000 ps equilibration was then carried out in the NPT ensemble at 1 atm to ensure stable thermodynamic conditions prior to mechanical analysis.

2.3 Force field

All molecular dynamics simulations were performed using the LAMMPS package[40]. Interatomic interactions were described using the reactive force field (ReaxFF), which enables dynamic bond formation and dissociation during simulation and is well-suited for modeling chemically reactive aluminosilicate–phosphate systems.

It should be noted that no existing ReaxFF parameter set can fully capture the complex chemistry of phosphoric acid-based geopolymers involving P–Al–Si–O–H interactions. Therefore, in this study, a modified ReaxFF parameter set was developed based on previously reported parameters[41–44], with targeted refinements to better describe the structural and reactive characteristics of phosphate–aluminosilicate networks.

The parameter optimization was guided by a combination of experimental data and first-principles calculations. In particular, the bond dissociation energy (BDE) of P–O bonds were calibrated to 261.91 eV, which is in close agreement with density functional theory (DFT) results (~ 262.3 eV) reported in the literature[37]. In addition, the Al–O interaction parameters were adjusted to reproduce experimentally observed bond lengths in the range of 1.88–1.92 Å[7, 11]. Cross-interaction parameters, including Si–Al, P–Al, and Si–P pairs, were further refined to reflect the coordination environments and connectivity characteristics typical of phosphoric acid-based geopolymer systems[36].

The reliability of the modified force field was validated by comparing key structural descriptors with available experimental and computational data. The simulated average bond lengths, including Si–O (~ 1.60 Å), Al–O (~ 1.90 Å), and P–O (~ 1.50 Å), are consistent with both first-principles calculations and experimental measurements reported in the literature[36, 45].

These results demonstrate that the modified ReaxFF parameter set provides a reliable and physically meaningful description of the structural and chemical properties of phosphoric acid-based geopolymer systems, and is therefore suitable for investigating their temperature-dependent behavior.

3. Results and Discussion

3.1 Structural evolution

To investigate the temperature-dependent structural evolution of the phosphoric acid-based geopolymer, radial distribution functions (RDFs) for the key atomic pairs Si–O, P–O, and Al–O were analyzed over the temperature range of 300–1173 K (Fig. 2).

At 300 K, all RDF curves exhibit well-defined first peaks, reflecting the pronounced short-range order within the geopolymer network. The first peak positions are located at approximately 1.60 Å for Si–O,

1.50 Å for P–O, and 1.90 Å for Al–O, which are consistent with the characteristic bond distances of tetrahedral [SiO₄], [PO₄], and [AlO₄] units. This confirms that the constructed model successfully reproduces the fundamental local structural features of phosphoric acid-based geopolymers.

With increasing temperature, the positions of the first RDF peaks remain nearly unchanged, suggesting that the average equilibrium bond distances are only weakly affected by thermal excitation. In contrast, an obvious decrease in peak intensity and a gradual peak broadening are observed for all atomic pairs, indicating enhanced thermal vibrations and a progressive loss of short-range order.

Notably, the attenuation of the first peaks for Si–O and P–O becomes more pronounced at higher temperatures, particularly above 873 K, implying increased distortion of the tetrahedral units. Meanwhile, the second and higher-order peaks gradually weaken and become less distinguishable, revealing the deterioration of medium-range connectivity within the geopolymer network.

Overall, the RDF analysis indicates that the primary tetrahedral units remain largely intact in terms of average bond distances, whereas the medium-range network order is progressively disrupted with increasing temperature. Such structural disordering is expected to have a pronounced influence on the thermal stability and mechanical response of the geopolymer.

3.2 Bond and coordination analysis

Building on the RDF results, bond populations and coordination environments were further analyzed to clarify the atomic-scale mechanisms governing the thermal evolution of the geopolymer network.

As shown in Fig. 3, the populations of all bond types decrease gradually with increasing temperature, indicating progressive thermal degradation of the network. However, the extent of reduction varies substantially among different bonds, revealing a clear preferential bond-breaking behavior.

Among the bridging linkages (Fig. 4), Si–O–P bonds exhibit the most significant decline, decreasing from 950 at 300 K to 805 at 1173K, corresponding to a reduction of 15.3%. Al–O–P bonds also decrease notably, from 744 to 661, representing an 11.2% decrease, whereas Si–O–Al bonds show a much smaller reduction, from 1939 to 1853, with a reduction of only 4.4%. This trend suggests that P-containing linkages, especially Si–O–P bonds that connect silicate and phosphate tetrahedra, are more vulnerable to thermal disruption than aluminosilicate linkages.

A similar tendency is observed for the total bond populations. The number of P–O bonds show a reduction of 7.1%, which is more pronounced than the decreases observed for Si–O bonds (reduced by 1.2%) and Al–O bonds (reduced by 3.6%). This further indicates that phosphate-related structural units are relatively less thermally stable. These results suggest that the degradation of the geopolymer network is initiated primarily by the weakening of P-centered bonding environments.

To further examine local structural evolution, the coordination states of aluminum were analyzed. As presented in Fig. 5, five-coordinated Al species (Al(V)) dominate the Al population at all temperatures,

accounting for approximately 60%, followed by six-coordinated Al species (Al(VI)) at about 30–35% and a minor fraction of four-coordinated Al species (Al(IV), ~ 4–8%). This distribution is consistent with phosphate-rich systems, where phosphate linkages can stabilize higher-coordination Al environments.

With increasing temperature, the fraction of Al(VI) decreases, accompanied by a corresponding increase in Al(IV), particularly at 1173 K. This indicates thermal-induced local rearrangement and partial relaxation of the Al-centered coordination environment. In contrast, the Al(V) population remains relatively stable, suggesting that five-coordinated Al serves as a structurally robust intermediate state within the phosphate-aluminosilicate network.

Combining the typical atomic configurations shown in Fig. 3–5, the analysis of bond evolution and coordination reveals the main characteristics of the thermal degradation mechanism. The preferential weakening of P-related linkages, especially Si–O–P bonds, reduces the connectivity between structural units, while the conversion of higher-coordinated Al species toward lower-coordinated environments reflects local structural relaxation. It also explains that these coupled processes gradually decrease the connectivity of the phosphate–aluminosilicate network and promote temperature-induced depolymerization.

3.3 Atomic mobility at different temperatures

The RDF and bond statistics presented above indicate that increasing temperature does not lead to an abrupt collapse of the phosphoric acid-based geopolymer network, but instead induces gradual bond weakening and progressive disruption of medium-range connectivity. In particular, the preferential reduction of P-related linkages and the redistribution of Al coordination environments suggest that thermal excitation mainly promotes local structural rearrangement. To further characterize this process from a dynamic perspective, the atomic mobility of the main network-forming species was examined through the mean-squared displacement (MSD) of Si, Al, and P atoms, together with the corresponding apparent diffusion coefficients estimated from the MSD curves.

As shown in Fig. 6 (a–c), the MSD values of all three species increase with temperature, indicating enhanced atomic motion under thermal activation. At 300 and 373 K, the MSD curves remain at relatively low levels, suggesting that the geopolymer network is still largely constrained and only limited local fluctuations occur. When the temperature increases to 573 K, the atomic mobility rises moderately, while a much more pronounced increase is observed at 873 and 1173 K, reflecting substantial thermally induced structural rearrangement.

Among the three species, P atoms show the most significant increase in MSD with temperature. This behavior indicates that phosphate-related structural units are the most thermally activated part of the network. Such a trend is consistent with the bond analysis in Section 3.2, where Si–O–P and Al–O–P linkages were found to be more sensitive to temperature than aluminosilicate bridges. Once these P-related bridges are weakened, the associated phosphate units can undergo more frequent local displacement, bond reorientation, and structural relaxation.

The MSD values of Si and Al atoms also increase with temperature, but to a lesser extent than those of P. This suggests that the silicate and aluminate units remain relatively more constrained within the phosphate–aluminosilicate framework, even at elevated temperature. In particular, the more limited mobility of Al is consistent with the coordination analysis, which suggests that the thermal response of Al is mainly expressed through local coordination adjustment rather than large atomic displacement.

The apparent diffusion coefficients estimated from the MSD curves further support this trend, as shown in Fig. 6(d). All three species exhibit increasing diffusion coefficients with temperature, confirming the progressive enhancement of thermally activated motion. Among them, P atoms show the most pronounced increase, especially at high temperature, further indicating that phosphate-related structural units are the most dynamically responsive part of the network. By contrast, Al atoms exhibit the lowest diffusion coefficients over the whole temperature range, suggesting that their thermal response remains more localized.

Overall, the MSD and diffusion-coefficient analyses show that the atomic mobility of the geopolymer network increases progressively with temperature, with P atoms exhibiting the strongest response. This result provides dynamic support for the structural evolution discussed above and indicates that thermally induced rearrangement in the PABG system is primarily associated with the activation of phosphate-related structural units.

3.4 Temperature dependence of mechanical properties

To examine the mechanical response of the phosphoric acid-based geopolymer at the atomic scale, uniaxial tensile simulations were carried out along the X-, Y-, and Z-directions using molecular dynamics. After thermal equilibration at each target temperature in the NVT ensemble, a tensile load was imposed at a constant strain rate of $1 \times 10^{-4} \text{ fs}^{-1}$ using the Fix Deform command in LAMMPS. During deformation, a Nose–Hoover thermostat was employed to maintain thermal equilibrium. Representative atomic configurations before and after tensile loading are shown in Fig. 7.

As illustrated in Fig. 7, the tensile process induces an obvious elongation of the network and a more pronounced structural rearrangement in the deformed state. Although the overall framework remains continuous, local distortions and chain-like stretching of the network become evident after loading, indicating that the geopolymer accommodates tensile deformation through bond stretching and local reorganization rather than abrupt structural failure.

The corresponding stress–strain responses at different temperatures are presented in Fig. 8. For all three loading directions, the initial segment of the curves exhibits an approximately linear relationship between stress and strain, reflecting the elastic response of the network. With increasing temperature, the slope of the elastic region decreases progressively, and the stress response becomes less stiff. This trend indicates that the geopolymer loses part of its resistance to tensile deformation as thermal activation intensifies. Compared with the low-temperature state, the curves at higher temperatures show

earlier departure from the linear regime, suggesting that local structural relaxation and bond rearrangement are more readily activated under elevated thermal conditions.

The tensile stiffness is further quantified by the Young's modulus, as shown in Fig. 9. The modulus decreases from 42.5 GPa at 300 K to 39.3 GPa at 373 K, followed by a more substantial reduction to 28.9 GPa at 573 K. At higher temperatures, the modulus continues to decline to 26.0 GPa at 873 K and 25.5 GPa at 1173 K. Relative to the value at 300 K, the Young's modulus decreases by approximately 7.5% at 373 K, 32.0% at 573 K, 38.8% at 873 K, and 40.0% at 1173 K. The most pronounced softening occurs between 373 K and 573 K, after which the reduction becomes less significant, implying that a large portion of the thermally induced loss in stiffness has already taken place in the intermediate temperature range.

This temperature-dependent weakening of tensile stiffness is consistent with the structural evolution discussed in the previous sections. The preferential reduction of P-related linkages, especially Si–O–P and Al–O–P bonds, reduces the effective connectivity between phosphate, silicate, and aluminate units. In parallel, the enhanced mobility of P atoms and the increase in porosity promote local rearrangement and create additional free volume, which makes the network more compliant under tensile loading. As a result, the load-bearing skeleton becomes less efficient in transferring stress, leading to a lower elastic modulus.

The tensile results therefore provide a direct macroscopic reflection of the atomic-scale changes induced by temperature. The progressive loosening of the phosphate-aluminosilicate network weakens the ability of the material to sustain tensile deformation, and this effect is most clearly expressed in the decline of the Young's modulus with increasing temperature.

3.5 Temperature-induced structural evolution: porosity and bulk density effects

To further characterize the temperature-induced structural evolution of the phosphoric acid-based geopolymer, the changes in porosity and bulk density were examined, as shown in Fig. 10. These two parameters provide complementary information on the compactness of the phosphate–aluminosilicate network and therefore serve as useful indicators of structural loosening under thermal exposure.

The porosity remains nearly unchanged between 300 and 373 K, with values of 35.32% and 35.26%, respectively, indicating that the network packing is still largely preserved at low temperature. When the temperature increases to 573 K, the porosity rises to 37.61%, suggesting the onset of more evident free-volume generation. At higher temperatures, the increase becomes much more pronounced, reaching 43.46% at 873 K and 47.44% at 1173 K. In contrast, the bulk density decreases monotonically from 1.885 g/cm⁻³ at 300 K to 1.390 g/cm⁻³ at 1173 K. The opposite trends of porosity and bulk density indicate that the geopolymer network becomes progressively more open and less compact with increasing temperature.

This behavior is consistent with the atomistic results discussed in the preceding sections. The preferential weakening of P-related bridging bonds, together with the enhanced mobility of phosphate-related structural units, facilitates local rearrangement of the network and the accumulation of additional free volume. As a result, the structure gradually loses its original compactness, even though the primary short-range tetrahedral units remain generally preserved. In this sense, the increase in porosity and the simultaneous decrease in bulk density provide direct structural evidence for the progressive loosening of the phosphate–aluminosilicate framework under thermal loading.

The influence of this structural change on the mechanical response is further illustrated in Fig. 9, which shows the variation of Young's modulus as a function of porosity. An evident inverse correlation can be observed: as porosity increases, Young's modulus decreases continuously. The most pronounced reduction occurs between 373 and 573 K, where the increase in porosity is accompanied by a marked loss of mechanical resistance. At higher temperatures, the modulus continues to decrease as the porosity further increases, indicating that pore growth is closely associated with the deterioration of mechanical performance.

These results suggest that porosity development is an important structural factor governing the temperature-dependent behavior of the geopolymer. As the network becomes more porous and less dense, load transfer through the framework becomes less effective, which contributes directly to the reduction in Young's modulus at elevated temperature.

3.6 Temperature-dependent structure–property relationship

The temperature-dependent mechanical response of PABGs is intrinsically related to their structural evolution under thermal exposure. As temperature increases, the phosphate–aluminosilicate network undergoes progressive changes at multiple structural levels, which are directly reflected in the corresponding variation of macroscopic properties.

Among these structural changes, the degradation of phosphate-related linkages appears to be particularly important. From 300 to 1173 K, the population of Si–O–P bonds decrease by 15.3%, and that of Al–O–P bonds decrease by 11.2%, whereas Si–O–Al bonds show a much smaller reduction of 4.4%. This trend indicates that the phosphate-linked segments are the most temperature-sensitive part of the network. At the same time, the strong increase in P mobility further suggests that thermally induced rearrangement occurs preferentially around phosphate-containing structural units. These results provide atomistic evidence that temperature does not directly destroy the local tetrahedral motifs, but progressively weakens the connectivity between them.

The evolution of porosity and bulk density further clarifies how these atomic-scale changes translate into macroscopic behavior. As temperature increases from 300 to 1173 K, the porosity rises from 35.32% to 47.44%, corresponding to a relative increase of 34.3%, while the bulk density decreases from 1.885

g/cm^{-3} to 1.390 g/cm^{-3} , representing a reduction of 26.3%. These changes indicate that the PABG network becomes progressively more open and less compact under thermal exposure. The corresponding Young's modulus decreases from 42.5 to 25.5 GA, with an overall reduction of 40.0%. The inverse relationship between porosity and Young's modulus confirms that pore growth and network loosening are closely associated with the deterioration of mechanical performance.

From the perspective of the present work, the main contribution is to establish an atomistic picture of the temperature-induced degradation process in PABGs. The results show that the thermal response of this system is governed primarily by the instability of phosphate-related bridges, followed by local coordination rearrangement, increased atomic mobility, and progressive pore development. In this sense, the high-temperature mechanical degradation of PABGs is not caused by a sudden collapse of the short-range framework, but by the gradual loss of medium-range connectivity and structural compactness. This finding helps clarify the role of phosphate-linked structural units in controlling the thermal stability of PABGs and provides useful insight for the design of phosphate-based geopolymer materials with improved high-temperature resistance.

4. Conclusion

The temperature-dependent structural evolution and mechanical response of PABGs were investigated by molecular dynamics simulation. The results show that increasing temperature does not directly destroy the local Si–O, P–O, and Al–O units, but progressively weakens the medium-range connectivity of the phosphate–aluminosilicate network.

Phosphate-related linkages are the most temperature-sensitive structural components. From 300 to 1173 K, the populations of Si–O–P and Al–O–P bonds decrease by 15.3% and 11.2%, respectively, while Si–O–Al bonds decrease by only 4.4%. This evolution is accompanied by enhanced atomic mobility, particularly for P atoms, porosity increase from 35.32% to 47.44%, and bulk density decrease from 1.885 g/cm^{-3} to 1.390 g/cm^{-3} , indicating progressive network loosening under thermal exposure.

The tensile simulations further show a clear deterioration in mechanical performance, with Young's modulus decreasing from 42.5 Ga at 300 K to 25.5 Ga at 1173 K, corresponding to an overall reduction of 40.0%. These results indicate that the thermal degradation of PABGs is governed by gradual loss of network connectivity, increased atomic mobility, and pore growth, rather than abrupt collapse of the local framework.

This work provides an atomistic understanding of the temperature-dependent structure–property relationship of PABGs and offers useful guidance for the design of phosphate-based geopolymer materials with improved high-temperature performance.

Declarations

Author Contribution

J.L. : calculations, plot figures, analysis, writes the main manuscript A.Z. :Methodology, investigation, analysis, editing and reviewing the manuscript W. S. : Investigation, analysis; editing and reviewing the manuscript

Acknowledgments

The authors would like to thank the China Scholarship Council (CSC) for providing the CSC Scholarship and the FEDER (Fonds Européen de Développement Régional) for financial support of DECA GEO.

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Figures

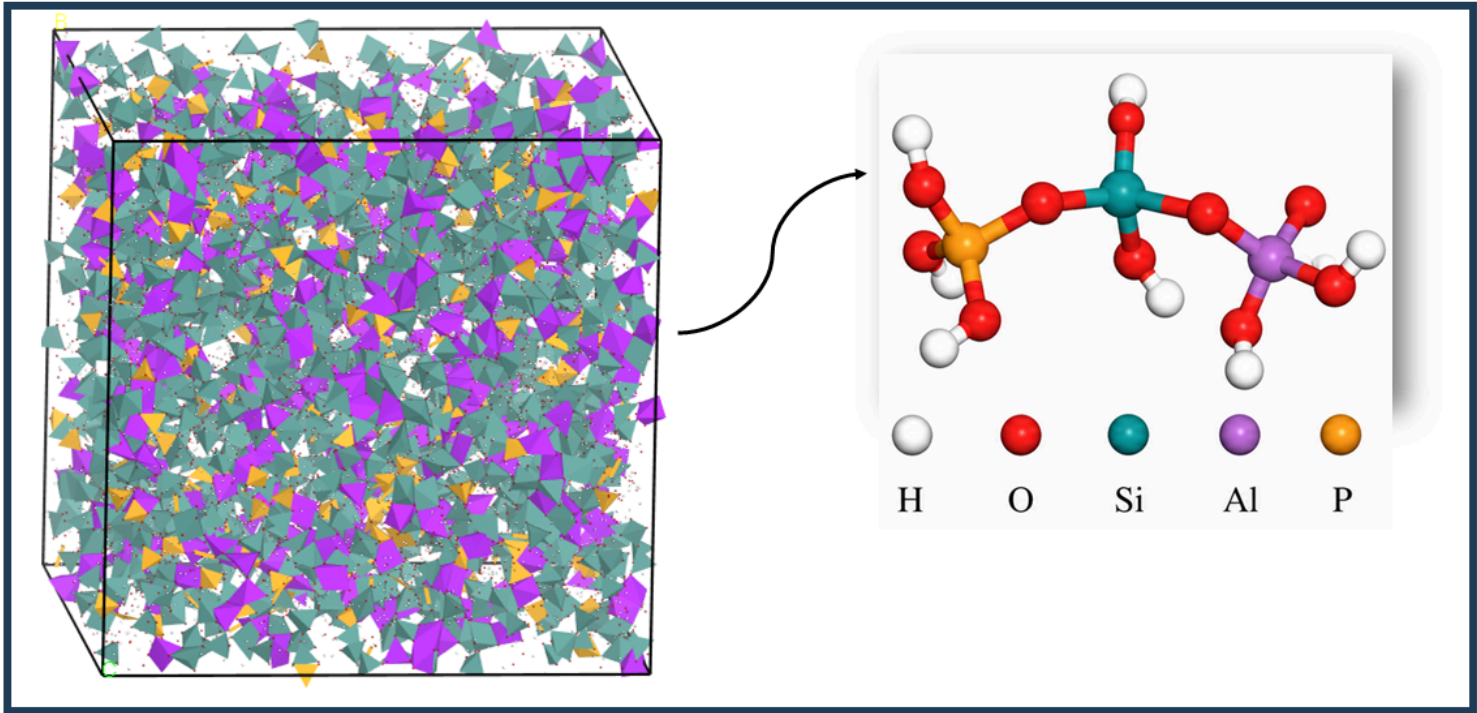


Figure 1

Initial PABG model structure.

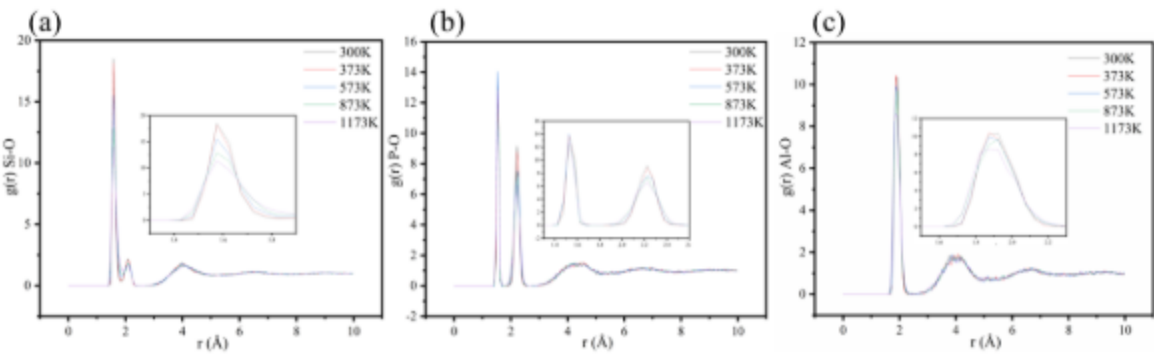


Figure 2

RDF curves at different temperatures (a)Si-O, (b)P-O, (c)Al-O.

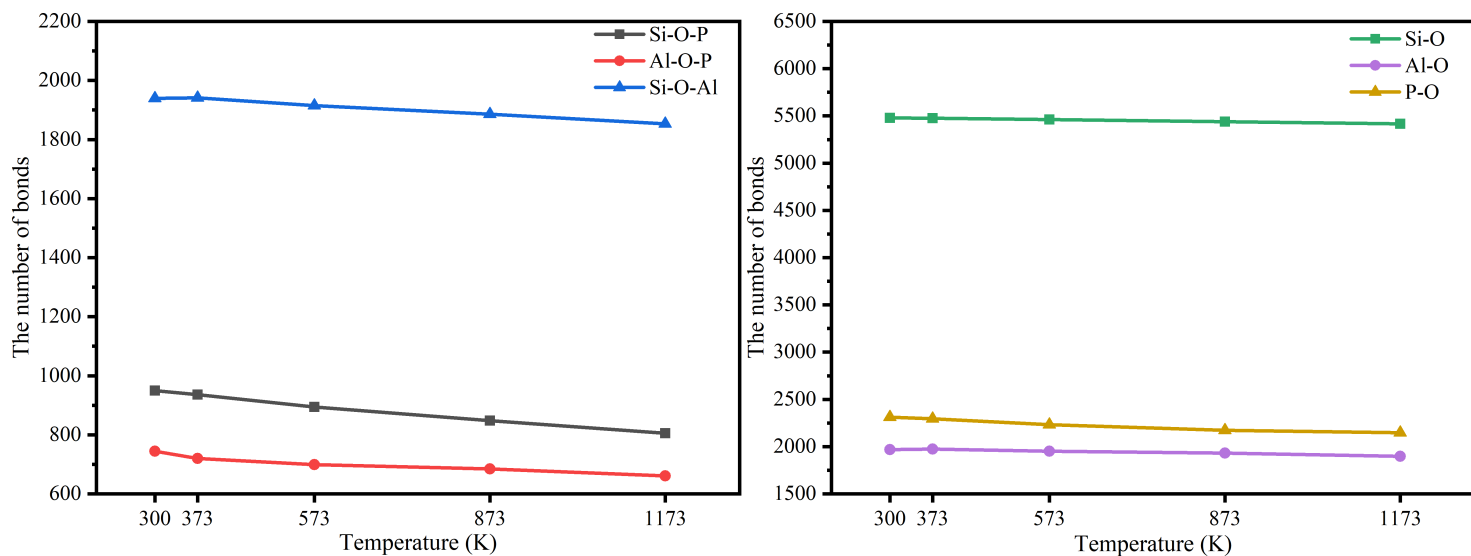


Figure 3

Temperature-dependent evolution of bond number in PABGs.

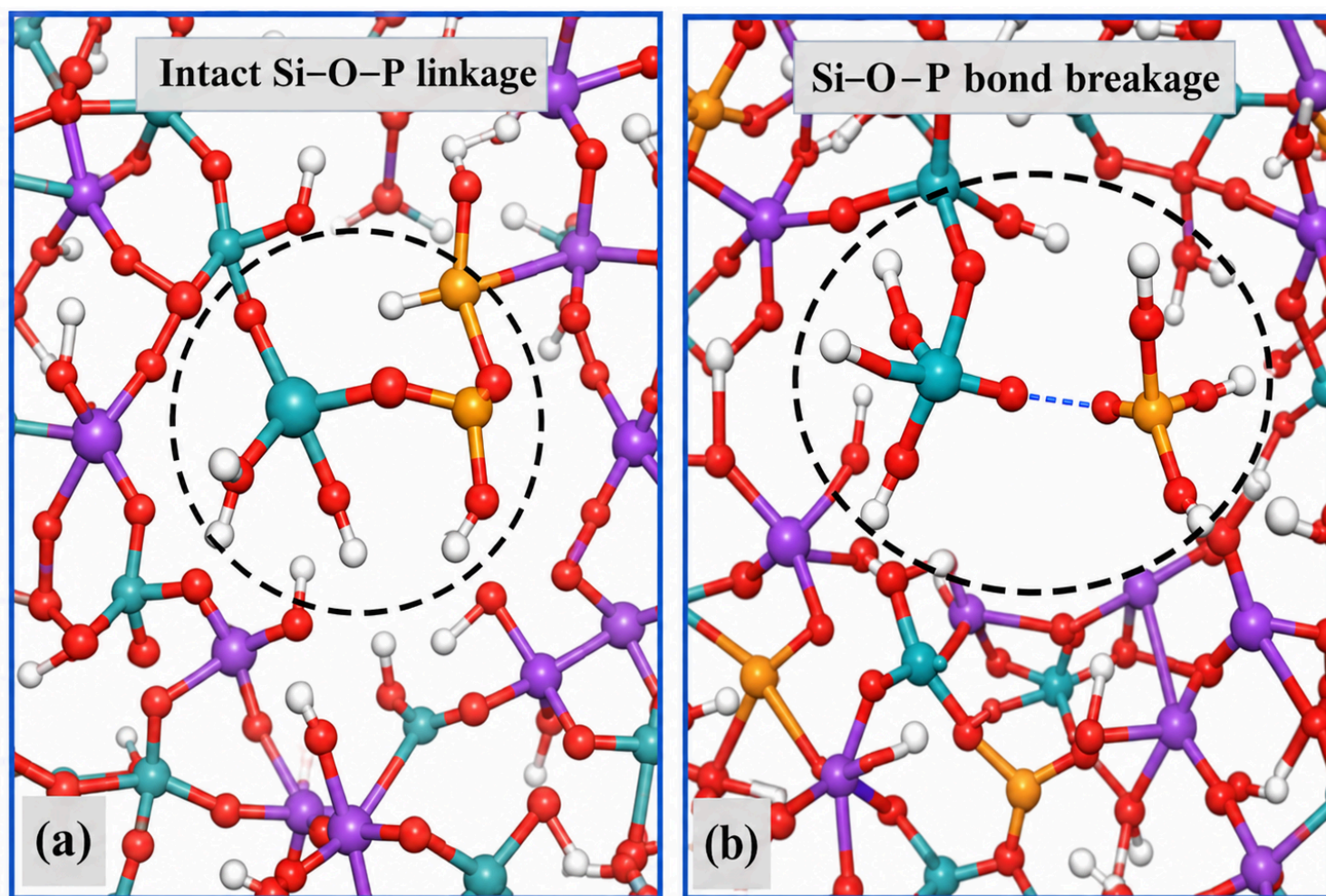


Figure 4

Atomistic illustration of Si–O–P bond cleavage in PABGs.

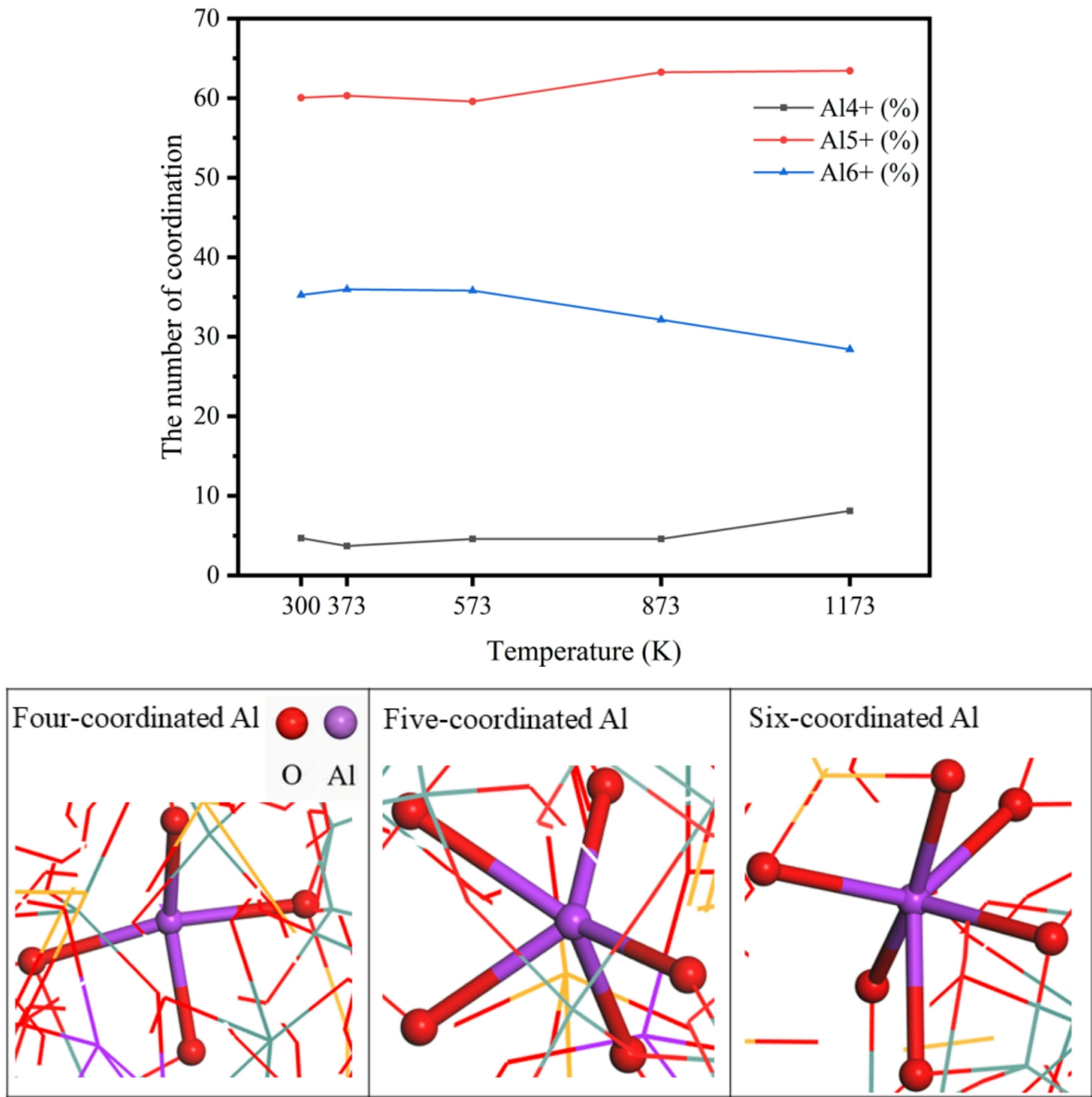


Figure 5

Temperature-dependent distribution of aluminum coordination states (Four-coordinated Al, Five-coordinated Al, and Six-coordinated Al).

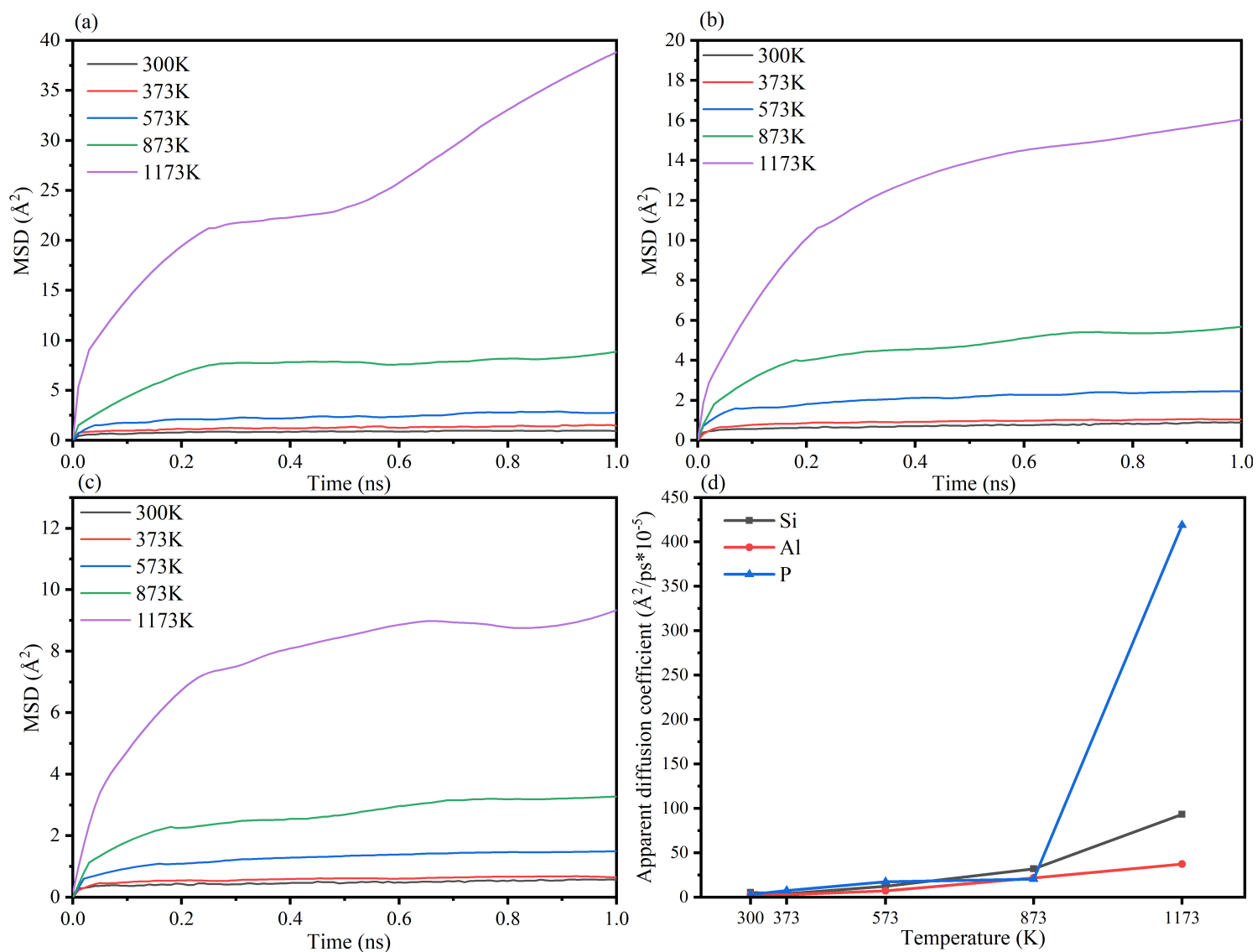


Figure 6

Temperature-dependent MSD in PABGs. (a) P MSD, (b) Si MSD, (c) Al MSD. And (d) apparent diffusion coefficient of atoms.

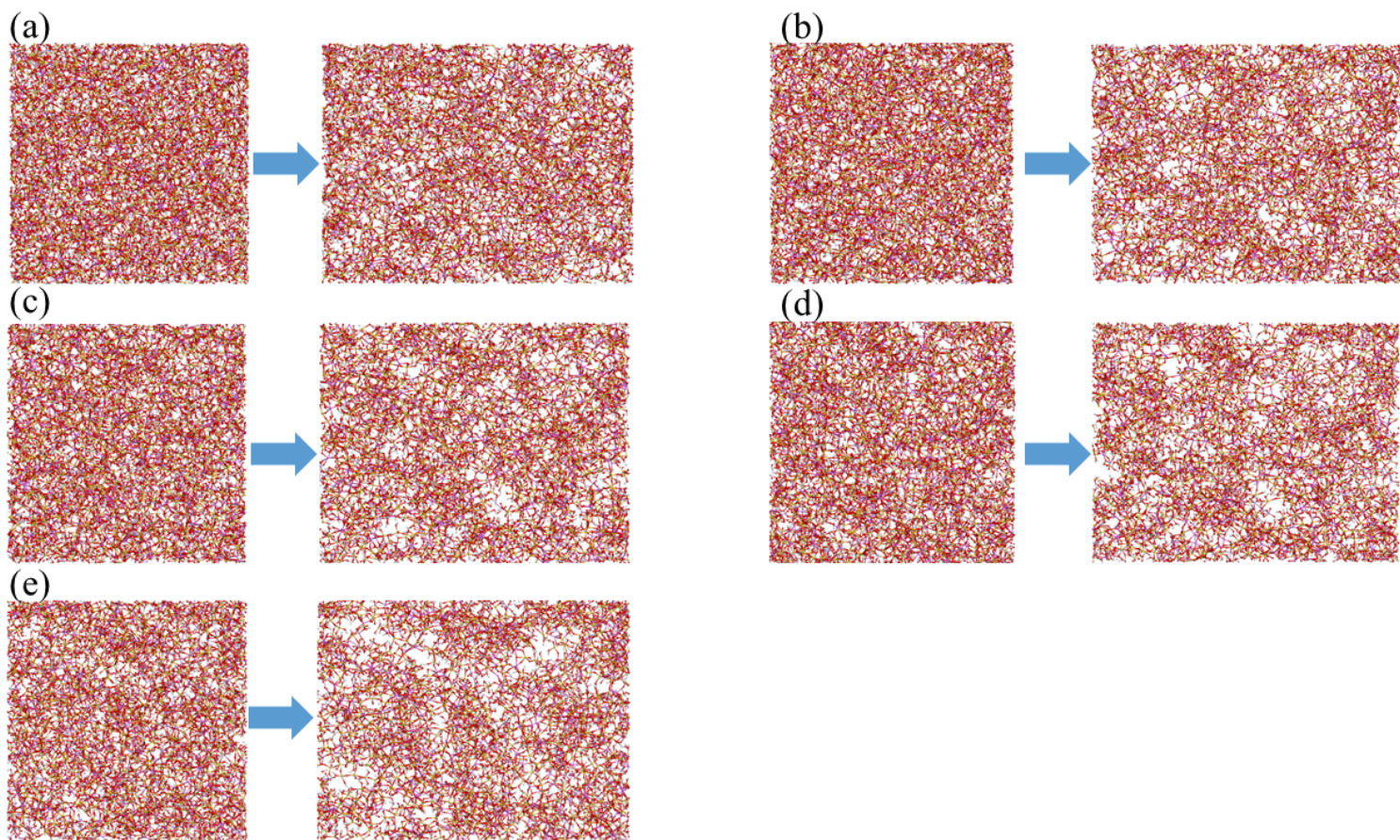


Figure 7

Representative atomic configurations of PABGs before and after uniaxial tensile deformation (a)300K, (b)373K, (c)573K, (d)873K, (e)1173K.

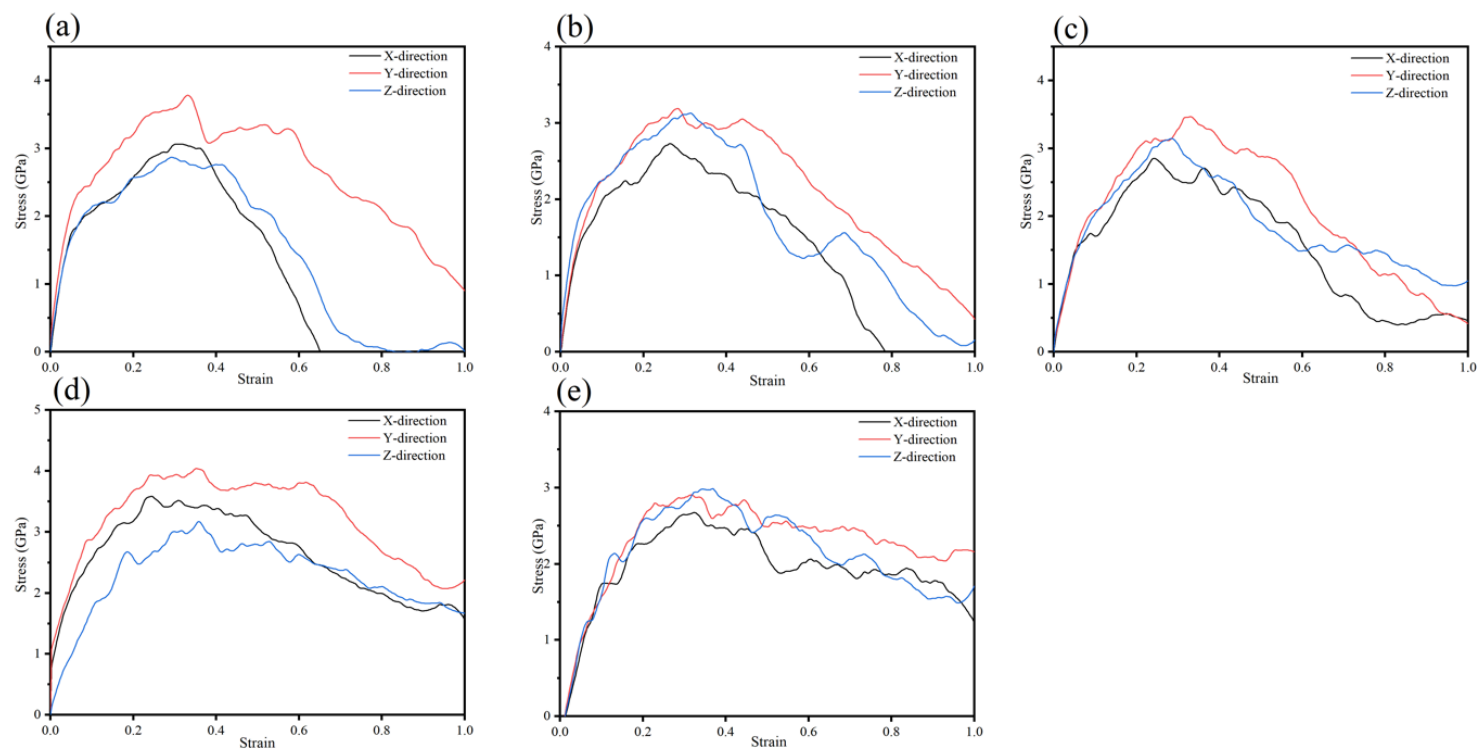


Figure 8

Uniaxial tensile stress–strain curves of PABGs along the X-, Y-, and Z-directions at different temperatures (a)300K, (b)373K, (c)573K, (d)873K, (e)1173K.

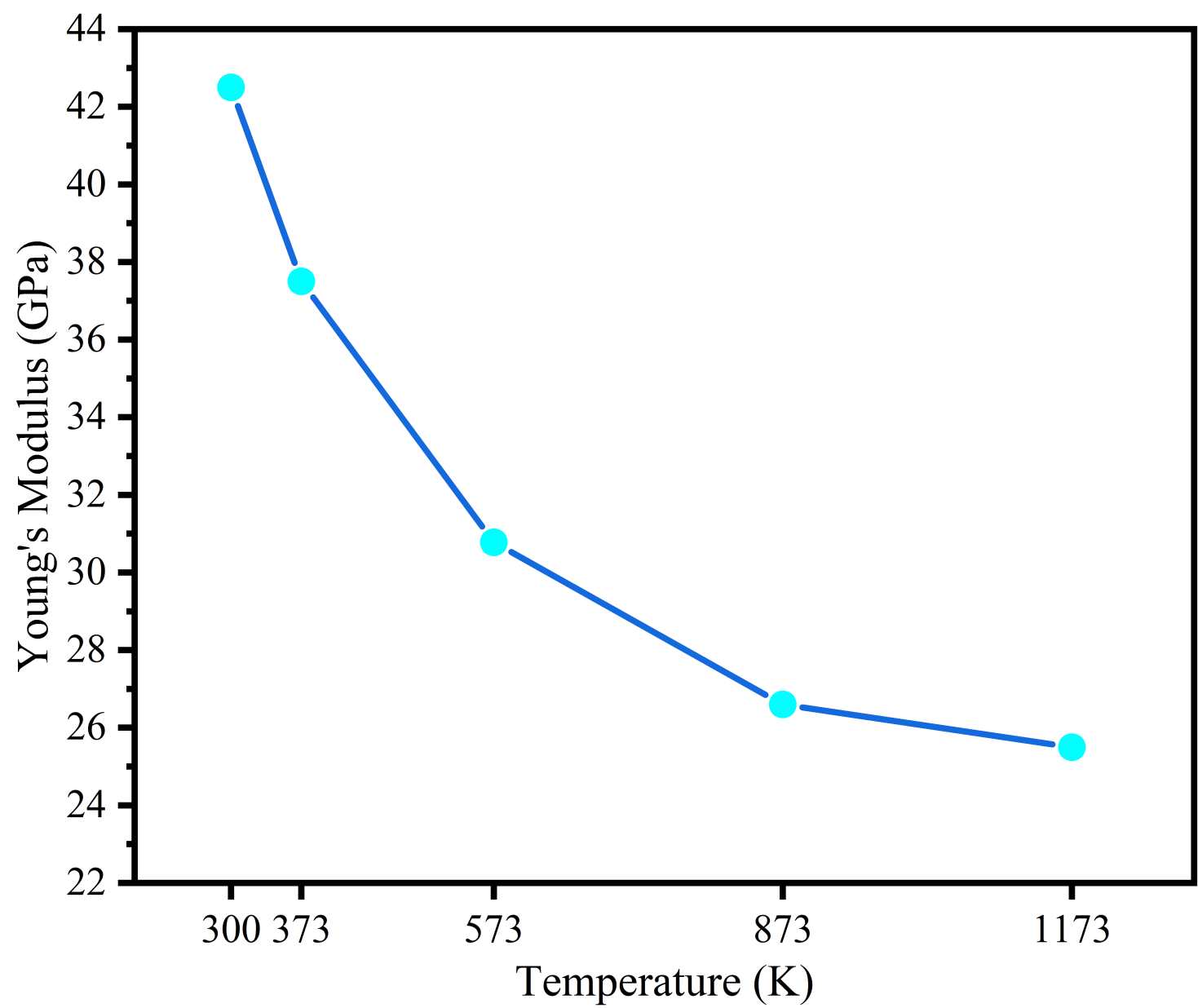


Figure 9

Temperature-dependent of the Young's modulus of PABGs.

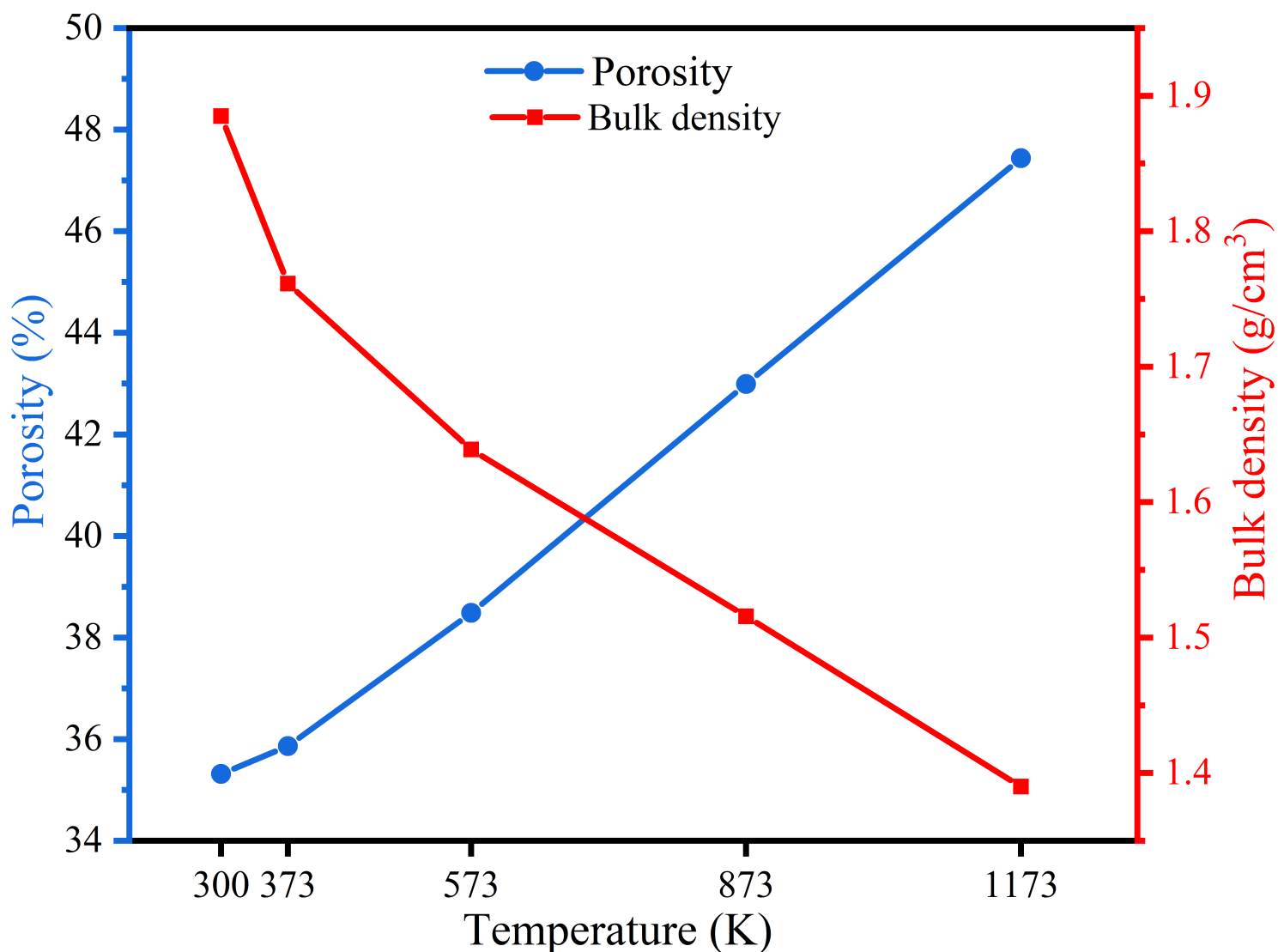


Figure 10

Temperature-dependent of porosity and bulk density of PABGs.