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Thermal conductivity of calcium-doped aluminium nitride ceramics

Part II *Polymer-derived ceramics*

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Metallic aluminium, calcium and yttrium were anodically dissolved in a purely organic electrolyte. Mixing of these solutions and subsequent drying and sintering led to aluminium nitride ceramics with oxygen contents down to 0.34 wt% and thermal conductivities up to 155 $\mathrm{W\,m^{-1}\,K^{-1}}$. The presence of homogeneously dispersed calcium and yttrium compounds led to an effective removal of oxygen from the aluminium nitride lattice due to short diffusion paths.

1. Introduction

In the last few years, aluminium nitride has generated a great deal of interest, predominantly due to its potential use as material for highly and ultra-highly integrated circuit carriers [1]. The predominant properties of aluminium nitride ceramics are their high thermal conductivity (theoretical value 320 $\mathrm{W\,m^{-1}\,K^{-1}}$), their high ohmic resistance, their high mechanical strength and their low wettability by molten metals. The experimental thermal conductivities of aluminium nitride ceramics, however, are always much below the theoretically predicted value. The reason for this behaviour are point defects in the aluminium nitride lattice, mainly due to oxygen impurities (e.g. [2]).

Conventional synthesis routes for aluminium nitride are the direct nitridation of metallic aluminium [3] or the carbothermic reaction of alumina, carbon and nitrogen [4]. Besides these two routes, the gas-phase reaction of aluminium chloride with ammonia has been used during the last few years for the preparation of aluminium nitride, [5]. The powders obtained by these high-temperature processes cannot be pressurelessly densified without a sintering aid. The most commonly used sintering aids are yttrium or calcium compounds, and in Part I [6] the use of calcium-based additives was studied. These compounds possess moreover the ability to act as an oxygen getter and form separate phases (e.g. aluminium yttrium garnet) with oxygen impurities of the aluminium nitride lattice. Thus the concentration of oxygen inside the grains, and hence the phonon–defect interaction, decreases. This leads to an increase in thermal conductivity.

In the last few years, pyrolytic routes which yield aluminium nitride have also been investigated. Most routes reported in the literature use aluminium hydride or alkyles as starting materials [7–11]. Another route, starting from inexpensive compounds, is the anodic dissolution of metallic aluminium, and subsequent drying and calcining of the obtained precursor [12–15]. This route enables pressureless sintering of aluminium nitride without the addition of sintering aids [13, 14]. Pyrolytic routes, in principle, also enable a homogeneous mixing of aluminium nitride precursors with other precursor solutions, e.g. those containing calcium or yttrium compounds. This should drastically influence the thermal conductivity of the aluminium nitride ceramic. This paper provides a study of the thermal conductivity of aluminium nitride ceramics, prepared from polymeric aluminium nitride precursors homogeneously mixed with calcium- and yttrium-containing precursor solutions.

2. Experimental procedure

Metallic aluminium was anodically dissolved in an organic electrolyte consisting of acetonitrile acting as a solvent, n-propylamine and tetraalkylammonium bromide as a supporting electrolyte. The latter was required to achieve a sufficiently high ionic conductivity of the electrolyte, necessary to reduce ohmic drops. A double-walled glass vessel contained the electrodes as well as the electrolyte. Cathodes and anodes were both formed by sheets of metallic aluminium (thickness 1 mm) and the distance between two electrodes was also 1 mm. The electrodes were alternately connected to a thick aluminium wire inserted from the top for the power supply. The polarity of the electrodes was inverted every 15 min to achieve a homogeneous dissolution of all electrodes. At the top of the vessel a condenser recovered solvent and amine which were

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vaporized or carried along with the gas stream. The electrolysis was carried out at a voltage of 5–20 V and a current of about 20 A. The current remained almost constant over a period of about 4 h and then decreased, due to increasing viscosity of the solution. Then the electrolysis was stopped, and the electrolyte drawn off to another vessel. The experimental details and the apparatus have already been discussed elsewhere [12, 13].

In order to obtain soluble calcium- and yttrium-containing precursors, the apparatus was modified. Calcium granules or yttrium powder were placed on metallic mercury, which subsequently was anodically polarized versus a platinum counterelectrode. The applied currents were much lower (4 A). Viscous solutions were obtained in this case. In order to obtain a homogeneous dosage of the aluminium nitride powders, the aluminium nitride precursor solution was mixed with those containing yttrium or calcium.

To obtain small particles and a narrow size distribution, the precursor solution was dried in the following manner: paraffin was placed in a glass vessel, heated up to around 450 °C and heavily stirred. Then the precursor solutions were dropped in. Excess solvent and other volatile compounds were vaporized immediately. Afterwards, the polymeric powder was obtained by means of filtration under argon. Although rinsed with petroleum ether, a small amount of paraffin remained, and the surface of the particles is presumed to be covered with a thin paraffin layer. Best results were obtained if the viscosity of the precursor solution was previously adjusted to a value of around 0.7 Pa s by adding propylamine. For a more detailed description of the experimental procedure see Distler and Rüssel [14].

For calcining, the polymeric powders were placed on carbon felt and calcined in dried ammonia at a temperature of 950 °C. The powders were isostatically cold-pressed (Weber, 480 MPa, 1 min). For sintering, a carbon tube furnace (Ruhrstrat, HTR 21) purged with pure nitrogen was used. Sintering was carried out at 1850 °C using a heating rate of 800 K h^{-1} and a soaking time of 3 h. The samples were embedded in aluminium nitride powder.

Polymeric, calcined and sintered samples were characterized by Fourier transformed infrared spectroscopy (FTIR) (Mattson Inst., Polaris), X-ray diffraction (XRD) (Siemens D 500), scanning electron microscopy (SEM) (Cambridge Instruments), energy-dispersive X-ray analysis (EDX) (Tracor Northern), and wavelength-dispersive X-ray analysis (WDX) (Microspec WDX 2 A). The oxygen content was measured by high-temperature extraction (Leco TC 136) and the yttrium and calcium contents by ICP (Leeman Labs. Inc. 2.5). The thermal conductivity was measured by a flash method, already described [2].

3. Results and discussion

During the electrolytic dissolution, the metal is oxidized at the anode. At the cathode, propylamine is reduced and the corresponding anion and gaseous hydrogen (gas bubbles) are formed. As an intermediate, the monomeric amino compounds $\mathrm{Me(NHR)}_x$ can be assumed. The reaction mechanism suggested is as follows: for Anodic reaction

$$\mathrm{Me} \rightarrow \mathrm{Me}^{x+} + x\,\mathrm{e}^-$$

and for Cathodic reaction

$$x\mathrm{NH_2R} + x\mathrm{e}^- \rightarrow x\mathrm{NHR}^- + (x/2)\mathrm{H_2} \quad (1)$$

$$x\mathrm{NH_2R} + \mathrm{Me} \rightarrow \mathrm{Me(NHR)}_x + (x/2)\mathrm{H_2}$$

where $x = 3$ for Al, Y and $x = 2$ for Ca. The amino compound $\mathrm{Me(NHR)}_x$ is assumed to be formed as an intermediate which polycondenses.

Fig. 1 shows an FTIR spectrum of precursors dried at 250 °C. All spectra show strong absorptions both in the region at about 3300–3500 cm^{-1} and at about 1600 cm^{-1}, indicating that considerable numbers of N–H bonds were still present and a complete polycondensation according to Equation 2 below did not occur:

$$\mathrm{Me(NHR)}_x \rightarrow \mathrm{Me(NR)}_{x/2} + (x/2)\mathrm{NH_2R} \quad (2)$$

C–H bonds can be seen at 2850–2950 cm^{-1} and at 1370–1470 cm^{-1}. The absorption at about 2100 cm^{-1} may be due to metal–hydrogen bonds. The broad absorption in the region at 500 to 1000 cm^{-1} is predominantly due to metal–nitrogen bonds.

The calcination behaviour of aluminium nitride precursors has already been described in detail [14, 11]. The main weight loss occurred in the temper-

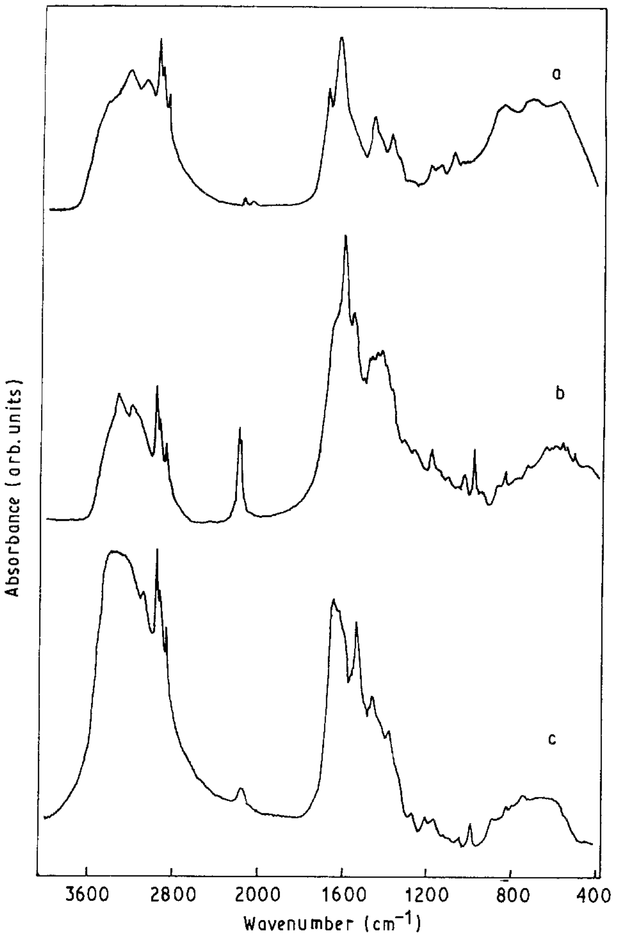

Figure 1 FTIR spectra of dried precursors: (a) aluminium compound, (b) calcium compound, (c) yttrium compound.

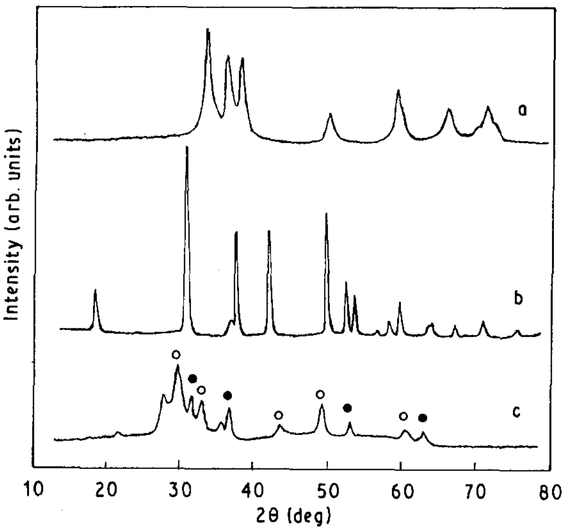

Figure 2 XRD patterns of products calcined at 950°C: (a) aluminium compound, (b) calcium compound, (c) yttrium compound (●) YN (o) $Y_{0.45}$ $C_{0.55}$.

TABLE I Chemical composition of the powders used (calcination temperature 950 °C, soaking time 1 h)

Sample	Ca content (wt %)	Y content (wt %)
A	0	0
B	2.90	0
C	5.24	0
D	7.14	0
E	2.21	1.53
F	3.99	1.36
G	6.06	1.27

ature region 250–500 °C. Fig. 2 shows the XRD patterns of aluminium-, calcium- and yttrium-containing precursors. The XRD pattern of the aluminium compound, calcined at 950 °C (Fig. 2 graph a) completely matches that of commercially available aluminium nitride. The lines, however, are considerably broadened due to small crystallite sizes. Fig. 2 graph b shows a sample prepared by calcining the calcium-containing precursor at 950 °C. Very sharp lines are seen which match those of calcium cyanamid (ASTM card No. 32-161). Graph c shows the XRD pattern of a calcined yttrium precursor. Notable broadened lines attributable to yttrium nitride (ASTM card No. 10-221) and to yttrium carbides (predominantely $Y_{0.45}C_{0.55}$, ASTM card No. 21-1443) can be seen.

If mixed precursor solutions are dried and subsequently calcined, however, the obtained XRD patterns can be different. Fig. 3 graph a shows the XRD pattern of sample B (Table I). The calcium content of the calcined sample was 2.9 wt %. Only lines attributable to aluminium nitride can be observed. By contrast, in graphs b and c which represent samples with a calcium content of 5.24 and 7.14 wt %, respectively, additional lines attributable to calcium cyanamid are observed. Graph d represents a sample containing both calcium and yttrium compounds. Here, besides lines related to aluminium nitride and calcium cyanamid, lines attributable to yttrium oxycarbide are also observed. It should be noted that lines

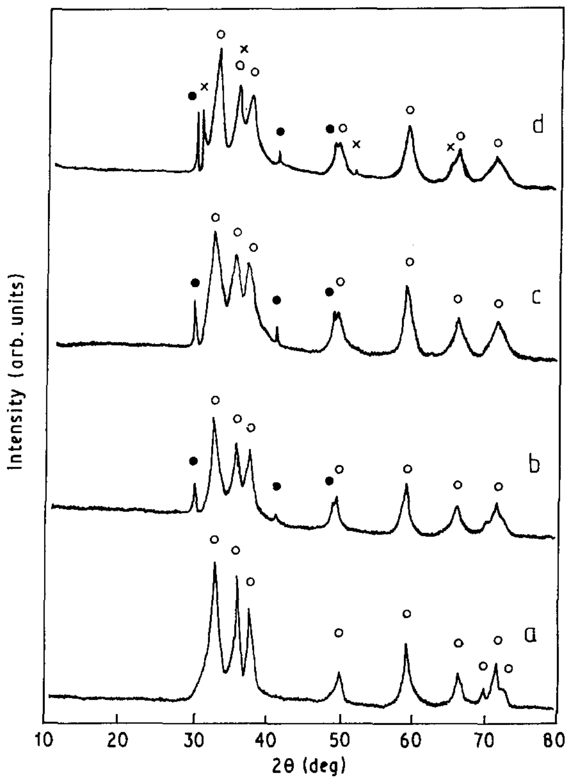

Figure 3 XRD patterns of mixed products calcined at 950°C: (a) 2.90 wt % Ca (sample B), (b) 5.24 wt % Ca (sample C), (c) 7.14 wt % Ca (sample D), (d) 6.06 wt % Ca and 1.27 wt % Y (sample G). (○) AlN (●) $CaCN_2$ (×) $Y_{0.45}C_{0.55}$.

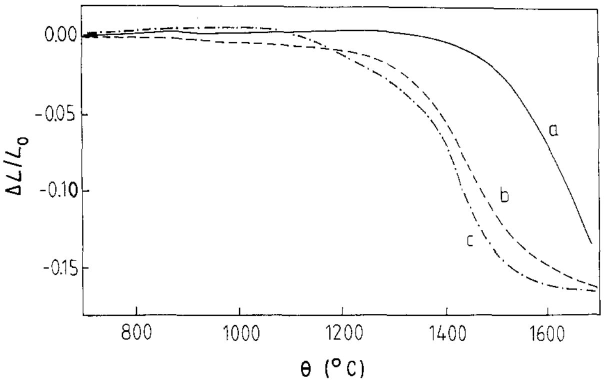

Figure 4 Dilatometric curves of (a) conventionally produced aluminium nitride powder with the addition of 3 wt % CaO; (b) polymer-derived aluminium nitride powder without any additions; (c) polymer-derived powder prepared by homogeneous mixing of calcium and aluminium nitride precursor solutions.

related to aluminium oxynitride could never be observed.

Fig. 4 shows dilatometric curves of aluminium nitride samples. Curve a represents a commercially available aluminium nitride powder (Tokuyama Soda Grade F) which was sintered by the addition of 3 wt % CaO. Sintering starts at about 1400 °C, and at 1650 °C a complete densification can be achieved. By contrast, curve b shows a curve of pyrolytically prepared aluminium nitride powder without the addition of calcium compounds. The densification starts at around 1200 °C and an almost horizontal line is reached at 1500 °C. In comparison to curve a, curve b is shifted about 180 °C to lower temperatures. Curve c shows the dilatometric curve of a sample prepared from mixed calcium and aluminium precursors. Although sintering starts even earlier than shown in curve b, the sintering process is not drastically influenced by the addition of calcium compounds.

Pressureless sintering at 1850 °C always resulted in densities of > 98% of the theoretical density. Figs 5 to 8 show SEM micrographs of sintered samples which were prepared by adding different quantities of calcium precursor solution (Figs 5 and 6) or by adding both calcium and yttrium precursor solutions (Figs 7 and 8) to the aluminium nitride precursor solution with subsequent drying, calcining and sintering. The microstructures obtained were fairly homogeneous with mean grain sizes in the range of 4 µm. The microstructure as well as the mean grain size did not notably depend on the amount of calcium or yttrium precursor solution added. In all samples only very few pores and no additional phases, such as calcium or yttrium aluminates, can be seen. It should be noted that the microstructure is fairly similar to that of samples obtained from conventionally produced aluminium nitride powder sintered with the aid of calcium or yttrium-containing additives (see e.g. [2, 16]).

The oxygen content of the sintered samples (Table II column 2) decreased with the amount of calcium precursor solution added. It was 2.0 wt % for a sample prepared without the addition of calcium precursor and decreased to a value of 0.55 wt % if the

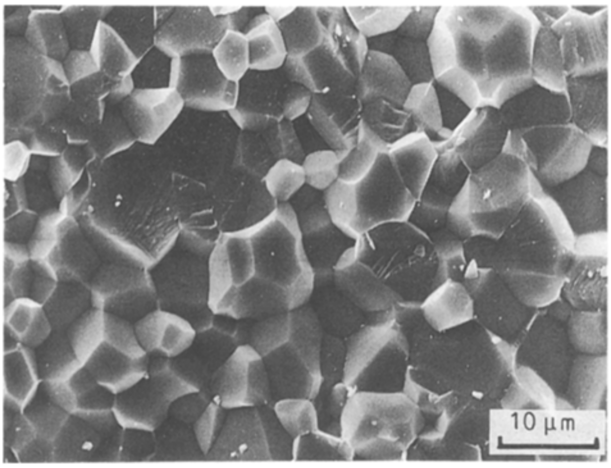

Figure 5 SEM micrograph of aluminium nitride sample prepared from powder containing 2.90 wt % calcium.

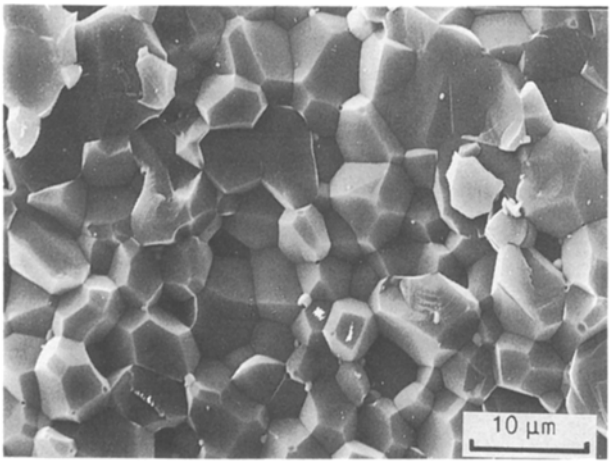

Figure 6 SEM micrograph of aluminium nitride sample prepared from powder containing 7.14 wt % calcium.

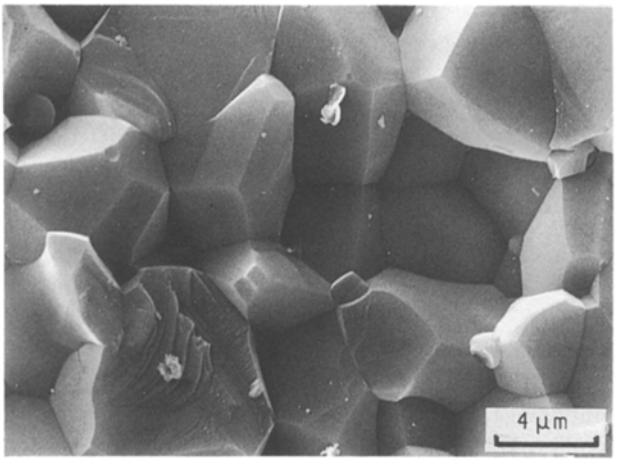

Figure 7 SEM micrograph of aluminium nitride sample prepared from powder containing 2.21 wt % calcium and 1.53 wt % yttrium.

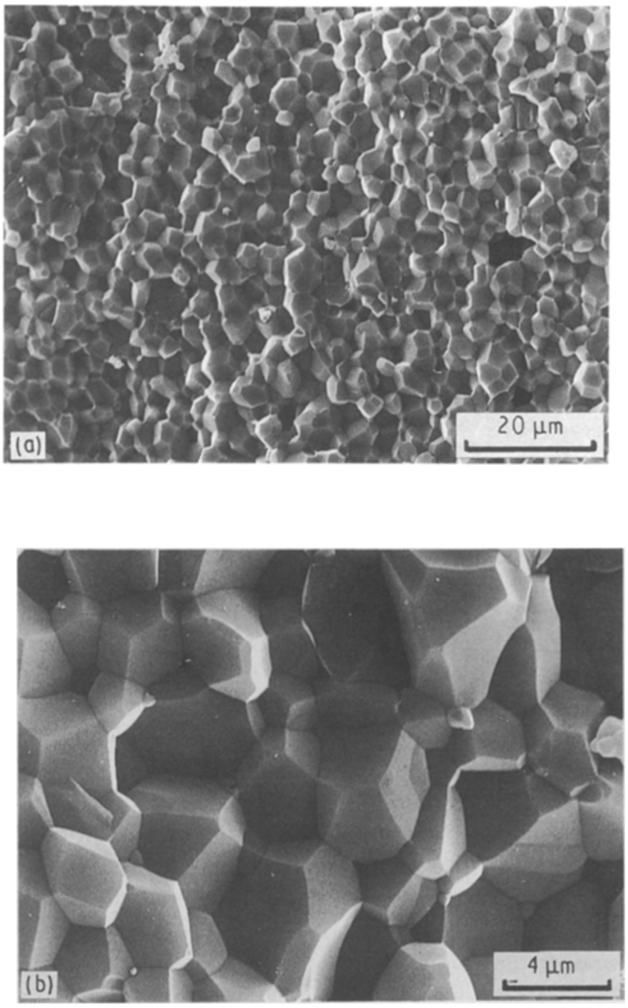

Figure 8 (a) SEM micrograph of aluminium nitride sample prepared from powder containing 6.06 wt % calcium and 1.27 wt % yttrium; (b) higher magnification.

TABLE II Chemical composition and thermal conductivity of sintered aluminium nitride samples (sintering temperature 1850 °C, soaking time 3 h)

Prepared from powder sample	Oxygen (wt %)	Thermal conductivity ($\mathrm{W\,m^{-1}\,K^{-1}}$)
A	2.0	40
B	0.94	51
C	0.73	80
D	0.55	95
E	1.29	71
F	0.82	123
G	0.34	155

calcium content of the powder was 7.14 wt %. A further decrease of the oxygen content was achieved if both calcium and yttrium precursor solutions were used. Sintering of powder sample E (calcium content 2.21 wt %, yttrium content 1.53 wt %), resulted in a ceramic with an oxygen content of 1.29 wt %, while powder sample G (calcium content 6.06 wt %; yttrium content, 1.27 wt %) could be densified to a ceramic containing 0.34 wt % oxygen. The use of powders doped with both calcium and yttrium generally resulted in lower oxygen contents than the use of powders doped solely with comparably quantities of calcium. By analogy, the calcium and yttrium contents decreased during sintering. In samples prepared from powders B and D (calcium content 2.90 and 7.14 wt %, respectively), the calcium content decreased to values of 0.034 and 0.014 wt %, respectively. The same effect was observed in samples prepared from powders doped with both calcium and yttrium: while the calcium content decreased from 2.21 (powder E) to 0.031 wt % and from 6.06 (powder G) to 0.054 wt %, the decrease in the yttrium content was not as pronounced. From an initial concentration of 1.53 (powder E) and 1.27 wt % (powder G), the yttrium content decreased to values of 0.58 and 0.51 wt %, respectively.

Table II column 3 summarizes thermal conductivities of the obtained ceramics. Aluminium nitride ceramics prepared without the addition of calcium precursors showed a fairly poor thermal conductivity of 40 $\mathrm{W\,m^{-1}\,K^{-1}}$. If calcium-containing precursors were added, the thermal conductivity increased with increasing quantity of calcium in the initial powder up to a value of 95 $\mathrm{W\,m^{-1}\,K^{-1}}$ for a powder containing 7.14 wt % Ca (powder D). The same effect could also be observed if additionally yttrium precursors were used. Then the thermal conductivity increased up to a value of 155 $\mathrm{W\,m^{-1}\,K^{-1}}$ for a sample prepared from powder G (calcium content 6.06 wt %, yttrium content 1.27 wt %). Although densification of the obtained powders is also possible without the addition of sintering aid, calcium and yttrium compounds are necessary in order to obtain good thermal conductivities. This effect may be due to the ability of calcium and yttrium compounds to act as an oxygen getter and therefore to remove oxygen contamination from inside the grains. The higher the quantity of calcium compounds added, the more effective is the removal of oxygen from the aluminium nitride lattice. It can be assumed that by analogy with ceramics prepared from conventionally produced aluminium nitride powders, residual yttrium compounds form binary aluminium yttrium oxides such as aluminium yttrium garnet at the grain boundaries, and therefore fix the oxygen in separate phases outside the aluminium nitride lattice.

4. Conclusions

Addition of calcium- and yttrium-containing precursor solutions to aluminium nitride precursor solutions and subsequent drying, calcining and sintering resulted in dense ceramics with comparatively low oxygen content. These ceramics possessed thermal conductivities up to 155 $\mathrm{W\,m^{-1}\,K^{-1}}$. It is assumed that the calcium compounds formed during calcination act as both sintering aid and oxygen getter. The presence of homogeneously dispersed calcium compounds also kinetically facilitates an effective removal of oxygen impurities from the aluminium nitride lattice due to short diffusion paths.

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