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Chemical Preparation of the Binary Compounds in the Calcia–Alumina System by Self-Propagating Combustion Synthesis

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The binary compounds $Ca_3Al_2O_6$ (C_3A), $Ca_{12}Al_{14}O_{33}$ ($C_{12}A_7$), $CaAl_2O_4$ (CA), $CaAl_4O_7$ (CA_2), and $CaAl_{12}O_{19}$ (CA_6) in the CaO–Al_2O_3 system have been synthesized as high-compound-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 diffractometry (XRD), Fourier transform infrared spectroscopy, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. The structural characterization of the $C_{12}A_7$ 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, CA_2, and $C_{12}A_7$ at 850°C, C_3A at 1050°C, and CA_6 at 1200°C in a dry-air atmosphere.

I. Introduction

THE binary compounds of the calcia–alumina (CaO–Al_2O_3) 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 Al_2O_3 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–Al_2O_3 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–Al_2O_3 system, as well as those of the above-mentioned binary line compounds, were recently compiled and assessed by Hallstedt[1] and by Eriksson and Pelton.[2] $Ca_3Al_2O_6$ (C_3A)† is known to melt incongruently[3] at 1544°C, by transforming to a mixture of a liquid phase and CaO. C_3A (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 Al_2O_3 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 Al_2O_3 as impurity phases. $CaAl_2O_4$ (CA) melts congruently at ~1600°C,[4–7] and, when prepared by using conventional methods, the final product of solid-state reactive firing contains the CaO, $CaAl_4O_7$ (CA_2), and $Ca_{12}Al_7O_{33}$ ($C_{12}A_7$) 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.*[8] to be chemically prepared at temperatures <900°C by using a Pechini-type[9] synthesis process. CA compositions have been prepared[10] via the sol–gel technique, by using the starting materials of aluminum sec-butoxide and calcium nitrate ($Ca(NO_3)_2$). $CaAl_4O_7$ (CA_2) melts congruently at 1745°C[11] (or 1775°C[1]) and is also known as calcium dialuminate. CA_2 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°–1450°C. $CaAl_{12}O_{19}$ (hibonite, CA_6) melts incongruently[1,12] at a temperature of 1885°C by transforming to a mixture of a liquid phase and α-Al_2O_3. CA_6 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, CA_2, C_3A, and $C_{12}A_7$). When CA_6 is blended with other calcium aluminates, it causes a decrease in the mechanical strength of the cement.[12]

Cinibulk and Hay[13] studied the evolution of the CA_6 phase from alumina sols that contained calcium acetate. They reported that, after calcining the gelled sols at 1200°C, CA_6 was the major phase, with a significant presence of α-Al_2O_3 and CA_2. After air calcination at 1400°C, an almost-single-phase powder of CA_6 was obtained;[13] this CA_6 powder still displayed traces of α-Al_2O_3 and CA_2. CA_6 sols were also used[13] to coat single-crystal yttrium aluminum garnet (YAG) fibers and alumina plates with the CA_6 phase; then, the CA_6-coated plates were used to study the behavior of the textured fiber–matrix interphases.

An and Chan[14] studied the microstructural and mechanical properties of Al_2O_3–CA_6 ceramic composites manufactured by the reactive sintering of alumina with CaO or $CaCO_3$ 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 CA_6 platelets. The control of the sintered grain morphology[15] and the mechanical properties[16] of the CA_6-containing ceramic composites have also been studied.

The refractory properties of the CA_6 phase, and its application in high-temperature calcium aluminate cements, have previously been discussed by Kopanda and MacZura.[17] $C_{12}A_7$ ($Ca_{12}Al_{14}O_{33}$) has previously been shown to be unstable in the anhydrous CaO–Al_2O_3 system.[1,2,6] Earlier determinations[4,18] of the phase diagram have identified four intermediary phases: C_3A, C_5A_3, CA, and C_3A_5. The C_5A_3 and C_3A_5 phases were later assigned the formulas $C_{12}A_7$ and CA_2, respectively.[1,2,19] Nurse *et al.*[6,20] determined the phase diagram in a moisture-free atmosphere and concluded that $C_{12}A_7$ is not stable under strictly anhydrous conditions. The formula $Ca_{12}Al_{14}O_{32}(OH)_2$

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†Cement chemistry notation is used throughout this paper (i.e., C = CaO, A = Al_2O_3, and H = H_2O).

has been proposed for this phase.[21] Structural ambiguity is still believed to persist over this compound. The $C_{12}A_7$ compound has previously been synthesized[22,23] via the solid-state reactive firing of reagent-grade starting materials such as $CaCO_3$, CaO, or Al_2O_3, mixed in appropriate amounts. The formation of the $C_{12}A_7$ 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.*[21] that the final product may contain up to 1.30–1.40 wt% H_2O (corresponding to the composition $C_{12}A_7H$) after heating to ~1100°C in air of normal humidity. This water was claimed to be absorbed reversibly and without any major structural change; therefore, Roy and Roy[22] termed $C_{12}A_7$ a ''zeolitic'' phase.

Several binary compounds, including the $C_{12}A_7$ phase, in the $CaO–Al_2O_3$ system have been synthesized by Morozova *et al.*[24] via the preparation of mixed aluminum/calcium hydroxides in aqueous solutions. Their report claimed a reduction of the synthesis temperature of $C_{12}A_7$ 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 ~5% in the calcined body.

The structure of the $C_{12}A_7$ phase was first studied by Büssem and Eitel,[25] and they reported a cubic structure with a lattice parameter *a* of 11.95 Å, and a possible space group of T_d^6. They claimed that this structure is formed by the 12:7 site ratio, and a three-dimensional network of AlO_4 tetrahedra constitutes the backbone of the structure whereas all the oxygen atoms

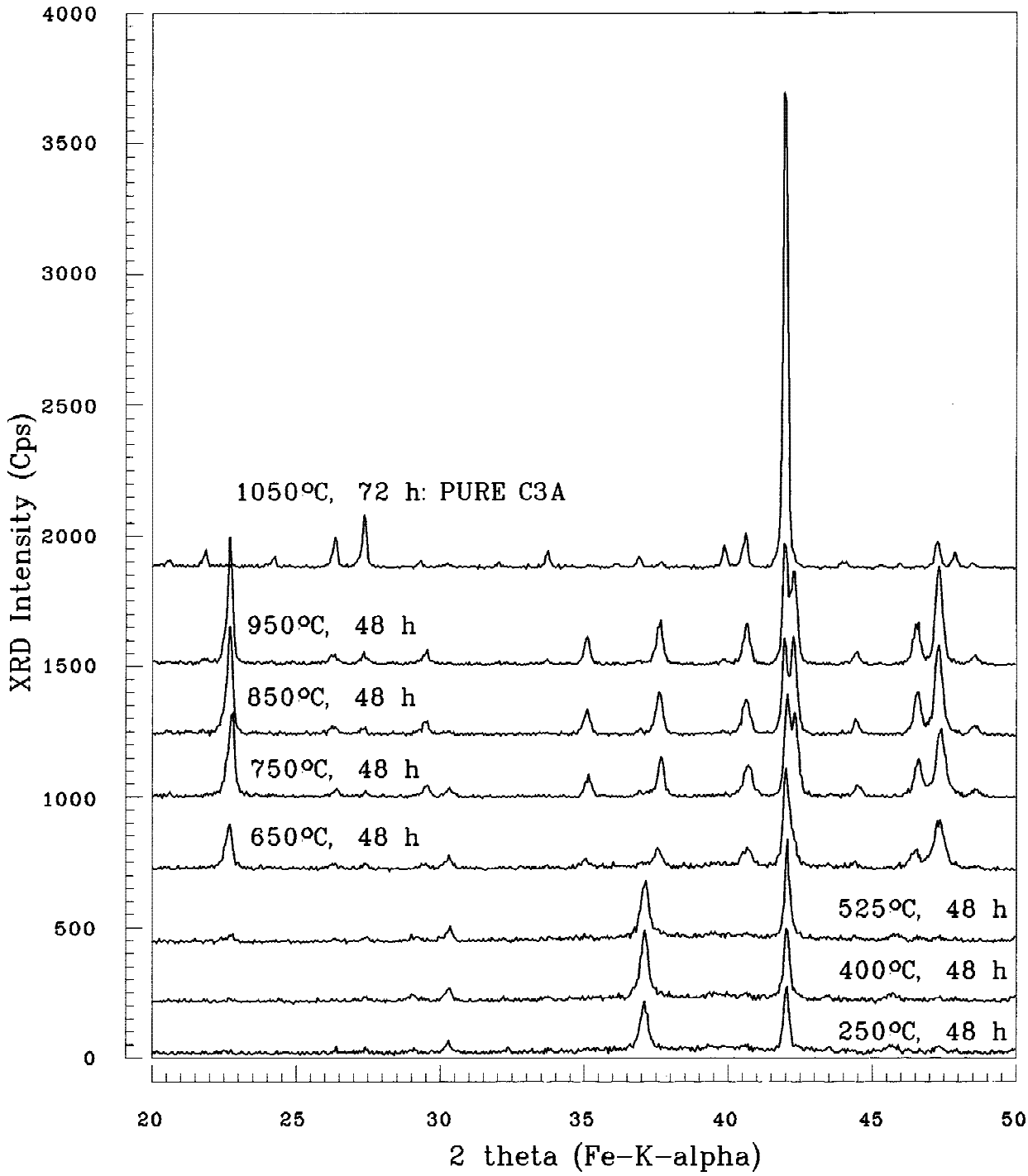

Fig. 1. XRD spectra of combustion-synthesized C_3A powders.

belong to every two such tetrahedra. Jeevaratnam *et al.*[26] later determined the space group of the $C_{12}A_7$ unit cell to be T_d^6 or *I*-43*d* 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., $11CaO \cdot 7Al_2O_3 \cdot CaF_2$) of cubic $C_{12}A_7$ was refined by Williams,[27] and the structure was confirmed to belong to the space group *I*-43*d* 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 α-Al_2O_3 and related oxides, such as metal aluminates, rare-earth orthoaluminates, and Ce^{3+}- or 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 $LaCrO_3$,[30] $Ba_2YCu_4O_8$,[31] and Y-Ba-Cu-O phases.[32] Recently, combustion methods that used glycine[33] and urea[34] as the fuel have been reported to successfully synthesize calcium-doped $LaCrO_3$ and $LaAlO_3$ powders, respectively. A similar combustion technique was also demonstrated for the successful synthesis of YAG:Cr and Y_2O_3:Eu[35] and of YAG:Nd and YIG: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 CaO–Al_2O_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 $Ca(NO_3)_2 \cdot 4H_2O$ (99+%, Merck, Darmstadt, Germany), and $Al(NO_3)_3 \cdot 9H_2O$ (99+%, Riedel-de Haën AG, Seelze, Germany) were weighed in appropriate amounts and then dissolved in distilled water at room temperature to yield 0.4*M* 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 (CH_4N_2O; 99.5%, Riedel-de Haën AG) was then added to this solution. Following the dissolution of urea in the cations solution, the beaker contents were transferred into a Pyrex™ (Corning Glass Works, Corning, NY) 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-

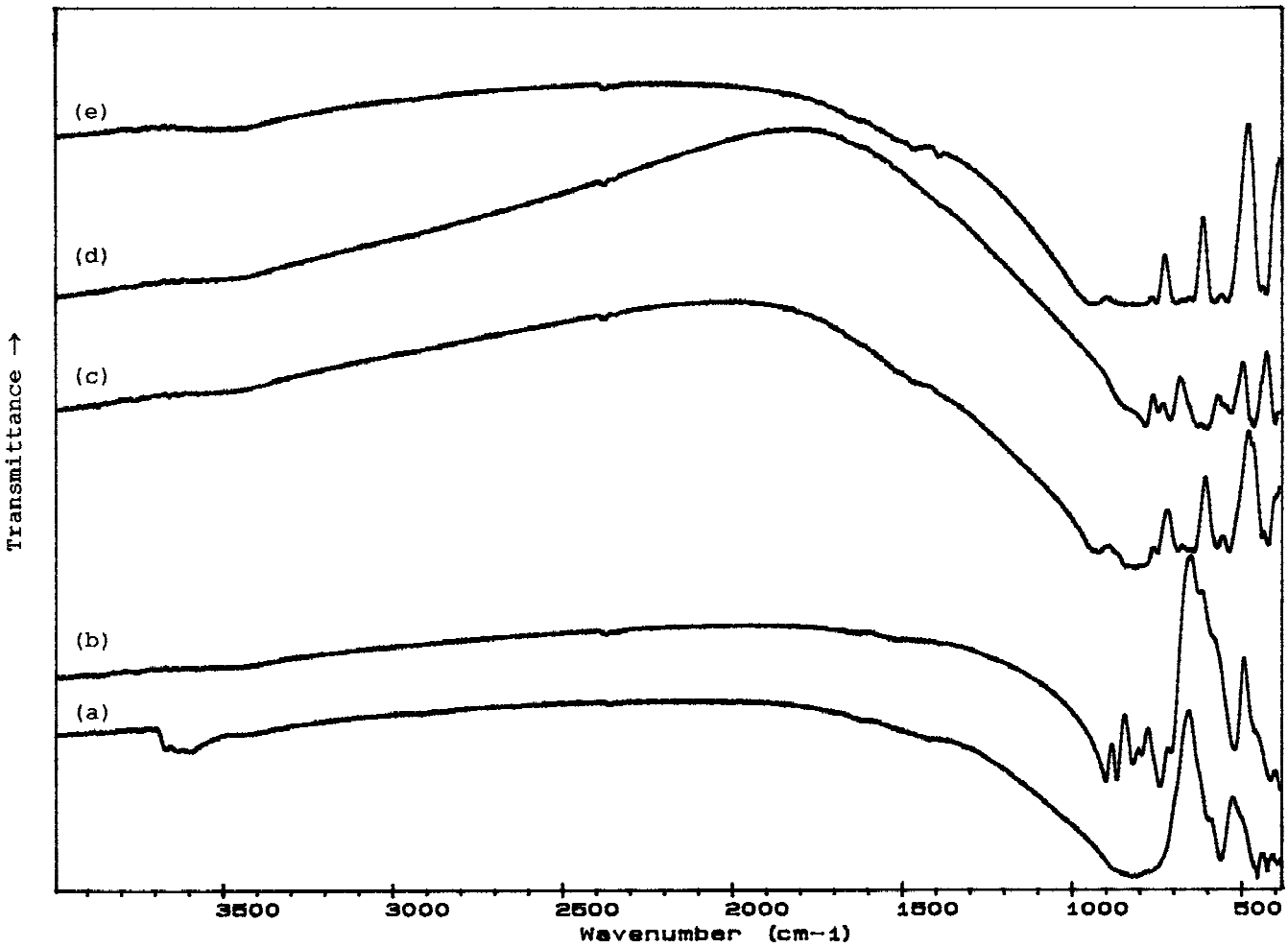

Fig. 2. FT-IR spectra of combustion-synthesized calcium aluminate powders calcined in air at 1100°C ((a) $C_{12}A_7$, (b) C_3A, (c) CA_2, (d) CA_6, and (e) CA).

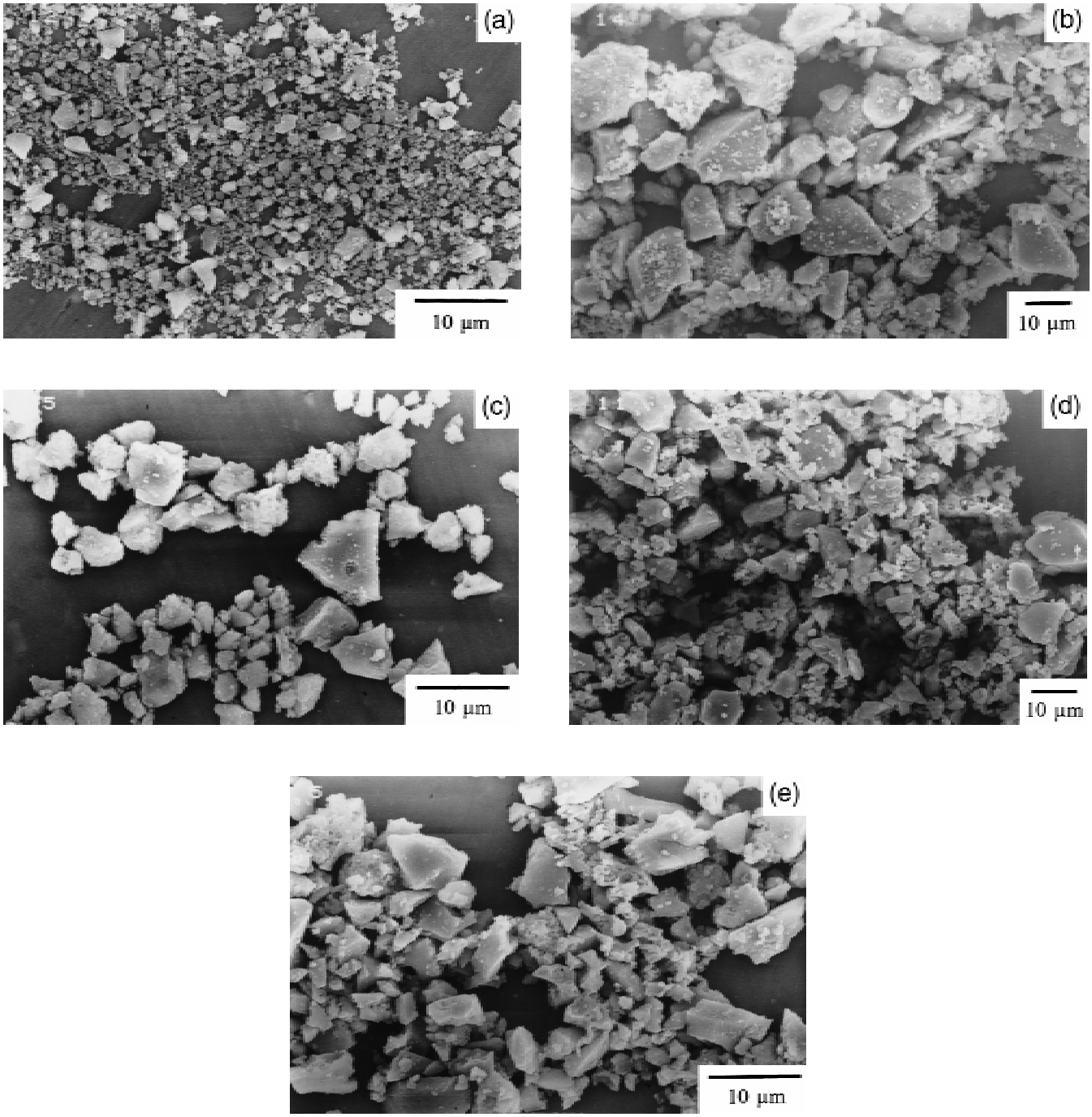

Fig. 3. SEM micrographs of combustion-synthesized calcium aluminate powders calcined in air at 1100°C ((a) C_3A, (b) CA, (c) CA_2, (d) CA_6, and (e) $C_{12}A_7$).

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.[28] 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 C_3A, 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-Al_2O_3 plates, in a dry-air atmosphere, over a temperature range of 250°–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 Fe$K\alpha$ 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

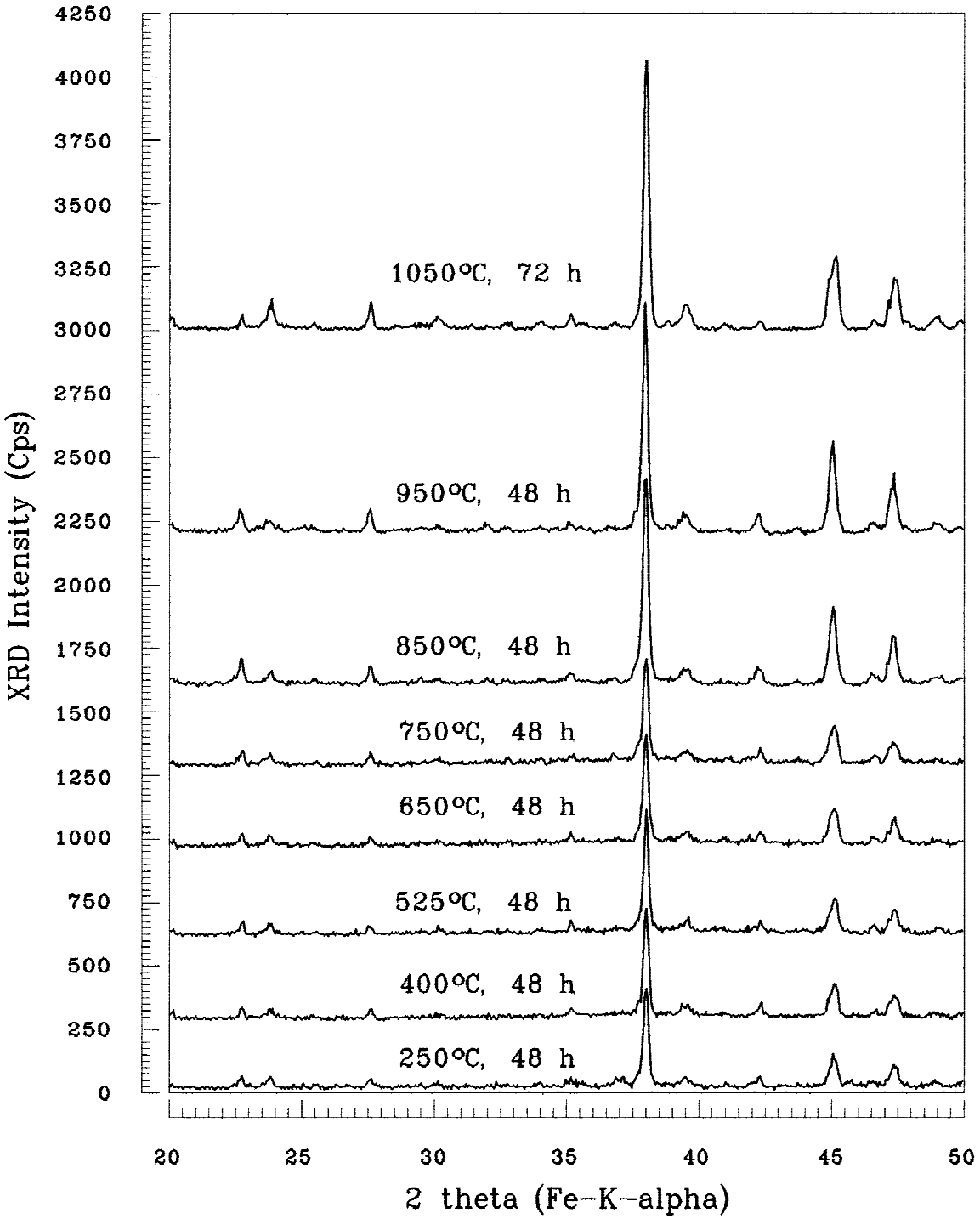

Fig. 4. XRD spectra of combustion-synthesized CA powders.

XRD data of $C_{12}Al_7$ samples by using the Rietveld method[38,39] on the DBWS-9411 Rietveld Analysis package.[40] 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 ~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_2O_5.[32] Urea is also known[32] to decompose into biuret (H_2N–CO–NH–CO–NH_2, i.e., $C_2H_5N_3O_2$), cyanuric acid (HCNO), and ammonia (NH_3) when it is heated to ~200°C. Biuret itself then decomposes when heated at

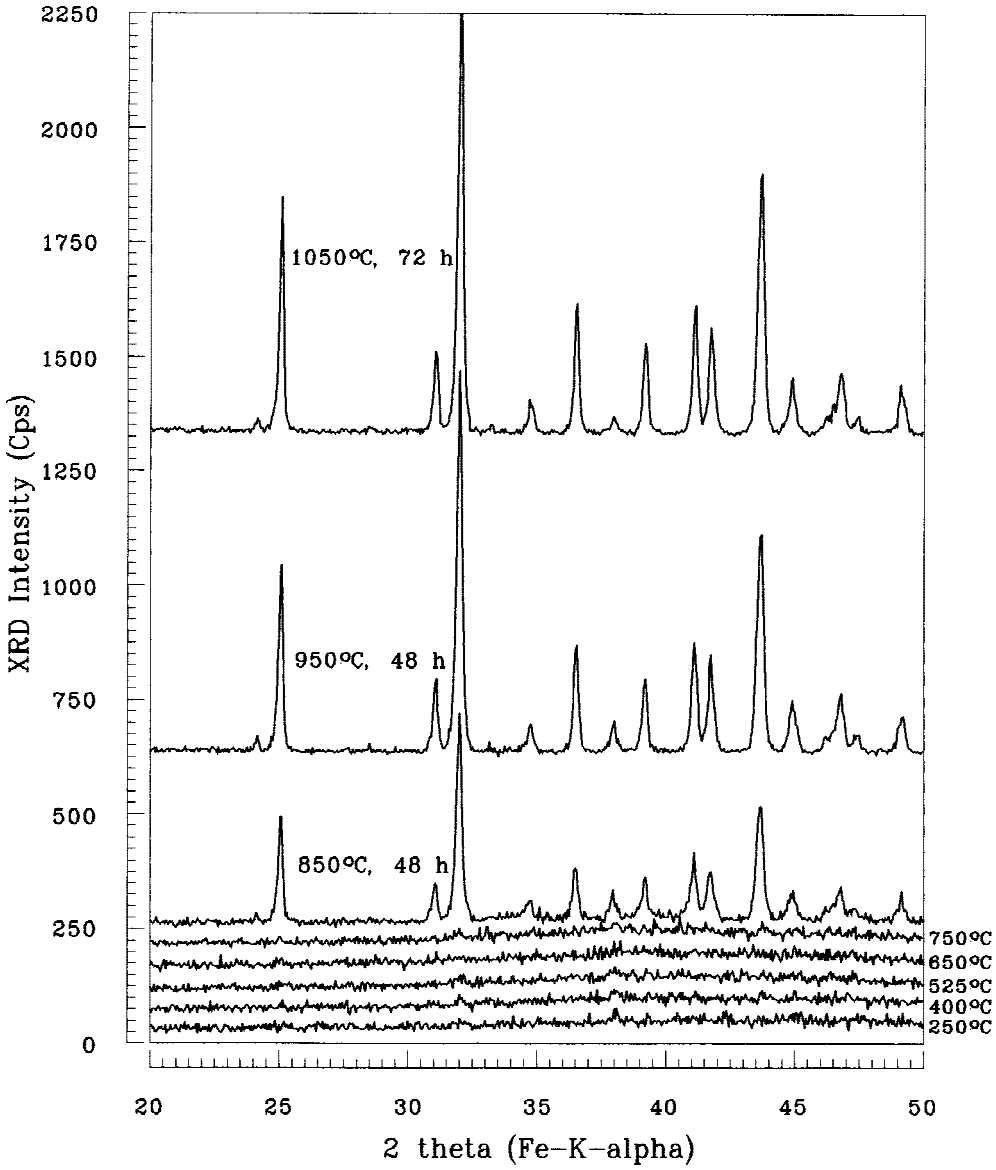

Fig. 5. XRD spectra of combustion-synthesized CA_2 powders.

temperatures >300°C. Therefore, in an aqueous mixture of metal nitrates and urea, the decomposition products are expected to consist of nitrous oxides, NH_3, and HCNO. This gaseous mixture will spontaneously ignite when the ambient temperature is ~500°C. This ignition is believed to instantaneously increase the local temperature of the dried foam to ~1300°C,[32] which, in a sense, is similar to the case of flash pyrolysis.

(1) Synthesis of C_3A, CA, CA_2, and CA_6

Figure 1 shows the XRD spectra of the combustion-synthesized C_3A 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 C_3A and $C_{12}A_7$. The calcined powders heated over the range of 650°–950°C did display a mixture of three phases: C_3A, $C_{12}A_7$, and CA. Single-phase C_3A 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 C_3A 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 C_3A powders (heated at 1100°C) is depicted in the SEM micrograph shown in Fig. 3(a).

The XRD spectra of the combustion-synthesized 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 CA phase. Powder samples heated at 850°C displayed an acceptable level of crystallization. A typical FT-IR spectrum of CA powders heated at 1100°C is given in Fig. 2 (spectrum ''(e)''). The particle morphology of the SPCS-synthesized CA powders (heated at 1100°C) is depicted in the SEM micrograph shown in Fig. 3(b).

The XRD spectra of the combustion-synthesized 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 CA_2. Spectrum ''(c)'' in Fig. 2 shows the FT-IR spectrum of CA_2

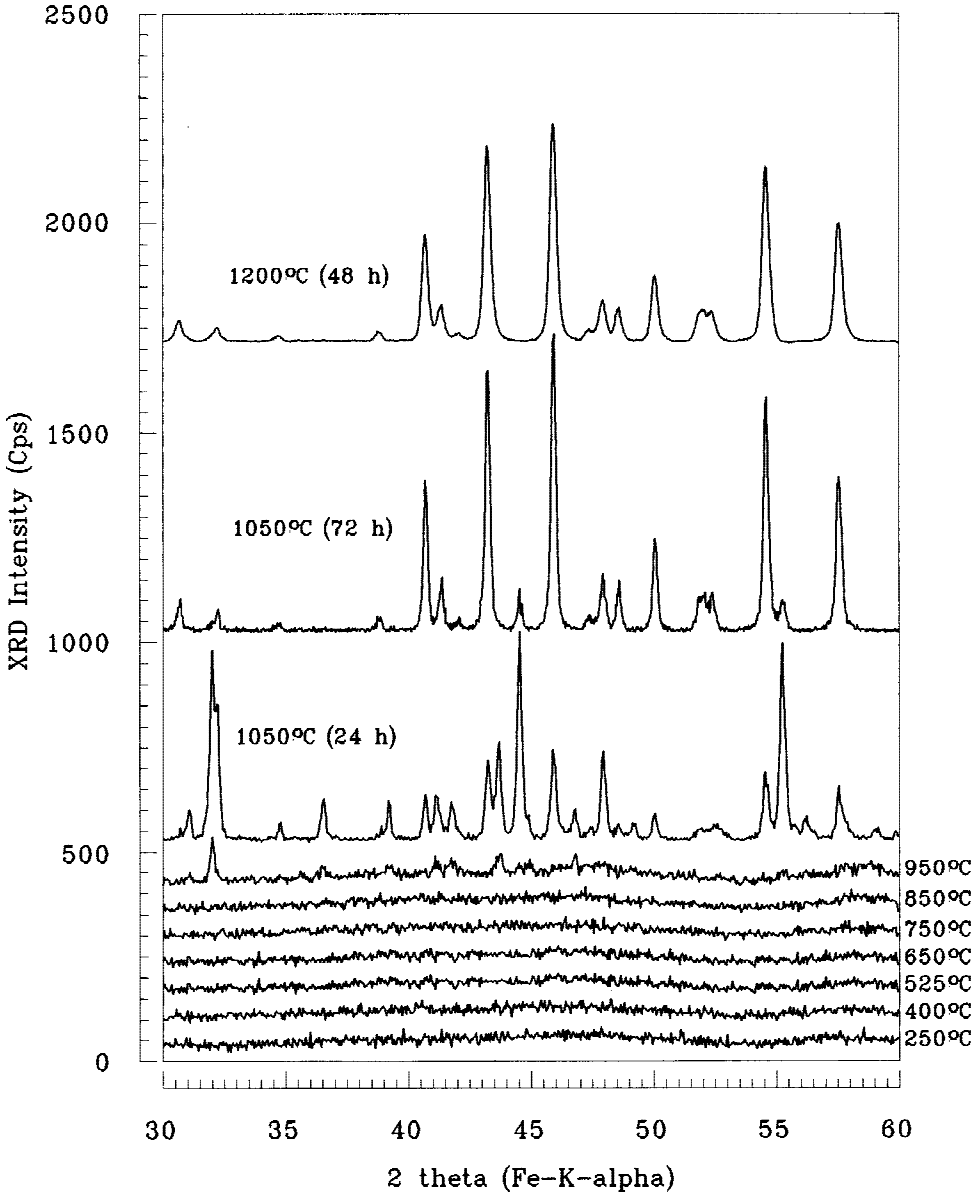

Fig. 6. XRD spectra of combustion-synthesized CA_6 powders.

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, α-Al_2O_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 α-Al_2O_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°–

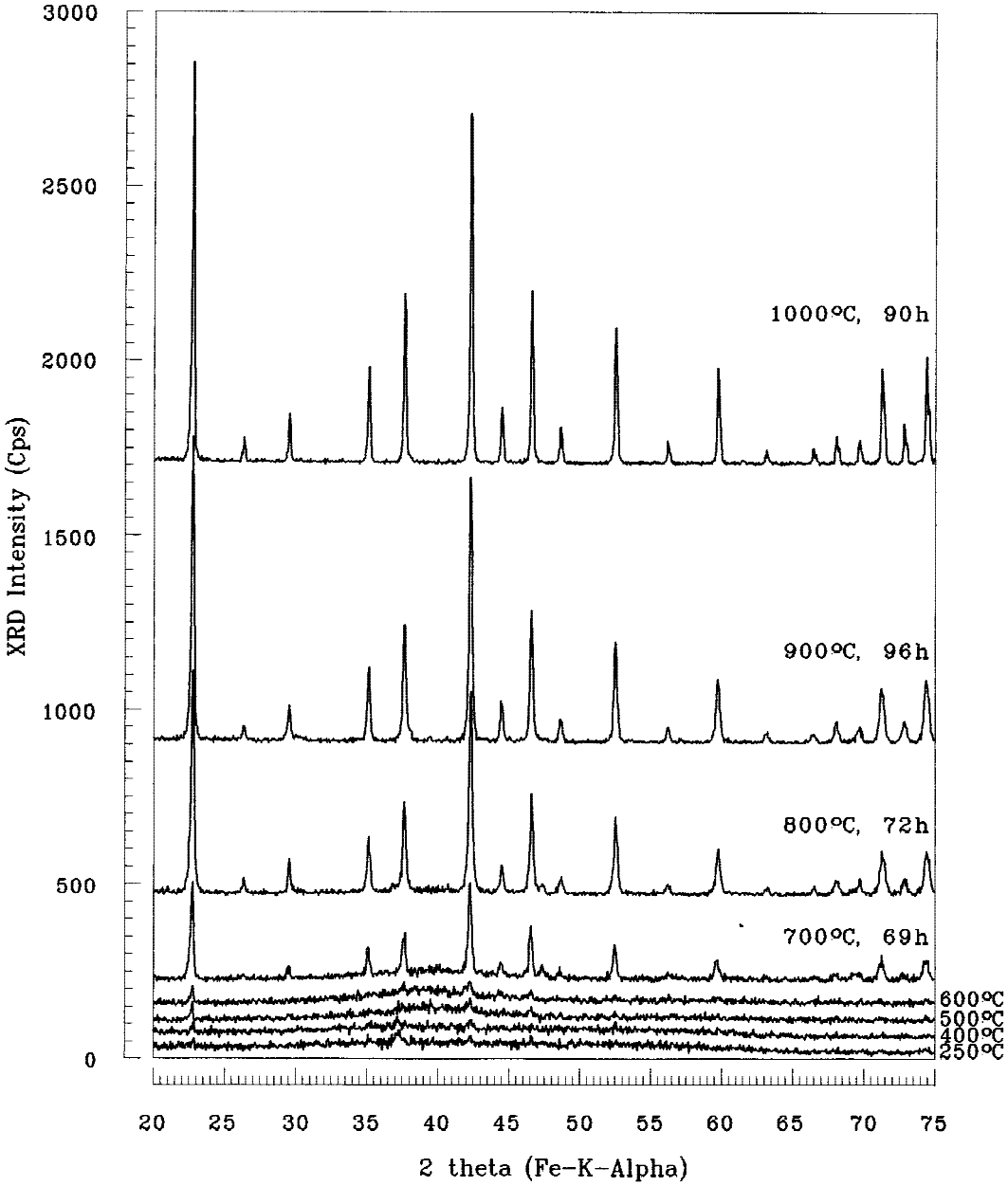

Fig. 7. XRD spectra of combustion-synthesized $C_{12}A_7$ powders.

1000°C, for prolonged times, did not cause any phase contamination (with any of the other binary compounds of the CaO–Al_2O_3 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 $C_{12}A_7$ sample heated at 1100°C. The particle morphology of the SPCS-synthesized $C_{12}A_7$ 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 $C_{12}A_7$ 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 $C_{12}A_7$

Structural refinements were performed on the powder samples of $C_{12}A_7$ 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 $C_{12}A_7$ ($Ca_{12}Al_{14}O_{33}$) was confirmed[25,26] 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[38–40] 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 R_{wp} 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 $C_{12}A_7$ powders (heated at 1000°C) by using the Warren–Averbach method.[41] The average crystallite size was ~14 Å, as shown in Fig. 8.

The unit cell of $Ca_{12}Al_{14}O_{33}$ 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

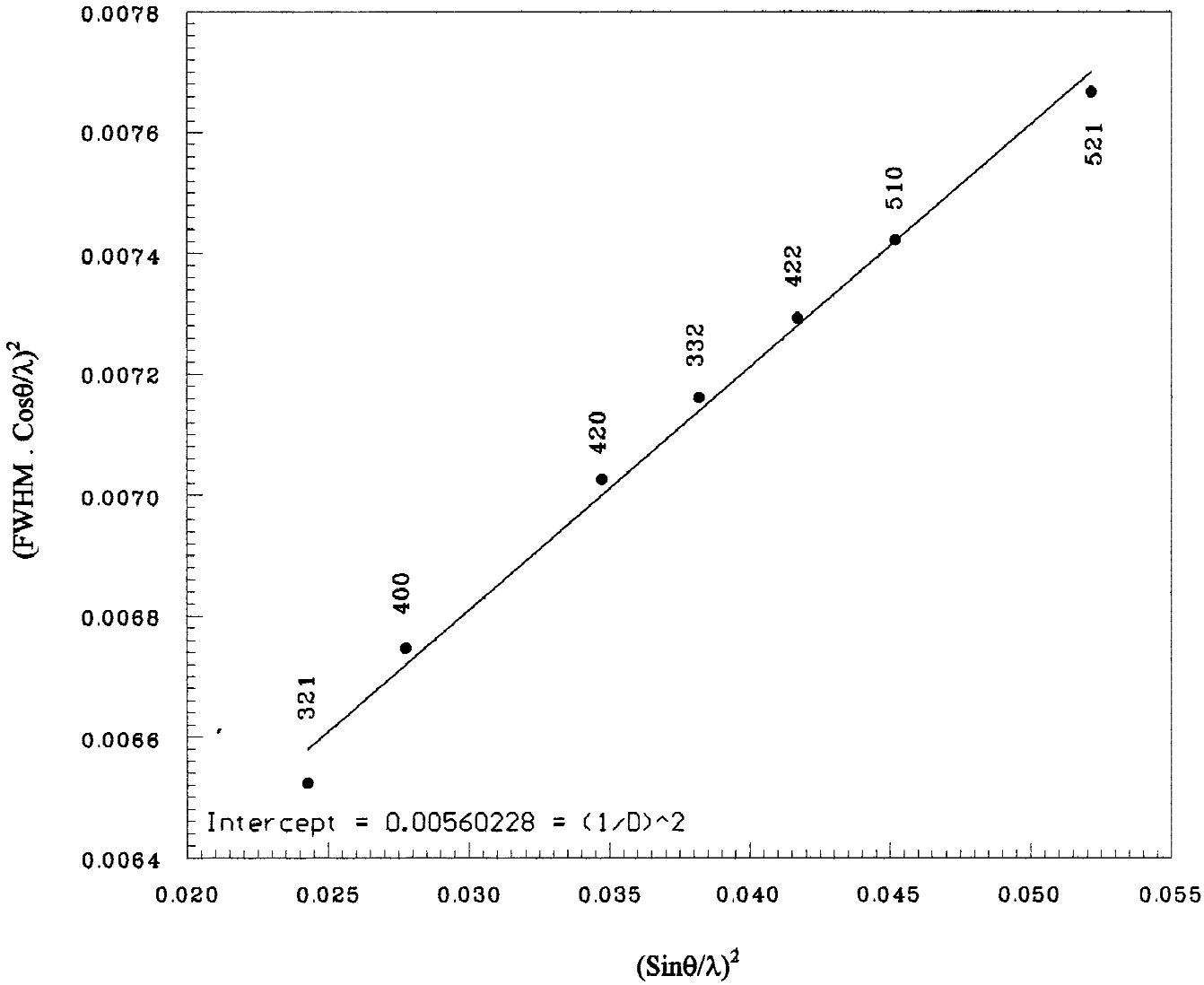

Fig. 8. Warren–Averbach[41] plot of $C_{12}A_7$ powders used to determine crystallite size.

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.

Table I. Refined Positional Parameters of the $Ca_{12}Al_{14}O_{33}$ Phase

Atom	Positional parameter		
	x	*y*	*z*
Ca	0.1026	0.0000	0.2500
Al(1)	0.3750	0.0000	0.2500
Al(2)	0.2335	0.2335	0.2335
O(1)	0.1987	0.2846	0.1033
O(2)	0.3105	0.3105	0.3105

IV. Conclusions

The binary compounds $Ca_3Al_2O_6$ (C_3A), $Ca_{12}Al_{14}O_{33}$ ($C_{12}A_7$), $CaAl_2O_4$ (CA), $CaAl_4O_7$ (CA_2), and $CaAl_{12}O_{19}$ (CA_6) of the CaO–Al_2O_3 system were, for the first time, prepared via the self-propagating combustion synthesis (SPCS) technique. Significant decreases in the synthesis temperatures (C_3A, 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_2O_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_6N_4O) and glycine ($C_2H_5NO_2$). The C_3A, $C_{12}A_7$, 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-

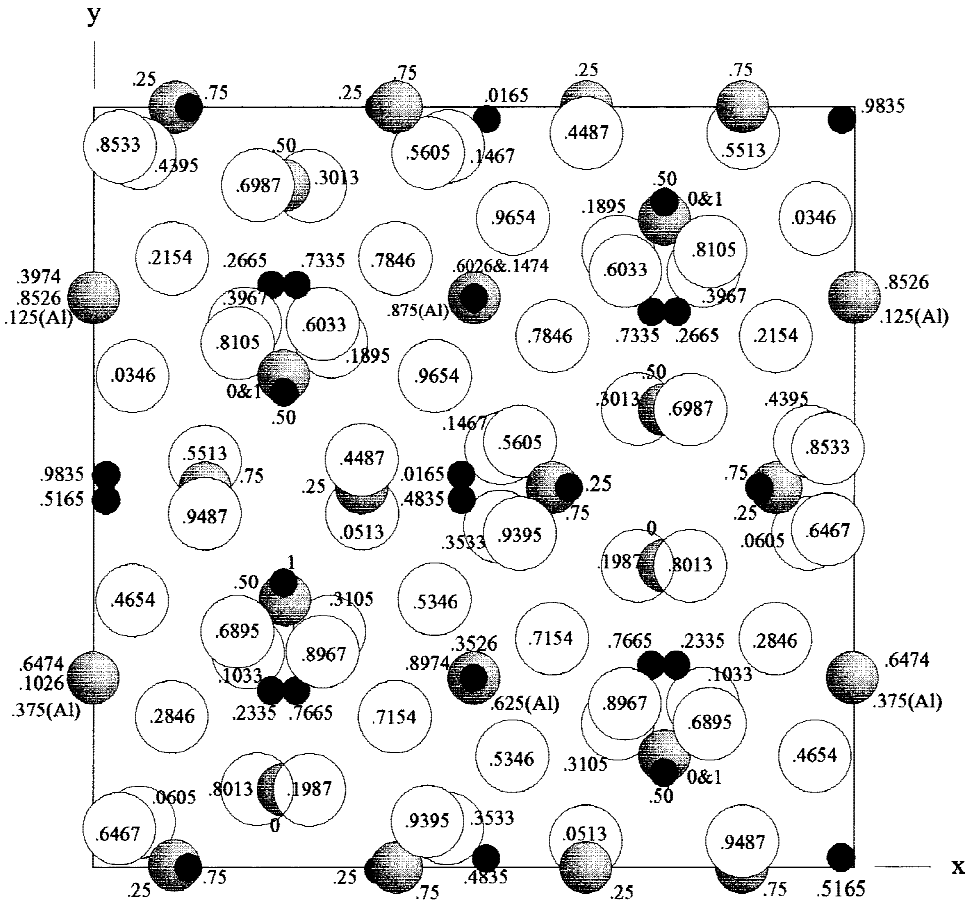

Fig. 9. Schematic of the $Ca_{12}Al_{14}O_{33}$ unit cell. Large open circles are O^{2-} anions, shaded circles are Ca^{2+} cations, and small solid circles are Al^{3+} cations.

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 $CaO–Al_2O_3$ 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.

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