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Low-temperature fabrication of anorthite ceramics from kaolinite and calcium carbonate with boron oxide addition

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Abstract

Anorthite ceramics were fabricated by using groleg kaolinite, calcite and quartz with addition of boron oxide and without the need of very fine particles. Single phase anorthite ceramic with a density of 87% of the therotical was obtained at a sintering temperature of 950 °C. Moreover, no single anorthite phase could be obtained from boron free specimens even at a sintering temperature of 1100 °C. SEM investigation revealed that although boron free samples contain very small crystals together with some larger grains, boron containing samples generally had a fine grained matrix of crystals.

Keywords: A. Sintering; Anorthite; Kaolinite; Calcite; Boron oxide

1. Introduction

Ceramic substrates for multilayer ceramic packaging should have low sintering temperatures (below the melting point of copper, 1082 °C), low dielectric constant ($\leqslant 5$) and low thermal expansion. Alumina ceramics, which have relatively lower dielectric constant at high frequency, have been used as substrate material in this area in the past decade. Cordierite ($2MgO.Al_2O_3.5SiO_2$) based glass ceramics have also great potential as a substrate material for integrated circuit boards [1]. In addition, anorthite ($CaO.Al_2O_3.2SiO_2$) polycrystalline ceramics also satisfy the requirements of ceramic substrates due to its lower thermal expansion (4.82×10^{-6}/°C) and lower dielectric constant (6.2 at 1 MHz) than alumina [2,3].

In order to be an effective substrate material, the anorthite ceramic must have sufficiently low sintering and densification temperatures to allow the cofiring of inexpensive conductive metals such as copper and silver. In addition to sol-gel and glass-ceramics processes, which are very expensive and complicated [3,4], Kobayashi and Kato [5] have reported the production of dense anorthite ceramics by sintering at 1000 °C, using kaolin and finely milled calcite. In their study, they observed that when 12 μm calcite was used, very low bulk density values of around 1.5 g/cm^3 were obtained even at sintering temperatures of 1100 °C (anorthite has a theoretical density of 2.763 g/cm^3). However, employment of fine calcite (1.5 μm) led to the formation of dense anorthite ceramics with a relative density of 94% at 950 °C.

Another method of improving the sinterability of stoichiometric anorthite ceramics made from coarse particles is the addition of sintering aids. In the present study, B_2O_3 was used to obtain dense anorthite ceramics at low sintering temperatures from kaolinite, calcite and quartz without the necessity of very fine particles. B_2O_3 was used as a sintering aid due to its low melting point and less harmful effect on the insulating characteristics than other sintering aids.

2. Experimental procedure

Groleg kaolinite (China), quartz and calcite (99.5%) were used as starting materials. The chemical analysis of kaolinite and quartz, performed by atomic absorption

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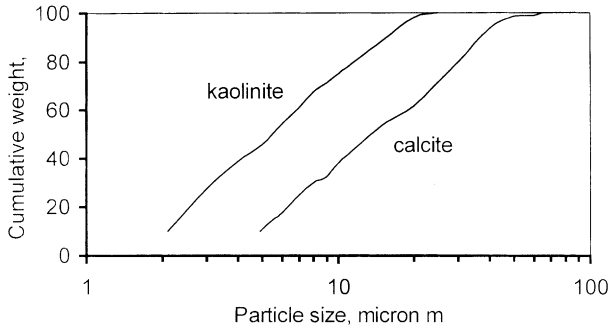


Fig. 1. Particle size distribution of raw materials.

spectrophotometer (Varian SpectraAA-300) and X-ray fluorescence (Shimadzu, XRF-1700), are given in Table 1. The particle size distribution of starting materials determined with a Malvern 2600 particle sizer indicated that the mean particle sizes of the kaolinite and calcite were 5 and 18 μm respectively (Fig. 1). DTA-TG analysis (SETARAM Labsys 3.0 DTA-TG System) of kaolinite revealed around 11.3% of weight loss between 25 and 1100 °C with an associated endothermic peak at around 562 °C. The exothermic peak at around 985 °C was due to recrystalization reaction in the dehydrated kaolinite [6].

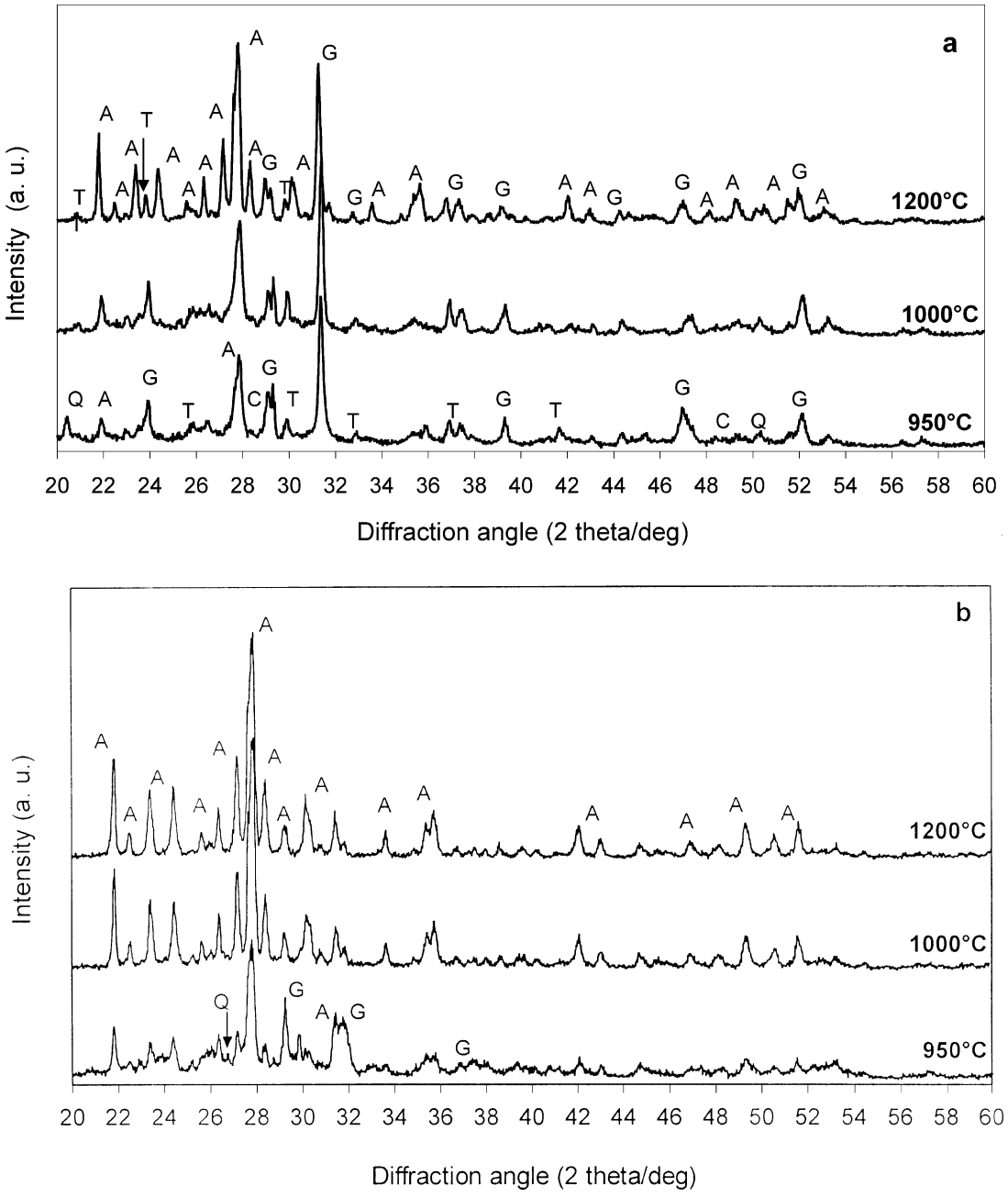


Fig. 2. XRD spectra of specimens sintered at different temperatures for 1 h (a) boron free samples and (b) with 3 wt.% B_2O_3 (A = anorthite, G = gehlenite, T = tridymite, Q = quartz, C = cristobalite).

Table 1
Chemical analysis of kaolinite and quartz

Oxide	Composition (mass%)		
	Kaolinite	Quartz	Calcite
Al_2O_3	37	15	–
SiO_2	48	78	0.1
CaO	–	0.2	53.5
Na_2O	–	0.1	0.03
K_2O	2.5	0.1	0.2
MgO	–	0.1	0.1
Fe_2O_3	0.75	0.5	0.05
TiO_2	–	0.3	–
Ignition loss[a]	–	5.5	–
Total		99.8	

[a] Ignition loss was determined at 1100 °C.

Kaolinite, quartz and calcite were weighed according to the stoichiometric anorthite composition ($CaO.Al_2O_3.2SiO_2$) and 3 wt.% of boron oxide (B_2O_3) was added to the mixture as boric acid (H_3BO_3). These powders were wet mixed and milled in deionised water for 4 h using alumina balls in a plastic container. In order to compare the results, anorthite powders were also produced without boron addition using the same raw materials. After drying the resulting slurry at 80 °C for 24 h, it was uniaxially pressed at 70 MPa into pellets approximately 10 mm diameter. Afterwards, the green compacts were sintered at a temperature in the range 950–1100 °C for 1 h with a heating and cooling rate of 300 °C/h. The phases formed after sintering were identified by XRD (Siemens) using CuK_α radiation from $2\theta = 20$–$60°$ at a speed of $1°$ min^{-1}.

3. Results and discussion

XRD analysis of boron free powders sintered at temperatures between 950–1100 °C revealed that no single anorthite phase could be obtained (Fig. 2a). After 950 °C for 1 h, mainly gehlenite and anorthite phases were observed with minor quartz, tridymite and cristobalite phases. After sintering at 1000 °C for 1 h, quartz and cristobalite disappeared. Although the peak intensities of anorthite phase increased sharply at 1100 °C, there were still two main phases, anorthite and gehlenite, at this temperature with minor trdymite phase. XRD of boron containing specimens indicated that at 950 °C there was mainly anorthite phase together with some minor phases like gehlenite and quartz (Fig. 2b). However, these minor phases disappeared at 1000 °C and only a single anorthite phase was obtained at sintering temperatures of 1000 and 1100 °C. It is clear that boron addition causes a significant change on the phase development of anorthite ceramics from groleg kaolinite, calcite and quartz with moderate particle sizes. Boron addition leads to formation of single anorthite

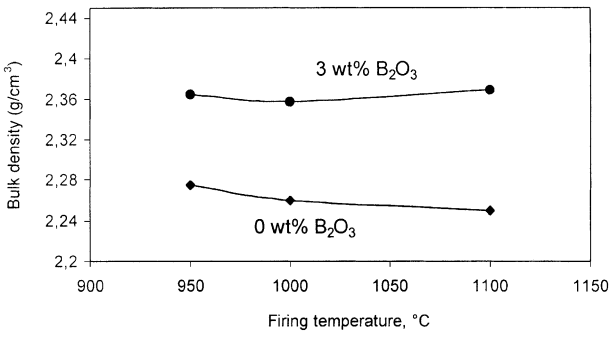
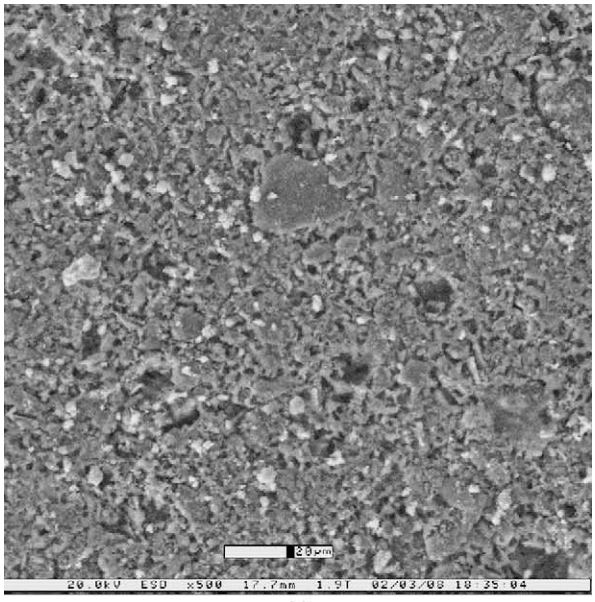
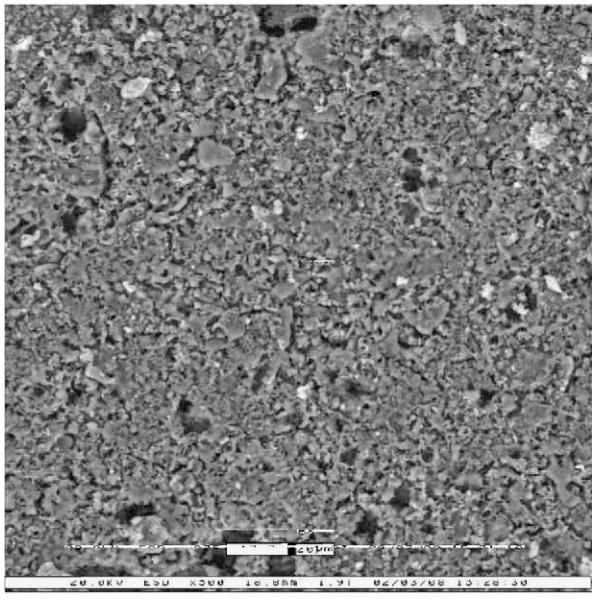


Fig. 3. Bulk densities of fired specimens.



(a)



(b)

Fig. 4. SEM photographs of (a) boron free and (b) boron containing (3 wt.% B_2O_3) specimens sintered at 950 °C for 1 h.

phases at lower temperatures, although no single anorthite ceramic could be obtained from boron free samples even at 1100 °C.

Fig. 3 shows the variation in bulk density in relation to sintering temperatures between 950 and 1100 °C. Boron containing ceramics always had higher density values than the boron free specimens, as expected. Boron containing specimens had a density of around 87% of theoretical density at 950 °C but the density of the specimens did not change significantly with sintering temperature. In another work [5], anorthite ceramics were prepared from kaolinite and calcite having mean particle sizes of 0.3 and 12 μm respectively and a density of only around 55% of theoretical was obtained by sintering at 1100 °C for 1 h and the density of anorthite ceramics increased to 90% theoretical by employment of smaller calcite powders of 2.5 μm. Nevertheless, in the present study higher density values of around 2.37 g/cm^3 (around 87% of theoretical) were obtained at 950 °C by incorporating boron oxide as the sintering aid in spite of starting with raw materials having larger particle sizes. In addition, boron free specimens sintered at 950 °C had a theoretical density of around 82% and the density decreased to 81% at 1100 °C. However, it should be taken into account that there was always more than one phase in boron free specimens but the density was calculated according to the single anorthite phase.

The SEM micrographs of sintered boron free and boron containing samples are shown in Fig. 4. Boron free samples had very small crystals together with some larger grains. However, boron containing samples generally revealed a fine grained matrix of crystals. A small amount of glassy phase and a number of pores were observed both in boron free and boron containing specimens.

4. Conclusion

By using boron oxide additions, single phase anorthite ceramic with a density of 87% of the therotical can be obtained at a sintering temperature of 950 °C from groleg kaolinite, calcite and quartz without need of very small particle size. There were always anorthite and gehlenite phases coexisting together in boron free specimens even at sintering temperature of 1100 °C.

References

[1] S.H. Knickerbocker, A.H. Kumar, L.W. Herron, Cordierite glass-ceramics for multilayer ceramic packaging, Am. Ceram. Soc. Bull. 72 (1) (1993) 90–95.
[2] R.A. Gdula, Anorthite ceramic dielectrics, Am. Ceram. Soc. Bull. 50 (6) (1971) 555–557.
[3] M.G.M.U. Ismail, H. Arai, Sol–gel synthesis of B_2O_3-doped anorthite and its characterisation, J. Ceram. Soc. Jap. 100 (12) (1992) 1385–1389.
[4] B. Samuneva, Y. Ivanova, P. Djambaski, S. Stefanova, Y. Dimitriev, M.D. Lukacs, Phase formation in gels of the apatite–anorthite system, J. Sol–Gel Sci. Technol. 13 (1998) 255–259.
[5] Y. Kobayashi, E. Kato, Low-temperature fabrication of anorthite ceramics, J. Am. Ceram. Soc. 77 (3) (1994) 833–834.
[6] W. Ryan, C. Radford, Whitewares: Production, Testing and Quality Control, Pergamon Press, UK, 1987.