Low temperature synthesis of 12CaO·7Al2O3 from calcium sulfite waste

Takahiro TAKEI,*† Maho NAKAMURA, Akira MIURA, Nobuhiro KUMADA and Kiyohiko OGIHARA*†

Center for Crystal Science and Technology, University of Yamanashi, 7–32 Miyamae, Kofu 400–8511, Japan
*Ogihara INC., Ltd, 1861–2 Enzankamiozo, Koshu, Yamanashi 404–0012, Japan

One of the calcium aluminates, 12CaO·7Al2O3, was synthesized from calcium sulfite hemihydrate waste which was produced as a by-product of calcium polysulfide. The calcium sulfite waste was at first pre-treated by sodium salts, Na2CO3 and Na2C2O4. Then, the waste was converted to the CaCO3 and CaC2O4 respectively. From these pre-treated sample, 12CaO·7Al2O3 phase was formed at 850°C for the converted CaCO3 from Na2CO3 and at 650°C for the converted CaC2O4 from Na2C2O4. These crystallization temperatures are much lower than from reagent CaCO3 and CaC2O4 at 1250 and 850°C, respectively. The reason of such reduction of crystallized temperature may result from impurity Fe2O3 including in the by-product. Actually, addition of Fe2O3 into the reagent CaCO3 posed decrease of crystallization temperature of 12CaO·7Al2O3 from 1250 to 1050°C.

1. Introduction

Sulfite salts can be used for the additive of food as an antioxidant because SO3²⁻ anion tends to oxidize itself to protect oxidation of food.1)2) One of the sulfite salts, calcium sulfite hemihydrate (CaSO3·0.5H2O) forms as a by-product of lime sulfur (CaS), which is useful as a pesticide. In the case of this sample, the by-product, calcium sulfite, cannot use for the food additives. Especially relatively large amount of the by-product assumed to be generated with around several tens ton/year in Japan.

The calcium sulfite has a low solubility in water, on which is around 4.3 mg per 100 g of water. On the other hand, the solubility of gypsum (CaSO4·2H2O) is around 240 mg/100 g from such difference between these solubilities, reactivity of the calcium sulfite may be lower than that of gypsum and is assumed to be relatively stable in the environment in which human can live. Under this environment, the calcium sulfite oxidizes itself very slowly in atmosphere. Such slow oxidation, however, tends to remove oxygen from the ground to prevent plant growth. Thus, the calcium sulfite waste might not be left on the ground, if possible.

In CaO–Al2O3 system, some sorts of oxides with different composition can be formed such as 3CaO·Al2O3 (C3A), 12CaO·7Al2O3 (C12A7), CaO·Al2O3 (CA), CaO·2Al2O3 (CA2) and CaO·6Al2O3 (CA6). Most of the calcium aluminates can be used for luminescent materials with rare earth elements.3) 7) In the addition, the C12A7 phase shows unique property. The C12A7 includes O²⁻ anion clathrated within the cage in the crystal structure. This O²⁻ anion can work as oxidant. When O³⁻ anion was exchanged by e⁻, the crystal shows electronic conductivity, designated as electride.8) 9) However, these compounds in calcium aluminate system can be prepared at relatively high temperature. For example, C12A7 is prepared at 1100°C or higher temperature from the reagent, at 900°C from gel for bulk or powder state, and 700°C for thin film state.9) 10) Such heat treatment at relatively high temperature spends a large amount of energy. Therefore, reduction of the synthesis temperature should be reduced for decrease of energy consumption. In this paper, low-temperature syntheses of the calcium aluminate phase are examined from calcium sulfite waste as a green energy synthesis process.

2. Experimental

2.1 Preparation of C12A7

The typical process of the preparation of C12A7 is explained as follows. The calcium source explained in the next section was intimately mixed with γ-Al2O3 by wet mixing and then heated at the range from 550 to 1250°C in the O2 flow. The crystal phases in the heated compounds are identified by XRD with monochromated Cu Kα radiation. (RINT-2000, RIGAKU) The chemical composition of the samples was measured by ICP elementary analysis. (SPS-1700, SII) The particle shapes of samples were observed by FE-SEM. (JSM-6500F, JEOL) The vibrational state of some groups in the samples were examined by FTIR with ATR attachment. (FT/IR-4100, Jasco).

2.2 Calcium sources

The ‘calcium sulfite waste’ was designated as WCS hereafter in this paper. The WCS with and without pre-treatment was used for the preparation. CH3COONa, Na2CO3 and Na2C2O4 were used for the pre-treatment of WCS as follows. The WCS was put into an aqueous solution including stoichiometric these sodium salts. The solution was stirred at RT for 24 h, and then the sample was separated from the solution by filtration and dried at 50°C. The resultant powders were used for starting material of the preparation of C12A7. The powders were designated as AW, CW and OW for the pre-treated wastes with CH3COONa, Na2CO3 and Na2C2O4, respectively. In addition, reagents CaCO3 and CaC2O4 were used as Ca sources, which were designated as CR and OR, respectively.

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3. Results and discussion

3.1 Characterization of the calcium sulfit waste and its pre-treated waste

Calcium sulfit waste was examined for its chemical composition by the ICP measurement. As the result, Fe$_2$O$_3$ was detected at the fraction of 0.2 mass%. From these results, the calcium sulfit waste is found to include a small amount of Fe$_2$O$_3$ as an impurity. Generally, CaS was prepared from CaO, H$_2$O and S by heating at around 150°C. The calcium source CaO was produced by burning lime hydrate which includes small amount of iron in mineral. In addition, the heating process at 150°C was carried out in large metal vessel which may include Fe. The Fe$_2$O$_3$ impurity from CaO and reaction vessel possibly moves into the waste. Thus, Fe$_2$O$_3$ probably derives from calcium source in the waste.

**Figure 1** shows XRD patterns of the mixture of WSC and γ-Al$_2$O$_3$ heated at 850 and 1250°C for 6 h under O$_2$ flow. The WSC was changed to CaSO$_4$ by heating at 850°C. At 1250°C, around half of the sample seems to be converted to calcium aluminate oxysulfate, Ca$_3$Al$_2$O$_5$SO$_4$. The result show that the sulfur oxide anion still remains in the heated samples even by heat treatment at 1250°C under O$_2$ flow. From these patterns, the conversion from the calcium salt including sulfur to calcium aluminate cannot occur below or at 1250°C. Therefore, the WSC was pre-treated chemically by some sodium salts to change crystal phase.

**Figure 2** shows the XRD patterns of the mixture of WCS and γ-Al$_2$O$_3$ heated at 850 and 1250°C for 6 h under O$_2$ flow. The WCS was changed to CaSO$_4$ by heating at 850°C. At 1250°C, around half of the sample seems to be converted to calcium aluminate oxysulfate, Ca$_3$Al$_2$O$_5$SO$_4$. The result show that the sulfur oxide anion still remains in the heated samples even by heat treatment at 1250°C under O$_2$ flow. From these patterns, the conversion from the calcium salt including sulfur to calcium aluminate cannot occur below or at 1250°C. Therefore, the WSC was pre-treated chemically by some sodium salts to change crystal phase.

3.2 Formation of C12A7

**Figure 3** shows the XRD patterns of the mixed CW or CR sample with stoichiometric γ-Al$_2$O$_3$ heated at 550–1250°C. These patterns confirm that C12A7 phase crystallized at 850°C or higher for CW with γ-Al$_2$O$_3$. On the other hand, C12A7 crystallize at 1250°C from the mixed powder of CR and γ-Al$_2$O$_3$. The difference between crystallization temperatures is around 400°C. In these patterns of heated samples at lower the temperature, γ-Al$_2$O$_3$ cannot recognize due to their broad peaks.

**Figure 4** shows the XRD patterns of the mixed OW or OR with γ-Al$_2$O$_3$ heated at 550–1250°C. From these patterns, Ca$_3$Al$_2$O$_5$SO$_4$ phase completely decomposed to form CaSO$_4$ at 550°C in both samples. The crystallization of C12A7 begins at 650 and 850°C, respectively. For the mixed oxalate salt with γ-Al$_2$O$_3$, the crystallization temperature of C12A7 reduces drastically compared to that of carbonates. However, for OW samples, significant amounts of Ca$_3$Al$_2$O$_5$SO$_4$ seem to form at higher than 950°C. These phases imply residual sulfur in the treated samples with Na$_2$C$_2$O$_4$.

**Figure 5** shows the thermal tendency of mass ratios of consisting crystalline phases in these samples. These amounts are calculated from structural factor [F], multiplicity, density, cell volume, Lorentz–polarization factor and the intensity of a diffraction line of each phases existing in the samples, as follows; 131 (2θ ≈ 23.6°) in Ca$_4$Al$_2$O$_7$SO$_4$, 800 (2θ ≈ 47.6°) in 3CaO·Al$_2$O$_3$·(C3A), 211 (2θ ≈ 18.1°) in 12CaO·7Al$_2$O$_3$·(C12A7), 111 (2θ ≈ 32.0°) in CaO and 104 (2θ ≈ 29.4°) in CaSO$_4$. From these plots, for the sample from reagents (CR and OR), CaO phase emerges by decomposition of calcium sources, CaCO$_3$ and CaC$_2$O$_4$. At 850°C, C3A was crystallized. C12A7 phase was crystallized simultaneously to C3A for OR samples, and at higher the temperature at 1250°C for CR. Finally, C12A7 was occupied more than 70 mass % of the samples, and the coexisted phase C3A less than 30 mass %. On the other hand, for the sample from the waste (CW and OW), CaO phase is not observed in these patterns. C12A7 phases formed directly at 850°C for CW and at 650°C for OW. The C12A7 crystallizations seem to occur by decomposition of CaCO$_3$. At further higher the temperature, the amount of
Ca$_4$Al$_6$O$_{12}$SO$_4$ increased, implying incomplete removal of sulfur from the waste. At the crystallization temperature of C$_{12}$A$_7$ phase, S$^{2-}$ anion may clathrate in the cage of the C$_{12}$A$_7$ structure in cases of the CW and OW samples.

Figure 6 shows the FTIR spectra of the heated sample mixtures of pre-treated waste by Na$_2$CO$_3$ and Na$_2$C$_2$O$_4$ with γ-Al$_2$O$_3$ at 850 and 1250°C.

Ca$_4$Al$_6$O$_{12}$SO$_4$ increased, implying incomplete removal of sulfur from the waste. At the crystallization temperature of C$_{12}$A$_7$ phase, S$^{2-}$ anion may clathrate in the cage of the C$_{12}$A$_7$ structure in cases of the CW and OW samples. Figure 6 shows the FTIR spectra of the CW and OW with γ-Al$_2$O$_3$ samples heated at 850 and 1250°C. In these spectra, we can confirm the absorption bands of the SO$_4^{2-}$ at 644 and 1100 cm$^{-1}$ especially in the spectra of the OW at 1250°C. On the other hand, at least in the spectra of
CW and OW at 850°C, there are no absorptions related to the SO$_4^{2−}$. The emergence of the bands in the spectrum of OW at 1250°C sample which includes the largest amount of Ca$_6$Al$_6$O$_{12}$SO$_4$ can be regarded as collateral evidence of the clathrated S$^{2−}$. As the results, the clathrated S$^{2−}$ exists in the cage of the sample heated at 850°C, and changes to SO$_4^{2−}$ at 1250°C. In addition, quantitative analysis of these samples was examined by EDX. The quantitative analysis confirms that the ratio S/Al of around 0.65/14.0. From these results, the amount of occupation of the clathrated S$^{2−}$ ion can be estimated to around two thirds using theoretical formula of Ca$_{12}$Al$_{14}$O$_{32}$S. Heating at the higher temperature such as 1250°C possibly poses decomposition of S$^{2−}$ clathrated C$_{12}$A$_7$ to generate pure C$_{12}$A$_7$ and Ca$_6$Al$_6$O$_{12}$SO$_4$.

Such clathrated structure with S$^{2−}$ anion might decrease some functionality of the C$_{12}$A$_7$. Therefore, the sulfur should be diminished from the samples in the future work. Generally, one of the most important function of the C$_{12}$A$_7$ may be electride. C$_{12}$A$_7$ electride was synthesized by substitution of clathrated O$^{2−}$ by other ions or electron. Therefore, the clathrated S$^{2−}$ ion may not be disadvantage for the functionality of the C$_{12}$A$_7$.

Figure 7 shows the FE-SEM micrographs of the four heated samples at 650, 850, 1050 and 1250°C. From these micrographs, we can see the thermal change of the texture of the samples. For CR samples, very small particles can be observed below or at 1050°C, and these particles seem to be diminished at 1250°C. For CW samples, the small particles preserved at 650°C and the particles cannot be observed at 850°C or higher. For OR samples, the small particles can be confirmed at 650°C and then coalescence seems to be occurs at 850°C or higher. The small particles observed in these samples are plausibly identified to γ-Al$_2$O$_3$ because generally γ-Al$_2$O$_3$ composed of very small particles. For OW samples, the small particles cannot observed at even 650°C.

### 3.3 Effect of Fe$_2$O$_3$ addition

From ICP measurement, sodium cannot be detected in these samples. On the other hand, the starting material, calcium sulfite waste includes very small amount of Fe$_2$O$_3$ (≤0.2 mass%), though diffraction peak of hematite phase cannot be observed. This impurity implies hematite phase may affect to the crystallization of C$_{12}$A$_7$. To confirm effect of the impurity, the hematite of 1.0% was added to the CR sample and heated at 1050°C for 6h. Figure 8 shows the XRD patterns of the heated CR samples at 1050°C with and without hematite addition of 1%. In the XRD patterns of heated CR with hematite addition, we can observe the diffraction pattern of coexisting C$_{12}$A$_7$ and C$_3$A phases. These XRD patterns confirm that the addition of hematite surely affects the crystallization temperature of the C$_{12}$A$_7$. The reason of such crystallization seems to be a kind of catalytic behavior. Sometimes transition metal or metal oxide has an active surface due to some reasons as follows. Electron transition occurred in outer orbital, relatively small electronegativity, and relatively large surface energy. The relatively small electronegativity poses that surface OH groups can be easily dissociate to release proton. Thus, especially transition metal oxide may work as a solid acidity site. Relatively large surface energy can advance the crystallization by inhomogeneous nucleation reaction by minimize effect of surface energy. For example, crystallization on catalyst surface including catalyst particles as a core decrease total surface energy. For crystallization of inorganic compounds, transition state of catalyst or large surface energy might be influenced.
4. Conclusions

Calcium sulfito was used for synthesis of C12A7 via pre-treatment for the calcium sulfito in Na2CO3, CH3COONa or Na2C2O4 aqueous solution. The treated calcium sulfito was mixed with γ-Al2O3 and then heated at 550–1250°C under O2 flow to synthesize C12A7 phase. Following results can be obtained.

1. The calcium sulfito hemihydrate can be converted by Na2CO3 and Na2C2O4 to CaCO3 and CaC2O4, respectively.
2. The C12A7 can be formed at 850°C from the converted CaCO3, at 650°C from the converted CaC2O4 from the waste. These formation temperatures are very lower than the temperatures from CaCO3 and CaC2O4 reagent, which are around 1250 and 850°C, respectively.
3. Especially for the converted CaC2O4, considerable amount of Ca4Al6O12SO4 forms at temperature higher than 950°C.
4. The reduction of the formation temperature may result from catalytic effect of the Fe2O3 impurity.

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