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Effect of CaO Addition on the Sintering Behaviour of Anorthite Formed from Kaolin and CaO

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Thermal reactions and sintering behavior of kaolin DD3 (Djebel Debbagh, Algeria) and CaO mixtures to obtain dense anorthite ceramics were investigated. Mixed powders were uniaxially pressed and fired between 850 and 1150 °C. Firing the pressed specimens yielded a dense anorthite ceramics. The sintered density increased with increase of CaO content and reached the maximum value of 2.57 g/cm^3 for the composition containing 10 wt% CaO and fired at 1150 °C. Their coefficient of linear expansion of the sintered samples at 1100 °C decreases with the addition of CaO. X-ray diffraction experiments carried out on the samples containing varied amount of CaO and fired at the temperatures higher than 1000 °C for 2 h showed the presence of only anorthite phase.

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1. Introduction

Many studies have been directed at developing alternative ceramics to replace conventional alumina substrate for an increase in semiconductor integrated circuit performance, such as high density. Ceramic substrates should have low sintering temperatures [1–6]. Anorthite is the best member in place of alumina substrate with a relatively low density of 2.76 g cm^{-3} [7]. Anorthite polycrystalline ceramics also satisfy the requirements of ceramic substrates due to its lower thermal expansion coefficient and lower dielectric constant than alumina. The sinterability of anorthite substrates at low temperature have never been fabricated due to the difficulty of sintering anorthite particles below 1000 °C. Harabi et al. [8] investigated the sintering phenomenon in kaolin–calcite mixtures for application as porous ceramic supports. However, they concluded that the sintering of these mixtures never proceeded below 1200 °C. Probably, the kaolin used in their studies was too coarse to get sinterable mixtures [9].

In this study, we are using kaolin DD3 from Djebel Debbagh (Algeria) and CaO mixture. A dense anorthite was obtained with low-temperature firing below 1000 °C. Also, we studied the effect of CaO additions, on the sintering of the prepared anorthite by several methods such as X-ray diffraction (XRD) and dilatometry.

2. Experimental procedure

Algerian raw kaolin DD3 (from Djebel Debbagh, Algeria) and calcium hydroxide ($Ca(OH)_2$) were used as starting materials. Before preparing the mixture, the crystalline kaolin was calcinated at 700 °C for 2 h to yield metakaolin in amorphous state. The chemical analysis of metakaolin by X-ray fluorescence spectroscopy is given in previous work [10]. The mean particle sizes of the mixture before and after ball-milling were 8.01 µm and 1.5 µm, respectively (Fig. 1). As it can be clearly seen, the powder presents a bimodal distribution with size between 0.25 and 44 µm and between 0.125 and 32 µm for the raw and the milled mixture powder, respectively (Fig. 1a,b). Metakaolin and calcium hydroxide were weighed according to the stoichiometric anorthite composition. These powders were wet mixed and milled in distilled water for 5 h using zirconia balls. All mixtures powder were dried at 110 °C for hours and then uniaxially pressed at 50 MPa to form a disk of 13 mm in diameter. Afterwards, the green compacts were sintered at temperature in the range 850–1150 °C with a heating and cooling rate of up 5 °C/min. The phases formed after sintering were identified by XRD using Cu K radiation.

Powders were characterized by differential thermal analysis (DTA/TG) using Setaram Labevo with heating at 20 °C/min. The phases formed after sintering were identified by powder X-ray diffractometry (Shimadzu model 5600 with Cu K_α radiation). The thermal expansion of sintered samples was determined using a dilatometer (Netzsch Dil 402C). Bulk density was determined by the Archimedes immersion.

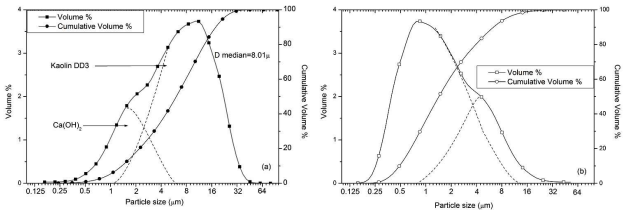

Fig. 1. Particle size distribution [vol.%] and [cumulative vol.%] of raw materials before (a) and after (b) ball-milling.

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3. Results and discussion

Figure 2 shows DTA and TG and their derivative (DTG) curves of kaolin DD3. The DTA results of the samples revealed two endothermic peaks at 110 °C from vaporization of absorbed water and at 510 °C due to loss of structural water. The exothermic peak observed at 987 °C corresponded to the formation of mullite and spinel from the metakaolin. The bulk density of fired (kaolin–CaO) mixtures is changing with firing temperature between 850 and 1150 °C and CaO amount. With the increase in CaO content (Fig. 3), bulk density significantly increased at temperature in the range between 1100 and 1150 °C. Difference in sintering at temperatures between 850 and 950 °C was significant in all specimens. Nevertheless, in firing temperature from 950 to 1100 °C the bulk density is practically constant. Sample with (anorthite+0%CaO) and (anorthite+10%CaO) have an apparent bulk density of 2.37 g/cm^3 and 2.57 g/cm^3, respectively, calculated from the relative density of the triclinic anorthite (2.76 g/cm^3).

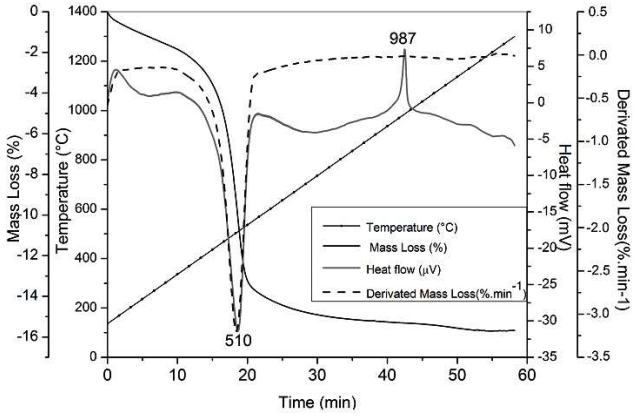

Fig. 2. DTA and TG curves of kaolin DD3 at a rate of 10 °C/min to a range of temperature up to 1300 °C.

Thermal expansion is important in evaluating any material's applications. We plotted thermal expansion against temperature for anorthite+0.0%CaO and anorthite+10%CaO fired at 1100 °C for 2 h (Fig. 4). The samples anorthite+0.0%CaO and anorthite+10%CaO have the same thermal expansion coefficient between 200 and 1000 °C. Thermal expansion of the sintered sample with anorthite+0.0%CaO, almost the monolithic phase of anorthite, is equal to 6.69×10^{-6}/K and 6.98×10^{-6}/K in the range of 300–900 °C and 100–1000 °C, respectively. Sintered samples with anorthite+10%CaO have a higher thermal expansion coefficient, 8.41×10^{-6}/K and 8.79×10^{-6}/K in the range of 300–800 °C and 100–1000 °C, respectively.

XRD patterns of the specimens fired at 1000 °C for 2 h for the mixture (kaolin–CaO) were presented in Fig. 5. Peaks corresponding of anorthite phase were detected in all samples. Continuous increase in anorthite content with increase of CaO addition was observed.

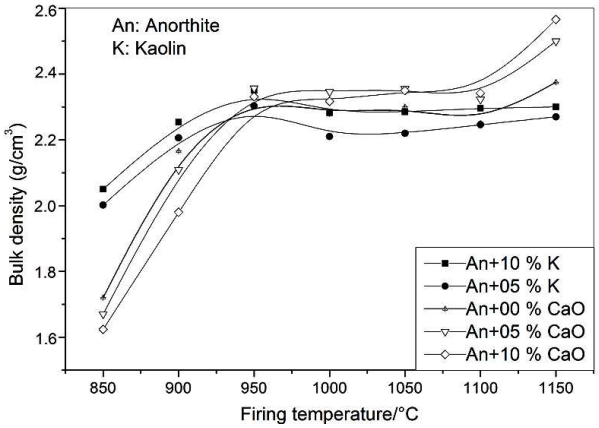

Fig. 3. Bulk density of fired specimens plotted against temperature and additive ratio of CaO.

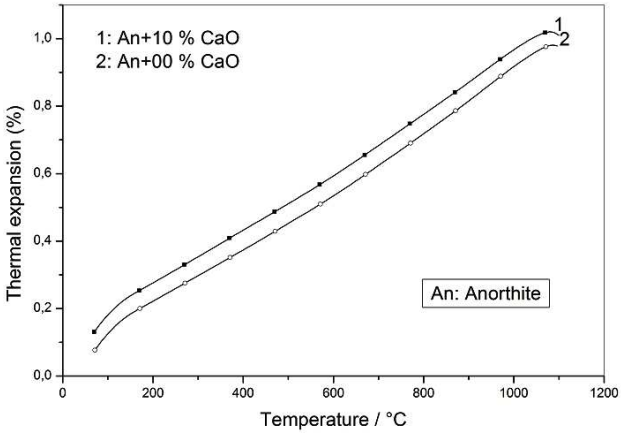

Fig. 4. Thermal expansion behavior curves of fired specimens at 1100 °C.

The SEM micrographs of fractured surfaces of anorthite+0.0%CaO samples sintered at 1000 °C for 2 h in two scale 5000 and 2500 are shown in Fig. 6a and 6b, respectively. Sintering led to the formation of a homogeneous microstructure characterized by anorthite grains with irregular shape. We note the presence of small

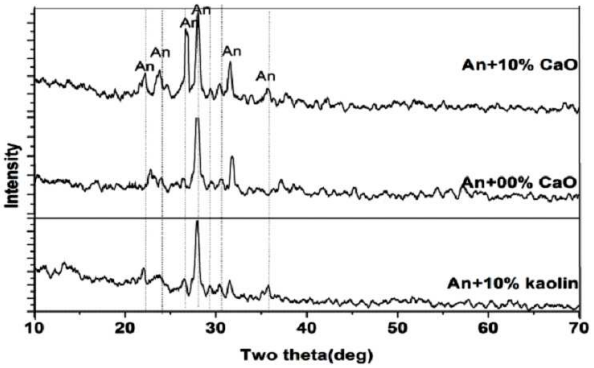

Fig. 5. XRD patterns of specimens fired for 2 h at 1000 °C.

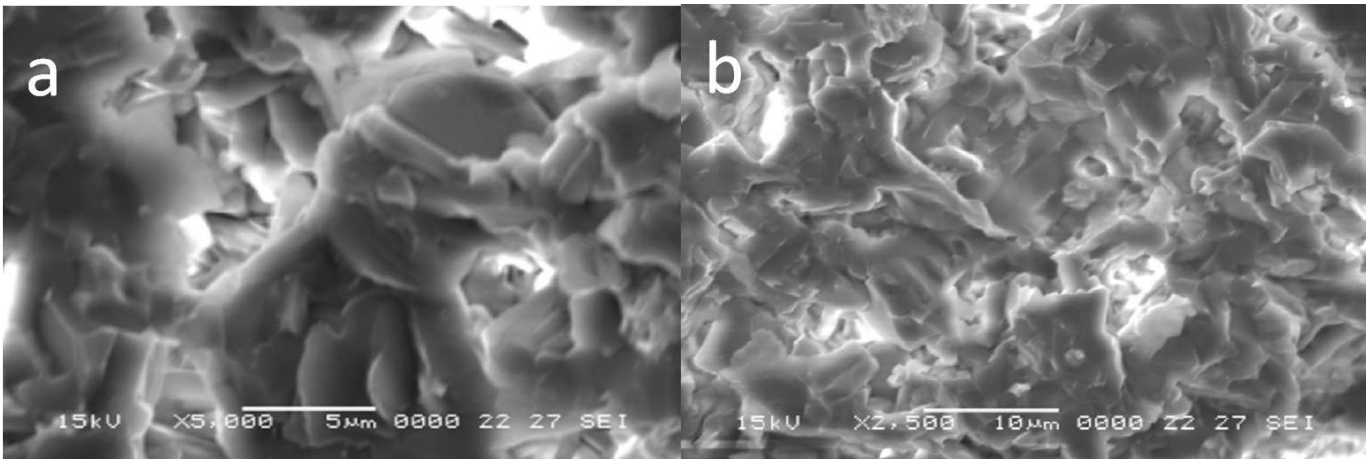

Fig. 6. SEM micrographs of fractured surface of anorthite+0.0%CaO samples sintered for 2 h at 1000 °C.

quantity of porosity of 3 µm of diameter as shown in Fig. 6b. The glass phase was observed between the grains of anorthite in these samples.

4. Conclusion

Fine calcium oxide and kaolin particles were used as starting materials to study reactions and mechanisms of sintering at 1150 °C or less. We studied the effect of CaO additions on the sintering of the prepared anorthite. A starting composition with anorthite+0.0%CaO and anorthite+10%CaO sinters into a dense body with varied amounts of anorthite. The sintered density increased with increase of CaO content and reached a maximum of 2.57 g/cm^3 for the sample anorthite+10%CaO fired at 1150 °C. Thermal expansion coefficient being controllable from 6.69 to 8.79 $\times$ 10^{-6}/K in the case of anorthite+0.0%CaO and anorthite+10%CaO samples. From these results, a dense anorthite ceramics have been produced at low temperatures (1000 °C) would be applicable as dielectric and multilayered substrates for integrated circuit.

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