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Identification of Calcium Sulphoaluminate Formation between Alunite and Limestone

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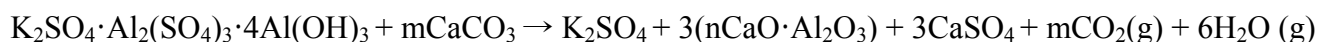
Abstract: This study was carried out to identify the conditions of formation of calcium sulphoaluminate ($3CaO \cdot 3Al_2O_3 \cdot CaSO_4$) by the sintering of a limestone ($CaCO_3$) and alunite [$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3$] mixture with the following reagents: K_2SO_4, $CaCO_3$, $Al(OH)_3$, $CaSO_4 \cdot 2H_2O$, and SiO_2. When K_2SO_4, $CaCO_3$, $Al(OH)_3$, $CaSO_4 \cdot 2H_2O$ were mixed in molar ratios of 1:3:6:3 and sintered at 1,200~1,300 °C, only $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ and calcium langbeinite ($2CaSO_4 \cdot K_2SO_4$) were generated. With an amount of CaO that is less than the stoichiometric molar ratio, $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ was formed and anhydrite ($CaSO_4$) did not react and remained behind. With the amount of $CaSO_4$ that is less than the stoichiometric molar ratio, the amounts of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ and $2CaSO_4 \cdot K_2SO_4$ decreased, and that of $CaO \cdot Al_2O_3$ increased. In the K_2SO_4-CaO-Al_2O_3-$CaSO_4$-SiO_2 system, to stabilize the formation of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$, $2CaSO_4 \cdot K_2SO_4$, and β-$2CaO \cdot SiO_2$, the molar ratios of CaO: Al_2O_3: $CaSO_4$ must be kept at 3:3:1 and that of CaO/SiO_2, over 2.0; otherwise, the generated amount of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ decreased and that of gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$) with no hydration increased quantitatively. Therefore, if all $SO_3(g)$ generated by the thermal decomposition of alunite reacts with $CaCO_3$ (or CaO, the thermal decomposition product of limestone) to form $CaSO_4$ in an alunite-limestone system, 1 mol of pure alunite reacts with 6 mol of limestone to form 1 mol of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ and 1 mol of $2CaSO_4 \cdot K_2SO_4$.

1. Introduction

Cement has been prepared using alunite [1], and a type of special cement containing calcium aluminate, anhydrite, and potassium sulfate has been prepared using anhydrite formed by the reaction between $SO_3(g)$ that evolves from alunite and limestone via the following reaction:

$$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3 + mCaCO_3 \rightarrow K_2SO_4 + 3(nCaO \cdot Al_2O_3) + 3CaSO_4 + mCO_2(g) + 6H_2O~(g)$$

Choi *et al.* [2] synthesized a calcium sulphoaluminate clinker consisting of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$, CaO and $CaSO_4$ through the sintering for 2 hrs at a temperature of 1,200 °C of alunite, limestone and an anhydrite mixture at a weight ratio of 1:13:5. Their research results showed that alunite could be used in the preparation of a $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ clinker provided that adequate mixing conditions are provided, despite that the expansion is relatively small compared to that of a clinker synthesized from reagents. However, the exact formation conditions of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ in the sintering state were not discussed. In addition, Han *et al.* [3,4] synthesized a clinker containing calcium fluoroaluminate ($C_{11}A_7 \cdot CaF_2$) from domestic alunite and investigated its characteristics in an effort to develop a type of fast-hardening cement.

The authors [5] carried out an investigation of the conditions under which $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ is formed when mixtures of alunite and limestone are sintered. It was concluded that calcium langbeinite ($2CaSO_4 \cdot K_2SO_4$) forms from 700 °C and that calcium sulphoaluminate forms from 800 °C. Both are stable up to 1,300 °C, as shown in the equation below:

$$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3 + 6CaCO_3 \rightarrow 4CaO \cdot 3Al_2O_3 \cdot SO_3 + 2CaSO_4 \cdot K_2SO_4 + 6H_2O(g) + 6CO_2(g)$$

However, when alunite or limestone is incorporated in SiO_2 so as to enable the formation of calcium sulphoaluminate, the molar ratios of CaO/alunite and CaO/SiO_2 must be kept over 6.0 and 2.0, respectively. A clinker composed of calcium sulphoaluminate and calcium langbeinite was transformed into ettringite($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) in water as calcium langbeinite is transformed into $CaSO_4 \cdot 2H_2O(s)$ and K_2SO_4 (aq) in water.

In the present study, the formation of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ is identified in a K_2SO_4-CaO-Al_2O_3-$CaSO_4$-SiO_2 system using reagents of various types in a detailed investigation of the formation conditions of this species through the sintering of a mixture of alunite and limestone.

2. Experimental

The reagents listed in Table 1 were used to investigate the reaction products arising from the K_2SO_4-CaO-Al_2O_3-$CaSO_4$-SiO_2 system. K_2SO_4 and $Al(OH)_3$ were used in substitution for the components of alunite; calcium carbonate ($CaCO_3$) substituted for limestone, and $CaSO_4 \cdot 2H_2O$, substituted for anhydrite ($CaSO_4$), which is formed by the sintering reaction between alunite and limestone.

The mixture of reagents were sintered in a programmable electric furnace (Barnstead /Thermolyne F46120 CM High-Temperature Furnace : 240 V, 40 A, 2,500 Watt, 50/60 Hz, 1 Phase) below 1,300 °C in an air atmosphere. The mineral phases of the manufactured clinker were then analyzed by XRD(PW-1700, Philips, 30kV, 25mA, Cu target, Ni filter, at a scanning rate of 2°/min). After the prepared clinker was finely milled with a laboratory ball mill, the mineral phases of the crushed clinker were analyzed by XRD.

Table 1. List of reagents used in this study.

Reagents	Chemical formula	Purity	Manufacturer
Potassium Sulfate	K_2SO_4	First grade	Ducksan Pharmaceutical Co., Ltd
Aluminum Hydroxide	$Al(OH)_3$	First grade	Shinyo Pure Chemical Co., Ltd
Calcium Carbonate	$CaCO_3$	min 98.0%	Kanto Chemical Co., Inc.
Gypsum	$CaSO_4 \cdot 2H_2O$	Extra pure	Junsei Chemical Co., Ltd.
Silicate Dioxide	SiO_2	Extra pure	Junsei Chemical Co., Ltd.

3. Results and Discussion

Alunite ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)$) is transformed into $KAl(SO_4)_2$ and Al_2O_3 by dehydration at 500～580 °C and $KAl(SO_4)_2$, K_2SO_4 and Al_2O_3 by desulphurization at 700～780 °C via the reaction of $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3 \rightarrow K_2SO_4 + 2Al_2O_3 + 3SO_3(g) + 6H_2O(g)$, regardless of the partial pressure of $CO_2(g)$. However, limestone decomposes from 650 °C in air and from 900 °C in a $CO_2(g)$ saturated atmosphere [6].

When the mixture of alunite and limestone is sintered in air and in a $CO_2(g)$ saturated atmosphere, the rate of formation of anhydrite is relatively low, at 76.0% and 67.0%, respectively, at a $CaCO_3$/alunite stoichiometric molar ratio of 3. However, the rate of formation increases as the molar ratio of $CaCO_3$/alunite (particle size, 37～44 μm) exceeds 6, showing rates of more than 99.0% and 95.0% in air and in a $CO_2(g)$ saturated atmosphere, respectively [7].

As shown in the results of aforementioned experiment, if alunite and limestone are mixed and sintered in air, most of the generated SO_3 reacts with limestone to form anhydrite ($CaSO_4$). Additionally, ignoring impurities such as Fe_2O_3, TiO_2, and P_2O_5 included in the alunite, because alunite ore is composed of alunite, quartz(SiO_2), and the aluminum silicate minerals of kaolinite, dickite, and pyrophyllite, the alunite and limestone mixture can be said to have five components, as does K_2SO_4-CaO-Al_2O_3-$CaSO_4$-SiO_2.

If 1 mol if pure alunite is heated to temperatures that exceed 800 °C, it is pyrolyzed as $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3 \rightarrow K_2SO_4 + 3Al_2O_3 + 3SO_3 + 6H_2O$. Therefore, to formulate $SO_3(g)$ of 3 mol into anhydrite, 3 mol of $CaCO_3$ is required, and to change 3 mol of Al_2O_3 into $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$, 3 additional mol of $CaCO_3$ and 1 mol of $CaSO_4$ will be needed. Therefore, to change all of the Al_2O_3 in alunite into $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$, and to generate $SO_3(g)$ by the thermal decomposition of alunite into anhydrite, theoretically, pure alunite and limestone should be mixed at a molar rate of 1:6. This mixture will be composed of five component systems as in K_2SO_4-CaO-Al_2O_3-$CaSO_4$.

The present study aims to determine the mineral phases of a clinker generated in the K_2SO_4-CaO-Al_2O_3-CaSO$_4$ and the K_2SO_4-CaO-Al_2O_3-CaSO$_4$-SiO$_2$ systems, using several types of reagents, including K_2SO_4, $Al(OH)_3$, SiO_2, $CaSO_4 \cdot 2H_2O$, and $CaCO_3$.

Figure 1 shows X-ray diffraction patterns of the materials generated, when a compound consisting of K_2SO_4-3CaO-3Al_2O_3-3CaSO$_4$ was sintered at 1,100 °C, 1,200 °C, and 1,300 °C, respectively, for 2 hours. As shown in this figure, $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ and $2CaSO_4 \cdot K_2SO_4$ is formed, but $CaSO_4$ does not react and remains at 1,100 °C. Meanwhile, at temperatures in excess of 1,200 °C $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ and $2CaSO_4 \cdot K_2SO_4$ were mainly generated. Accordingly, 1 mol of pure alunite reacts with 6 mol of limestone to form 1 mol of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ and 1 mol of $2CaSO_4 \cdot K_2SO_4$ as follows;
$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 4Al(OH)_3 + 6CaCO_3 \rightarrow 2CaSO_4 \cdot K_2SO_4 + 3CaO \cdot 3Al_2O_3 \cdot CaSO_4 + 6H_2O(g) + 6CO_2(g)$.

Figure 1. X-ray diffraction patterns of sintered products of mixtures of K_2SO_4-3CaO-3Al_2O_3-3CaSO$_4$ at various temperatures in air.

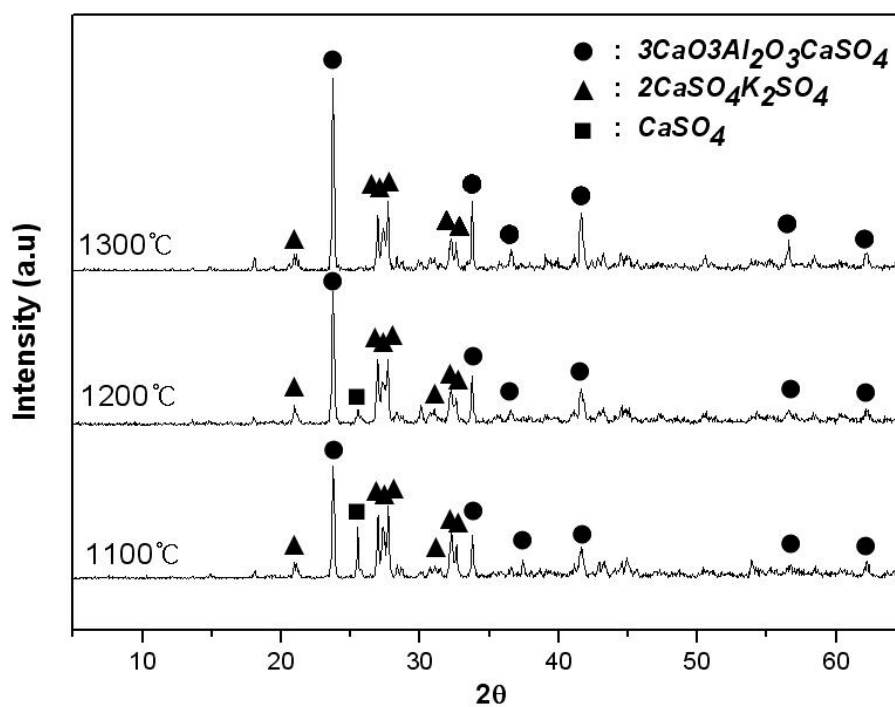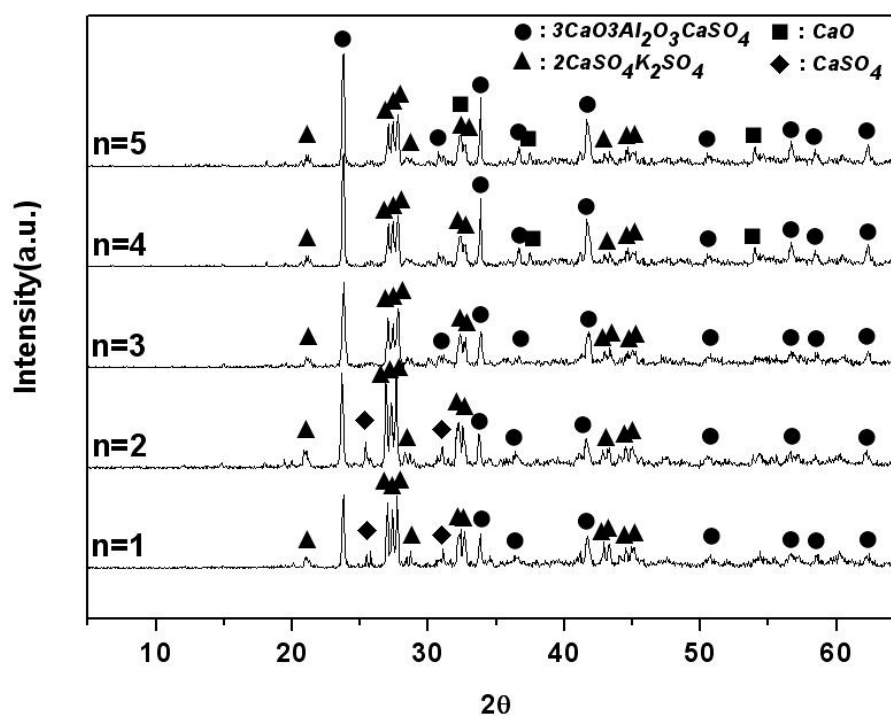Figure 2 displays the materials generated from K_2SO_4-nCaO-3Al_2O_3-3CaSO$_4$ with various amounts of CaO sintered at 1,200 °C for two hours, as determined via an XRD analysis.

Figure 2. X-ray diffraction patterns of sintered products of mixtures of K_2SO_4-nCaO-3Al_2O_3-3CaSO$_4$ with various amounts of CaO in air (sintering temp.: 1,200 °C, sintering time: 2 hrs).
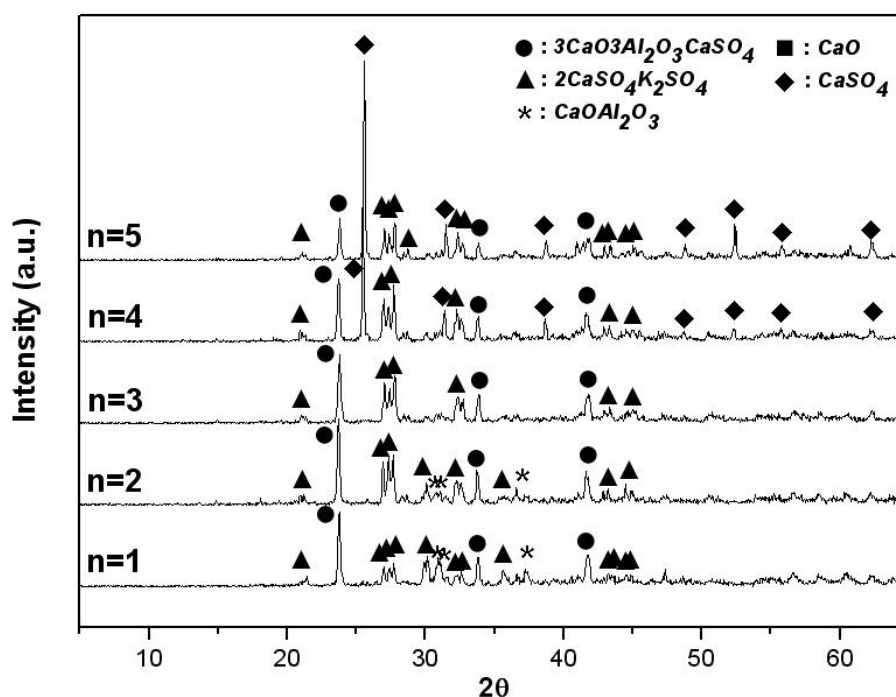

When it CaO is included in at an amount of 3 mol, 3CaO·3Al_2O_3·CaSO$_4$ and 2CaSO$_4$· K_2SO_4 are mainly generated. However, it was found that as the amount of CaO is increased from 3 mol to 5 mol, CaO does not participate in the formation reaction of 3CaO·3Al_2O_3·CaSO$_4$. Thus, it can be said that 3CaO·3Al_2O_3·CaSO$_4$ and 2CaSO$_4$· K_2SO_4 are generated stably when CaO is 3 mol in the K_2SO_4-nCaO-3Al_2O_3-3CaSO$_4$ system.

According to Fukuda [8] 3CaO·3Al_2O_3·CaSO$_4$ is the only compound in the CaO-Al_2O_3-SO$_3$ system. This line of research was started in 1962 by Halstead, *et al.* [9] with Ca^{2+} and SO_4^{2-} ions in a three-dimensional crystal structure sharing the angular point of a AlO$_4$ tetrahedron; an Al^{3+} ion is coordinated with four O^{2-} ions, a Ca^{2+} ion is surrounded asymmetrically by O^{2-} ions, and an isolated SO_4^{2-} ion is characterized by its ability to readily react with water. Kondo [10] discovered that these ions become hardened in water. In general, they are produced by re-sintering after producing 3CaO·Al_2O_3 and regulating the mixture ratio of 3CaO·Al_2O_3, CaSO$_4$·2H_2O and Ca(OH)$_2$ and by sintering a mixture of CaCO$_3$, Al_2O_3, and CaSO$_4$· 2H_2O.

2CaSO$_4$· K_2SO_4 is easily generated in the CaO-Al_2O_3-SiO$_2$-Fe$_2O_3$-MgO-CaSO$_4$-K_2SO_4 system and has a considerable influence on the condensation time and the hardening characteristics of cements. Known as a water-soluble alkali, as 2CaSO$_4$· K_2SO_4 can be easily separated from the liquid state of a clinker oxide and is said to become K_2SO_4·CaSO$_4$·H_2O(syngenite) and CaSO$_4$·2H_2O upon exposure to water [11].

Figure 3 shows the materials generated from the K_2SO_4-3CaO-3Al_2O_3-nCaSO$_4$ system sintered at 1,200 °C for two hours with varying amounts of anhydrite, as determined via an XRD analysis.

Figure 3. X-ray diffraction patterns of sintered products of mixtures of K_2SO_4-$3CaO$-$3Al_2O_3$-$nCaSO_4$ with various amounts of $CaSO_4$ in air (sintering temp.: 1,200 °C, sintering time: 2 hrs).


As shown in this figure, when anhydrite is included in an amount of 3 mol, $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ and $2CaSO_4 \cdot K_2SO_4$ are generated. However, as the amount of anhydrite is decreased from 3 mol to 1 mol, it was observed that the K_2SO_4 that did not react with $CaO \cdot Al_2O_3$ remained. As the amount of anhydrite is increased from 3 mol to 5 mol, only the diffraction strength of the $CaSO_4$ that does not react increases. Thus, it can be said that an amount of $CaSO_4$ in excess of the stoichiometric molar ratio is necessary to generate $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ stably.

As noted above, $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ and $2CaSO_4 \cdot K_2SO_4$ were mainly generated in the K_2SO_4-$3CaO$-$3Al_2O_3$-$3CaSO_4$ system. However, because alunite from nature has impurities of SiO_2 and aluminum silicate minerals such as kaolinite, dickite, and pyrophyllite, the alunite and limestone mixture is believed to be comprised of a K_2SO_4-CaO-Al_2O_3-$CaSO_4$-SiO_2 system to which SiO_2 is added.

Figures 4 and 5 show, by XRD analysis, the materials generated from the K_2SO_4-$3CaO$-$3Al_2O_3$-$3CaSO_4$-$nSiO_2$ system and the K_2SO_4-$(3+m)CaO$-$3Al_2O_3$-$3CaSO_4$-$nSiO_2$ system, respectively, sintered at 1,200 °C for 2 hours, with various amounts of CaO (3 + m : mol number) and SiO_2(n: mol number). In Figure 4, when there is no SiO_2 in the mixture, the result is identical to that obtained when 3 mol of CaO is used (Figure 2). It is expected that $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ and $2CaSO_4 \cdot K_2SO_4$ will be generated. However, as the amount of SiO_2 is increased from 1 mol to 5 mol, the amount of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ generated is reduced, because gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$) and wollastonite ($\alpha$-$CaO \cdot SiO_2$), which do not react with water, are generated. In addition, as shown in Figure 5, when the mol rate of CaO/alunite is less than 6 (m less than 3), and that of CaO/SiO_2 is less than 2, the synthetic clinker contained $2CaO \cdot Al_2O_3 \cdot SiO_2$ and $CaSO_4$; these compounds do not participate in the formation reaction of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ because $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ is the only compound in the CaO-Al_2O_3-SO_3 system as noted above[8] and CaO and Al_2O_3 participate

preferentially in the formation reaction of $2CaO \cdot Al_2O_3 \cdot SiO_2$. Accordingly, if all $SO_3(g)$ generated by thermal decomposition of alunite reacts with $CaCO_3$ (or CaO, the thermal decomposition product of limestone) to form $CaSO_4$ in the alunite-limestone system, when the molar ratios of CaO/alunite exceed 6 and that of CaO/SiO_2 exceeds 2, $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$, $2CaSO_4 \cdot K_2SO_4$ and β-$2CaO \cdot SiO_2$ are generated stably.

Figure 4. X-ray diffraction patterns of sintered products of mixtures of K_2SO_4-3CaO-3Al_2O_3-3CaSO_4-nSiO_2$ with various amounts of SiO_2 in air (sintering temp.: 1,200 °C, sintering time: 2 hrs).
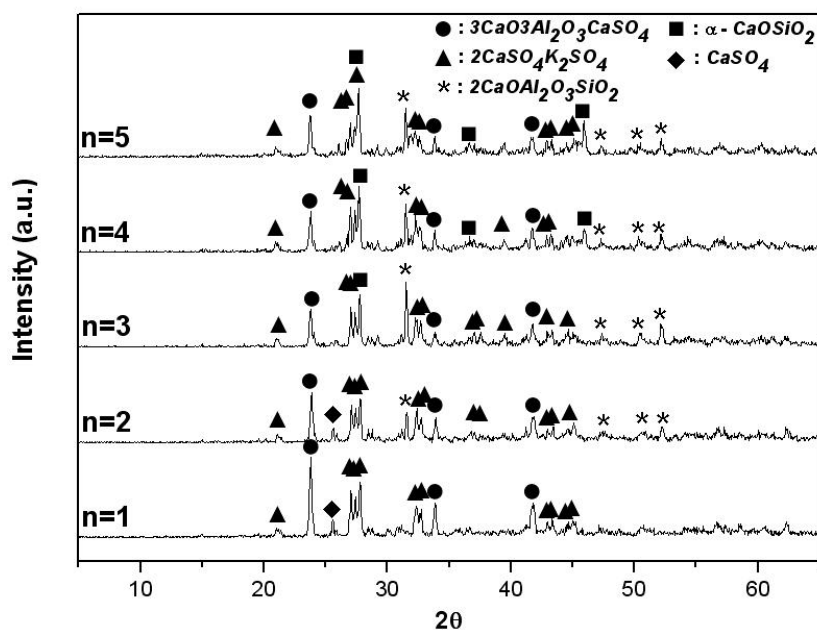
Figure 5. X-ray diffraction patterns of sintered products of mixtures of K_2SO_4 -[(3+m)CaO]-3Al_2O_3-3CaSO_4-nSiO_2$ with various amounts of CaO and SiO_2 in air (sintering temp.: 1,200 °C, sintering time: 2 hrs).
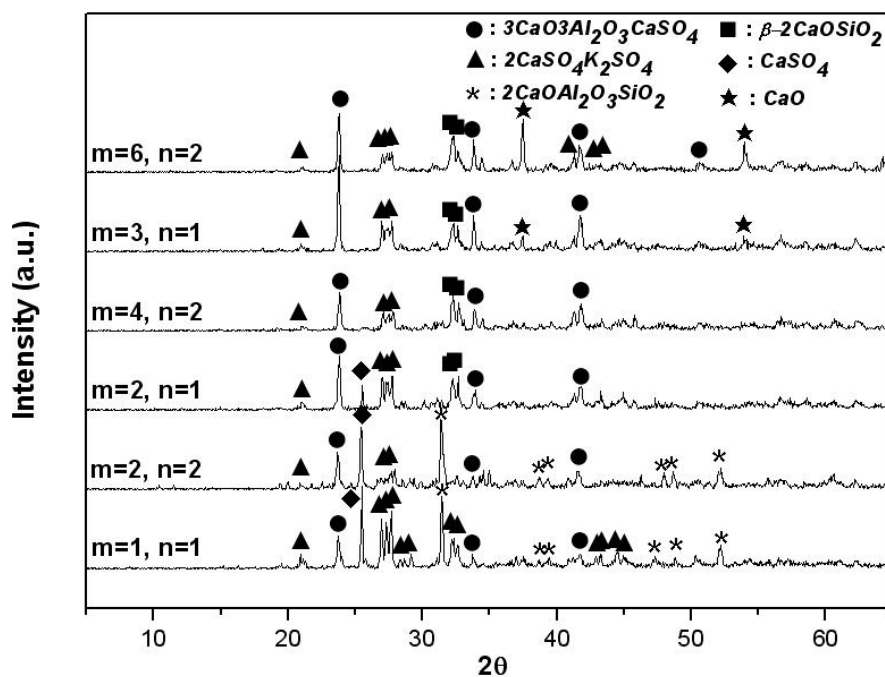
4. Conclusions

This study investigated the formation characteristics of calcium sulphoaluminate ($4CaO \cdot 3Al_2O_3 \cdot SO_3$) in a K_2SO_4-CaO-Al_2O_3-$CaSO_4$-SiO_2 system using reagents of various types in an effort to identify the formation conditions of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ by the sintering of a mixture of alunite and limestone. In experiments with reagents for the mineral phases generated from the compound system (the K_2SO_4-CaO-Al_2O_3-$CaSO_4$-SiO_2 system), if all $SO_3(g)$ from alunite reacts with limestone to form anhydrite, it was found that 1 mol of pure alunite reacts with 6mol of limestone to form 1 mol of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ and 1 mol of $2CaSO_4 \cdot K_2SO_4$, as of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ and $2CaSO_4 \cdot K_2SO_4$ are generated stably at a component ratio of K_2SO_4-$3CaO$-$3Al_2O_3$-$3CaSO_4$. Over-mixing of CaO and $CaSO_4$ has a slight effect on the generation of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$. However, it is thought that under-mixing will have a substantial effect on the mineral phase of the clinker and on the amount of $3CaO \cdot 3Al_2O_3 \cdot CaSO_4$ that is generated. Moreover, if the impurities of SiO_2 are incorporated in the alunite and limestone, the molar ratio of CaO/alunite must exceed 6 and that of CaO/SiO_2 must exceed 2 in order to ensure the stable formation of calcium sulphoaluminate, calcium langbeinite, and the β-$2CaO \cdot SiO_2$ phases. Otherwise, the amount of gehlenite($2CaO \cdot Al_2O_3 \cdot SiO_2$), which does not react with water, may be increased.

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