

## RAPID COMMUNICATION

## Thermal history driven molecular structure transitions in alumino-borosilicate glass

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## Abstract

The glass network structure governs various thermos-physical properties such as viscosity, thermal, and electrical conductivities, and crystallization kinetics. We investigated the effect of temperature on structural changes in a Na<sub>2</sub>O-CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> glass system using <sup>27</sup>Al MAS NMR spectroscopy. Around the glass transition temperature, most of aluminate structures exist as AlO<sub>4</sub>, acting as a glass former. When the temperature is above the melt crystallization temperature, the AlO<sub>4</sub> structure is drastically decreased and glass structures are mainly composed of AlO<sub>5</sub> and AlO<sub>6</sub>, acting as glass modifiers. Thermodynamic assessment based on Gibbs energy minimization was used to confirm the dependency of aluminate structure's amphoteric characteristic on temperature by calculating the site fraction of aluminate molecular structures at different temperatures. Temperature-induced aluminate structural variation can also influence silicate and borate structural changes, which have been confirmed by the <sup>29</sup>Si and <sup>11</sup>B NMR spectra.

## KEYWORDS

glass network, molecular structure, solid-state MAS NMR, structural variations, temperature effect

## 1 | INTRODUCTION

Understanding structural variations of aluminate in amorphous structure had been an object of research for a long time due to its importance for industrial applications. Typical examples are sealing materials for solid oxide fuel cells (SOFCs),<sup>1-3</sup> electrolytes for lithium-ion batteries,<sup>4,5</sup> and glass lubricants for continuous casting of steel.<sup>6,7</sup>

Smeacetto et al.<sup>1,2</sup> reported that sodium calcium aluminosilicate glass-ceramic could be an ideal sealing material for SOFC because it provides an interface free from pores and cracks, and has low reactivity under humidified hydrogen condition. Aluminosilicate glass can also be potential electrolyte material for a solid lithium-ion battery due to high-temperature durability and ionic conductivity by ion-exchangeable network structure.<sup>4,5</sup> Moreover, aluminosilicate glass can be a promising lubricant during continuous casting of Advanced High Strength Steels

(AHSS) with larger amount of aluminum.<sup>6</sup> As the conventional silicate-based glass lubricant tends to be easily reduced by aluminum in AHSS, developing chemically stable aluminosilicate glass is desirable to enhance both the quality and productivity of continuously cast AHSS.<sup>7</sup> Thus, understanding structural variation in aluminate is crucial in designing appropriate materials for various industrial applications.

As an amphoteric substance, alumina can act either as an acid or as a base in the multi-oxide system. Therefore, depending on the surrounding conditions, alumina can be either a network former or a network modifier within an amorphous network structure. The molecular ratio between R<sub>x</sub>O (R = Alkali cation or alkaline-earth cation) and Al<sub>2</sub>O<sub>3</sub> has been widely used to determine aluminate structure.<sup>8-10</sup> The aluminate unit has a fully 4-folded structure under the condition of R<sub>x</sub>O/Al<sub>2</sub>O<sub>3</sub> = 1. A certain amount of Al<sup>3+</sup> modifier is present within the network structure when

$R_xO/Al_2O_3 < 1$ . On the contrary, when  $R_xO/Al_2O_3 > 1$ , the aluminate unit has a 4-fold structure and a certain amount of NBO arise from residual alkali or alkaline-earth cations.

Furthermore, several recent studies have claimed that the aluminate structure could be determined by not only the  $R_xO/Al_2O_3$  ratio but also the temperature.<sup>11-15</sup> Stebbins et al<sup>15</sup> showed that the structure of CaO- $Al_2O_3$ - $SiO_2$  ternary glass-forming liquid changes depending on temperature. Despite of their pioneering achievement on the temperature-driven structural variation, there are serious limitations. Because the structural variation was induced by insignificant range of fictive temperature adjustment, their study only considered structure of glass-forming liquid at high temperature. Thus, their results cannot be directly applied to the glass-ceramic industry where both high-temperature glass-forming liquid and low temperature non-crystalline solids are frequently used in glass sealant for SOFC and glass electrolytes for batteries, respectively. Moreover, the structure of a multi-glass system needs to be studied further due to its industrial needs.

This paper presents a novel approach to control alumina structure by imposing different temperature ranges. Using MAS NMR, we studied the different structural variation in aluminate structure at around glass transition temperature and above melt crystallization temperature.

## 2 | MATERIALS AND METHODS

We synthesized alumino-borosilicate glass using a melting and quenching technique (see Supplementary S1). The chemical composition of the glass was analyzed by X-ray fluorescence (XRF) (see Table 1). Also, the glass transition, the crystallization, and melting temperatures of the glass were measured by a Differential Scanning Calorimeter (DSC) (see Supplementary S2 and S4, Figure S4 and S5). The sample preparation for MAS NMR was started by quenching the melts at 1400°C to obtain fully glassy state. Then, the glass has been thermally equilibrated at different temperatures: at 610°C, slightly above the glass transition temperature, and at 1250°C, above the melt crystallization temperature. The glass was rapidly quenched to room temperature. Structural investigations conducted using <sup>27</sup>Al, <sup>29</sup>Si, and <sup>11</sup>B solid-state MAS NMR (see Supplementary S3).

**TABLE 1** Chemical compositions (in mol %) of studied sample in the present work

Glass	Chemical composition (mol %)				
	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	CaO
Contents	33.2	7.4	6.2	8.8	44.4

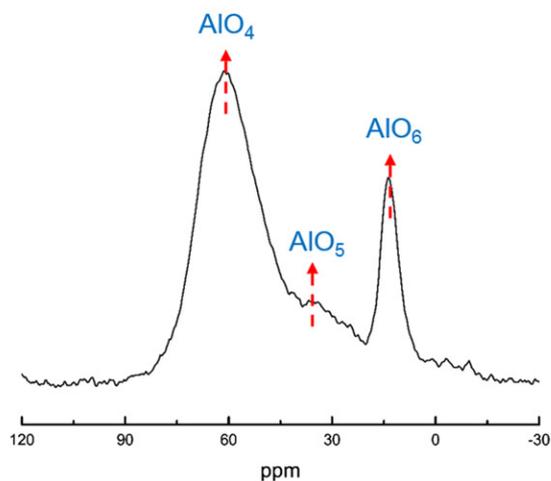
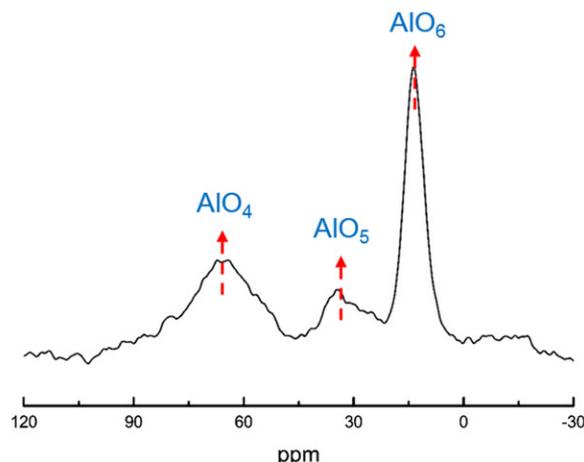
## 3 | RESULTS AND DISCUSSION

When  $Al_2O_3$  is more basic than its surroundings, it acts as a network modifier, which disconnects the network structure in the form of either  $AlO_5$  units or  $AlO_6$  units (see Supplementary S5, Figure S6). Conversely, when  $Al_2O_3$  is more acidic than its surroundings, it acts as a network former in the form of  $AlO_4$  units because it compensates charges with alkali or alkaline-earth cations including  $Na^+$  and  $Ca^{2+}$ .<sup>8,16,17</sup>

To understand aluminate structure variation induced by temperature change, the chemical shifts from solid-state <sup>27</sup>Al MAS NMR spectra were investigated. Figure 1A, B show <sup>27</sup>Al NMR spectra results of glass samples acquired at 610°C and 1250°C, respectively. It is obvious that <sup>27</sup>Al chemical shifts are dependent on the Al-O coordination number. The spectra show three resolved peaks for  $AlO_6$ ,  $AlO_5$ , and  $AlO_4$  units. In Figure 1A, the <sup>27</sup>Al NMR analysis confirms that the aluminate in the glass sample obtained at 610°C is mostly present in the form of  $AlO_4$  network former, and partially present in the forms of  $AlO_5$  and  $AlO_6$  network modifiers. In Figure 1B, the aluminate in the glass sample obtained at 1250°C is mostly present as  $AlO_5$  and  $AlO_6$  within the glass network. It should be emphasized that charge compensators preferentially bond with  $AlO_4$  in a peralkaline glass structure.<sup>3,11,18-20</sup> However, despite of  $Na_2O/Al_2O_3 > 1$  as shown in Table 1, the <sup>27</sup>Al NMR spectra in Figure 1 confirm that a number of aluminate units do not act as formers but as modifiers within the network structure. Thus, it implies that the temperature affects the quantity of aluminum modifiers.

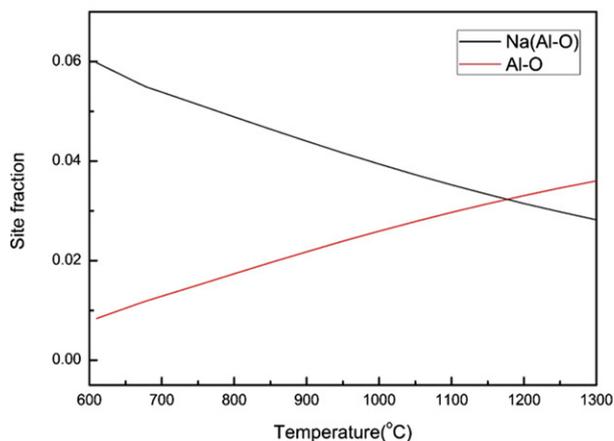
To properly explain the temperature-induced variation in an aluminate structure within a glass sample, we used site fraction functions in a computational thermodynamic program based on Gibbs energy minimization, FactSage 6.4, to assess the degree of charge compensation between a  $Na^+$  and an aluminate structure. Albeit the employed chemical composition contained a large number of  $Ca^{2+}$ , the thermodynamic calculation was conducted by considering only  $Na^+$  because charge compensation degree of alkaline-earth cation is much smaller than that of alkali cation.<sup>8,16</sup> In Figure 2A, the red solid line represents the site fraction of Al-O molecules bound with charge compensators,  $Na^+$ , and the black solid line represents the site fraction of Al-O molecules without any bond with  $Na^+$ .

As shown in Figure 2A, B, the thermodynamic assessment also showed that Al-O molecules are dominantly present as a network modifier without any charge compensator in the form of  $AlO_5$  and  $AlO_6$  at a high temperature. However, at lower temperature,  $Na^+$  bonds with Al-O molecules resulting in  $AlO_4$  network formers within the network structure. The results suggest that the temperature greatly affects the degree of charge compensation and

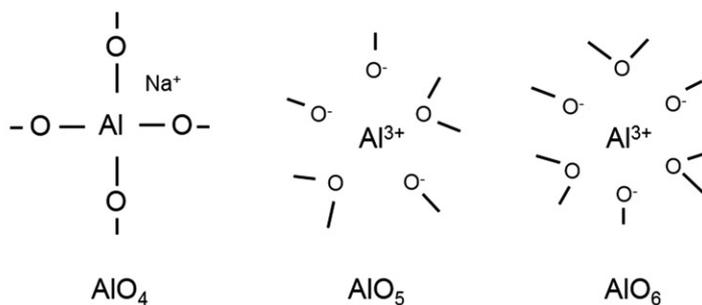
(A)  $^{27}\text{Al}$  MAS NMR spectrum of glass at 610 °C(B)  $^{27}\text{Al}$  MAS NMR spectrum of glass at 1250 °C

**FIGURE 1**  $^{27}\text{Al}$  MAS NMR spectra of glass sample thermally treated at 610°C and glass sample quenched at 1250°C collected at 11.7 T. A,  $^{27}\text{Al}$  MAS NMR spectrum of the glass at 610°C. B,  $^{27}\text{Al}$  MAS NMR spectrum of the glass at 1250°C [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

(A) site fraction of aluminate structural units VS Temperature



(B) 2D structural units of aluminate molecule



**FIGURE 2** FactSage calculation for site fraction of aluminate molecular units with respect to temperature and that of structural units of aluminate. A, Site fraction of aluminate molecular units versus temperature. B, two-dimensional aluminate structural units: Na charge compensated  $\text{AlO}_4$ ,  $\text{AlO}_5$ , and  $\text{AlO}_6$  [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

the structure of aluminate. Therefore, controlling the amphoteric property of alumina is feasible within a glass structure.

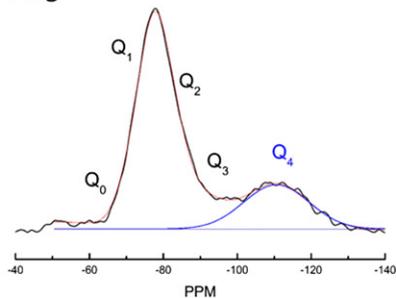
Figure 3A, B show the  $^{29}\text{Si}$  MAS NMR spectra for the glass samples obtained at 610°C and 1250°C, respectively. The molecular structure of silicate can be in one of five different forms,  $\text{Q}_0$ – $\text{Q}_4$  units (see Supplementary S6, Figure S7). Each spectrum shows two distinct peaks at  $\sim -78$  ppm and  $\sim -110$  ppm. By comparing two spectra, we confirmed the structural variations in silicate network

structure. Especially, two spectra differ greatly at  $\sim -110$  ppm, which corresponds to  $\text{Q}_4$  units of silicate.<sup>21</sup>  $\text{Q}_4$  units can be considered as polymerization degree of silicate network. In Figure 3A, B, the polymerization level at 1250°C is considerably lower than that at 610°C. Therefore, the connectivity of the silicate network should become lower at higher temperature.

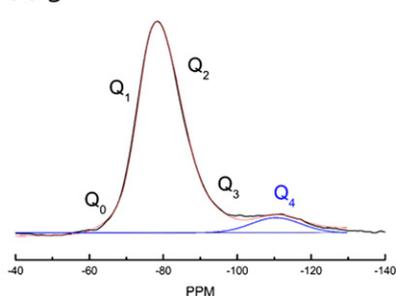
Figure 3C, D show the  $^{11}\text{B}$  MAS NMR spectra for the glass samples acquired at 610°C and 1250°C, respectively. Generally, the borate structure can be any of a  $\text{BO}_3$

**$^{29}\text{Si}$  MAS NMR spectra**

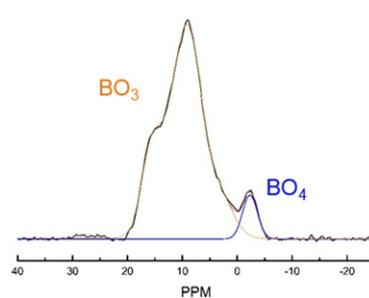
(A) glass at 610°C



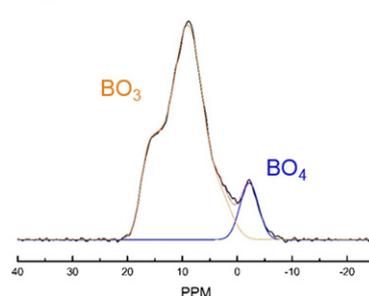
(B) glass at 1250°C

 **$^{11}\text{B}$  MAS NMR spectra**

(C) glass at 610°C



(D) glass at 1250°C



**FIGURE 3**  $^{29}\text{Si}$  and  $^{11}\text{B}$  MAS NMR spectra of the glasses at 610°C and 1250°C obtained at 11.7 T. For each color line in  $^{29}\text{Si}$  and  $^{11}\text{B}$  MAS NMR spectra represents the Gaussian fit curve of each structural unit. A,  $^{29}\text{Si}$  MAS NMR spectrum of the glass at 610°C. B,  $^{29}\text{Si}$  MAS NMR spectrum of the glass at 1250°C. C,  $^{11}\text{B}$  MAS NMR spectrum of the glass at 610°C. D,  $^{11}\text{B}$  MAS NMR spectrum of the glass at 1250°C [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

triangular ring, a  $\text{BO}_3$  triangular non-ring, or a  $\text{BO}_4$  tetrahedron.<sup>22</sup> The tetrahedral borate structure can form only when a charge compensator is bound with a triangular borate in a same way  $\text{AlO}_4$  is formed by compensating with an alkali or alkaline-earth metal ion (See Supplementary S7, Figure S8). In Figure 3C, D,  $\text{BO}_4$  tetrahedron is more active in the glass sample obtained at 1250°C than the sample obtained at 610°C. The variation in silicate and borate structures can be caused by the change in the charge compensation degree of aluminate-alkali cations induced by temperature variation.

All the above discussions in this study strongly suggest that the  $\text{Na}^+$  cations preferentially bond with an aluminate structure at lower temperature while it is expected that  $\text{Na}^+$  cations are released due to low charge compensation ability and produce a large amount of non-bridging oxygen at higher temperature.<sup>3,11,18-20</sup> On the contrary, the  $\text{BO}_4$  structure becomes more abundant at higher temperature because the  $\text{Na}^+$  cations are released from an aluminate structure due to lower bonding energy between  $\text{AlO}_4$  and  $\text{Na}^+$  cation, which act as charge compensators for making  $\text{BO}_4$  units<sup>23</sup> (see schematic illustrations of a microstructure in Supplementary S8, experimental evidences in S9, reproducibility of molecular structures at studied temperatures in S10, and S11).

## 4 | CONCLUSIONS

We successfully investigated molecular structure variations of a  $\text{Na}_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{B}_2\text{O}_3$  glass system that is driven by not only the chemical composition but also a

temperature variation. Such structural variations are caused by alumina's amphoteric property, which is affected by the temperature-induced change in the charge compensation ability. Understanding the aluminate structure within a glass system according to temperature and charge compensation ability can be beneficial to various industrial applications.

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## SUPPORTING INFORMATION

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**How to cite this article:** Baek J-Y, Shin S-H, Kim S-H, Cho J-W. Thermal history driven molecular structure transitions in alumino-borosilicate glass. *J Am Ceram Soc*. 2018;101:3271-3275.  
<https://doi.org/10.1111/jace.15553>