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CHEMICAL PREPARATION OF THE BINARY COMPOUNDS OF $CaO-Al_2O_3$ SYSTEM BY COMBUSTION SYNTHESIS

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ABSTRACT

The binary compounds (C_3A : $Ca_3Al_2O_6$, $C_{12}A_7$: $Ca_{12}Al_7O_{33}$, CA : $CaAl_2O_4$, CA_2 : $Ca_2Al_2O_5$) and CA_6 : $CaAl_{12}O_{19}$) of $CaO-Al_2O_3$ system have been synthesized as high-purity ceramic powders by using the Combustion Synthesis (CS) method. Materials characterization of the above-mentioned phases were performed by powder XRD, FTIR, SEM and EDXS. It has hereby been shown that by using this synthesis procedure it would be possible to manufacture high-purity ceramic powders of CA_6 , CA_2 and $C_{12}A_7$ at 850°C, and of C_3A and CA at 1050°C in a stagnant air atmosphere.

INTRODUCTION

The binary compounds of the $CaO-Al_2O_3$ system do hold a significant place in a wide spectrum of applications of metallurgical slags, ceramic materials, and cement technology. The superior refractory properties of these binary line compounds, which are between 2900°C melting CaO and 2050°C melting Al_2O_3 terminal members, make them progressively attractive, in recent years, in the cement manufacturing technology. Products containing these binary compounds are especially used in casting, trowelling and grouting applications. The pure, alkali-free binary compounds of $CaO-Al_2O_3$ system are also being considered for replacing the alkali-containing chemical additives used in cement technology.

The chemical and thermodynamic properties of the $CaO-Al_2O_3$ system, as well as of the above-mentioned binary line compounds, were recently compiled and assessed by Leucht [1]. $Ca_3Al_2O_6$ (C_3A) is known to melt incongruently [2] at 1544°C, by transforming into a mixture of a liquid phase and CaO . $CaAl_2O_4$ (CA) melts congruently at about 1600°C [3-6] and when prepared by conventional methods the final product of solid-state reactive firing contains the impurity phases of CaO , CA_2 and $C_{12}A_7$ below 1300°C. $CaAl_2O_7$ (CA_2) melts congruently at 1745°C [7] (or 1775°C) and is also known as di-calcium aluminate. CA_2 is preferred in use to a large extent among all the high-alumina cements, and is utilized as a high commercial value mineral substance, especially in casting, trowelling and grouting applications. Al_2O_3 (CA_6) melts incongruently [1, 8] at 1885°C, by transforming into a mixture of a liquid phase and $\alpha-Al_2O_3$. CA_6 does not take its place among "high-alumina cements" since it is stable against water, and since it does not get "hydrated" in contrast to other (i.e., CA , CA_2 , C_3A and $C_{12}A_7$) binary calcium aluminates. Combustion synthesis (CS) is not a new technique to be used in the field of advanced materials synthesis and chemistry. It has first been used by Kingsley and Patil [9] for the manufacture of high purity α -alumina powders. The same researchers have also

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successfully used this method of materials synthesis in preparing several compositions in the $ZrO_2-Al_2O_3$ binary system [10]. The combustion being instantaneous and energy-saving have attracted much interest and been successfully utilized in the synthesis of $LaCrO_3$ [11], $Ba_2YCu_3O_8$ [12] and $Y-Ba-Cu-O$ phases [13]. Recently, combustion methods using "glycine" as the fuel [14], and "urea" as the fuel [15] have been reported for the successful synthesis of Ca-doped $LaCrO_3$ and pure $LaAlO_3$ powders, respectively. A similar combustion technique was also demonstrated for the successful synthesis of $YAG:Cr$ and $Y_2O_3:Eu$ [16], and of $YAG:Nd$ and $YIG:Nd$ [17] powders using both of the above-mentioned fuels.

In the present work, the experimental conditions and parameters of the preparation of binary calcium aluminate ceramic powders have been studied and presented by the powder route of combustion synthesis.

EXPERIMENTAL PROCEDURE

Starting powders of $Ca(NO_3)_2 \cdot 4H_2O$ (99+%, Merck, Germany), and $Al(NO_3)_3 \cdot 9H_2O$ (99+%, Riedel-de Haën AG, Germany) were weighed, and then dissolved in distilled water at room temperature to yield 0.4 M stock solutions. A total of 250 ml of 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 hour at room temperature. A proprietary amount [18] of urea (CH_4N_2O ; 99.5%, Riedel-de Haën AG, Germany) was then added to this solution. Following the dissolution of urea in the cations solution, the beaker contents were transferred into a 400-ml capacity Pyrex beaker. The Pyrex beaker with the liquid mixture was then placed in a muffle furnace maintained at $510 \pm 10^\circ C$. Initially, the mixture boils and undergoes dehydration followed by decomposition, with swelling and frothing, resulting in a foam which ruptures with a flame and glows to incandescence [10]. The entire combustion process was complete in less than 15 minutes. The product of combustion was a voluminous, foamy and amorphous (or crystalline) precursor of the desired calcium aluminate phase. The foamy precursors were lightly ground in an agate mortar into a fine powder and then calcined and crystallized on α -alumina plates, in a dry air atmosphere, over the temperature range of 250 to $1050^\circ C$ for prolonged times to yield the crystalline and phase-pure calcium aluminate binary compounds.

Powder X-ray diffraction spectra were obtained from the calcined samples for phase characterization purposes. A Rigaku DMax/B powder diffractometer was used with FeK_α radiation at the step size of 0.02° and a preset time of 1 second for the runs performed to accomplish phase characterization and to check the phase purity of the synthesized ceramic powders. The FTIR spectra of calcium aluminate powders were collected by a Nicolet DX-510 spectrometer. Dried (at $70^\circ C$) powder samples were mixed in an agate mortar with 3 wt% KBr prior to pellet formation.

Particle size and morphology of the powders were monitored from the photomicrographs taken with a JEOL/JSM6400 scanning electron microscope. The samples were, first, sputter coated with an approximately 25 nm-thick layer of gold-palladium alloy. EDXS (Kevex, USA) analysis were carried out on the samples to

perform a semi-quantitative analysis for the determination of the elemental distribution in the powder samples. The EDXS runs were believed to be accurate to about ± 3 wt%.

RESULTS AND DISCUSSION

The amorphous or crystalline (depending on the specific calcium aluminate compound), while precursor powders obtained, following the "combustion synthesis," were lightly ground in an agate mortar and then calcined at different temperatures, in dry air, in the form of consecutive isothermal heatings for pre-determined periods. Powder XRD spectra were gathered following each isothermal heating step. Samples for SEM and EDXS studies were also collected after each isothermal heating step.

Figure 1 shows the XRD spectra of the combustion synthesized $Ca_3Al_2O_6$ (C_3A) powder samples heated at different, consecutively increasing temperatures. The already crystalline precursor powders heated in the temperature range of 250 to $525^\circ C$ exhibited a phase mixture of C_3A and $C_{12}A_7$. The calcined powders heated over the range of 650 to $950^\circ C$ did display a mixture of three phases; C_3A , $C_{12}A_7$ and CA . Single-phase C_3A powders (deduced by XRD and EDXS analysis) could only be obtained by heating the precursors at $1050^\circ C$ for periods of 48 to 72 hours. Figure 2 shows the FTIR spectra of C_3A samples as a function of increasing calcination temperature.

The XRD spectra of $Ca_{12}Al_{14}O_{33}$ ($C_{12}A_7$) samples are shown in Figure 3. The precursors were found to remain significantly amorphous over the temperature range of 250 to $600^\circ C$. Crystallization of $C_{12}A_7$ precursors began above $600^\circ C$, and the crystallization product was $Ca_{12}Al_{14}O_{33}$. Further heating, over the temperature range of 600 to $1000^\circ C$, 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, and only improved the extent of crystallization achieved in the powder samples. Figure 4 displays the FTIR spectra of $C_{12}A_7$ samples.

The XRD spectra of the combustion synthesized $CaAl_2O_4$ (CA) powder samples heated at different temperatures, in dry air, are given in Figure 5. It was seen that even the powders heated at $250^\circ C$ were crystalline, and did only possess the characteristic spectrum of the desired CA phase. Powder samples heated at $850^\circ C$ displayed an acceptable level of crystallization. The FTIR spectra of CA powders are given in Figure 6.

Figure 7 shows the XRD spectra of the combustion synthesized $CaAl_2O_7$ (CA_2) powder samples heated at different, consecutively increasing temperatures. The "as-synthesized" precursor powders were found to be amorphous, and the bottom five spectra (amorphous) do correspond to the isothermal heatings at 250, 400, 525, 650, and $750^\circ C$ (48 hours, each), respectively. The amorphous body crystallized at temperatures above $750^\circ C$, and the crystallization product was pure CA_2 . Figure 8 shows the FTIR spectra of CA_2 powders.

The XRD spectra of the combustion synthesized $CaAl_{12}O_{19}$ (CA_6) powder samples heated at different temperatures, in dry air, are plotted in Figure 9. The "as-synthesized" precursor powders of CA_6 composition were found to be amorphous, and

The SEM micrographs of all the samples showed the presence of micron-range, irregularly shaped particles after calcination at each temperature. The FTIR spectra of the combustion synthesized calcium aluminate precursor powders did exhibit the typical "nitrate (NO_3^-)" vibrations over the range of 1250 to 1650 cm^{-1} . The nitrate peaks in the FTIR plots did disappear with the calcination temperature increasing beyond 900°C.

"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 "carbonyltriazide" ($\text{CH}_6\text{N}_4\text{O}$) and "glycine" ($\text{C}_2\text{H}_5\text{NO}_2$). It was also noted in this study that the samples of C_3A , C_{12}A_7 , CA , CA_2 , and CA_6 prepared with the stoichiometric amounts of either carbonyltriazide or glycine did all yield single-phase, "pure" (deduced only by XRD and EDXS analysis) binary calcium aluminates, followed by isothermal heatings (for 48 to 72 hours) at 1050, 800, 850, 900, and 1050°C, respectively.

CONCLUSIONS

The binary compounds (C_3A , C_{12}A_7 , CA , CA_2 , and CA_6) of the $\text{CaO-Al}_2\text{O}_3$ system were, for the first time, prepared by combustion synthesis. Significant decreases (C_3A : 1050°C, C_{12}A_7 : 800°C, CA : 850°C, CA_2 : 900°C, and CA_6 : 1050°C) in the synthesis temperatures (together with improved compound purities 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). It is also hereby shown that, in the combustion synthesis processing of binary calcium aluminate compounds, one can reliably and interchangeably use *urea*, or *carbonyltriazide*, or *glycine* as the fuel/oxidizer.

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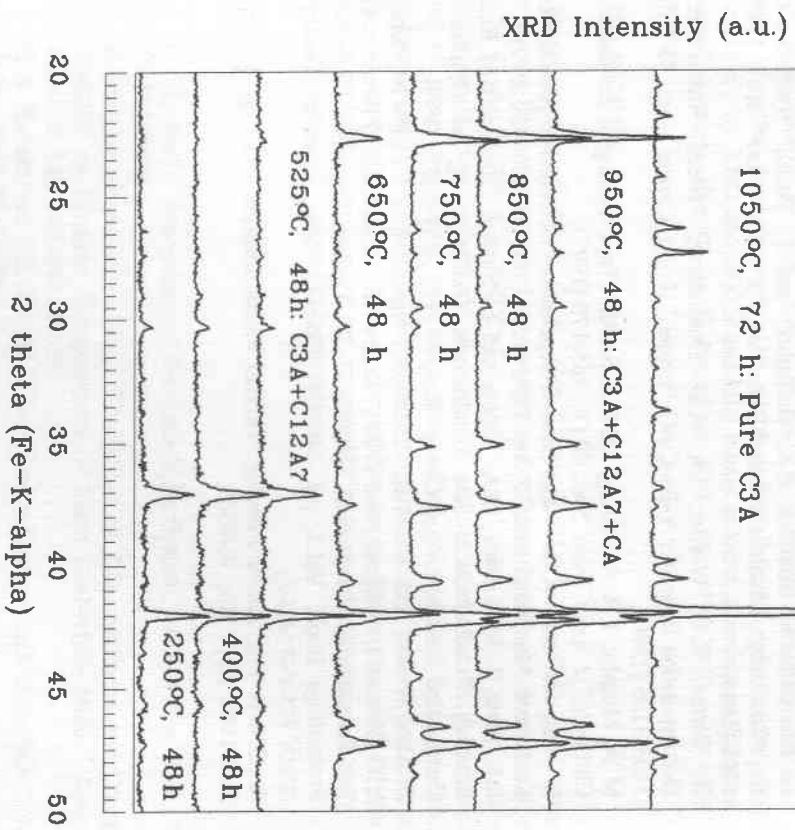


Figure 1. XRD spectra of $\text{Ca}_3\text{Al}_2\text{O}_6$ (C_3A) powders

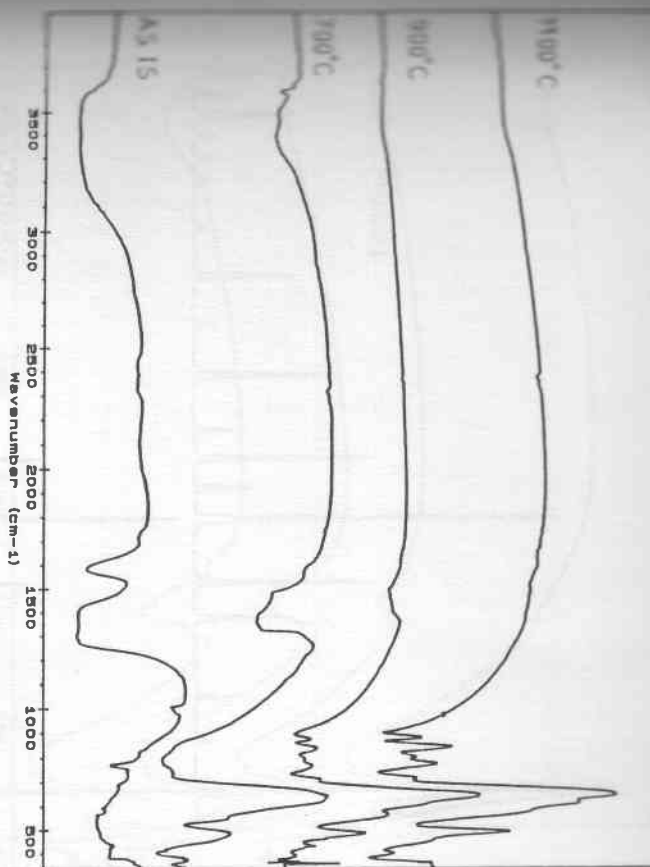


Figure 2. FTIR (%transmittance) spectra of $\text{Ca}_3\text{Al}_2\text{O}_6$ (C_3A) powders

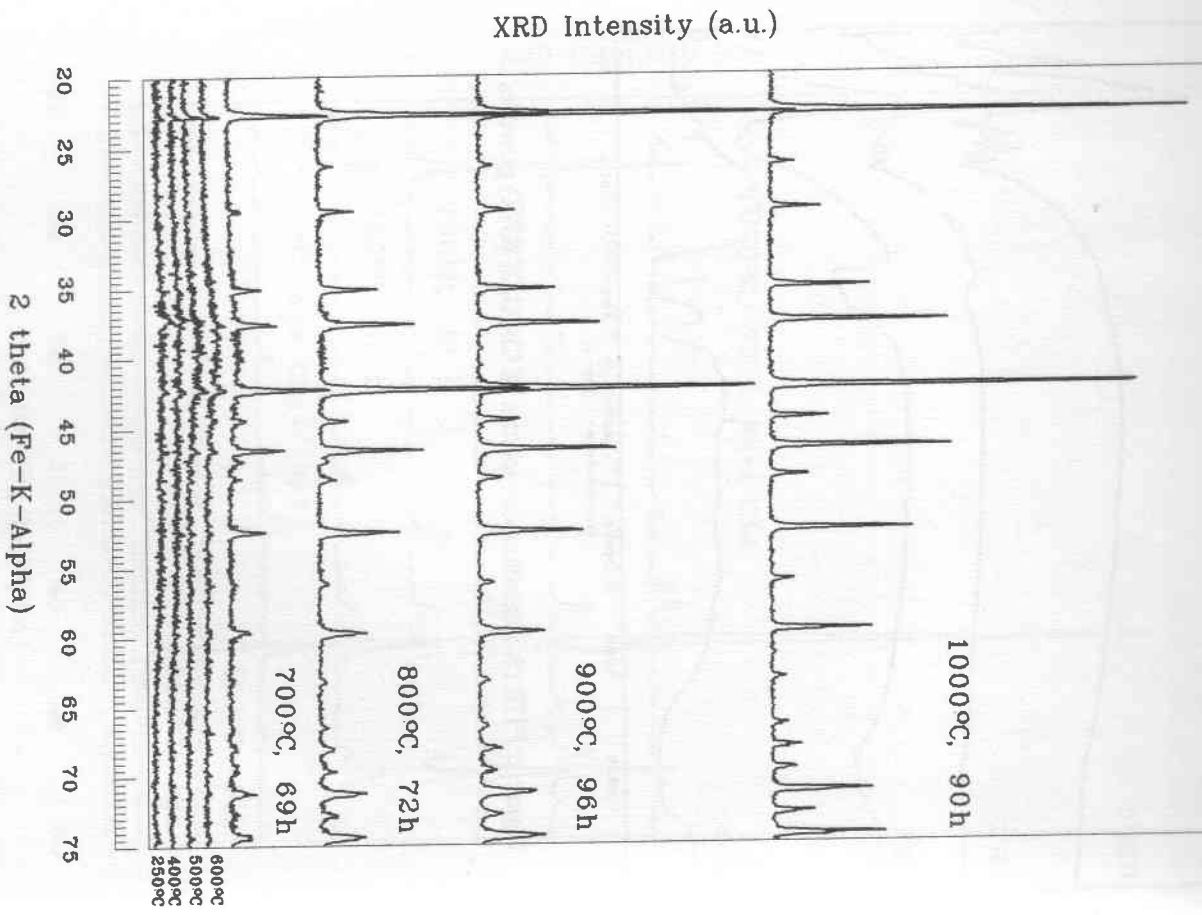


Figure 3. XRD spectra of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (C_{12}A_7) powders

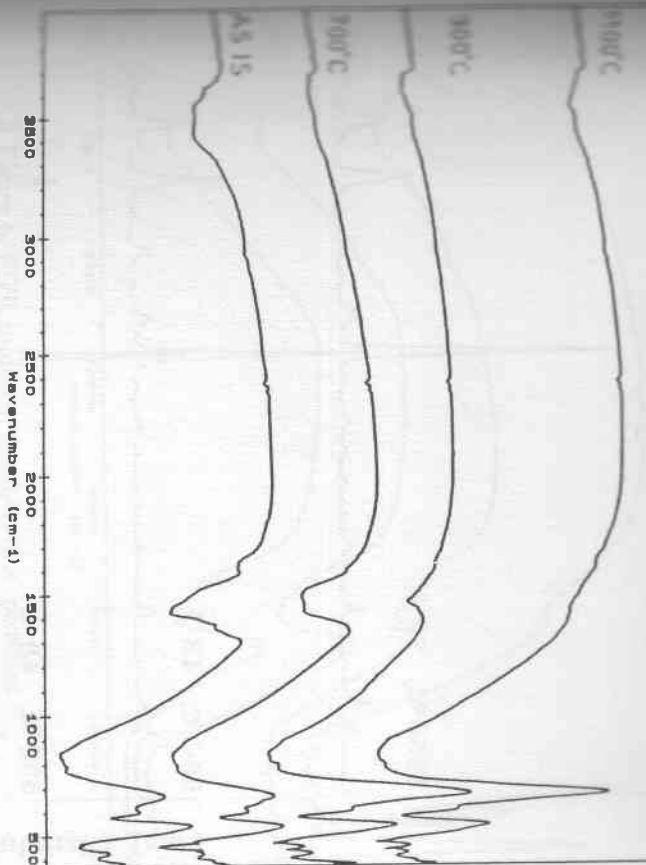


Figure 4. FTIR spectra of $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (C_{12}A_7) powders

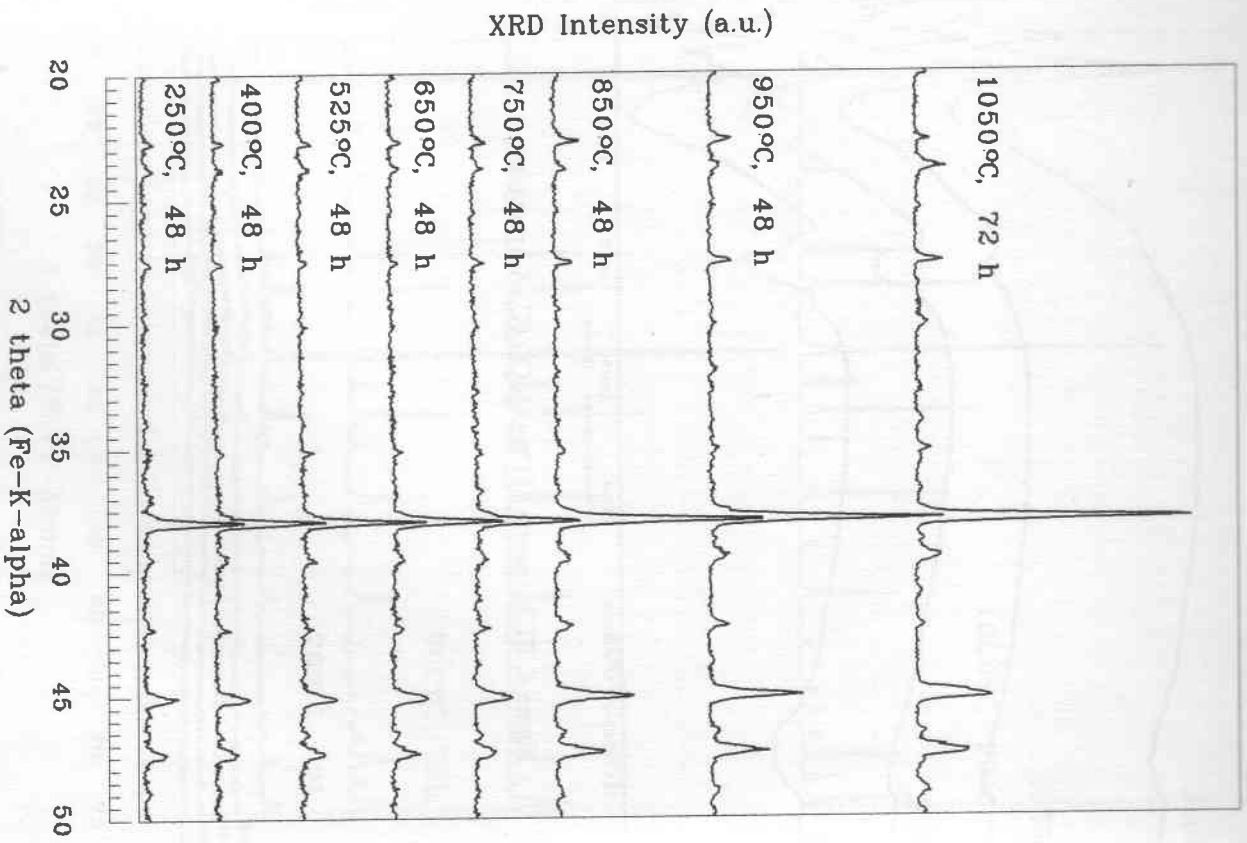


Figure 5. XRD spectra of CaAl₂O₄ (CA) powders

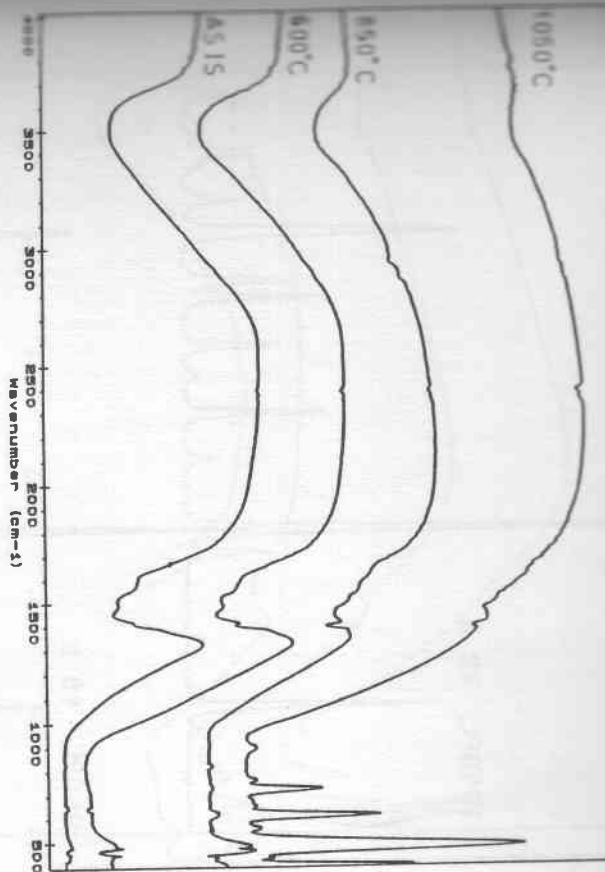


Figure 6. FTIR spectra of CaAl₂O₄ (CA) powders

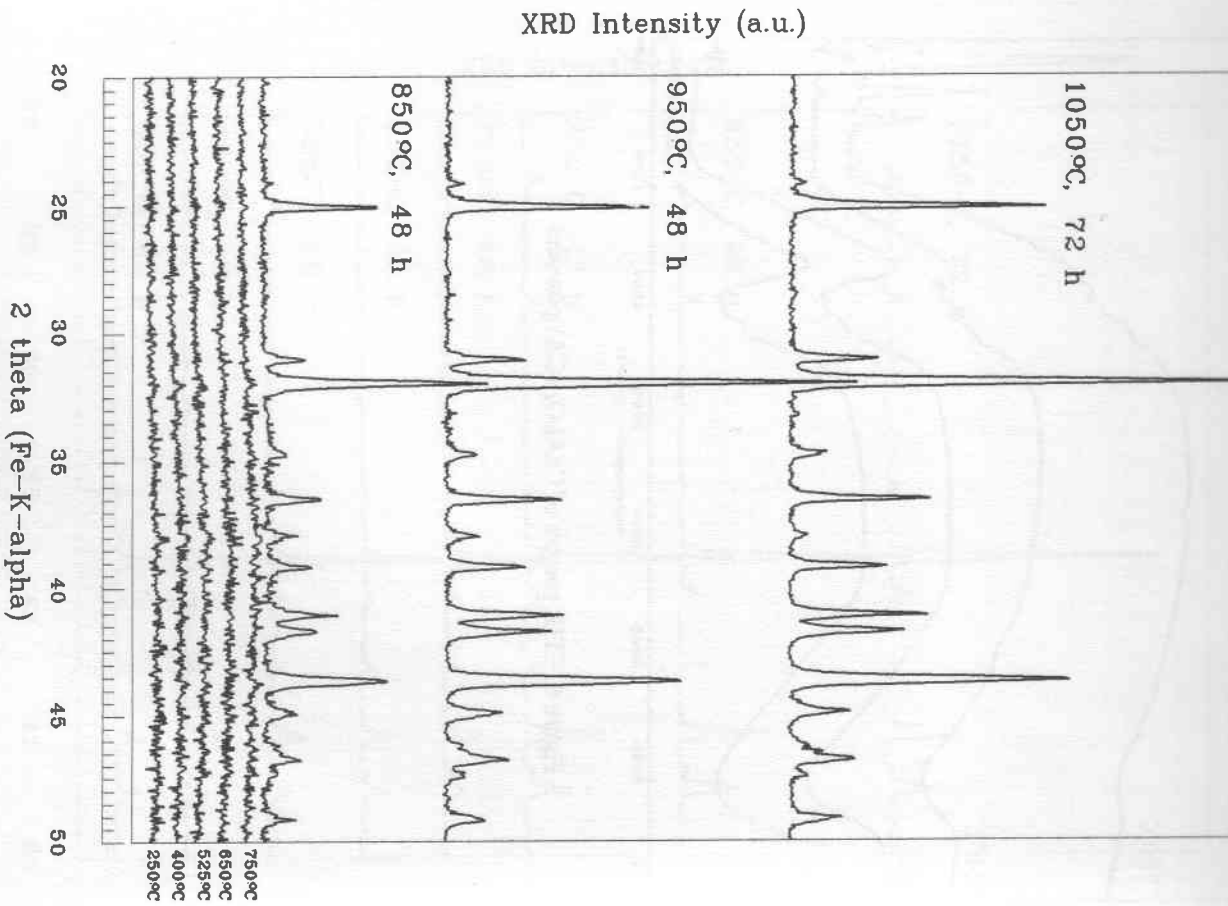


Figure 7. XRD spectra of CaAlO₇ (CA₂) powders

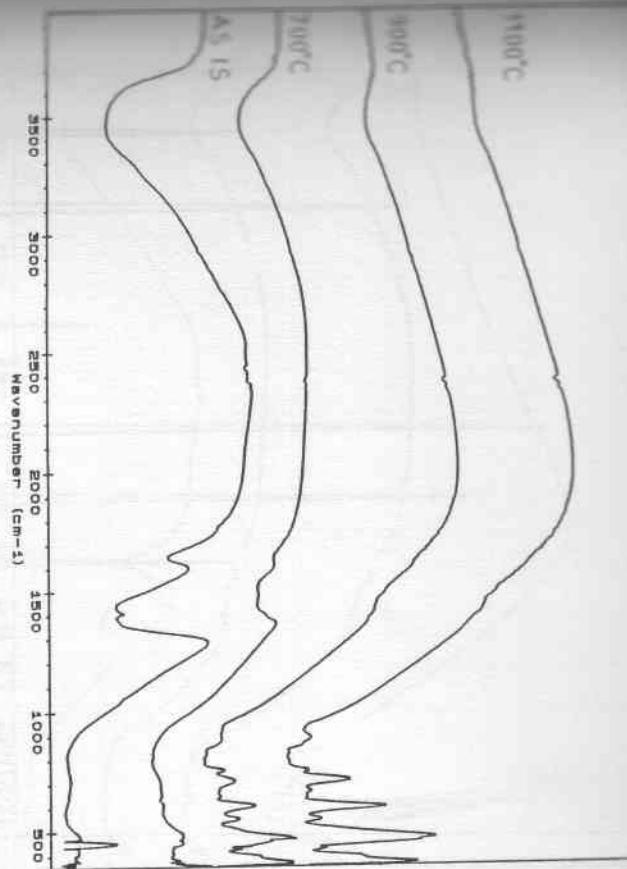


Figure 8. FTIR spectra of CaAlO₇ (CA₂) powders

XRD Intensity (a.u.)

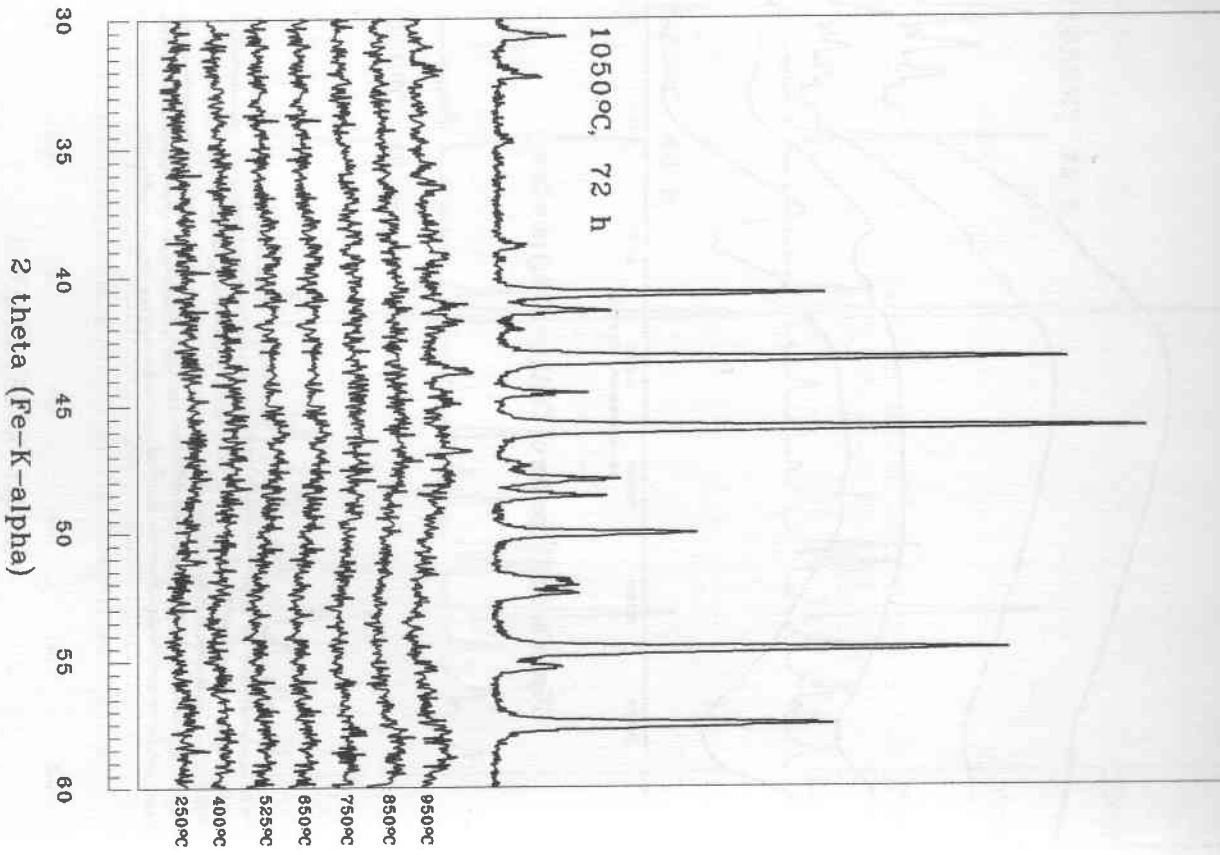


Figure 9. XRD spectra of CaAl_2O_9 (CA_6) powders

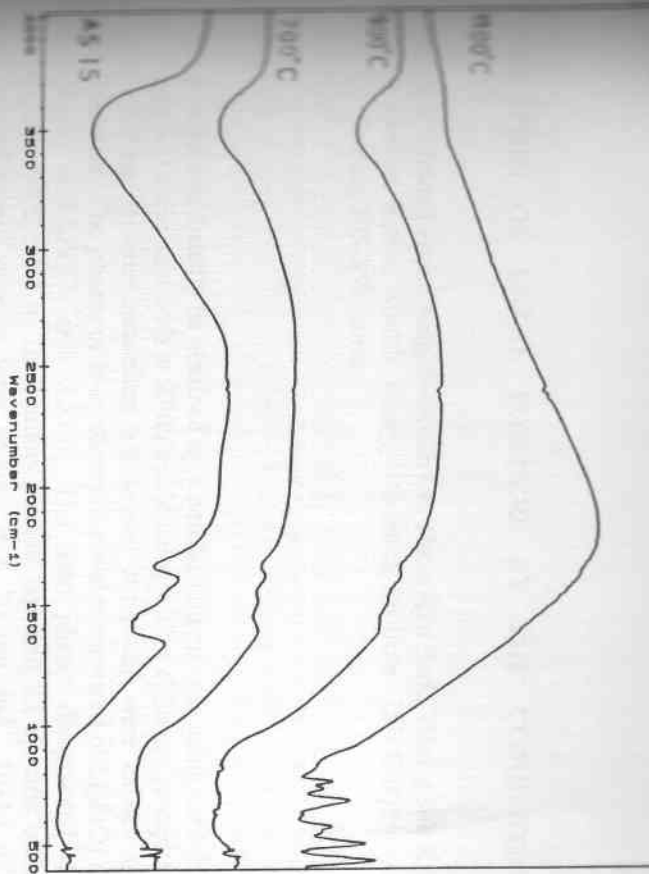


Figure 10. FTIR spectra of CaAl_2O_9 (CA_6) powders