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The influence of different CaO source in the production of anorthite ceramics

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Abstract

The effects of starting raw materials and firing conditions on anorthite ($CaAl_2Si_2O_8$) phase formation are investigated by differential thermal analysis (DTA)–thermogravimetry (TG) and X-ray powder diffraction (XRD). Four different sources of CaO were used for anorthite production such as $Ca(OH)_2$, $CaCO_3$, marble powder and gypsum mould waste. The mixture of raw materials was prepared in stoichiometric ratio of anorthite. Sintering of samples was carried out at various temperatures (1000–1300 °C). In all samples before the formation of anorthite phase, formation of layered alimunosilicate phase (LAS) and of gehlenite phase were observed at low temperatures (<1200 °C). All the samples showed similar crystallization behaviour at 1200 °C. The densification characteristic and the flexural strength of samples were affected by the nature of starting raw materials. The maximum density (~80%) was reached in sample ACH which was prepared from $Ca(OH)_2$.

Keywords: C. Thermal properties; C. Mechanical properties; X-ray diffraction; Anorthite

1. Introduction

Anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) is the most important mineral that has formed at earth's surface and it is the lime-rich end-member of the plagioclase feldspar solid solution series. It is very interesting from a technological point of view because crystallization of anorthite in microstructure increases material's strength, chemical stability, and density due to changes of its crystallographic structure during passing from albite to anorthite. In addition to the above-mentioned properties, it receives common uses in ceramics production. For example, it is a good candidate to satisfy the requirements in view of fabrication of ceramic substrates due to its lower thermal expansion ($4.82 \times 10^{-6}\ {}^{\circ}C^{-1}$) and lower dielectric constant (6.2 at 1 MHz) than alumina [1–3]. In order to be an effective substrate material, the anorthite ceramic must have sufficiently low sintering and densification temperatures to allow the co-firing of inexpensive conductive metals such as copper and silver. In addition to sol–gel and glass–ceramics processes, which are very expensive and complicated [2,4], Kobayashi and Kato [5] have reported the production of dense anorthite ceramics by sintering at 1000 °C, using kaolin and finely milled calcite. Mergen and Aslanoglu improved the sinterability of stoichiometric anorthite ceramics by using coarse particles and B_2O_3 as a sintering aid [6].

According to the Al_2O_3–SiO_2–CaO phase diagram pure anorthite melts congruently at 1553 °C. Its theoretical density is 2.76 g/cm^3. These properties make it interesting for producing wall tiles, floor tiles and porcelain.

In most of the investigations concerning the production of anorthite ceramics, kaolin, calcite, and quartz have been selected as raw materials so far. Mineral raw materials have been extensively used for more or less complex ceramics starting compositions since quite a long time in a large range of possible applications. Recent experimental results concerning sintering of anorthite at low temperature have induced great attention in view of a better understanding of the effect of starting materials. All these studies investigated the effect of kaolin and sintering aid (as flux) on anorthite sintering temperature [6].

In the present investigation; the production of anorthite ceramics, was studied with different sources of CaO such as $Ca(OH)_2$, $CaCO_3$, marbel powder and gypsum mould waste. These different CaO sources were selected to investigate the effect of the calcia source.

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2. Experimental

Quartz and Al_2O_3 were used as starting materials. As a source of CaO, different raw materials were used such as $Ca(OH)_2$, calcite ($CaCO_3$), marble powder and gypsum mould waste. Compositions are prepared according to the stoichiometric anorthite composition ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) and will be labelled as ACH, ACC, AMM, AGW, respectively. These powders were wet mixed and milled in deionised water for 4 h using alumina balls in alumina jar. After drying the resulting slurries at 80 °C for 24 h, they were pressed to pellets or bars uniaxially in a steel die.

Typical dimensions of circular pellet-shaped (pressed at 1.96 MPa) samples were 15 mm in diameter and 5 mm in thickness. Typical dimensions of rectangular bar-shaped samples were longer than 50, 6.5 ± 0.1 mm in width, and 6.0 ± 0.1 mm in thickness. Afterwards, the green compacts were sintered in air at temperature in the range 1000–1300 °C for 2 h. The heating rate was 5 °C/min up to 550 °C, 1 °C/min to 960 °C and 2 °C/min to dwell temperatures.

The crystalline phases were identified by using an X-ray diffractometer (Rigaku Co., Tokyo, Japan) from 5° to 60° with scanning speed of 2°/min. Thermal transformations were investigated by using a STA 409 PG-Netzsch model differential thermal analysis (DTA). Samples were heated in air up to 1250 °C at 5 °C/min with alumina reference in order to observe behaviour during heating.

Mechanical properties of the samples have been determined at room temperature. They were tested using an Instron 5581 flexture testing machine in three-point configuration with a support roller span of 40 mm, at a 2 kN load cell with 0.5 mm/min cross-head speed. For every sintering condition, five sintered specimen from each composition were used to carry out the flexural strength test. Using the standard equations for strength (σ) [7] and Young's modulus (E) [8], these values were determined and average taken for each sample.

$$\sigma = \frac{3}{2} \times \left[\frac{P \times L}{W \times D^2}\right] \tag{1}$$

$$E = \frac{L^3 \times m}{4 \times W \times D^3} \tag{2}$$

where P [N] is the load at fracture, L [mm] is the length of support span, W [mm] is the width of the specimen, D [mm] is the thickness of the specimen and m is the slope of the tangent of initial straight-line portion of the load–deflection curve.

The sintered pellets were batched at 150 °C for 24 h, and then the weight of the sintered pellets was measured. In order to get the density, the sintered specimens were immersed in boiled deionized water for 3 h. Then the volume of immersed samples was measured by Archimedes method. After that, the weight of immersed samples was measured again in order to calculate the density.

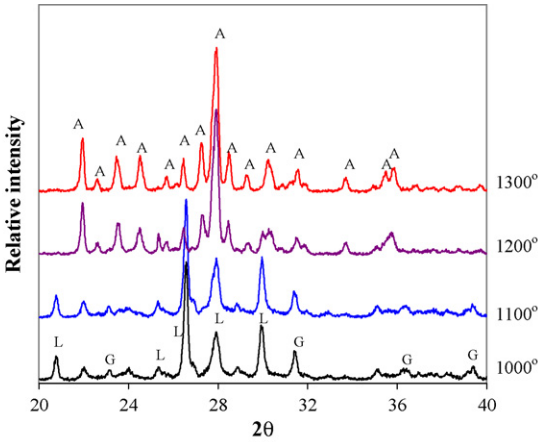


Fig. 1. XRD patterns of AMM samples for after sintering at different temperatures (A: anorthite, L: LAS, G: gehlenite).

3. Results and discussion

3.1. X-ray diffraction analysis of sintered products

The phases formed in the samples fired at various temperatures were determined from the corresponding XRD patterns, some of which are shown in Figs. 1 and 2 and summarized in Table 1. The strong dependence of crystallization on sintering temperature was reflected in the X-ray diffraction patterns. In the samples, gehlenite and layered aluminosilicate (LAS, $CaAl_2Si_2O_8$) phases are the main phases observed at low temperatures (1000–1100 °C). This result is in a good agreement with literature [9]. In the sample of AGW, LAS phase disappeared at 1200 °C by crystallisation of anorthite phase (Fig. 2). Above the 1200 °C anorthite was observed as a main phase. As explained in the study of Okado et al., the amount of LAS phase depends on the firing temperature [9]. Additionally, in our study it was observed that LAS phase formation is not related to the source of CaO. At higher sintering temperatures (>1100 °C) the amount of gehlenite phase decreased or it disappeared related to starting compositions. On the other side, anorthite started to crystallize at 1200 °C by melting of gehlenite and LAS at this temperature.

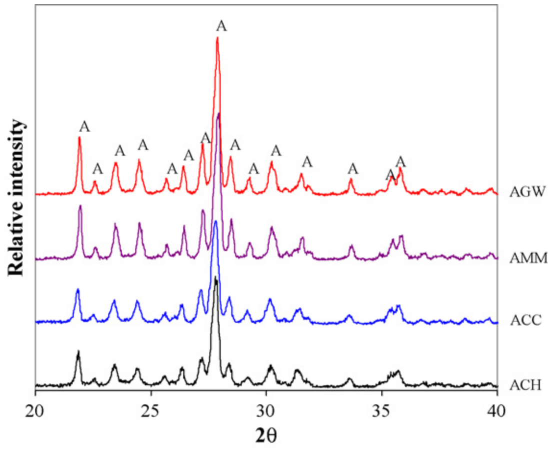


Fig. 2. XRD patterns of all samples sintered at 1300 °C (A: anorthite).

Table 1
Crystalline phases of samples prepared with different CaO sources at different temperatures

Code	Temperatures (°C)	Phase		
		LAS	Anorthite	Gehlenite
ACH	1000	vvs	–	s
	1100	vvs	–	s
	1200	–	vvs	–
	1300	–	vvs	–
ACC	1000	vvs	–	s
	1100	vvs	–	s
	1200	–	vvs	–
	1300	–	vvs	–
AMM	1000	vvs	–	s
	1100	vvs	–	s
	1200	–	vvs	vvw
	1300	–	vvs	vvw
AGW	1000	vvs	–	s
	1100	vvs	–	s
	1200	–	vvs	vvw
	1300	–	vvs	vvw

v: very; s: strong; w: weak, LAS: $CaAl_2Si_2O_8$ (layered aluminosilicate).

3.2. Properties changes upon sintering and crystallisation

The DTA and thermogravimetry (TG) curves of all samples are shown in Fig. 3. Some differences were observed in endothermic and exothermic peaks related to the source of CaO. The DTA–TG curves of all samples supported the crystallisation behaviour of anorthite phase determined by XRD analysis (Table 1).

In the DTA curve of ACH sample three endothermic peaks and one exothermic peak are observed at 300, 450, 700 and 980 °C, respectively (Fig. 3a). These endothermic peaks can be explained with TG-curve. TG-curve of ACH sample shows slightly weight loss at these temperatures. Thus, it is clear that the endothermic peaks result from the dehydration of $Ca(OH)_2$ while the exothermic peak occurred from crystallisation of gehlenite and LAS.

According to the thermal analyses results ACC and AMM samples showed a different behaviour than ACH samples. In these samples one endothermic peak and three exothermic peaks were observed at 790, 950, 980 and 1200 °C, respectively. The TG curve of these two samples clearly shows weight losses at about 790 °C, which correspond to the decomposition of $CaCO_3$. As different from the other two samples (ACH and AGW), pre-anorthite formation started under the form of LAS. The exothermic peak at 950 °C represents the formation of gehlenite. On the other side, crystallisation of $CaAl_2Si_2O_8$ from gehlenite is represented by the exothermic peak at 980 °C. The third exothermic peak indicates the crystallisation of anorthite. In the DTA–TG results of sample AGW, endothermic peaks were observed at 160 °C. This was attributed to the dehydration of gypsum. According to the TG curve, weight loss started at 1000 °C and increased beyond 1170 °C, which is due to the decomposition of $CaSO_4$ into CaO and SO_2. Although in AGW (Fig. 3d) crystallization peak of gehlenite could not be seen slightly, the formation of anorthite at about 1185 °C was clearly observed as indicated in Table 1.

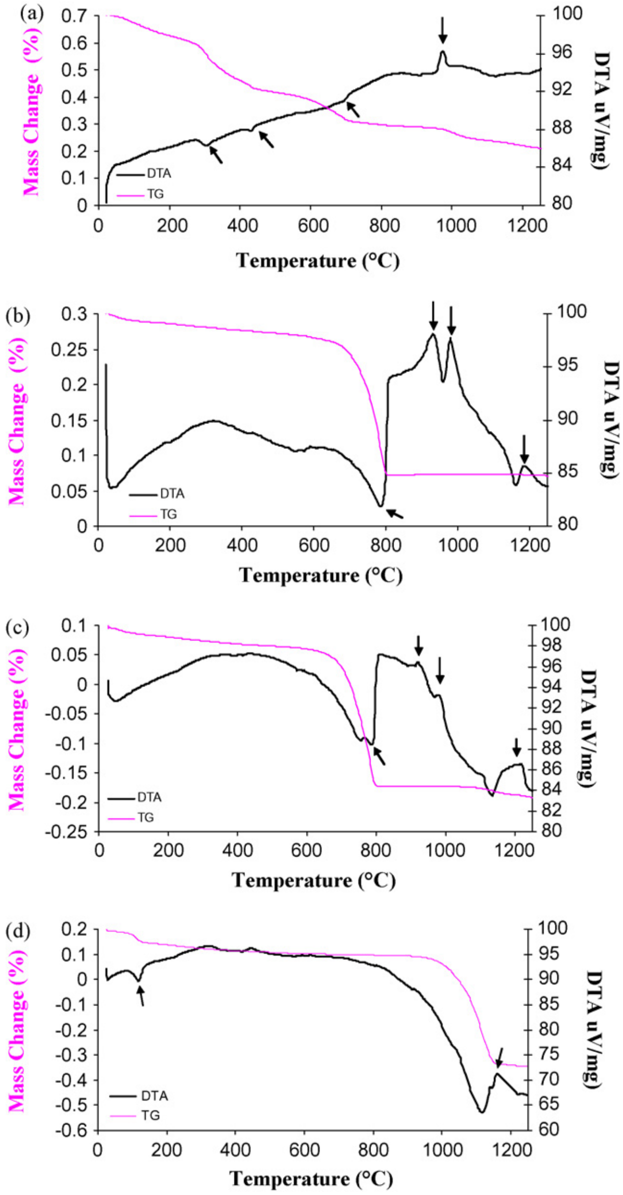


Fig. 3. Thermal analyses of (a) ACH; (b) ACC; (c) AMM and (d) AGW.

3.3. Mechanical properties of samples

The variations of shrinkage versus firing temperature are plotted in Fig. 4. According to these results, three compositions, ACC, AGW and AMM, show similar sintering behaviour. For these three, the shrinkage increases continuously with the sintering temperature. ACH composition shows a different behaviour. During the sintering process, in ACC, AGW and AMM samples a large weight loss is observed. The reason of this weight loss is the decomposition of carbonates and sulphates. After the loss of CO_2 and SO_2 gas from the samples, they contain a higher amount of porosity than the others.

For three samples (ACC, AMM and AGW) the shrinkage increased up to 1200 °C whereas in ACH samples this value

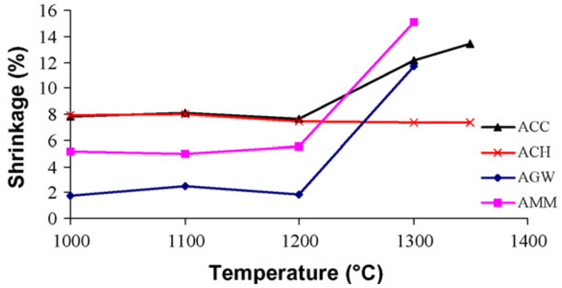
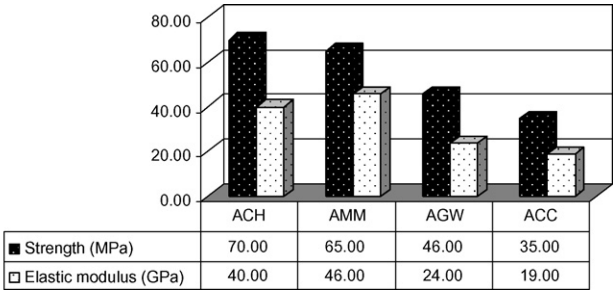


Fig. 4. Shrinkage behaviour of samples prepared with different CaO sources vs. sintering temperature.



	ACH	AMM	AGW	ACC
■ Strength (MPa)	70.00	65.00	46.00	35.00
□ Elastic modulus (GPa)	40.00	46.00	24.00	19.00

Fig. 5. The average flexural strength and elastic modulus of samples (sintered at 1300 °C for 2 h) as a function of CaO source (standard deviations for strength ±4.0 MPa and elastic modules ±2.0 GPa).

remained constant. This result indicates that densification starts at lower temperatures for ACH sample than for others. The ACH sample, sintered at 1300 °C, reached ~80% percent of theoretical density whereas others reached only ~75% of theoretical density.

Changes of strength and elastic modulus values related to starting raw materials are given in Fig. 5. The strength values are low due to the low density of samples. Additionally, the strength of the samples was affected by type of CaO source. As seen from Fig. 5, AMM, AGW and ACC samples have lower strength than ACH. The reasons of this decrease are the low density and the loss of CO_2 and SO_2 gasses during the decomposition of samples. The variation of the elastic modulus follows the same trends as the strength of samples.

4. Conclusions

The effect of using different raw material sources of CaO on formation of anorthite was investigated. It is observed that by using different raw material sources of CaO gehlenite phase was formed at low temperatures (1000–1100 °C) with some minor pre-anorthite (LAS) phase.

LAS phase depends on the firing temperature. Additionally; it was observed that LAS phase formation is not related to the source of CaO. At higher sintering temperatures (>1100 °C) lower amount of gehlenite phase observed or it disappeared related to starting compositions. On the other side, anorthite started to crystallize at 1200 °C by melting of gehlenite and LAS at this temperature. The results also showed that the waste materials (gypsum mould waste and marble powder) can be used successfully as CaO source in production of anorthite ceramics.

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