Understanding the Formation of CaAl$_2$Si$_2$O$_8$ in Melilite-Based Glass-Ceramics: Combined Diffraction and Spectroscopic Studies

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Supporting Information

ABSTRACT: An assessment is undertaken for the formation of anorthite crystalline phase in a melilite-based glass composition (CMAS: 38.7CaO–9.7MgO–12.9Al$_2$O$_3$–38.7SiO$_2$ mol %), used as a sealing material in solid oxide fuel cells, in view of the detrimental effect of anorthite on the sealing properties. Several advanced characterization techniques are employed to assess the material after prolonged heat treatment, including neutron powder diffraction (ND), X-ray powder diffraction (XRD), $^{29}$Si and $^{27}$Al magic-angle spinning nuclear magnetic resonance (MAS-NMR), and in situ Raman spectroscopy. ND, $^{29}$Si MAS-NMR, and $^{27}$Al MAS-NMR results revealed that both Si and Al adopt tetrahedral coordination and participate in the formation of the network structure. In situ XRD measurements for the CMAS glass demonstrate the thermal stability of the glass structure up to 850 °C. Further heat treatment up to 900 °C initiates the precipitation of melilite, a solid solution of akermanite/gehlenite crystalline phase. Qualitative XRD data for glass-ceramics (GCs) produced after heat treatment at 850 °C for 500 h revealed the presence of anorthite along with the melilite crystalline phase. Rietveld refinement of XRD data indicated a high fraction of glassy phase (~67%) after the formation of crystalline phases. The $^{29}$Si MAS-NMR spectra for the CMAS-GC suggest the presence of structural units in the remaining glassy phase with a polymerization degree higher than dimer units, whereas the $^{27}$Al MAS-NMR spectra revealed that most Al$^{3+}$ cations exhibit a 4-fold coordination. In situ Raman spectroscopy data indicate that the formation of anorthite crystalline phase initiated after 240 h of heat treatment at 850 °C owing to the interaction between the gehlenite crystals and the remaining glassy phase.

1. INTRODUCTION

In recent years, planar-solid oxide fuel cells (p-SOFC) have been considered as one of the most efficient and versatile power generation systems. However, a major hurdle that needs to be overcome for their commercialization is the development of a hermetic high-temperature sealing material.1–4 Durable sealants are required to prevent gas mixing between the anode and cathode compartments, to bond the cell stacks, and to provide electrical insulation. Among the various types of sealing materials, glasses and glass-ceramics (GCs) are considered to be the most efficient and attractive sealants for SOFCs because of their ability to form hermetic and durable seals at high temperatures and at relatively low cost.3–6

Glass-based materials are promising for many technological applications because of their flexible chemical compositions combined with ease of handling and manufacturing and relative cheapness.4,7 Glasses are known to be more stable at room temperature (RT) because of the short-range order of the bonding ions. Although the stability of vitreous phase usually decreases with increasing temperature or during isothermal heat treatments,7 the thermal, mechanical, and electrical properties of the heat-treated materials may be improved through the formation of crystalline phases, forming GCs. The chemical formulae of the formed crystalline phases are closely related to that of the parent glass composition. In general, GCs are polycrystalline materials, normally obtained from parent glasses by partial devitrification.7 However, the polymorphism of the crystalline phase is another important feature that can affect the properties of GCs. For example, barium-rich, aluminosilicate-based glasses are known to exhibit appropriate...
coefficients of thermal expansion (CTEs) for their operation as sealing materials in SOFCs. However, these glasses have a tendency to devitrify at around 800–850 °C, resulting in the appearance of hexacelsian (BaAl₂Si₂O₈). During SOFC operation, the crystalline phase gradually transforms into its monoclinic polymorph, which has a low CTE associated with the deterioration of the mechanical properties. Hence, understanding the formation and development of crystalline phases in GC-based materials during devitrification is of crucial importance for industrial applications.

In search of a suitable glass sealant material for p-SOFCs, with high chemical resistance and appropriate CTE, we have investigated a glass composition in the CaO–MgO–Al₂O₃–SiO₂ (CMAS) system and within the primary crystallization field of akermanite (Ca₂MgSi₂O₇)/gehlenite (Ca₂Al₂SiO₇). Nevertheless, the formation of triclinic anorthite (CaAl₂Si₂O₈), an important member of the feldspar family, as the second dominant crystalline phase after 300 h of heat treatment at 850 °C, puts into question the reliability of CMAS as a glass seal. The most important aspects of anorthite in relation to sealant applications are the temperature-induced reversible phase transformation and its CTE value. Anorthite adopts triclinic symmetry (space group P1̅) at RT but transforms to the body-centered I̅I space group at a transition temperature (Tc) of approximately 240 °C. The framework structure is more crumpled in the P1̅ symmetry and more expanded in the I̅I phase. Moreover, the apparent CTE value of anorthite was reported to be 11 × 10⁻⁶ K⁻¹ within the temperature range 20–1000 °C. This contrasts with the value of ~5.3 × 10⁻⁶ K⁻¹ determined within the temperature range of 250–800 °C from high-resolution data of the I̅I phase. Hence, the CMAS glass may not be completely satisfactory in real SOFC operating conditions under repeated thermal cycling, under which even a minor mismatch in the CTE gives rise to thermal stresses in the GC sealant during startup and shutdown.

Although the induced stresses may not cause an immediate seal failure, they may generate cracks during long-term operation. The formation of undesired crystalline phases in the technologically applicable GC materials therefore should be avoided.

In view of the above, we endeavor to better understand the formation of undesired secondary crystalline phase in CMAS-GC-based sealant materials. In the present study, a range of structurally sensitive investigation tools are employed to this end, including neutron powder diffraction (ND), X-ray powder diffraction (XRD), ²⁹Si and ²⁷Al magic-angle spinning nuclear magnetic resonance (MAS-NMR), and in situ Raman spectroscopy.

2. RESULTS

2.1. Glass Structure. Figure 1 shows the total experimental structure factor S(Q) (dotted line) and simulated S(Q) from the reverse Monte Carlo (RMC) model (continuous line) for the CMAS glass composition derived from neutron diffraction for Q values in the range 0.95–9.5 Å⁻¹. It is known that the ND technique is highly sensitive to hydrogen, the presence of which in glass samples due to hydrolysis results in well-identified peaks in the final ND spectrum. Here, the ND pattern reveals that the specimens are fully amorphous, and no hydrogen was detected. The most striking feature of the S(Q) data is the relatively high intensity and sharp distribution of the first and second peaks of the CMAS glass, which is a fingerprint of a network structure formed by well-defined units. The intensity of the third and fourth peaks of the glass becomes broader, indicating a complex network structure.

Several partial atomic pair correlation functions and coordination number distributions have been revealed with moderately good stability. Herein, we focus on the characteristic features of oxygen coordination of the Si and Al network formers by analyzing the polyhedral units and their linkages. The derived atomic pair correlation functions gᵢᵢ(r) and the coordination number distributions from the RMC simulations for the CMAS glass composition are shown in Figures 2 and 3, respectively. In general, the position and width of the peak in the pair correlation function gᵢᵢ(r) reflect the value and the distribution of the distances for different atomic correlations, respectively. The oxygen-linked gᵢ₋O(r) (where i = Ca, Mg, Al, Si, and O) are shown in the plots of Figure 2. The peaks for Si–O, Al–O, Mg–O, and Ca–O pairs are located at 1.6, 1.75, 1.7, and 2.35 Å, respectively. These values concur with the characteristic lengths of 1.6 Å for Si–O and 1.75 Å for Al–O for multicomponent aluminosilicate glasses.

The peak corresponding to Si–O correlations is narrow, whereas those corresponding to Al–O, Mg–O, and Ca–O are broader and more asymmetric, resulting from a larger distribution of distances between oxygen and aluminum, magnesium, and calcium. From the coordination number distribution of Si and Al, shown in Figure 3, it is clear that the CMAS glass contains a high fraction of 4-fold-coordinated Si and Al atoms, which is consistent with a silicate network formed from corner-sharing SiO₄ tetrahedra. For the CMAS sample, an average coordination number CNₜₐₐ = SiO₄ = 3.83 ± 0.2 (Figure 3) is obtained. Considering the gᵢ₋O(r) distribution (Figure 2d), it is reasonable to consider that the shorter distance of 1.6 Å can be attributed to the SiO₄ units which form the network or partake in the network formation. The initial RMC constraint of Si connectivity is, therefore, justified because the Si atoms are coordinated on average to four oxygen neighbors.

2.2. In Situ XRD Studies. Figure 4 shows the high-temperature (HT)-XRD patterns of the CMAS glass recorded from RT to 900 °C. The CMAS glass is highly stable and amorphous up to 850 °C. However, from 850 to 900 °C, low-intensity XRD reflections are observed, indicating that the crystals have started to precipitate. The observed XRD reflections correspond to the melilitic-based akermanite/gehlenite crystals (ICDD: 76-7527). Notably, a slow cooling rate (~2 K min⁻¹) from 900 °C to RT led to an increase in the intensity of the XRD reflections. However, no additional XRD
reflections corresponding to new crystalline phases were observed during the cooling process. The position of the HT-XRD reflections is similar to that of the XRD reflections obtained for the glass-powder compacts sintered at 900 °C for 1 h, although differences in intensities are observed. The time for the growth of anorthite nuclei from their own melts at 900 and 1050 °C has been reported as 92 and 48 h, respectively.22 On the basis of previous studies12,23,24 and from the in situ XRD results, it is confirmed that a thermal treatment of 900 °C for 1 h is sufficient to grow the melilite-based nucleus from the CMAS glass composition.

2.3. Quantitative Rietveld Refinement. Quantitative phase analysis proceeded with the Rietveld refinement of melilite-based phase, employing a composition of Ca2Mg0.35Al1.3Si1.35O7 and anorthite, CaAl2Si2O8, in the space groups P42/m and P1̅, respectively. The structural models were based on published structural data.25 Because of the large number of refinable parameters in the two structures, thermal vibration factors, occupancies, and certain atomic positions were fixed throughout the refinement. The observed diffraction pattern and difference between the observed and calculated data on the termination of refinement are shown in Figure 5. Selected structural parameters and agreement factors are given.
in Table 1. The calculated amounts of melilite and anorthite were 25.6 and 8.1 wt %, respectively, with the remaining 66.3 wt % amorphous phase.

2.4. $^{29}$Si and $^{27}$Al MAS-NMR Spectroscopic Studies. $^{29}$Si and $^{27}$Al MAS-NMR spectra of glass and GC samples are displayed in Figure 6. The $^{29}$Si MAS-NMR spectrum of the CMAS glass shows a single broad resonance Q-site distribution with the center of gravity (CG) at $-78$ ppm. Numerous studies indicate that SiO$_4$ tetrahedra in glasses normally occur in more than one polymerization state, the distribution of which is a function of composition.\textsuperscript{26–28} The appearance of CG at $-78$ ppm indicates that this glass is mostly enriched in Q$^1 + Q^2$ units, whereas other Q units including Q$^0$(mAl) units, where $n$ (ranging from 0 to 4) is the number of bridging oxygens (BOs) associated with Si and $m$ (ranging from 0 to 4) is the number of Al in the next-nearest neighbor (NNN), are below the detectable levels.\textsuperscript{29} However, $^{27}$Al MAS-NMR can provide valuable information on the glass composition as the $^{27}$Al chemical shift is strongly dependent on the aluminum coordination.\textsuperscript{30} The $^{27}$Al MAS-NMR spectrum of the CMAS glass exhibits a broad asymmetric peak with a tail toward the lower ppm region.

Table 1. Selected Structural Parameters and Agreement Factors for CMAS-GC Obtained from XRD Data\textsuperscript{a}

|                  | CMAS-GC | melilite, P42/m | anorthite, P1̅ |
|------------------|---------|-----------------|----------------|
| $a$ (Å)          | 8.243(3)| 7.7421(4)       |                |
| $b$ (Å)          | 12.863(6)|                 |                |
| $c$ (Å)          | 14.154(6)|                 |                |
| $\alpha$         | 91.01(5)|                 |                |
| $\beta$         | 115.08(4)|                 |                |
| $\gamma$        | 88.15(4)|                 |                |
| $V$ (Å$^3$)      | 1359(1) | 302.20(4)       |                |

\textsuperscript{a}$\chi^2 = 2.30$, $R_p = 3.59\%$, $R_{wp} = 4.70\%$, $R_B$ (anorthite) = 10.2, and $R_B$ (melilite) = 2.60.
negative parts per million, which is a typical profile in disordered materials such as glass. The appearance of the peak at an isotropic shift of about 70 ppm (the isotropic shift is usually set on the left end of the spectra because of the second-order quadrupolar shift) but with a maximum at 59 ppm indicates that most of the Al resides in tetrahedral environments, consistent with the results obtained from the RMC simulation. This is also confirmed by the satellite-transition magic-angle spinning (STMAS) spectra (Figure S1), in which only AlO₄ sites are observed and no penta- or octahedrally coordinated Al environments are distinguishable.

Solid-state ²⁹Si NMR spectra are highly sensitive to the number and type of silicon environments present within the crystal material, providing a direct correlation between the number of resonances and the number of crystallographically distinct silicon sites. For crystalline silicates, the ²⁹Si chemical shift becomes more negative as the degree of polymerization increases. However, the substitution of Al for Si on the tetrahedral sites of framework and sheet silicates caused the ²⁹Si chemical shift to become less negative by 3–5 ppm per NNN Al. Moreover, a careful comparison of NMR and diffraction results revealed that a change in the Si–O bond length of 0.001 Å produced a difference in the shift of ca. 1 ppm and a change of 1° in the Si–O–T bond angle led to changes in the ²⁹Si solid-state chemical shift between ca. 0.3 and 0.9 ppm.

Considerable differences are observed in the ²⁹Si MAS-NMR spectra of the GC samples compared to those of the CMAS glass, most notably the presence in the former of two main components (Figure 6). The largest contribution found at ~−71.9 ppm corresponds to that of aluminum-rich melilite minerals, also observed in the XRD patterns, whereas the smaller component located at ~−84 ppm is typical of anorthite. The presence of several overlapping peaks in the ~−71 to ~−85 ppm region can be easily explained by the presence of various types of silicate tetrahedral units surrounded by different cations in the melilite-type crystalline phase. However, deconvolution analysis reveals the appearance of four overlapping Gaussian peaks, which appear at ~−71.6, −72, −73.2, and ~−76 ppm, in the ~−71 to ~−85 ppm range. In addition to the peak at ~−84 ppm, the smaller component of the CMAS-GC sample exhibits two shoulders at ~−89 and ~−93 ppm. It is worth mentioning that the smaller component of the GC sample is similar to but comparatively less well-resolved than that of the synthetic anorthosite synthesized from the parent glass after a heat treatment at 1400 °C for 179 h.

Heat treatment at 850 °C for 500 h significantly reduced the width of the ²⁷Al MAS-NMR spectrum of the glass (Figure 6), but the peak maximum remains at 56 ppm, indicating that Al is essentially unchanged with increasing time of thermal treatment. The similarity between the glass and the GC samples is not surprising because anorthosite and melilite are the dominant crystalline phases in the GC, with most Al residing in tetrahedral sites with four BOs and four Si neighbors. By contrast, a small shoulder at 80 ppm appears in the GC sample, which is not evident in the glass. The ²⁷Al peak maxima for ⁵¹Al are known to fall in the range 75–80 ppm for aluminas. The formation of linkages between two different tetrahedral aluminum sites existing in anorthosite and in magnesium-rich melilite is another possible reason for the appearance of the shoulder at 80 ppm. This feature may correspond to the structural characteristic frequency of layer-lattice aluminosilicates, the structures of which consist of two-dimensional octahedral AlO₆ sheets alternating with tetrahedral SiO₄ sheets, in which some replacement of Si by Al can also occur; the charge imbalance is compensated by the presence of interlayer cations.

### 2.5. Raman Studies

Raman spectroscopy is widely used to investigate the structural changes in aluminosilicate glasses because of its capacity to distinguish crystalline phases and provide indirect information about the structural role of Al+ ions. Raman intensities from the vibrations of electrostatic bonds, generally appearing between modifier (M) cations and nonbridging oxygens (NBOs), are approximately 2 orders of magnitude less than those generated from the vibrations of covalent bonds between the network-former cations and BOs. Because of this, the intermolecular vibration modes of silicate cations dominate the Raman spectra of silicate crystals and glasses. However, as explained in a previous report, the bonding forces between the modifier cation and NBOs strongly influence the intensity of covalent bonds because greater covalent character between NBOs and the metal ion tends to reduce the degree of electron sharing in the Si–O–O bonds. Such a behavior explains the variation in the intensity and the interaction between modifier cations and network formers with increasing heat treatment time.

The Raman spectrum of CMAS-GC heat-treated at 850 °C for 500 h, together with the spectra of akermanite and anorthosite, is shown in Figure 7. Within the limits of experimental error, ±2 cm⁻¹, the Raman frequencies observed from the CMAS-GC spectrum correspond well to the characteristic frequencies of both melilite-based akermanite/gehlenite and anorthosite crystalline phases. The phase analysis is also consistent with the corresponding XRD results. The following features are identified as the corresponding frequencies of akermanite- and gehlenite-based crystalline phases: (i) the broad band with a peak position at 912 cm⁻¹ is attributed to a symmetric stretching motion of terminal NBOs of SiO₄ which can be represented as νₛ(SiO₄); (ii) the band at 988 cm⁻¹ is attributed to an asymmetric stretching vibration of BOs situated between two tetrahedra (T), which can be represented as ν₃(SiO₃); (iii) the bands at 661 and 619
cm$^{-1}$ are ascribed to the symmetric stretching vibrations of BOs $\nu_s$(TOT), where $T = Si$ or $Al$, present in akermanite and gehlenite crystalline phases, respectively, and (iv) the vibration band in the lower frequency region at 311 cm$^{-1}$ is attributed to a lattice vibrational mode. The broad band with peak positions at 484 and 504 cm$^{-1}$ corresponds to the symmetric stretching vibrations of BOs $\nu_s$(TOT), where $T = Si$ or $Al$, in the anorthite crystalline phase. The peak appearing at 790 cm$^{-1}$ is attributed to a vibration of $Al$ in the tetrahedral form.

Figure 8 shows the Raman spectra of CMAS glass powders in the region 300–1100 cm$^{-1}$ recorded on varying the heat treatment time from 0 to 400 h at 850 °C. The spectrum at 0 h shows a broad resonance band, consistent with the amorphous nature of the glass. Thereafter, well-resolved peaks associated with the crystalline phase are observed with increasing heat treatment time from 0 to 240 h then shifts toward a higher wave number with increasing heat treatment time from 240 to 264 h, before stabilizing with further increasing time of treatment. A shoulder appearing at the low-frequency side of the $\nu_s$(SiO$_4$) band at $\sim$790 cm$^{-1}$ is attributed to the AlO$_4$ units present at a site with point group symmetry 4 in melilite. The intensity of this shoulder decreases with increasing time of heat treatment up to its disappearance after 240 h. Nevertheless, an additional new peak with very low intensity appears again at $\sim$790 cm$^{-1}$ after 260 h, the intensity of which increases with increasing time of heat treatment. The second, high-intensity, broad band appearing at 577 cm$^{-1}$ after 240 h of heat treatment is attributed to the symmetric stretching vibrations of BO situated between two $Si$ tetrahedra, represented as $\nu_s$(SiOSi). A shoulder at 647 cm$^{-1}$ accompanied by a band peaking at 620 cm$^{-1}$ due to the symmetric stretching mode of $\nu_s$(TOT) (where $T = Si$ or $Al$) is also observed up to 288 h; these bands then tend to overlap with the $\nu_s$(SiOSi) broad band with further increasing heat treatment time. The third intense band observed at 311 cm$^{-1}$ corresponds to the lattice vibrational mode, which is not much influenced by increasing heat treatment time. All three strong bands, appearing at 912, 661, and 311 cm$^{-1}$, are characteristic frequencies of melilite, as reported previously. In addition, bands of low intensity with the characteristic frequencies of anorthite appear at 504 cm$^{-1}$, accompanied with a shoulder at 484 cm$^{-1}$, and 998 cm$^{-1}$, corresponding to the symmetric and antisymmetric stretching vibrations of BO, $\nu_s$(SiOSi) and $\nu_a$(SiOSi), respectively. The intensity of these bands increases with increasing heat treatment time from 240 h. The band appearing at 504 cm$^{-1}$, characteristic of the feldspar structure, is attributed to the four-membered-ring structure in anorthite, whereas the shoulder at 484 cm$^{-1}$, although not well-studied, arises from the combinations of six- and three-membered-ring structures.

3. DISCUSSION

The average oxygen coordination number around $Si$ should be very close to four atoms, which is required for the formation of tetrahedral units in the network. Nevertheless, the obtained average value for CN$_{Si-O}$ of 3.833 from the RMC simulations indicates the presence of slightly distorted tetrahedral units in the glass structure. We have also found that $Al$ atoms are 4-fold oxygen-coordinated and have formed AlO$_4$ tetrahedral units, as also confirmed by the $^{27}$Al MAS-NMR glass spectrum, similar to the basic SiO$_4$ network units. Therefore, the formation of slightly distorted SiO$_4$ tetrahedral units in the CMAS glass structure is likely attributable to the formation of mixed Si–O–Al chains, where $Al$ atoms are coordinated by four oxygen atoms.

The appearance of sharp peaks at $\sim$71.6 and $\sim$73.2 ppm in the NMR spectra for the CMAS-GC represents two different types of dimer units, gehlenite AlSi$_O$ and akermanite $Si$O$_2$ units, respectively. Because the $^{29}$Si MAS-NMR chemical shifts of crystalline silicates are highly sensitive to short-range order effects, the presence of additional broad peaks at $\sim$72 and $\sim$76 ppm represents a glassy phase with structural units longer than dimers precipitated after the formation of melilite crystalline phase. This polymerization may occur because of the role of alumina, which converts NBOs to BOs through the formation of Si–O–Al linkages as postulated by Stebbins et al. It can be concluded, therefore, that anorthite has formed from the heterogeneous glass composition that remains after the growth of melt-based
crystalline phase. However, the $^{29}$Si MAS-NMR spectrum of well-ordered anorthite should contain eight equally intense peaks because the structural units are composed of eight nonequivalent Si sites. As shown previously, the $^{29}$Si peaks can shift with higher temperature, resulting in only three overlapping peaks with a relative ratio of 3:3:2. Therefore, the peaks in the range of $-93$ to $-81$ ppm (Figure 6) are assigned to the $Q^2(4Al)$ units, which are characteristics of anorthite.49

On the other hand, the broad peak appearing at a more negative chemical shift can be assigned to a disordered aluminosilicate framework, which commonly contains 0–4$^3$Al units as NNNs for Si.

The peak at 577 cm$^{-1}$ in the Raman spectrum for 0 h of heat treatment is more typical of the glass structure of gehlenite, in which Al$^{3+}$ ions act to a large extent as a network former, existing as (AlSiO$_4$) dimers. The broad and highly intense $\nu_s$(SiO$_2$) vibration band, in comparison to the $\nu_r$(TOT) vibration band, in the present spectrum recorded at 850 °C after 0 h indicates a large distribution of $Q^4$ units. The peak at 926 cm$^{-1}$ appears at a shift similar to that of the peak observed in the Raman spectrum of the akermanite glass.43 This is expected because, as confirmed by XRD, the CMAS glass is based on the melilite solid solution. The shift in the $\nu_r$(SiO$_2$) mode toward a lower wave number, along with the decrease in the peak width with increasing heat treatment time up to 240 h, is credited to the formation of the melilite crystalline phase. It has been reported that for clinoxyroxene crystalline materials containing Al, that is, CaAl$_2$Si$_2$O$_6$ (CaTs), the $\nu_r$(SiO$_2$) band appears at lower frequencies (953 cm$^{-1}$) than aluminum-free pyroxene, CaMgSi$_2$O$_6$ (~1000 cm$^{-1}$).42 This shift in frequency is attributed to the isomorphous substitution of Al$^{3+}$ for Si$^{4+}$ in the chains, resulting in longer T–O bonds (1.636 Å) in CaTs than the average Si–O bond length (1.634 Å) in diopside. In the present glass system, the small shift in frequency (30 cm$^{-1}$) indicates that during the formation of crystalline phases, T–O bond lengths may increase and therefore exhibit correspondingly lower force constants.

Sharma et al. reported that the $\nu_r$(SiO$_2$) mode in Raman spectra is highly sensitive to the bond angle, bond length, and short-range connectivity.30 The frequencies of the $\nu_r$(TOT) bands in the spectra of the crystalline melilites exhibit a distinct linear relationship with the T–O–T bridging angle of the pyrosilicate unit, whereby increasing bond angle increases the resonance frequency.32 In the present case, the shift in band frequency toward higher values with the increase in heat treatment time from 0 to 240 h suggests structural rearrangement around the BO through increasing the T–O–T bond angle. This increase may be due to the formation and the participation of AlO$_4$ and MgO$_4$ tetrahedral units in melilite crystal formation because the structure is composed of layers of (Si,Al) and (Mg,Al) tetrahedra connected by Ca in 8-fold coordination between the layers.31,32 A small cation size, high field strength, and the possible existence of MgO$_4$ tetrahedra suggest that Mg can compete with aluminum in network-forming positions. The main peak corresponding to MgO$_4$ tetrahedral vibrations should appear at 587 cm$^{-1}$.45,55 However, because of the broadness of the spectra, features attributable to the Mg–O stretching vibrations were not identified accurately. In any case, the increase in frequency and the appearance of peaks at 620 and 646 cm$^{-1}$, which are characteristic frequencies of gehlenite and akermanite crystalline phases, in the spectrum for 240 h of heat treatment confirm that AlO$_4$ and MgO$_4$ units participate in the formation of melilite-type gehlenite/akermanite crystalline phase with increasing duration of heat treatment.

With a further increase in the heat treatment time from 240 to 290 h, the peak appearing at 794 cm$^{-1}$ diminishes in intensity, placing in doubt the presence of AlO$_4$ units in the melilite solid solution.52 However, the peak at 507 cm$^{-1}$, attributable to the characteristic $\nu_r$(SiO$_2$) vibration mode of anorthite crystalline phase, increases in intensity. This result suggests that a fraction of AlO$_4$-containing dimer units may have reacted with the glassy phase that remains after the formation of melilite crystalline phase and then converted into four-membered rings. The increase in the bandwidth of the $\nu_r$(SiO$_2$) mode further confirms the disproportion reaction 2Q$^4$ ⇔ Q$^{4−1}$ + Q$^{4+1}$. Gelenite, usually considered as an intermediate compound that becomes unstable in the presence of SiO$_2$ and Al$_2$O$_3$, has likely reacted to give anorthite (CaAl$_2$Si$_2$O$_6$) through the following reaction:34,55

$$\text{CaAl}_2\text{Si}_2\text{O}_6 + 3\text{SiO}_2 + \text{Al}_2\text{O}_3 \rightarrow 2\text{CaAl}_2\text{Si}_2\text{O}_8$$ (1)

Moreover, on the basis of the in situ XRD results at various temperatures, it is reported that akermanite does not decompose into other compounds; otherwise, wollastonite and monticellite should appear.56,57 No such crystalline phases have been encountered in the present glass system.

As already mentioned, the $^{27}$Al MAS-NMR spectra clearly reveal that most Al exists in the form of AlO$_4$ units. Therefore, assuming that Mg$^{2+}$ ions participate in the formation of melilite-like crystalline phase, the presence of four-membered rings along with eight-coordinated Ca$^{2+}$ cations leads to the formation of crystalline anorthite from the residual glassy phase, confirmed from the presence of a band at 327 cm$^{-1}$. The increases in the bandwidth and frequency and the decrease in the intensity of the $\nu_r$(SiO$_2$) band further confirm the structural rearrangement and disproportion reaction which occur with further increase in the heat treatment time. The decrease in the intensity can be attributed to the degree of covalence of the Al–O bonds. However, no additional crystalline phases have been observed even after 500 h of heat treatment. The presence of a broad band may, therefore, be assigned to the resonance vibrations of melilite and anorthite crystalline structural units. This clearly confirms that anorthite crystalline phase forms during the period of 240–290 h of heat treatment time from the residual phase, which is rich in Al$_2$O$_3$, SiO$_2$, and CaO.

The present study clearly illustrates that the CMAS chemical composition is highly stable up to 850 °C, forming crystals with a composition close to that of the parent glass. Nevertheless, during prolonged heat treatment at 850 °C, anorthite crystallizes owing to the interaction with the glassy phase, which is rich in Al$_2$O$_3$, SiO$_2$, and gehlenite crystalline units. This suggests that decreasing the concentration of Al$_2$O$_3$ in the precipitated glassy phase would inhibit the formation of undesired anorthite phase. This could be realized with the partial replacement of MgO for Al$_2$O$_3$ in the initial CMAS glass position. The rationale behind the selection of MgO is that it may increase the fraction of akermanite and does not much alter the properties of the CMAS glass sealing material.12 Studies of such glass compositions are under progress, and the results will be reported in our forthcoming articles.

4. CONCLUSIONS

The mechanism for the deleterious formation of anorthite in a melilite-based CMAS-GC composition with the potential as a
sealing material for SOFCs has been revealed from the experimental data gathered through a number of complementary advanced characterization techniques (ND, XRD, MAS-NMR, and in situ Raman). The glass network, as revealed by ND data and MAS-NMR spectra, is mainly composed of SiO$_4$ and AlO$_4$ structural units. The high stability of CMAS glass up to 850 °C was confirmed by in situ XRD. In addition to SiO$_4$ and AlO$_4$ units, quantitative XRD and MAS-NMR analyses also suggest that the melilite phase homogeneously forms along with the inclusion of MgO$_4$ tetrahedral units above the glass-transition temperature at 900 °C during the initial heat treatment period. Peaks at ~72° and ~76 ppm in the $^2$Si MAS-NMR spectrum of the GC confirm that the glassy phase remaining after the melting process has a more polymerized structure than simple dimer units, attributable to the glass-forming role of alumina present in the remaining glass composition. The gehlenite crystalline phase in the melilite solid solution is not stable beyond 240 h of heat treatment as concluded from the decreasing intensity of the Raman peak at $947 \pm 1$ cm$^{-1}$ attributed to AlO$_4$ units. A late and gradual reaction between gehlenite and the highly polymerized remaining glassy phase leads to the formation of crystalline anorthite.

5. EXPERIMENTAL DETAILS

5.1. Material Preparation. CMAS glass of composition 38.7CaO–9.7MgO–12.9Al$_2$O$_3$–38.7SiO$_2$ (mol %)$^{12}$ was prepared by melting the batch in a Pt-crucible at 1590 °C for 1 h and then quenching the glass melts in cold water. The experimental procedure for the preparation of glasses and glass powders has been detailed in our previous report.$^{12}$ The glass-transition temperature was observed around 730 °C. GC sample was obtained using a powder-processing technique, in which the glass powders with a mean particle size in the range 10–15 μm were pressed uniaxially (80 MPa) to form rectangular bars with dimensions of 4 mm × 5 mm × 50 mm. The as-formed rectangular glass-powder compacts were first sintered at 900 °C for 1 h and then further heated at 850 °C for 500 h in air at a heating rate of 5 K min$^{-1}$.

5.2. Neutron Diffraction. Neutron diffraction measurements were performed at the 10 MW Budapest research reactors using the two-axis position sensitive detector diffractometer (monochromatic wavelength $\lambda_0 = 1.068$ Å)$^{58}$.$^{58}$ A powder specimen of ~3 g was placed in a cylindrical vanadium sample holder (8 mm diameter, 50 mm height, and 0.07 mm wall thickness). The diffraction pattern was measured in the momentum transfer range of 0.95 ≤ Q ≤ 9.5 Å$^{-1}$. Correction and normalization procedures were utilized to obtain the structure factor, $S(Q)$, from the raw experimental data using program packages available at the facility.

The experimental $S(Q)$ data were simulated by the RMC method$^{59}$ using the software package RMC++$^{60}$. The RMC method minimizes the squared difference between the experimental $S(Q)$ and the calculated value from a three-dimensional atomic configuration. The RMC algorithm calculates the one-dimensional partial atomic pair correlation functions $g_i(r)$, which are then inverse-Fourier-transformed to calculate the partial structure factors, $S_i(Q)$

$$S_i(Q) = 1 + \frac{4\pi\rho_i}{Q} \int_0^{r_{\text{max}}} [g_i(r) - 1] \sin Qr \, dr$$

where $r_{\text{max}}$ is the half edge length of the simulation box of the RMC calculation. The actual computer configuration is modified by moving the atoms randomly until the calculated $S(Q)$ agrees with the experimental data to within the limits of experimental error. For the RMC starting model, a disordered atomic configuration was built up with a simulation box containing 10 000 atoms. The density value was 0.070 atomsÅ$^{-3}$, and the corresponding RMC half-box length was 26.13 Å. Moves are accepted only if they are in accordance with certain constraints.

Here, two types of constraints were applied to obtain a reliable three-dimensional atomic configuration, described by the partial atomic pair correlation functions, $g_i(r)$. These included the minimum interatomic distances between atom pairs (cutoff distances) and connectivity of the network-former Si–O atom pairs, assuming that the silicon atoms are surrounded by four-coordinated oxygen atoms, forming tetrahedral SiO$_4$ units; the silicon atoms were thus required to have four oxygen neighbors at a distance of between 1.5 and 2.1 Å.

Several RMC runs were completed by modifying the cutoff distances, and the results of each run were carefully checked to obtain reliable data for each $g_i(r)$ and coordination number distributions, CN$_i$(n). The partial atomic pair correlations, $g_i(r)$, were revealed from the RMC simulation with good reproducibility and acceptable statistics.

5.3. X-ray Diffraction. The initiation of crystalline phase formation with temperature in the glass powders was monitored from RT to 900 °C by in situ HT-XRD, employing a Philips XPert diffractometer. The implemented heat treatment schedule for the hot stage was as follows: RT to 550 °C at a heating rate of 30 K min$^{-1}$ and from 550 to 900 °C at 5 K min$^{-1}$ followed by a dwell at 900 °C for 1 h. The XRD data were collected at RT, at 550 °C, and at 900 °C in the interval from 550 to 900 °C without any significant dwell. The XRD data were also collected at RT after the completion of the hot stage-heating schedule to identify the formation of any additional crystalline phases during the cooling process.

The powder XRD patterns at RT were collected using monochromatic Cu K$_\alpha$ radiation over the range 15° ≤ 2θ ≤ 100° (step width of 0.02°) with a conventional Bragg–Brentano diffractometer (Philips PW3710, Ni-filter). The fraction of crystallized components in the GC after thermal treatment for 500 h was estimated by Rietveld quantitative analysis in a manner similar to that described previously.$^{61}$ The GCs were powdered in an agate mortar with the addition of Al$_2$O$_3$, which served as an internal weight standard, prior to sieving through a 60 μm mesh. Rietveld refinement was carried out with the FullProf software$^{62}$ using interpolation of points to model the background.

5.4. Solid-State MAS-NMR. $^{27}$Al solid-state NMR experiments were performed on a Bruker Avance-III HD operated at a $B_0$ field of 14.1 T. The $^{27}$Al (156.4 MHz) 1D experiments were carried out after a small 5° flip angle of 0.5 μs at a spinning speed of 20 kHz using a 3.2 mm MAS HFXY quadruple resonance probe (Bruker). The reference was set using a solution of AlCl$_3$ adjusted to a pH of 1 with hydrochloric acid.

$^{29}$Si MAS-NMR spectra were recorded on a Bruker Avance-II spectrometer operated at 59.62 MHz (7.1 T) using a 7 mm probe at a spinning rate of 5 kHz. The one-pulse experiments were carried out with a 90° pulse length of 4.4 μs and recycle times of 60 s for CMAS glass and 1800 s for CMAS-GC. The chemical shift was referenced to TMS using N(SiMe$_3$)$_3$ as a secondary reference.
5.5. Raman Spectroscopy. RT Raman spectra were obtained using a Horiba LabRAM HR 800 Evolution confocal Raman microscope, with a 532 nm excitation laser and a 100X objective lens (NA = 0.9). The incident laser power projected on the samples was ~10 mW, and the spot size was ~3.14 μm². The collected Raman radiation was dispersed with a 600 lines-mm⁻¹ grating and focused on a Peltier-cooled charge-coupled device (CCD) detector, allowing a spectral resolution of ca. 5 cm⁻¹. All spectra were recorded in the range 200–1200 cm⁻¹ with an integration time of 1 s and three accumulations per spectrum.

Raman spectra were collected on samples placed in a controlled-atmosphere chamber at elevated temperatures, which was recently developed for in situ studies of p-SOFC interfaces. The optical system of the setup comprises a 50 mW green (532 nm) laser with 20–25 μm spot size, a polarizer which decreases the power of the laser radiation when necessary, a mechanical shutter stopping the excitation beam for system tuning, and a set of collecting lenses and mirrors. The scattered light is distributed into different directions by a 600 lines-mm⁻¹ diffraction grating monochromator MDR-12 (LOMO, Russia) and registered with a Peltier-cooled CCD camera (Princeton Instruments, 1024 × 1024 pixel resolution). The spectra were recorded in the range 70–2050 cm⁻¹ with an integration time of 1 s and 5–300 accumulations per spectrum. The measurements reported in this work were performed at 25–900 °C in atmospheric air, with glass or GC samples placed onto a single-crystal sapphire support; the accuracy of temperature control was ±1 °C.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00598.

27Al double-quantum filtered STMAS-split-t1 spectra of CMAS glass and CMAS-GC (PDF)

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Notes
The authors declare no competing financial interest.

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