Development of dense Sr-substituted CaAl$_{12}$O$_{19}$ (CA$_6$) ceramics synthesized by sol-gel combustion method

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1. Introduction

Calcium hexa-aluminate (CaO-6Al$_2$O$_3$ or CaAl$_{12}$O$_{19}$, typically denoted as CA$_6$) is the highest alumina retaining intermediate phase in the CaO-Al$_2$O$_3$ system and naturally, it is found as hibonite mineral [1,2]. CA$_6$ has a hexagonal (P6$_3$/mmc) system with magnetoplumbite structure. The structure is made of alternating layers of spinel blocks [Al$_{11}$O$_{16}$]$^+$ stacked with mirror planes [CaAlO$_3$]$^-$. CA$_6$ grains favorably grow along the basal planes and form platelet morphology [3–5]. It is a promising refractory material due to its high melting point (~1860°C), good slag corrosion, creep resistance, good thermal stability, and low thermal expansion coefficient [6–8]. It is also proposed for other potential applications such as high-temperature filters, thermal insulators, catalyst supports, biomedical implants, and absorber for radioactive materials [9,10]. However, the flake morphology of CA$_6$ ceramics restrains its densification by the suppressed interlayer ion diffusion. Generally, the bulk density (BD) of CA$_6$ ceramics is reported in-between 1.9 and 2.5 g/cm$^3$ (theoretical density ~3.79 g/cm$^3$) at the sintering temperature range 1550–1650°C [11–13], and even at 1700°C sintered CA$_6$ cannot attain a BD of 3 g/cm$^3$ [2]. The loose-packed plate-like grains of CA$_6$ ceramics result in poor-sintered density and low strength. These are creating a boundary to use CA$_6$ ceramics in different fields like petrochemical, cement, iron, and glass industries, where a high density is very much required. Thus, the development of dense CA$_6$ ceramics within the processing temperature of 1650°C is essential for its applications in those above fields.

Nagaoka and Kanzaki [14] and Iglesia et al. [15] have used hot pressing and spark plasma sintering techniques to attain the dense CA$_6$ ceramics. Chen et al. [2] have enhanced the density of CA$_6$ by creating defects in the mirror planes by introducing Ba$^{2+}$ in place of Ca$^{2+}$. Substituting Ba$^{2+}$at Ca$^{2+}$ site creates defects in the spinel block layers and makes it easier for the ions to diffuse along the c-axis, resulting in an increase of the CA$_6$ crystal’s thickness along the c-axis. However, the BD value of the doped (3 wt% BaO) CA$_6$ ceramics is still low (~2.19 g/cm$^3$). Liu et al. [1] have added up to 4 wt% TiO$_2$ in CA$_6$ and found an open porosity of 8.2% in 1600°C sintered ceramics. However, as per the survey of existing literature, no research has reported the effect of Sr$^{2+}$ substitution on the physicomechanical properties of the CA$_6$ ceramics, synthesized by sol-gel auto combustion (SGC) method. L.Xu et al. [16] proposed nitrogen substitution for oxygen in CA$_6$ for enhanced densification.

The SrO-Al$_2$O$_3$ phase diagram shows a very similar behavior with the CaO-Al$_2$O$_3$ system, but the intermediate phase formation reaction temperatures and behaviors are slightly different [17]. The strontium hexa-aluminate (SrAl$_2$O$_{19}$, denoted as SA$_6$) is also a member of the “magnetoplumbite” structural group compound, and it exhibits properties quite similar to CA$_6$ [18]. In the present study, Sr$^{2+}$ substituted calcium...
hexa-aluminate (Ca$_{1-x}$Sr$_x$Al$_{12}$O$_{19}$ where, $x = 0, 0.1, 0.2,$ and 0.3) ceramics are synthesized by the SGC route. The SGC route is a convenient and economical method for the synthesis of fine particle size materials. It is known that the densification of CA$_6$ ceramics depends on the particle size, powder morphology, and synthesis method. The SGC synthesized powders are highly pure, reactive, homogeneous, and can be sintered at low temperature than conventional processed powder [18,19]. The effects of Sr$^{2+}$ substitution on the crystal structure, morphology, densification, and mechanical strength of the Ca$_{1-x}$Sr$_x$Al$_{12}$O$_{19}$ ceramics are comprehensively investigated.

2. Experimental procedure

2.1. Synthesis

Sr$^{2+}$ substituted calcium hexa-aluminate (Ca$_{1-x}$Sr$_x$Al$_{12}$O$_{19}$ where, $x = 0, 0.1, 0.2,$ and 0.3) ceramics were synthesized through the SGC route using analytical grade (AR) aluminum nitrate [$\text{[Al(NO}_3\text{)]}_3 \cdot 9\text{H}_2\text{O}$] (99.9% pure from Alfa Aesar), calcium nitrate [$\text{Ca(NO}_3\text{)]}_3 \cdot 4\text{H}_2\text{O}$] (99.9% pure from Alfa Aesar), strontium nitrate [Sr(NO$_3$)$_3$] (99.9% pure from Alfa Aesar), and citric acid [$\text{C}_6\text{H}_8\text{O}_7\text{H}_2\text{O}$] (99.9% pure from Alfa Aesar) as starting ingredients. The stoichiometric amounts of metal nitrates were dissolved in the least volume of double-distilled water. The citric acid as a chelating agent or fuel was mixed in the nitrate solution with a molar ratio of 1:1. The ammonia solution (30%) was slowly added to the nitrate-citrate solution to adjust the pH—7. The solution was heated at 80°C to evaporate the water and to form a viscous gel. The viscous polymerized mass was further heated above 200°C, and then the ignition started in a self-propagating way with the formation of fluffy burnt ash. The ground as-burnt powder was then calcined at 800–1200°C for 2 h to attain Ca$_{1-x}$Sr$_x$Al$_{12}$O$_{19}$ ceramics powders. For the pellet formation (15 mm diameter × 5 mm thickness), 3 wt% polyvinyl alcohol (PVA) as a binder was mixed with calcined powder and pressed at a pressure of 15 MPa using a uniaxial hydraulic press. Finally, the pressed pellets were sintered at 1500, 1550, and 1600°C, respectively for 3 h in air with a heating/cooling rate of 5°C/min.

2.2. Characterization

The phase identification of the calcined powder and sintered samples was made by X-ray Diffraction (XRD) analysis using Rigaku’s X-ray diffractometer, (Model: Ultima4, Japan) with Cu-ka radiation and a step size of 0.02° in the range from 20 to 80°. The Rietveld refinements of 1600°C sintered samples XRD patterns were carried out using MAUDWEB version 2.32 to determine the lattice parameters in the sintered ceramics. The bulk density (BD) and apparent porosity (AP) of sintered samples were measured according to the Archimedes’s principle. The morphology of the calcined and sintered specimen was examined by a field emission scanning electron microscope (SEM) (FESEM Model; Nova Nano SEM/FEI), and the grain size of sintered specimens was estimated from the SEM micrograph using “Image J1.48 V” software. The strength of sintered samples was determined by using Universal Testing Machine (Tinus Olsen, H10KLI0129) through the following equation (i):

$$\sigma = \frac{2F}{\pi dt} \quad (i)$$

where $F$ is the applied force, $d$ is the diameter, and $t$ is the thickness of the sintered pellet.

3. Results and discussion

Figure 1 shows the XRD analysis of raw and calcined (800, 1000,1100, and 1200°C) CA$_6$ (Ca$_{1-x}$Sr$_x$Al$_{12}$O$_{19}$ with $x = 0$) powder. The raw and 800°C calcined powders are amorphous in nature. Whereas 1000°C calcined sample shows some broad crystalline peaks of CaO·2Al$_2$O$_3$ (CA$_2$) (ICDD-46-1475) and Al$_2$O$_3$ (ICDD-04-0877). The unreacted CaO phase is not detected in the 1000°C calcined powder pattern. First, the CA$_2$ phase is formed at low temperature through a reaction between CaO and Al$_2$O$_3$. At high temperature, unreacted Al$_2$O$_3$ reacts with CA$_2$ phase to form CA$_6$ phase by the equation (ii). Thus, 1100°C calcined powder shows mostly CA$_6$ (ICDD-84-1613) phase with a small amount of unconverted CA$_2$ (ICDD-46-1475), and CA$_3$Al$_2$O$_{14}$ (ICDD-11-0357) phases. The 1200°C calcined powder shows pure CA$_6$ phase. Generally, the CA$_6$ phase is formed around 1600°C in the conventional solid-state reaction synthesis process [11,20], which is much higher than the temperature (~1200°C) found in the SGC process.

$$\text{CaO} \cdot 2\text{Al}_2\text{O}_3 + 4\text{Al}_2\text{O}_3 \rightarrow \text{CaO} \cdot 6\text{Al}_2\text{O}_3 \quad (ii)$$

Figure 2(a) depicts the XRD patterns of 1600°C sintered samples. As expected, the XRD pattern of $x = 0$ composition shows only CA$_6$ phase. Sr$^{2+}$ containing samples (x = 0.1, 0.2, and 0.3) also show the same diffraction peaks corresponding to single-phase magnetoplumbite structure like $x = 0$ (CA$_6$) sample. It may be due to the solid solution formation of Sr$^{2+}$ in the CA$_6$ phase. However, there is a slight shifting of peaks toward lower angles with Sr$^{2+}$ substitution (Figure 2(b and c)). The ionic radius of Sr$^{2+}$ and Ca$^{2+}$ are 1.13 and 0.99 Å, respectively. As the SA$_6$ phase has magnetoplumbite structure, it is expected that the Sr$^{2+}$ can effectively go into the crystal lattice of CA$_6$. The peak shifting toward the lower angle is supported by increased lattice parameters and cell volume found (Table 1) due to the higher ionic radius of Sr$^{2+}$.
The Rietveld refinement analysis has been performed to determine the change in lattice parameters of CA₆ with Sr²⁺ ions substitution. Rietveld refinement was carried out with space group number: 194 (Hermann-Mauguin symbol; P6₃/mmc). During the refinement, zero-correction, scale-factor, lattice parameters, asymmetry parameters, thermal parameters, and atomic positions were simultaneously refined. The result of Rietveld fitting for x = 0.2 sample XRD pattern is shown in Figure 3. The authenticity of the

![Figure 1. XRD patterns of as synthesized raw CA₆ precursor powder and precursor powders after calcination at different temperatures.](image1)

**Table 1.** Lattice parameter, cell-volume, and grain size of 1600°C sintered Ca₁₋ₓSrₓAl₁₂O₁₉ ceramics.

| Samples | a (Å)   | b (Å)   | c (Å)   | Cell-volume (Å³) | Avg. grain size (μm) |
|---------|---------|---------|---------|------------------|----------------------|
| x = 0   | 5.5739(2) | 5.5739(1) | 22.0296(4) | 592.7 | 2.18 ± 0.73 |
| x = 0.1 | 5.5747(3) | 5.5747(2) | 22.0417(5) | 593.2 | 2.43 ± 0.64 |
| x = 0.2 | 5.5760(3) | 5.5760(3) | 22.0512(2) | 594.2 | 2.69 ± 0.58 |
| x = 0.3 | 5.5766(4) | 5.5766(1) | 22.0703(2) | 594.4 | 2.59 ± 0.62 |

![Figure 2. (a) XRD patterns of 1600°C sintered samples, (b) and (c) show the peak shifting.](image2)
Figure 3. Rietveld refinement output of $x = 0.2$ composition RDX pattern. ($R_p = 11.67\%$, $R_{wp} = 7.9\%$, and GoF = 1.47). The observed data are represented in blue dots, calculated patterns are shown in black lines, differences are illustrated in lower block and the expected positions of the Bragg reflections are symbolized in black bars.

Table 2. Atom occupation information of Sr$^{2+}$ substituted ($x = 0.2$) CA$_6$.

| Atom | Position | Occupancy | $x$    | $y$    | $z$    | $b$ |
|------|----------|-----------|-------|-------|-------|-----|
| Ca   | 2d       | 0.8       | 0.6666| 0.3333| 0.25  | 0.16|
| Sr   | 2d       | 0.2       | 0.6666| 0.3333| 0.25  | 0.16|
| Al(1) | 2a     | 1         | 0.1692| 0.3335| -0.1092| 0.08|
| Al(2) | 4e     | 1         | 0.3333| 0.6667| 0.0285| 0.6 |
| Al(3) | 4f     | 1         | 0.3333| 0.6667| 0.1929| 0.01|
| Al(4) | 4f     | 1         | 0     | 0     | 0     | 0.5 |
| Al(5) | 12k    | 1         | 0     | 0     | 0.2497| 2   |
| O(1)  | 4e      | 1         | 0.1547| 0.3094| 0.0513| 1.5 |
| O(2)  | 4f      | 1         | 0.5035| 1.0070| 0.1469| 0.59|
| O(3)  | 6h      | 1         | 0.3333| -0.3333| -0.0507| 0.02|
| O(4)  | 12k     | 1         | 0     | 0     | 0.1488| 0.99|
| O(5)  | 12k     | 1         | 0.1767| -0.1768| 0.25  | 1.2|

Refinement is estimated by refined parameters; weighted residual error ($R_p$) = 11.67\%, expected error ($R_{wp}$) = 7.9\%, and goodness of fit (GoF) = 1.47. The lattice parameters and unit cell volume of 1600°C sintered samples are shown in Table 1. The atomic occupation information for $x = 0.2$ composition is shown in Table 2. From Table 1, it is found that the lattice parameters (LP) gradually increase. This increase in LP is ascribed to the effect of incorporation of larger ionic radii Sr$^{2+}$ (1.13 Å) at the place of Ca$^{2+}$ (0.99 Å). This result is in harmony with the reported literature by Chen et al. [2]. Sr$^{2+}$ ions have entered into the lattice of CA$_6$ ceramics by increasing the crystal plane spacing (Figure 2 (b and c)). However, the variations of lattice parameters are not proportional to Sr$^{2+}$ substitution concentration. This could be due to the deformation of structure and/or non-stoichiometric composition. The c/a ratio values of these magnetoplumbite structures increase from 3.952 ($x = 0$) to 3.957 ($x = 0.3$) with Sr substitution. The higher c/a values in Sr-substituted CA$_6$ compositions suggest that the structures become distorted with Sr substitution, which may be the reason that the variations of lattice parameters are not proportional to Sr$^{2+}$ substitution concentration.

Figure 4 (a) and Figure 4 (b) illustrate the values of BD and AP of samples sintered at 1500, 1550, and 1600°C, respectively. It is observed that the AP of sintered samples is reduced significantly with increasing temperature. The BD of $x = 0$ composition is improved from 2.73 to 3.14 g/cm$^3$ with increasing sintering temperature from 1500 to 1600°C. It is ascribed due to the larger atomic diffusion in-between CA$_6$ particles with the increase in temperature. The BD value (3.14 g/cm$^3$) of 1600°C sintered CA$_6$ ceramic is expressively good compared to the previous reports (<3 g/cm$^3$) [1,2]. It may be due to the SGC synthesis process of CA$_6$ powder, which produced homogenous fine particles. The fine particles are helping for good packing and atomic diffusion due to high surface energy. Meanwhile, the BD of sintered samples is also progressively increased with Sr$^{2+}$ substitution up to $x = 0.2$ composition, and then it is slightly reduced for $x = 0.3$ composition. The ratio of BD to the theoretical density is depicted in Figure 4(c), which also expresses the same indication as Figure 4(a). The 1600°C sintered specimen with $x = 0.2$ composition shows highest BD (3.39 g/cm$^3$) and lowest AP (4.92%). Sr$^{2+}$ is replacing Ca$^{2+}$ to form solid solutions in the system. The key factors for solid solution formation include valence states and ionic
radius. The difference between Ca\(^{2+}\) and Sr\(^{2+}\) ionic radii is less than 15%, which favors the formation of a substitutional solid solution. The peak shifting in Figure 2 and increase in cell volume (Table 1) also supports the data. Around 90% theoretical density is achieved in x = 0.2 composition at 1600°C. The enhanced densification in CA\(_6\) with Sr\(^{2+}\) incorporation may be due to the formation of defects in the spinel blocks [2] and more easier diffusion of ions owing to the defects. In x = 0.3 composition, the decrease in density may be due to the increase of Sr\(^{2+}\), as SA\(_6\) has a higher liquidus temperature compared to CA\(_6\). CA\(_6\) – SA\(_6\) forms a complete solid solution; however, the liquidus increases with the increase in SA\(_6\) [21]; thereby, the densification will progressively be difficult due to the increase in SA\(_6\). The surface morphology of 1600°C sintered sample is displayed in Figure 5. The images showed a slight change in the microstructures due to a low porosity difference between the samples (maximum ~5%). Generally, the grain growth of CA\(_6\) ceramic is anisotropic, and the crystal grows along the basal plane to form a plate-like crystal. The most of the grains of all the samples were hexagonal in shapes, and the average grain (ab plane) sizes of the samples are shown in Table 1. The grain size increases up to x = 0.2 composition. The x = 0.2 sample also shows thicker flake than other samples. As the radius of Sr\(^{2+}\) (1.13 Å) is higher than Ca\(^{2+}\) (0.99 Å); when Sr\(^{2+}\) ions were entered into the CA\(_6\) lattice, the mirror layer structure was changed. Moreover, in the x = 0.2 composition, some grains are diffused with each other. It may be due to the changes of the surface energy of flakes due to the entering of Sr\(^{2+}\) into the crystal of CA\(_6\), which increased the rate of diffusion along the "c" axis. Therefore, an enhanced densification is achieved. Sr\(^{2+}\) substituted CA\(_6\) crystals are thicker than the undoped ceramics (Figure 6).

Figure 7 represents the maximum displacement in the elastic curve, and the inside image shows the diametral compression strength of 1600°C sintered samples at room temperature. The nature of the graph indicates their brittle behavior, which shows the failure at the highest loads without plastic deformation. The strength value of the samples increases with Sr\(^{2+}\) incorporation (up to x = 0.2). It can also be observed that the obtained strength values are related to the BD of the samples, that is, the strength is proportional to the BD of samples. More energy is required to propagate the cracks in the dense structure due to lower porosity, which increases the strength. A slight reduction of strength is observed for x = 0.3 samples due to an increase in the porosity of the ceramic.

4. Conclusions
Calcium hexa-aluminate ceramics has been synthesized at low temperature (1200°C) by the sol-gel auto combustion method. The refinement of XRD data

![Figure 4](image-url)
Figure 5. SEM images of 1600°C sintered samples with different magnification.

Figure 6. SEM images of calcined powder samples.
showed that the lattice parameters increases due to the incorporation of Sr\(^{2+}\) ions into the structure of CA\(_6\). Sr\(^{2+}\) substitution had mainly led to an increase in the c-axis dimension and volume of the CA\(_6\) unit cell. The combined effects, that is, SGC processed fine homogeneous particles and Sr\(^{2+}\) substitutions, have assisted the densification in CA\(_6\) ceramics. Enhanced densification has been found with Sr\(^{2+}\) substitution for Ca\(^{2+}\) in CA\(_6\) ceramics, and the bulk density above 3 g/cm\(^3\) has been achieved at a sintering temperature of 1600°C. The SEM micrograph showed an increase in grain size of Sr\(^{2+}\) substituted CA\(_6\) ceramics compared to pure CA\(_6\) ceramics. So, Sr\(^{2+}\) substitution and SGC process are feasible to develop a dense CA\(_6\) ceramic with improved mechanical strength for refractory applications.

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Disclosure of potential conflicts of interest

No potential conflict of interest was reported by the author(s).

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