

Thermal conductivity of calcium-doped aluminium nitride ceramics

Part I *Conventionally produced ceramics*

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Aluminium nitride ceramics were prepared with the addition of up to 12 wt% of calcium oxide as a sintering aid. Both the oxygen and the calcium content of the samples decreased during sintering with increasing sintering temperature and soaking time. Higher amounts of calcium oxide resulted in higher thermal conductivities, with values up to $142 \text{ W m}^{-1} \text{ K}^{-1}$. Moderate sintering temperatures, short temperature soaking times and the use of inexpensive Ca-based sintering additives should enable the production of aluminium nitride ceramics with sufficiently high thermal conductivity at relatively low cost.

1. Introduction

In the last few years, aluminium nitride has gained a great deal of interest due to its potential use as a substrate material for highly and ultra-highly integrated circuits [1]. With respect to this application, aluminium nitride offers the advantages of a high thermal conductivity, a high ohmic resistance, good mechanical properties, and a thermal expansion coefficient close to that of silicon.

Commercially available aluminium nitride substrates usually have thermal conductivities in the range of 100 to $200 \text{ W m}^{-1} \text{ K}^{-1}$. These values are about four to ten times higher than those of common alumina substrates and make such substrates very efficient for microelectronic applications as microchip carriers. Up to now, however, the theoretically calculated thermal conductivity of $320 \text{ W m}^{-1} \text{ K}^{-1}$ [2] has not been achieved experimentally, even with single crystals.

Generally, aluminium nitride powders prepared by high-temperature synthesis routes cannot be pressurelessly densified without sintering aids, with the exception of some aluminium nitride powders prepared by the pyrolysis of polymeric precursors [3–5]. The most commonly used sintering aids for aluminium nitride ceramics are yttrium compounds, mainly yttrium oxide. During the sintering process, oxygen impurities in the starting material which would negatively influence the thermal conductivity of the final product are trapped in secondary phases belonging to the binary system $\text{Al}_2\text{O}_3\text{--Y}_2\text{O}_3$, e.g. aluminium yttrium garnet, $\text{Y}_3\text{Al}_5\text{O}_{12}$. The influence of the yttrium content on the thermal conductivity of aluminium nitride has been intensively investigated (e.g. [6]). To achieve high thermal conductivities, however,

considerable quantities of Y_2O_3 must be added, and the sintering process usually requires sintering temperatures above 1850°C . Due to the high costs of yttrium compounds and the necessary high sintering temperatures, aluminium nitride substrates sintered with Y_2O_3 are too expensive for many electronic applications, in spite of the favourable physical properties of this material. This paper provides a study of the thermal conductivity of aluminium nitride ceramics prepared with calcium oxide as a sintering aid. The aim is to investigate a “low cost” route which enables the production of aluminium nitride ceramics of reasonably high thermal conductivity using cheap sintering aids, comparatively low sintering temperatures, and short soaking times. The influence of the calcium content of polymer-derived aluminium nitride powders on the thermal conductivity will be discussed in Part II [7].

2. Experimental procedure

Commercially available aluminium nitride powder (Tokuyama Grade F, Tokuyama Soda Ltd., Tokyo) was doped with 0.5 to 12 wt% of CaO and isostatically cold-pressed into cylinders at a pressure of 480 MPa. The relative green densities obtained ranged from 58 to 60%. The samples were placed in a graphite crucible and embedded in aluminium nitride powder. Sintering was carried out in a carbon tube high-temperature furnace (HTR, Ruhstrat KG, FRG) at temperatures between 1650 and 1950°C and soaking times between 1 and 8 h.

The sintered aluminium nitride samples were characterized by scanning electron microscopy, SEM (Cambridge Instruments), energy-dispersive X-ray

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analysis, EDX (Tracor Northern), wavelength-dispersive X-ray analysis WDX (Microspec WDX-2A), and X-ray diffractometry XRD (Siemens 500). The oxygen content was determined by high-temperature extraction (TC-136, Leco Corp.), and the calcium content by ICP (Leeman Labs Inc. 2.5). The thermal conductivity was measured on small aluminium nitride cylinders (diameter 5 mm, length 3–4 mm) by a flash method already described [8]. The accuracy limit of this method is assumed to be around 5%.

3. Results

3.1. Sintering behaviour

Dilatometric curves indicated that sintering starts at about 1500 °C. Almost complete densification with final densities >98% of the theoretical density could be achieved at sintering temperatures of 1650 °C or above (soaking time 3 h, 1 wt % CaO, heating rate 800 °C h⁻¹). At 1950 °C, the density decreased again due to the evaporation of aluminium nitride. The quantity of calcium oxide added had no significant influence on the density of the sintered samples. Even at a concentration of only 0.5 wt % CaO (sintering temperature: 1800 °C, soaking time 3 h, heating rate 800 °C h⁻¹), a sintering density of >98% of the theoretical density could be obtained. Furthermore, the sintered densities were also not significantly affected by a variation of soaking time (0.5 to 6 h) and heating rate (400 to 1200 °C h⁻¹).

3.2. Chemical composition of the sintered samples

The oxygen and calcium contents of the sintered samples were determined in order to check for variations in the chemical composition as a result of the different sintering conditions. In all samples, the calcium and oxygen contents decreased during sintering.

The oxygen content of the aluminium nitride powder used was 1.1 wt %. With the addition of 3 wt % of CaO, the total oxygen content of the powder mixture prior to sintering was around 2.0 wt %. After sintering at 1650 °C with a soaking time of 3 h, the oxygen content decreased to a value of 0.9 wt %, i.e. down to an oxygen level below that of the pure aluminium nitride powder (Fig. 1). At sintering temperatures of 1750 °C and above, the oxygen content was reduced to values between 0.4 and 0.45 wt %. The same effect was observed for samples sintered at 1800 °C with different soaking times. At a soaking time of 0.5 h, the oxygen content was 0.88 wt % and decreased to a value of 0.53 wt % for a temperature hold of 1 h (Fig. 2). By further raising the soaking time (2, 3, 4 and 6 h), the oxygen contents measured were also reduced to values of about 0.4 wt %.

Variation of the CaO addition up to 8 wt % had only a minor influence on the oxygen concentration in the sintered bodies. Samples sintered at 1800 °C for 3 h showed that the minimum quantity of CaO added (0.5 wt %) resulted in a fairly high oxygen content

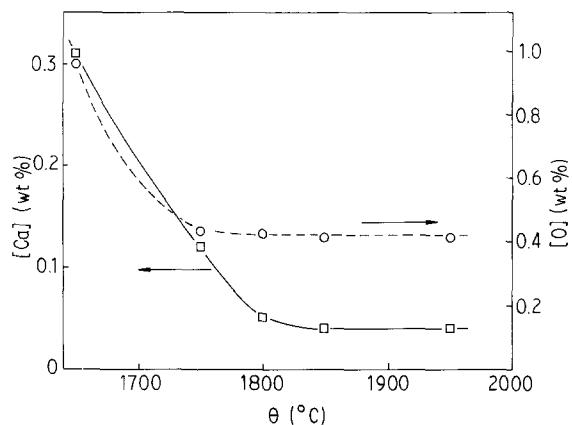


Figure 1 (□) Calcium and (○) oxygen content of aluminium nitride ceramics sintered at different temperatures (3 wt % CaO, soaking time 3 h).

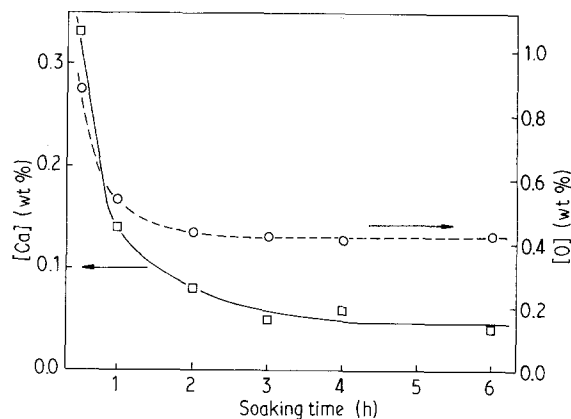


Figure 2 (□) Calcium and (○) oxygen content of aluminium nitride samples sintered with different soaking times (3 wt % CaO, sintering temperature 1800 °C).

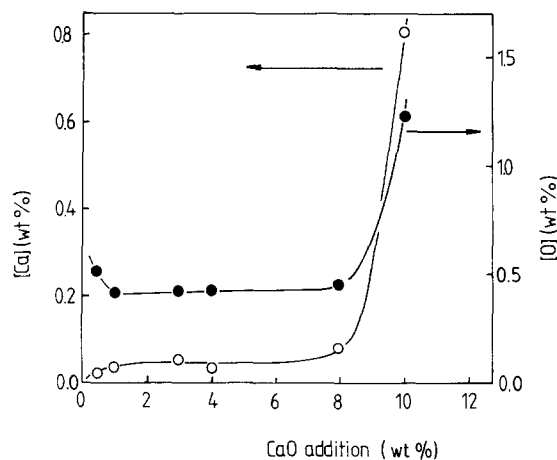


Figure 3 (○) Calcium and (●) oxygen content of aluminium nitride samples sintered with different quantities of CaO as sintering aid (sintering temperature 1800 °C, soaking time 3 h).

(0.51 wt %), whereas all samples with CaO additions in the range of 1 to 8 wt % had oxygen levels in the range of 0.4 to 0.45 wt % (Fig. 3). By contrast, the addition of 10 wt % of CaO resulted in a considerably higher oxygen content of 1.23 wt %.

Analogous to the results of the oxygen measurements, the calcium content also decreased during

sintering. With 3 wt % of CaO added, samples sintered at 1650 °C for 3 h showed a final calcium content after sintering of 0.31 wt % (see Fig. 1). An increase of the sintering temperature to 1850 °C or above resulted in a decrease of the calcium content down to a value of 0.04 wt % (see Fig. 1). The calcium level was also influenced by the soaking time. For a sintering temperature of 1800 °C and a CaO addition of 3 wt %, the calcium content was 0.33 wt % at a soaking time of 0.5 h, but dropped to a value of 0.05 wt % when the soaking time was increased to 3 h (see Fig. 2). Up to a quantity of 8 wt % of CaO, the amount of sintering aid had no explicit influence on the final calcium level in the samples (see Fig. 3). For a CaO addition of 10 wt %, however, a considerably higher calcium content of 0.81 wt % was measured, after sintering at 1850 °C for 3 h.

X-ray diffraction patterns recorded for samples sintered at temperatures of 1800 °C or more only showed peaks related to aluminium nitride. Additional phases, such as oxynitrides or calcium-containing compounds, could not be detected. For some samples with higher CaO additions which were prepared at lower sintering temperatures, additional phases such as $\text{CaO} \cdot \text{Al}_2\text{O}_3$ (10 wt % CaO addition, sintering temperature 1750 °C, soaking time 3 h) or $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$ (10 wt % CaO addition, sintering temperature 1750 °C, soaking time 1 h) could be observed.

3.3. Microstructure

Fig. 4 shows the fracture surface of a sample doped with 3 wt % of CaO and sintered at 1650 °C for 3 h. The microstructure is dense, homogeneous and very fine-grained, with a mean grain size of about 1–2 μm . As expected, an increase of the sintering temperature leads to grain growth (Figs 5–7), resulting in a mean grain size $> 10 \mu\text{m}$ for a sintering temperature of 1950 °C. In all samples, predominantly intergranular fracture can be observed (see Figs 4–7). Increased soaking times at temperature had a similar effect on the grain size and also led to grain growth.

Additional phases could not be observed by SEM, EDX and WDX in samples doped with CaO quantitatively up to 4 wt %.

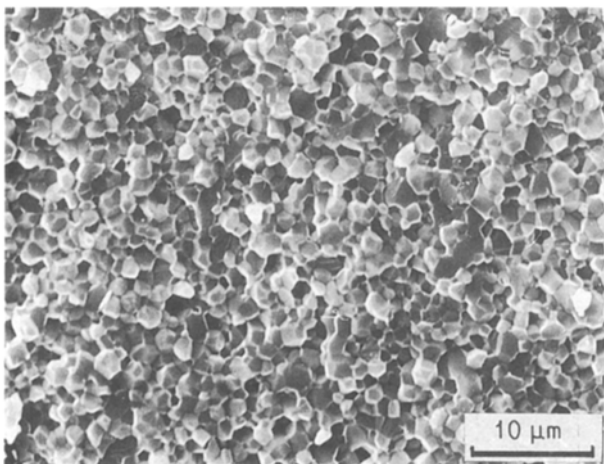


Figure 4 SEM micrograph of a fractured aluminium nitride sample sintered at 1650 °C (3 wt % CaO, soaking time 3 h).

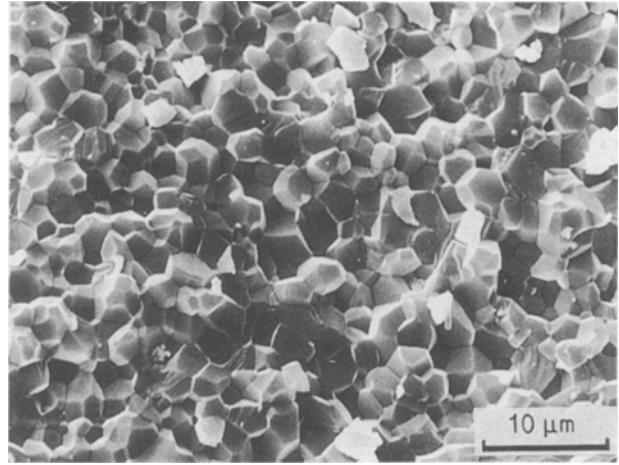


Figure 5 SEM micrograph of a fractured aluminium nitride sample sintered at 1750 °C (3 wt % CaO, soaking time 3 h).

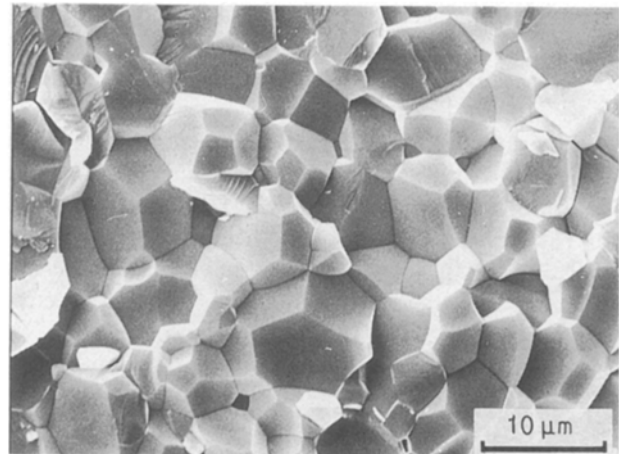


Figure 6 SEM micrograph of a fractured aluminium nitride sample sintered at 1850 °C (3 wt % CaO, soaking time 3 h).

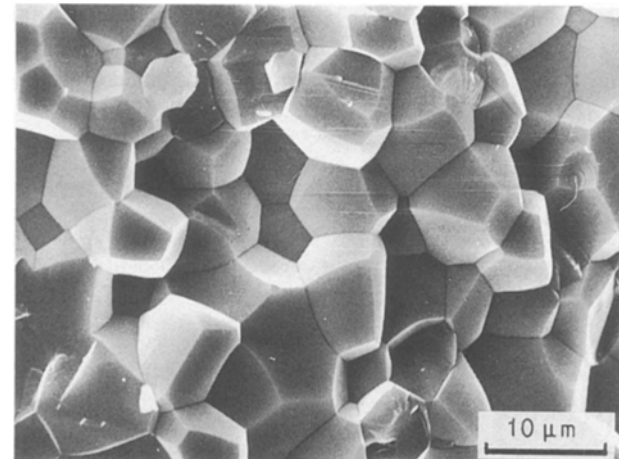


Figure 7 SEM micrograph of a fractured aluminium nitride sample sintered at 1950 °C (3 wt % CaO, soaking time 3 h).

ies up to 4 wt %. Fig. 8 shows an SEM micrograph of a sample initially containing 10 wt % CaO and sintered at 1800 °C for 3 h. At some triple points (see angle in Fig. 8) and grain boundaries, secondary phases containing calcium were detected, as shown by EDX

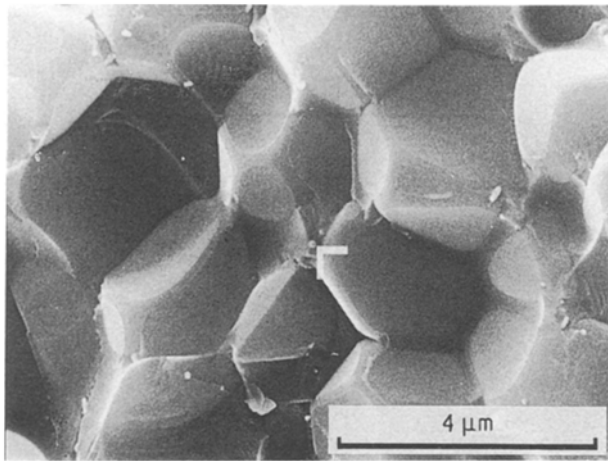


Figure 8 SEM micrograph of a fractured aluminium nitride sample sintered at 1800°C (10 wt % CaO, soaking time 3 h).

analysis. The mean grain size, however, was not strongly influenced by the amount of CaO addition.

3.4. Thermal conductivity

The results for the thermal conductivity measurements of samples sintered under different sintering conditions and with varying CaO contents are given in Table I. A variation of the heating rate (400, 600, 800 and 1200°C h⁻¹) did not have any significant effect on the thermal conductivity of the respective samples.

4. Discussion

The decrease of both calcium and oxygen content with increasing sintering temperature and soaking time is due to the evaporation of oxidic Ca–Al compounds from the samples during the sintering process. The relatively high content of residual oxygen in the sample sintered with 0.5 wt % of CaO indicates that this low amount of sintering aid was not sufficient to entrap the contained oxygen impurities in volatile, and therefore removable, Ca–Al compounds.

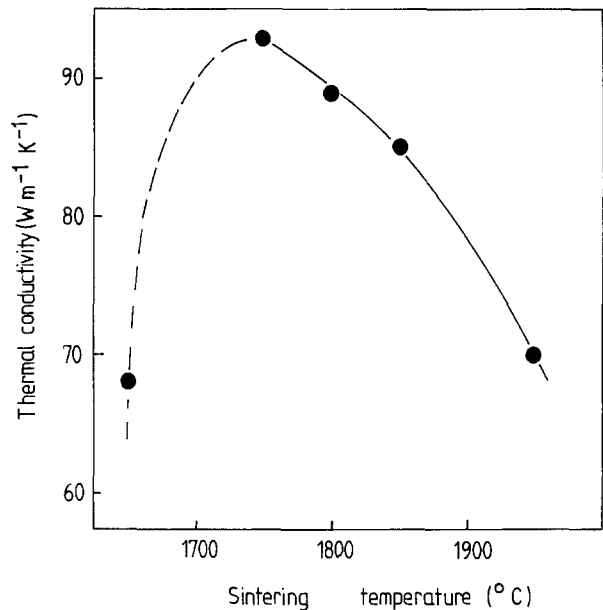


Figure 9 Thermal conductivity of aluminium nitride samples sintered at different temperatures (3 wt % CaO, soaking time 3 h).

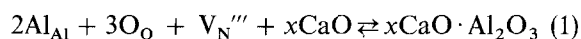
Fig. 9 shows the thermal conductivity as a function of the sintering temperature (3 wt % CaO, soaking time 3 h). The sample sintered at 1650°C exhibited a rather poor thermal conductivity of 68 W m⁻¹ K⁻¹. By increasing the sintering temperature to 1750°C, the thermal conductivity reached a value of 93 W m⁻¹ K⁻¹. A further increase in sintering temperature resulted in a decreasing thermal conductivity; at a sintering temperature of 1950°C, a thermal conductivity of 70 W m⁻¹ K⁻¹ was obtained. It should be noted that both calcium and oxygen contents remained nearly constant while varying the sintering temperatures in the range from 1800 to 1950°C.

For a sintering temperature of 1800°C and a CaO content of 3 wt % the dependence of the thermal conductivity on the soaking time was not very pronounced. All samples showed values of the thermal conductivity in the range of 85 to 98 W m⁻¹ K⁻¹, with the highest value measured for a sample sintered with a soaking time of 1 h.

TABLE I Density, oxygen and calcium content, and thermal conductivity of sintered aluminium nitride samples prepared with different quantities of calcium oxide, different soaking times and different sintering temperatures

Sintering temperature (°C)	Soaking time (h)	CaO addition (wt %)	Relative density (%)	Oxygen content (wt %)	Calcium content (wt %)	Thermal conductivity (W m ⁻¹ K ⁻¹)
1650	3	3	98	0.88	0.31	68
1750	3	3	> 99	0.43	0.12	93
1800	3	3	> 99	0.42	0.05	89
1850	3	3	> 99	0.41	0.04	85
1950	3	3	97	0.41	0.04	70
1800	0.5	3	> 99	0.88	0.33	94
1800	1	3	> 99	0.53	0.14	98
1800	2	3	> 99	0.43	0.08	85
1800	3	3	> 99	0.42	0.05	89
1800	3	0.5	98	0.51	0.02	59
1800	3	1	> 99	0.41	0.03	76
1800	3	3	> 99	0.42	0.05	89
1800	3	4	> 99	0.42	0.03	110
1800	3	8	> 99	0.45	0.08	122
1800	3	10	> 99	1.23	0.81	142

The main parameter influencing the thermal conductivity of the samples was the amount of calcium oxide added as a sintering aid (Fig. 10). CaO additions of 0.5 wt % only led to a thermal conductivity of $59 \text{ W m}^{-1} \text{ K}^{-1}$. Higher initial CaO contents, however, resulted in a considerable increase of the thermal conductivity up to a value of $142 \text{ W m}^{-1} \text{ K}^{-1}$ for 10 wt % CaO. A further increase of the CaO addition to 12 wt % again led to a slight drop in thermal conductivity of the respective samples. It should be noted that the residual calcium and oxygen contents did not increase when the amount of sintering aid was changed from 1 to 4 wt % CaO, but that the thermal conductivity was raised from 67 to $110 \text{ W m}^{-1} \text{ K}^{-1}$. The sample with the highest thermal conductivity measured ($142 \text{ W m}^{-1} \text{ K}^{-1}$) contained a considerable amount of residual calcium and oxygen (see Table I). In this case, additional calcium-containing phases could also be detected by EDX. It can be assumed that the presence of a sufficient amount of these secondary phases during the sintering process is the most important factor for a high thermal conductivity, due to the ability of such phases to act as impurity traps in the microstructure. CaO has the ability to wet the aluminium nitride grains during the sintering process and to reach an equilibrium with calcium aluminates, oxygen impurities, and nitrogen vacancies according to the equation.



This equilibrium is shifted to the right-hand side by increasing the amount of CaO added. It should be noted that higher quantities of CaO also result in a more complete wetting of the aluminium nitride grains

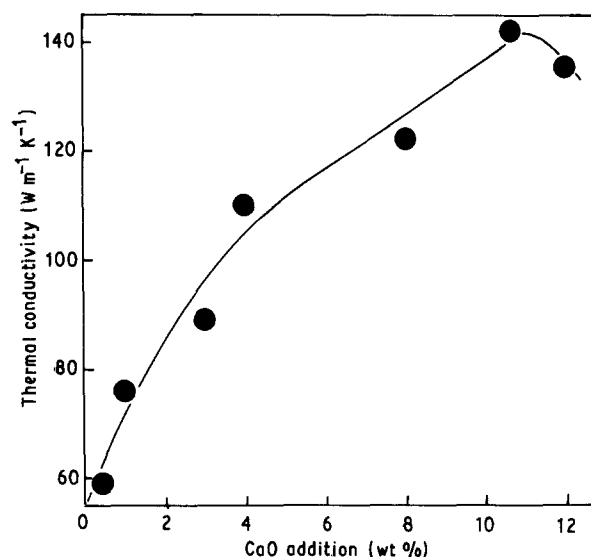


Figure 10 Thermal conductivity of aluminium nitride samples sintered with different quantities of CaO (sintering temperature 1800°C , soaking time 3 h).

during sintering and therefore also kinetically facilitate the removal of oxygen impurities from the bulk material. Both effects agree well with the observation of increasing thermal conductivities for higher CaO contents. From the phase diagram, it can be seen that at temperatures below 1850°C , $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ is formed and is in equilibrium with the liquid phase. At higher temperatures, however, $\text{CaO} \cdot 6\text{Al}_2\text{O}_3$ is decomposed and a solid phase of $\alpha\text{-Al}_2\text{O}_3$ is formed. The effect of a decreasing thermal conductivity with higher sintering temperatures can be possibly attributed to the re-diffusion of oxygen impurities from the α -alumina phase at the grain boundaries into the aluminium nitride lattice.

5. Conclusions

Aluminium nitride ceramics prepared by the addition of up to 10 wt % CaO as a sintering additive showed a fairly high thermal conductivity of up to $142 \text{ W m}^{-1} \text{ K}^{-1}$. This value should be sufficient for most applications as a substrate material. The use of cheap calcium oxide instead of comparably expensive yttrium compounds, relatively low sintering temperatures and short soaking times should enable the production of low-cost aluminium nitride ceramics.

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