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CRYSTAL CHEMISTRY AND STRUCTURAL CHARACTERIZATION OF $Ca_{12}Al_{14}O_{33}$

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Abstract

The chemically homogeneous powders of $C_{12}A_7$ phase ($Ca_{12}Al_{14}O_{33}$) of the CaO-Al₂O₃ binary system has been synthesized via a modified "self propagating combustion synthesis" technique. A significant reduction in the synthesis temperature of this compound has been achieved as compared to the conventional techniques of synthesis. The structural characterization of the synthesized materials has been performed by Rietveld analysis on the single-phase, powder XRD samples.

1. Introduction

The $C_{12}A_7$ ($Ca_{12}Al_{14}O_{33}$) has been shown not to be stable in the anhydrous CaO-Al₂O₃ system [1, 2]. The earlier determinations [3, 4] of the phase diagram have identified four intermediary phases: C₃A, C₅A₃, CA, and C₃A₅. The phases C₅A₃ and C₃A₅ were later assigned the formulas C₁₂A₇ and CA₂, respectively [1, 5]. Nurse *et al.* [2, 6] determined the phase diagram in a moisture-free atmosphere and concluded that C₁₂A₇ is not stable under strictly anhydrous conditions. The formula Ca₁₂Al₁₄O₃₂(OH)₂ has been proposed for this phase [7]. The structural ambiguity is still believed to persist over this compound.

The compound $C_{12}A_7$ has previously been synthesized [8, 9] by the solid state reactive firing of reagent grade starting materials like $CaCO_3$, 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 higher than 24 hours. It has been reported by Roy *et al.* [8] that the final product may contain up to 1.30 to 1.40 wt% H₂O (corresponding to the composition $C_{12}A_7H$) after heating to about 1100°C in air of normal humidity. This water was claimed to be absorbed reversibly and without any major structural change; therefore Roy *et al.* [8] termed $C_{12}A_7$ a "zeolitic" phase.

Several binary compounds, including the $C_{12}A_7$ phase, in the CaO-Al₂O₃ system have been synthesized by Kuznetsova *et al.* [10] via the preparation of mixed Al-Cahydroxides in aqueous solutions. This report claimed the reduction of the synthesis temperature of $C_{12}A_7$ to less than 1200°C, but the chemical precipitation process employed was not able to produce a single-phase substance, and the solid product of the subsequent air calcination was also found to contain other phases amounting to about 5% in the calcined body.

The structure of the $C_{12}A_7$ phase was first studied by Eitel et al. [11] and they reported a cubic structure with the lattice parameter, a=11.95 Å, and a possible space group of T_d^{6} . They claimed that this structure is the one that is build up by the 12:7 site ratio and

a three-dimensional network of AlO_4 tetrahedra constitutes the back bone of the structure while all oxygen atoms belong to every two such tetrahedra.

Glasser et al. [12] did later determine the space group of the $C_{12}A_7$ unit cell to be T_d^6 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., $11CaO.7Al_2O_3.CaF_2$) of cubic $C_{12}A_7$ was refined by Williams [13] and the structure was confirmed to belong to the space group I-43d with a=11.970 Å, Z=2.

It has been reported [14] 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 demonstrated for the first time [15] by the rapid synthesis of fine particle α -Al₂O₃ and related oxides such as metal aluminates, rare earth orthoaluminates, and Ce³⁺ or Cr³⁺ doped aluminous oxides. The process involves the combustion of corresponding metal nitrate plus either urea or carbohydrazide mixtures at 500°C or 250°C, respectively, under normal atmospheric pressure [14]. The process yields foamy, voluminous and fine oxide powders in less than 5 minutes. The combustion being instantaneous and energy saving has attracted much interest and been successfully utilized in the synthesis of LaCrO₃ and Ba₂YCu₄O₈ phases [16, 17].

One of the compounds of the CaO-Al₂O₃ binary system, $Ca_{12}Al_{14}O_{33}$, has been synthesized, for the first time, by self-propagating combustion synthesis, and the preparation and structural details of this phase is presented in this study.

2. Experimental Procedure

(1) Preparation of $Ca_{12}Al_{14}O_{33}$

Starting powders of $Ca(NO_3)_2.4H_2O$ (99+%, Merck, Germany), and $Al(NO_3)_3.9H_2O$ (99+%, Riedel-de Haën AG, Germany) were weighed, and then dissolved in distilled water at room temperature to yield 0.5 M stock solutions. A total of 50 ml of cations solution, taken from each of the stock solutions in appropriate amounts to give the stoichiometry of $Ca_{12}Al_{14}O_{33}$, was mixed with a magnetic stirrer in an uncovered 100 ml-capacity glass beaker for 1 hour at room temperature. 3 grams of urea (CH₄N₂O; 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 250-ml capacity Pyrex beaker.

The Pyrex beaker with the liquid mixture was placed in a muffle furnace maintained at 510 \pm 10°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 [14]. The entire combustion process was complete in less than 15 minutes. The product of combustion was a voluminous, foamy and amorphous precursor of the Ca₁₂Al₁₄O₃₃ phase.

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3. Results and Discussion

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The morphological were investigated by scandramatic change in the particular The foamy, amorphous precursors were ground in an agate mortar into a fine powder and then calcined on an α -alumina plate, in dry air, over the temperature range of 250 to 1000°C for prolonged times to yield the crystalline and phase-pure Ca₁₂Al₁₄O₁₃.

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Powder X-ray diffraction spectra were obtained from the 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 check the purity of the synthesized ceramic powders.

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 on the elemental distribution in the powder samples. The EDXS runs were believed to be accurate to about ± 3 wt%.

(3) Structural Refinements

Structural refinements were performed on the carefully gathered $(0.02^{\circ} \text{ step size}, 5 \text{ seconds count time})$ powder XRD data of $Ca_{12}Al_{14}O_{33}$ samples by using Rietveld method [18, 19] on the DBWS-9411 Rietveld Analysis package [20]. The refined structural parameters were then used to draw the unit cell of this phase.

3. Results and Discussion

The amorphous, white precursor powders obtained, following the "self-propagating combustion synthesis," were lightly ground in a hand mortar and then calcined at different temperatures in the form of consecutive isothermal heatings for pre-determined durations. Powder XRD spectra were collected following each isothermal heating step. Figure 1 shows the results of this study, and it displays the phase evolution characteristics of $Ca_{12}Al_{14}O_{33}$ samples upon heating in a dry air atmosphere. Figure 1 contains eight separate XRD spectra, each gathered at a different temperature; and the four spectra at the bottom portion of the figure do correspond to the isothermal heatings performed at 250, 400, 500 and 600°C, respectively, from bottom to top. The remaining four spectra were labeled with their respective heating temperatures on them. The precursors were found to remain *significantly* amorphous over the temperature range of 250 to 600°C.

Crystallization of the precursors began over the temperature range of 600 to 700°C, and the crystallization product was $Ca_{12}Al_{14}O_{33}$. Further heating, over the temperature range of 700 to 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, and only improved the extent of crystallization achieved in the powder samples.

The morphological features of the combustion synthesized $Ca_{12}Al_{14}O_{33}$ powders were investigated by scanning electron microscopy. Figure 2 shows the characteristic and dramatic change in the particle size and morphology of the precursors with increasing







A: Amorphous precursor j



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Figure 2. SEM microgram

temperature. The unitality formed, amergatory statute for the distancement of sowill berring the 16 office (), attractionate, were concerning of our mercin particles buryed and regulater of the former temperature), and at 230°C, as there in Figure 2A. To resurchedule, affect of increasing effertation from temperature (and string on the particle used in muscledule) or depreted in Party of the transformer margin is used in the contraction of the muscledule.



90h

96h

A: Amorphous precursor powders after being heated at 250°C for 48 hours



B: Precursor powders after being heated at 900°C for 96 hours



temperature. The initially formed, amorphous chunks (of the dimensions of 20 to 50 μ m) still having the Ca₁₂Al₁₄O₃₃ stoichiometry were consisting of sub-micron particles heavily fused together at the lower temperatures, such as 250°C, as shown in Figure 2A. The remarkable effect of increasing calcination temperature (and time) on the particle size and morphology is depicted in Figure 2B for a precursor sample heated at 900°C, in dry air, for 96 hours. The particle sizes were found to range from sub-micron (for quite a significant portion of the powder body) to about few microns for samples heated at temperatures above 700°C.

Structural refinements were performed on the powder samples heated at 1000°C, in a dry air atmosphere, on alumina plates for crystallization times ranging from 72 to 90 hours. The unit cell of $Ca_{12}Al_{14}O_{33}$ was confirmed [12, 13] to be cubic (a = 11.971 Å) with a space group of I-43d (*Hermann-Mauguin No. 220*) which possess the Laue symmetry of *m3m*. The unit cell of this phase contains 118 atoms (i.e., Z=2).

Rietveld analysis [18-20] were performed on the powder XRD data of the 1000°C samples. The positional (atomic) parameters, as well as the overall scale, temperature, site occupancy factors, and the cell, preferred orientation, mixing, halfwidth and background parameters were refined in the Rietveld cycles. Rietveld refinement was converged in 43 cycles to an $R_{wp} = 4.3\%$ with a Durban-Watson statistic of 0.46.

The unit cell of $Ca_{12}AI_{14}O_{33}$ was found to contain 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 Laue symmetry m3m. These five unique atomic positions as refined by the Rietveld analysis are reproduced in Table 1.

Table 1.	Refined	positional	parameters of	the	phase	Ca ₁₂ A	$l_{14}C$	3
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The unit cell of $Ca_{12}Al_{14}O_{33}$ was then plotted, as a two-dimensional (and to the correct scale) projection, by using the above information, as depicted in Figure 3. The numbers adjacent to the ions of the cell do represent their altitudes along the z-axis, which is perpendicular to the plane of paper.

4. Conclusions

Once debated and heavily questioned (to its existence) phase, $Ca_{12}AI_{14}O_{33}$ ($C_{12}A_{7}$), of the CaO-Al₂O₃ binary system has been synthesized, for the first time, by a patented self-propagating combustion synthesis technique, and a significant reduction in its synthesis temperature has been achieved with respect to conventional routes of solid-state reactive



Figure 3. Unit cell contents (Space group: 1-4



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Figure 3. Unit cell contents of the $Ca_{12}Al_{14}O_{33}$ phase projected onto the xy plane (Space group: I-43d, No:220).

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 find increasing use in the field of alkali-free, synthetic chemical additives in "cement" compositions.

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