The binary compounds Ca₃Al₂O₆ (C₃A), Ca₁₂Al₂O₃₃ (C₁₂A₃), CaAlO₄ (CA), CaAl₄O₇ (CA₂), and CaAl₁₂O₁₉ (CA₆) in the CaO–Al₂O₃ system have been synthesized as high-purity ceramic powders by using the self-propagating combustion synthesis (SPCS) method. Materials characterization of the above-mentioned phases was performed via powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. The structural characterization of the C₁₂A₇ phase has been performed via Rietveld analysis on the powdered XRD samples. It has hereby been shown that, by using this synthesis procedure, it should be possible to manufacture high-purity ceramic powders of CA, CA₂, and CA₆ at 850°C, CA₃ at 1050°C, and CA₆ at 1200°C in a dry-air atmosphere.

### I. Introduction

The binary compounds of the calcia–alumina (CaO–Al₂O₃) system are significant in a wide range of applications in metallurgical slags, ceramic materials, and cement technology. The superior refractory properties of these binary line compounds, which lie between the 2900°C-melting CaO and 2050°C-melting Al₂O₃ terminal members, have made them progressively attractive, in recent years, in the cement manufacturing technology. Cements that contain these binary compounds are especially used in casting, trowelling, and gunning applications. The pure, alkali-free binary compounds of the CaO–Al₂O₃ system are also being considered as replacements for the alkali-containing chemical additives that are used in cement technology.

The chemical and thermodynamic properties of the CaO–Al₂O₃ system, as well as those of the above-mentioned binary line compounds, were recently compiled and assessed by Hallstedt and by Eriksson and Pelton. Ca₂Al₄O₇ (C₃A) is known to melt incongruently at 1544°C, by transforming to a mixture of a liquid phase and CaO. Ca₃A (which is also known as tricalcium aluminate) is mainly used in portland cement compositions rather than high-alumina cements. The preparation of this compound via conventional methods (mixing and milling of CaO and Al₂O₃ in stoichiometric amounts, followed by solid-state reactive firing in kilns) has always been troublesome, and the final product of conventional syntheses almost always yields the other calcium aluminate compounds, together with some unreacted CaO and/or Al₂O₃ as impurity phases. CaAlO₄ (CA) melts congruently at ~1600°C, and when prepared by using conventional methods, the final product of solid-state reactive firing contains the CaO, CaAlO₄ (CA), and Ca₂Al₃O₃₃ (C₁₂A₇) impurity phases at temperatures <1300°C. Reheating this intermediate-phase mixture at a temperature of ~1450°C, after a homogenization milling, would then produce a single-phase CA powder body. On the other hand, high-purity and single-phase CA powders were also reported by Gulgun et al. to be chemically prepared at temperatures <900°C by using a Pechini-type synthesis process. CA compositions have been prepared via the sol–gel technique, by using the starting materials of aluminum sec-butoxide and calcium nitrate (Ca(NO₃)₂). CaAlO₄ (CA) melts congruently at 1745°C (or 1775°C) and is also known as calcium dialuminate. CA₂ is preferred for use, to a large extent, among all the high-alumina cements and is used as a high-commercial-value chemical substance, especially in casting, trowelling, and gunning applications. The typical temperature of synthesis of this calcium aluminate compound, in conventional practices, is over a temperature range of 1350°C–1450°C. Ca₁₂Al₁₄O₃₃ (C₁₂A₇) melts incongruently at 1885°C by transforming to a mixture of a liquid phase and α-Al₂O₃. CA₆ does not take its place among “high-alumina cements” because it is stable against water and it does not become “hydrated,” in contrast to other binary calcium aluminates (i.e., CA, CA₂, CA₃, and CA₆). When CA₆ is blended with other calcium aluminates, it causes a decrease in the mechanical strength of the cement.

Cinibulk and Hay studied the evolution of the CA₆ phase from alumina sols that contained calcium acetate. They reported that, after calcining the gelled sols at 1200°C, CA₆ was the major phase, with a significant presence of α-Al₂O₃ and CA₂. After air calcination at 1400°C, an almost-single-phase powder of CA₆ was obtained; this CA₆ powder still displayed traces of α-Al₂O₃ and CA₂. CA₆ sols were also used to coat single-crystal yttrium aluminum garnet (YAG) fibers and alumina plates with the CA₆ phase; then, the CA₆-coated plates were used to study the behavior of the textured fiber–matrix interphases.

An and Chan studied the microstructural and mechanical properties of Al₂O₃–CA₆ ceramic composites manufactured by the reactive sintering of alumina with CaO or CaCO₃ mixtures heated at a peak temperature of 1650°C for 2 h. It has been noted in this study that the enhanced toughening behavior observed in the samples is mainly due to the crack-bridging mechanism provided by the in situ formation of the CA₆ platelets. The control of the sintered grain morphology and the mechanical properties of the CA₆-containing ceramic composites have also been studied.

The refractory properties of the CA₆ phase, and its application in high-temperature calcium aluminate cements, have previously been discussed by Kopanda and MacZura. C₁₂A₇ (Ca₁₂Al₁₄O₃₁₃) has previously been shown to be unstable in the anhydrous CaO–Al₂O₃ system. Earlier determinations of the phase diagram have identified four intermediary phases: CA₆, C₁₂A₇, CA₂, and CA₆. The C₁₂A₇ and CA₂ phases were later assigned the formulas C₁₂A₇ and CA₂, respectively.

Nurse et al. determined the phase diagram in a moisture-free atmosphere and concluded that C₁₂A₇ is not stable under strictly anhydrous conditions. The formula Ca₁₄Al₁₄O₃₂(H₂O)₃
has been proposed for this phase. Structural ambiguity is still believed to persist over this compound. The $\text{C}_{12}\text{A}_7$ compound has previously been synthesized via the solid-state reactive firing of reagent-grade starting materials such as $\text{CaCO}_3$, $\text{CaO}$, or $\text{Al}_2\text{O}_3$, mixed in appropriate amounts. The formation of the $\text{C}_{12}\text{A}_7$ phase necessitated the attainment of temperatures in excess of 1400°C with equilibration times of $>24$ h. It has been reported by Eliezer et al. that the final product may contain up to 1.30–1.40 wt% $\text{H}_2\text{O}$ (corresponding to the composition $\text{C}_{12}\text{A}_7\text{H}$) after heating to $\sim1100°C$ in air of normal humidity. This water was claimed to be absorbed reversibly and without any major structural change; therefore, Roy and Roy termed $\text{C}_{12}\text{A}_7$ a “zeolitic” phase.

Several binary compounds, including the $\text{C}_{12}\text{A}_7$ phase, in the $\text{CaO–Al}_2\text{O}_3$ system have been synthesized via the preparation of mixed aluminum/calcium hydroxides in aqueous solutions. Their report claimed a reduction of the synthesis temperature of $\text{C}_{12}\text{A}_7$ to $<1200°C$; however, the chemical precipitation process used was unable to produce a single-phase substance, and the solid product of the subsequent air calcination also contained other calcium aluminate phases that amounted to $\sim5\%$ in the calcined body.

The structure of the $\text{C}_{12}\text{A}_7$ phase was first studied by Büssem and Eitel, and they reported a cubic structure with a lattice parameter $a$ of 11.95 Å, and a possible space group of $T_d$. They claimed that this structure is formed by the 12:7 site ratio, and a three-dimensional network of $\text{AlO}_4$ tetrahedra constitutes the backbone of the structure whereas all the oxygen atoms

![Fig. 1. XRD spectra of combustion-synthesized $\text{C}_3\text{A}$ powders.](image-url)
belong to every two such tetrahedra. Jeevaratnam et al.\(^{26}\) later determined the space group of the \(\text{C}_{12}\text{A}_7\) unit cell to be \(T_d\) or \(I-43d\) with a lattice parameter of 11.98 Å. Only 64 of the 66 oxygen atoms in the unit cell could be placed in this space group; the remaining two were assumed to be distributed statistically. The structure of the fluoride analogue (i.e., \(11\text{CaO}\cdot7\text{Al}_2\text{O}_3\cdot\text{CaF}_2\)) of cubic \(\text{C}_{12}\text{A}_7\) was refined by Williams,\(^{27}\) and the structure was confirmed to belong to the space group \(I-43d\) with \(a = 11.970\) Å and \(Z = 2\).

It has been reported\(^{28}\) that fine-particle oxide ceramics could be produced using exothermic redox reactions between an oxidizer (metal nitrates) and a fuel (amides, hydrazides, etc.). This concept was first demonstrated by Kingsley and Patil\(^{29}\) on the rapid synthesis of fine-particle \(\alpha\)-\(\text{Al}_2\text{O}_3\) and related oxides, such as metal aluminates, rare-earth orthoaluminates, and \(\text{Ce}^{3+}\)- or \(\text{Cr}^{3+}\)-doped aluminum oxides. The process involved the combustion of the corresponding metal nitrate plus either urea or carbohydrazide mixtures at temperatures of 500° or 250°C, respectively, under normal atmospheric pressure.\(^{28}\) The process yields foamy, voluminous, and fine oxide powders within 5 min. The combustion, being instantaneous and energy saving, has attracted much interest and has been successfully used in the synthesis of \(\text{LaCrO}_3\),\(^{30}\) \(\text{Ba}_2\text{YCu}_4\text{O}_8\),\(^{31}\) and \(\text{Y-Ba-Cr-O}\) phases.\(^{32}\) Recently, combustion methods that used glycine\(^{33}\) and urea\(^{34}\) as the fuel have been reported to successfully synthesize calcium-doped \(\text{LaCrO}_3\) and \(\text{LaAlO}_3\) powders, respectively. A similar combustion technique was also demonstrated for the successful synthesis of \(\text{YAG}:\text{Cr}\) and \(\text{Y}_2\text{O}_3:\text{Eu}^{35}\) and of \(\text{YAG}:\text{Nd}\) and \(\text{YIG}:\text{Nd}^{36}\) phosphor powders using both of the above-mentioned fuels.

In the present work, the experimental conditions and parameters of the preparation of the ceramic powders of the binary compounds of the \(\text{CaO}-\text{Al}_2\text{O}_3\) system have been studied. These conditions and parameters are presented by using the powder route of self-propagating combustion synthesis (SPCS).

II. Experimental Procedure

Starting powders of \(\text{Ca(NO}_3\text{)}_2\cdot4\text{H}_2\text{O}\) (99+%, Merck, Darmstadt, Germany), and \(\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}\) (99+%, Riedel-de Haén AG, Seelze, Germany) were weighed in appropriate amounts and then dissolved in distilled water at room temperature to yield 0.4M stock solutions. A total of 250 mL of the cations solution, taken from each of the stock solutions in appropriate amounts to give the stoichiometries of each of the studied calcium aluminates, was agitated and stirred with a magnetic stirrer in an uncovered glass beaker for 1 h at room temperature. A proprietary amount\(^{37}\) of urea (\(\text{CH}_4\text{N}_2\text{O}; 99.5\%\), Riedel-de Haén AG) was then added to this solution. Following the dissolution of urea in the cations solution, the beaker contents were transferred into a Pyrex™ beaker (capacity of 400 mL). The Pyrex™ beaker with the liquid mixture was then placed in a muffle furnace and maintained at a temperature of 510° ± 10°C. Initially, the mix-

![Fig. 2. FT-IR spectra of combustion-synthesized calcium aluminate powders calcined in air at 1100°C (a) \(\text{C}_{12}\text{A}_7\), (b) \(\text{C}_3\text{A}\), (c) \(\text{CA}_2\), (d) \(\text{CA}_6\), and (e) \(\text{CA}\).](image-url)
ture boils and undergoes dehydration, followed by decomposition, with swelling and frothing; this process results in a foam that ruptures with a flame and glows to incandescence. The entire combustion process was completed within 15 min. The product of combustion was a voluminous, foamy, and amorphous (or crystalline) precursor of the desired calcium aluminate phase or, as was the case with C₃A, a mixture of phases to maintain the overall stoichiometry. The foamy precursors were lightly ground in an agate mortar into a fine powder. The foams freshly recovered from the Pyrex™ reaction beakers were observed to become highly “hygroscopic.” Ground foams were then calcined and crystallized on α-Al₂O₃ plates, in a dry-air atmosphere, over a temperature range of 250°C–1050°C for prolonged times to yield the crystalline and phase-pure calcium aluminate binary compounds.

Powder X-ray diffractometry (XRD) spectra were obtained from the calcined samples, for purposes of phase characterization. XRD spectra could not be obtained from the “as-recovered” hygroscopic foams prior to the heatings at 250°C, because of the difficulties that were encountered in powder sample preparation for the XRD work. A powder diffractometer (Model DMax/B, Rigaku Co., Tokyo, Japan) was used, with FeKα radiation at a step size of 0.02° 2θ and a preset time of 1 s, for the runs performed to accomplish phase characterization and to check the phase purity of the synthesized ceramic powders. Structural refinements were performed on the slowly collected (step size of 0.02° 2θ, count time of 10 s) powder
XRD data of C$_{12}$A$_7$ samples by using the Rietveld method\textsuperscript{38,39} on the DBWS-9411 Rietveld Analysis package.\textsuperscript{50} The refined structural parameters were then used to draw the unit cell of this phase. The Fourier transform infrared analysis (FT-IR) spectra of the synthesized calcium aluminate powders were collected by using a spectrometer (Model DX-510, Nicolet, CA). Dried (at 70°C) powder samples (3 wt\%) were mixed in an agate mortar with potassium bromide (KBr) prior to pellet formation.

The particle size and morphology of the powders were monitored from photomicrographs taken via scanning electron microscopy (SEM) (Model JSM6400, JEOL, Tokyo, Japan). The samples were first sputter coated with a layer of gold–palladium alloy that was $\approx$25 nm thick. Energy-dispersive X-ray spectroscopy (EDXS) (Kevex, Valencia, CA) analysis was performed on the samples to obtain a semiquantitative analysis to determine the elemental distribution in the powder samples. The EDXS runs were believed to be accurate to approximately ±3 wt%.

III. Results and Discussion

Nitrate solutions usually decompose at temperatures $<$700°C with the evolution of the gases of nitrous oxides, such as NO$_2$, NO, and N$_2$O$_5$.\textsuperscript{32} Urea is also known\textsuperscript{32} to decompose into biuret (H$_2$N–CO–NH–CO–NH$_2$, i.e., C$_2$H$_5$N$_3$O$_2$), cyanuric acid (HCNO), and ammonia (NH$_3$) when it is heated to $\approx$200°C. Biuret itself then decomposes when heated at

\begin{figure}[h]
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\includegraphics[width=\textwidth]{xrd_spectra.png}
\caption{XRD spectra of combustion-synthesized CA powders.}
\end{figure}
temperatures >300°C. Therefore, in an aqueous mixture of metal nitrates and urea, the decomposition products are expected to consist of nitrous oxides, \( \text{NH}_3 \), and \( \text{HCNO} \). This gaseous mixture will spontaneously ignite when the ambient temperature is \( \sim 500^\circ\text{C} \). This ignition is believed to instantaneously increase the local temperature of the dried foam to \( \sim 1300^\circ\text{C} \), which, in a sense, is similar to the case of flash pyrolysis.

(1) Synthesis of \( \text{C}_3\text{A} \), \( \text{CA} \), \( \text{CA}_2 \), and \( \text{CA}_6 \)

Figure 1 shows the XRD spectra of the combustion-synthesized \( \text{C}_3\text{A} \) powder samples heated at different, consecutively increasing, temperatures. The already-crystalline precursor powders heated in the temperature range of 250°–525°C exhibited a phase mixture of \( \text{C}_3\text{A} \) and \( \text{C}_{12}\text{A}_7 \). The calcined powders heated over the range of 650°–950°C did display a mixture of three phases: \( \text{C}_3\text{A} \), \( \text{C}_{12}\text{A}_7 \), and \( \text{CA} \). Single-phase \( \text{C}_3\text{A} \) powders (as deduced by XRD and EDXS analysis) could only be obtained by heating the precursors at 1050°C for periods of 48–72 h. Spectrum "(b)" in Fig. 2 shows a typical FT-IR spectrum for a \( \text{C}_3\text{A} \) sample that has been heated at 1100°C for 72 h prior to the FT-IR runs. The nitrate peaks present in the FT-IR spectra of the as-formed, 700°, and 900°C samples disappeared in the powder samples heated at 1100°C for 12 h. The particle morphology of the SPCS-synthesized \( \text{C}_3\text{A} \) powders (heated at 1100°C) is depicted in the SEM micrograph shown in Fig. 3(a).

The XRD spectra of the combustion-synthesized \( \text{CA} \) powder samples heated at different temperatures, in dry air, are given in Fig. 4. Even the powders heated at 250°C were crystalline, and these powders only possessed the characteristic spectrum of the desired \( \text{CA} \) phase. Powder samples heated at 850°C displayed an acceptable level of crystallization. A typical FT-IR spectrum of \( \text{CA} \) powders heated at 1100°C is given in Fig. 2 (spectrum "(e)"). The particle morphology of the SPCS-synthesized \( \text{CA} \) powders (heated at 1100°C) is depicted in the SEM micrograph shown in Fig. 3(b).

The XRD spectra of the combustion-synthesized \( \text{CA}_2 \) powder samples heated at different, consecutively increasing, temperatures are given in Fig. 5. The "as-synthesized" precursor powders were amorphous, and the bottom five spectra (amorphous) correspond to the isothermal heatings at 250°, 400°, 525°, 650°, and 750°C (48 h each), respectively (from bottom to top). The amorphous powder body crystallized at temperatures >750°C, and the crystallization product was pure \( \text{CA}_2 \). Spectrum "(c)" in Fig. 2 shows the FT-IR spectrum of \( \text{CA}_2 \).
powder heated at 1100°C. The particle morphology of the SPCS-synthesized CA$_2$ powders (heated at 1100°C) is depicted in the SEM micrograph shown in Fig. 3(c).

The XRD spectra of the combustion-synthesized CA$_6$ powder samples heated at different temperatures, in dry air, are plotted in Fig. 6. The ‘‘as-synthesized’’ precursor powders of CA$_6$ composition were amorphous, and the bottom seven XRD spectra correspond to the isothermal heatings at 250°, 400°, 525°, 650°, 750°, 850°, and 950°C (48 h each), respectively (from bottom to top). An acceptable level of phase crystallization (of a phase mixture of CA$_2$, $\alpha$-Al$_2$O$_3$, and CA$_6$) could only be achieved in ~24 h at 1050°C. The peaks of the CA$_2$ phase almost disappeared when the soaking time at 1050°C was increased to 72 h. Phase-pure CA$_6$ could only be obtained after heating the SPCS foams at 1200°C for 48 h. Cinibulk and Hay$^{13}$ previously reported a similar behavior during the crystallization of CA$_6$ gels prepared from the calcium acetate and alumina sols, in the sense that producing phase-pure CA$_6$ would be difficult, even by heatings such gels at 1400°C (i.e., traces of CA$_2$ and $\alpha$-Al$_2$O$_3$ phases were still detected). Spectrum ‘‘(d)’’ in Fig. 2 depicts a typical FT-IR spectrum of CA$_6$ samples heated at 1150°C. The particle morphology of the SPCS-synthesized CA$_6$ powders (heated at 1100°C) is depicted in the SEM micrograph shown in Fig. 3(d).

(2) Synthesis of C$_{12}$A$_7$

The amorphous, white, C$_{12}$A$_7$ precursor powders obtained following the SPCS process were lightly ground in an agate mortar and then calcined at different temperatures (in the format of consecutive isothermal heatings for predetermined durations). Powder XRD spectra were collected following each isothermal heating step. Figure 7 shows the results of this study, and it displays the phase evolution characteristics of C$_{12}$A$_7$ samples when the samples are heated in a dry-air atmosphere. Figure 7 contains eight separate XRD spectra, each gathered at a different temperature; the four spectra at the bottom portion of the figure correspond to the isothermal heatings performed at 250°, 400°, 500°, and 600°C, respectively, from bottom to top. The remaining four spectra are labeled with their respective heating temperatures. The precursors remained significantly amorphous over the temperature range of 250°–600°C. Crystallization of the C$_{12}$A$_7$ precursors began at temperatures >600°C, and the crystallization product was C$_{12}$A$_7$. Additional heating, over the temperature range of 700°–
1000°C, for prolonged times, did not cause any phase contamination (with any of the other binary compounds of the CaO–Al₂O₃ system) or decomposition; rather, the additional heating only improved the extent of crystallization achieved in the powder samples. Spectrum "(a)" in Fig. 2 displays a typical FT-IR spectrum of a C₁₂A₇ sample heated at 1100°C. The particle morphology of the SPCS-synthesized C₁₂A₇ powders (heated at 1100°C) is depicted in the SEM micrograph shown in Fig. 3(e). Inductively coupled plasma (ICP) spectroscopy analysis performed on the 1100°C-heated C₁₂A₇ samples yielded a Ca:Al atomic ratio of 0.85. This value was considered to be in satisfactory agreement with the stated stoichiometry of this compound.

(3) Structural Characterization of C₁₂A₇

Structural refinements were performed on the powder samples of C₁₂A₇ heated at 1000°C, in a dry-air atmosphere, on alumina plates for crystallization times in the range of 72–90 h. The unit cell of C₁₂A₇ (Ca₁₂Al₁₄O₃₃) was confirmed to be cubic (a = 11.971 Å) with a space group of I-43d (Hermann–Mauguin No. 220), which possess the m₃m Laue symmetry. The unit cell of this phase contains 118 atoms (i.e., Z = 2). Rietveld analysis was performed on the powder XRD data collected from the samples heated at 1000°C. The positional (atomic) parameters were refined in the Rietveld cycles, as well as the overall scale, temperature, and site-occupancy factors; in addition, the cell, preferred orientation, mixing, and half-width and background parameters were also refined in this manner. Rietveld refinement was converged in 43 cycles to an Rwp value of 4.3%, with a Durban–Watson statistic of 0.46.

The full width at half maximum (FWHM) values obtained from the Rietveld runs were used to determine the average crystallite size of the SPCS-synthesized C₁₂A₇ powders (heated at 1000°C) by using the Warren–Averbach method. The average crystallite size was ~14 Å, as shown in Fig. 8.

The unit cell of Ca₁₂Al₁₄O₃₃ contained only five unique atomic positions, which were then manipulated within the cell to yield a total of 118 positions, according to the space-group operations of the m₃m Laue symmetry. These five unique

![Fig. 7. XRD spectra of combustion-synthesized C₁₂A₇ powders.](image)
atomic positions, as refined by the Rietveld analysis, are reproduced in Table I.

The unit cell of Ca$_{12}$Al$_{14}$O$_{33}$ was then drawn as a two-dimensional projection (and to the correct scale) by using the above-mentioned information, as depicted in Fig. 9. The numbers adjacent to the ions of the cell represent their altitudes along the $z$-axis, which is perpendicular to the plane of the page.

### IV. Conclusions

The binary compounds Ca$_3$Al$_2$O$_6$ (C$_3$A), Ca$_{12}$Al$_{14}$O$_{33}$ (C$_{12}$A$_7$), CaAl$_2$O$_4$ (CA), CaAl$_4$O$_7$ (CA$_2$), and CaAl$_{12}$O$_{19}$ (CA$_6$) of the CaO–Al$_2$O$_3$ system were, for the first time, prepared via the self-propagating combustion synthesis (SPCS) technique. Significant decreases in the synthesis temperatures (C$_3$A, 1050°C; C$_{12}$A$_7$, 800°C; CA, 850°C; CA$_2$, 900°C; and CA$_6$, 1200°C), together with improved compound purities that were attained in the final powder bodies, of these compounds have been achieved, as compared to the conventional methods and practices of solid-state reactive firing of the starting oxides (i.e., CaO and Al$_2$O$_3$), which require operation temperatures in the range of 1400°–1550°C for prolonged times in kiln-type furnaces.

Urea used (as a fuel and/or oxidizer) in the combustion-synthesis runs was, later, separately replaced (in the initial aqueous solutions) in a series of experiments with carbohydrazide (CH$_6$N$_4$O) and glycine (C$_2$H$_5$NO$_2$). The C$_3$A, C$_{12}$A$_7$, CA, CA$_2$, and CA$_6$ samples prepared with the proprietary amounts of either carbohydrazide or glycine were all noted to yield single-phase, “pure” (as deduced only by XRD and EDXS analysis) binary calcium aluminates, followed by isothermal heatings (for 48–72 h) at 1050°, 800°, 850°, 900°, and 1200°C, respectively.

SEM micrographs of each of the samples showed the presence of micrometer-range, irregularly shaped particles after calcination at each temperature. The FT-IR spectra of the combustion-synthesized calcium aluminate precursor powders exhibited the typical “nitrate (NO$_3$)” vibrations over a wave-

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**Fig. 8.** Warren–Averbach$^{14}$ plot of C$_{12}$A$_7$ powders used to determine crystallite size.
length range of 1250–1650 cm$^{-1}$. The nitrate peaks in the FT-IR plots disappeared as the calcination temperature increased beyond 1000°C.

The once debated and heavily questioned (as its existence) C$_{12}$A$_7$ phase (Ca$_{12}$Al$_{14}$O$_{33}$) of the CaO–Al$_2$O$_3$ binary system has been synthesized, for the first time, via the SPCS technique, and a significant reduction in its synthesis temperature has been achieved with respect to conventional routes of solid-state reactive firing practices. The structural ambiguity on this compound has also been resolved, and the structural parameters and the unit-cell contents of Ca$_{12}$Al$_{14}$O$_{33}$ are hereby refined and presented. This phase (together with other binary calcium aluminates) is also expected to have increasing use in the field of alkali-free, synthetic chemical additives in “cement” compositions.

Acknowledgment: The author gratefully acknowledges Ms. F. Arzum Simsek, from the Department of Chemistry of the Middle East Technical University, for performing the FT-IR runs used in this study.

References


Fig. 9. Schematic of the Ca$_{12}$Al$_{14}$O$_{33}$ unit cell. Large open circles are O$^{2-}$ anions, shaded circles are Ca$^{2+}$ cations, and small solid circles are Al$^{3+}$ cations.


