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Abstract

Recently, ceramic substrates have been of great interest for use in light emitting diode (LED) packaging materials because of their excellent heat transfer capability. The thermal conductivities of ceramic-based substrates are usually one or two orders of magnitude higher than those of conventional epoxy-based substrates. The demand for ceramic substrates with high mechanical strength and thermal conductivity is also growing due to their use in thin and high-power device packaging substrates. Examples are direct bonded copper or aluminum or direct plated copper substrates for insulated gate bipolar transistors; thin and robust ceramic packages for image sensor modules that are used in mobile smart phones; ceramic packages for miniaturized chip-type supercapacitors; and high-power LED packages. This chapter will cover the development and application of ceramics and ceramic composites with high thermal conductivity for the thermal management of integrated electronic packaging substrates such as high-power LED packaging, power device packaging, etc.

Keywords: thermal conductivity, ceramics, composites, electronic, packaging

1. Introduction

Ceramic materials with high thermal conductivity are of great interest in the thermal management of integrated electronic device packaging such as high-power light emitting devices (LEDs), power semiconductor modules, micro and nano fluidics, thermoelectrics, solar cells, and wireless communication devices. These electronic devices and packages generate more heat than before as the system design goes into more integrated, miniaturized, and increasing
data communication due to the multifunctional requirement in wireless communication and the Internet of things (IOT) environment. Moreover, a global movement for a clean environment has shifted the public interest from conventional cars with combustion engines to electric vehicles (EVs) and hybrid electric vehicles (HEVs), thus drastically increasing the use of integrated power modules with increased powers and operation frequencies. In this regard, the development of high thermal conductivity ceramics for packaging substrate and filler materials for composites is of great importance. This chapter briefly examines recent trends, development, and technical issues of selected high thermal conductivity ceramic materials and their composites.

2. High thermal conductivity ceramics and their composites

2.1. Aluminum nitride (AlN) base ceramics and composites

2.1.1. AlN ceramics with sintering additives

Aluminum nitride (AlN) has a highly covalent bonded wurtzite structure with a high thermal conductivity and a low thermal expansion coefficient (CTE) of 4.5 ppm/°C that matches well with silicon devices. Typical thermal conductivity of AlN is 140–180 W/mK but varies in the range 18–285 W/mK in polycrystalline AlN ceramics depending on the process condition, purity of starting materials, and microstructures [1]. AlN is stable at 700–1000°C in an oxygen atmosphere. It also has excellent dielectric properties: low dielectric constant ($\varepsilon_r = 9$ and low loss ($\tan \delta$) = 0.0003 at 1 MHz. With these outstanding physical and thermal properties, AlN ceramic is frequently selected as a candidate material for insulating substrate (direct band gap energy ~6.015 eV) for power electronics device and package. However, sintering of AlN with high density for effective heat transfer and high mechanical strength is challenging due to its highly covalent and low diffusive nature that requires very high sintering temperatures over 1900°C in a reducing atmosphere with applied pressure even though it is stable near 1000°C in air. Also, degradation of thermal conductivity due to oxygen inclusion is another confronting issue in high thermal conductivity AlN substrate fabrication.

Many works to promote the densification of AlN ceramic bodies using different kinds of sintering additives such as CeO, Sm$_2$O$_3$, Y$_2$O$_3$, CaO, CaZrO$_3$, and their multiple co-additions have been investigated [2–5]. Some of the recent results showing the thermal conductivities obtained in polycrystalline bodies are 90–156 W/mK as summarized in Table 1, which is far below the theoretical value and has a wide span from each other. Ceria (CeO) doped AlN exhibited a stiff increase in thermal conductivity and decent increase in mechanical strength with a small amount of addition (~1.5 wt%), compared to the yttria (Y$_2$O$_3$) addition [2]. High energy sintering method like spark plasma sintering (SPS) was applied [3, 4] as well as conventional solid state reaction (SSR) method [2] for effective low temperature densification process. The two-step sintering technique was also conducted using different temperatures to minimize grain growth and purification of AlN grains [5] (Figure 1).
2.1.2. AlN composites with GNP/GNS/rGO: electrically conducting

Carbon based nanostructured materials such as graphene nanoplatelets (GNP) or nanosheets (GNS) were added to AlN matrix to improve physical properties (Table 2). The electrical conductivity was increased with the addition of multilayer graphene as expected but the thermal conductivity was decreased with the addition in both in-plane and through-plane direction, which is adverse to other ceramic/graphene composites data. This sharp decline of thermal conductivity in both directions seems attributed to the large thermal resistance at the thin interaction zone existing in the interface between AlN and GNP [6]. The high directionality in the in-plane and through-plane of AlN/GNP composites, 74 W/mK for in-plane and 37 W/mK for through-plane, is ascribed to the thermal contact resistance existing in both phase interfaces that are severe in the perpendicular heat transfer direction of graphene nanoplatelets [7]. This strong directionality in heat transfer, thermal conductivity, can be easily found in the boron nitride (BN)/polymer composite system, in which 2D morphology BN filler materials are used [9–16]. In case of reduced graphene oxide (rGO) added AlN, the thermal conductivity decreased sharply from 92.5 to 37.4 W/mK when 2 wt% of rGO was added, though there are minor increases in flexural strength and fracture toughness at ≤1 wt% of rGO, which is due to the low crystallinity, high vacancy defects in rGO, and increased interfacial thermal resistance [8]. The declining thermal conductivity behaviors of AlN composites with these three carbon based 2D fillers exhibited almost similar results as GNP, GNS, and rGO basically.

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Sintering additives</th>
<th>Thermal conductivity (W/mK)</th>
<th>Mechanical properties</th>
<th>Sintering temp/ method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN</td>
<td>1.5 wt% CeO</td>
<td>156</td>
<td>72.46 kg/mm²</td>
<td>1900°C/SSR</td>
<td>[2]</td>
</tr>
<tr>
<td>AlN</td>
<td>2 wt% Sm₂O₃</td>
<td>120</td>
<td>—</td>
<td>1700°C/SPS</td>
<td>[3]</td>
</tr>
<tr>
<td>AlN</td>
<td>Y₂O₃-CaO-B</td>
<td>90</td>
<td>—</td>
<td>1650°C/SPS</td>
<td>[4]</td>
</tr>
<tr>
<td>AlN</td>
<td>CaZrO₂-Y₂O₃</td>
<td>156</td>
<td>560 MPa</td>
<td>1550°C/Two-step</td>
<td>[5]</td>
</tr>
</tbody>
</table>

Table 1. Physical properties of AlN ceramics with the addition of sintering additives and densification methods.

2.1.2. AlN composites with GNP/GNS/rGO: electrically conducting

Carbon based nanostructured materials such as graphene nanoplatelets (GNP) or nanosheets (GNS) were added to AlN matrix to improve physical properties (Table 2). The electrical conductivity was increased with the addition of multilayer graphene as expected but the thermal conductivity was decreased with the addition in both in-plane and through-plane direction, which is adverse to other ceramic/graphene composites data. This sharp decline of thermal conductivity in both directions seems attributed to the large thermal resistance at the thin interaction zone existing in the interface between AlN and GNP [6]. The high directionality in the in-plane and through-plane of AlN/GNP composites, 74 W/mK for in-plane and 37 W/mK for through-plane, is ascribed to the thermal contact resistance existing in both phase interfaces that are severe in the perpendicular heat transfer direction of graphene nanoplatelets [7]. This strong directionality in heat transfer, thermal conductivity, can be easily found in the boron nitride (BN)/polymer composite system, in which 2D morphology BN filler materials are used [9–16]. In case of reduced graphene oxide (rGO) added AlN, the thermal conductivity decreased sharply from 92.5 to 37.4 W/mK when 2 wt% of rGO was added, though there are minor increases in flexural strength and fracture toughness at ≤1 wt% of rGO, which is due to the low crystallinity, high vacancy defects in rGO, and increased interfacial thermal resistance [8]. The declining thermal conductivity behaviors of AlN composites with these three carbon based 2D fillers exhibited almost similar results as GNP, GNS, and rGO basically.
had the same morphology and physical properties. High thermal conductivity materials with high directionality in heat transfer can be used in specific directional heat dissipation applications as thermal interface materials (TIM) (Figures 2 and 3).

2.1.3. $\text{Si}_3\text{N}_4$ base ceramics

Silicon nitride ($\text{Si}_3\text{N}_4$) ceramics has been drawing a lot of interest as a high thermal conductivity dielectric material used in insulated metal substrate (IMS) for power electronic circuit modules. $\text{Si}_3\text{N}_4$ have several benefits: high mechanical properties (flexural strength >800 MPa, Vickers' hardness >10 GPa), high electrical resistivity, and excellent thermal properties with thermal resistance, high thermal conductivity 70–180 W/mK. However, in reality, fabrication of $\text{Si}_3\text{N}_4$ with high thermal conductivity and high mechanical strength is not easy due to difficulties in densification and morphological control in microstructure. Typical approaches to get such a high performance $\text{Si}_3\text{N}_4$ are: (i) using raw materials with low oxygen to remove Si vacancies that cause phonon scattering, (ii) fabrication of $\text{Si}_3\text{N}_4$ ceramics with textured microstructure to utilize thermal anisotropy in $\text{Si}_3\text{N}_4$ crystals, (iii) using non-oxide sintering additives with low oxygen content to avoid oxygen content from the oxide phase, and (iv) selecting optimal additives that can minimize the Si vacancies [9]. Some of selected results based on these approaches

$$\begin{array}{|c|c|c|c|c|}
\hline
\text{Chemical composition} & \text{Additives} & \text{Thermal conductivity (W/mK)} & \text{Mechanical properties} & \text{Sintering temp./ method} & \text{Ref.} \\
\hline
\text{AlN-2.9 wt%Y}_2\text{O}_3,\text{GNP-10 vol%} & \text{GNP 0.1 vol%} & 74 \text{ (in-plane)} & \text{—} & 1700-1750/\text{SPS} & [6] \\
\text{—} & 37 \text{ (through-plane)} & & & & \\
\text{AlN-2wt%Y}_2\text{O}_3 & \text{GNS 1.49 vol%} & \text{—} & \text{FS = 441 MPa} & 1850/\text{hot press} & [7] \\
\text{AlN} & \text{rGO 1 wt%} & 92.5 \text{ (2 wt%)} & \text{FS = 375 MPa} & 1550/\text{SPS} & [8] \\
\hline
\end{array}$$

Table 2. Physical properties of AlN with carbon nanomaterials addition.

Figure 2. AC electric conductivity (a) and thermal conductivity data (b) with GNP content in the AlN composites [6].
are summarized in Table 4. When non-oxide additives like YF$_3$ was added to Si$_3$N$_4$, the mechanical strength and thermal conductivities were improved from 40 to 52; it was further increased to 75 W/mK after the annealing treatment at 1850°C. However, Vickers’ hardness was decreased slightly due to larger particle sizes than with the Y$_2$O$_3$ addition [9]. The thermal conductivity of Si$_3$N$_4$ increased up to 100 W/mK when Yb$_2$O$_3$/SiO$_2$ was added and the dielectric loss was decreased from $11.5 \times 10^{-4}$ to $1.4 \times 10^{-4}$ (2 GHz) by adjusting the ratio from 0.33 to 1.3 [10]. The influence of nitration and sintering conditions on the mechanical and thermal properties of the sintered reaction bonded Si$_3$N$_4$ (SRBSN) with Y$_2$O$_3$-MgO additives, and the coarsening of grain size and aspect ratio decreased the hardness and fracture toughness while increasing the thermal conductivity. Vickers’ hardness of 17.32 GPa, fracture toughness of 8.36 MPa·m$^{1/2}$, and thermal conductivity of 98.52 W/m·K were obtained by adjusting nitration and gas pressure sintering (GPS) [11].

A comparative study of the effects of oxide and non-oxide additives on the microstructure, lattice oxygen content, and thermal conductivity of Si$_3$N$_4$ ceramic was investigated. Non-oxide additives such as MgSiN$_2$, YF$_3$, YbF$_3$ induced a decrease in the amount of secondary phases and lattice oxygen contents, thus increasing thermal conductivity from 65 to 101.5 W/mK, while the flexural strength was not affected significantly [12].

2.1.4. AlN-BN base composites: electrically insulating

Boron nitride (BN) was introduced in the AlN matrix to realize low dielectric constant and moderate thermal conductivity [17]. Boron nitride (h-BN) has a hexagonal structure with good thermal shock resistance and high thermal conductivity together with directional preference in heat transfer, i.e., anisotropy in thermal conductivities at in-plane and through-plane of the substrate due to the 2D shape of the BN flake or BN nanosheet. The in-plane and through-plane thermal conductivities are about 300 and 30 W/mK, and the average apparent value is 33 W/mK. The h-BN has low dielectric constant and loss tangent, $\varepsilon_r = 4-4.6$, tan $\delta = 0.0012-0.0017$ at 8.8 GHz, and dielectric strength at AC = 67–95 kV, which varies depending on the purity. BN has been used in many applications due to these excellent properties, for example, in microelectronic packaging especially in thermal management parts such as heat sinks and power electronic substrates, etc. The addition of BN to AlN also can improve chemical resistance and moisture resistance since the AlN can be hydrolyzed slowly in water (Table 3).
In the AlN–BN composites with 8 wt% $\text{Sm}_2\text{O}_3$-$\text{CaF}_2$ as sintering aid, the highest thermal conductivity of 85 W/mK and lowest loss tangent of $4 \times 10^{-3}$ were achieved at the sintering temperature of 1800°C by the SPS method. The obtained thermal conductivity was lower than that of pure AlN because the platelet BN particles randomly distributed along the AlN matrix hinders direct contact of AlN so that phonon scattering is inhibited [17]. When yttrium oxide ($\text{Y}_2\text{O}_3$) from 3 to 8 wt% is added to the AlN–15%BN composites, the thermal conductivity was increased from 110 to 140 W/mK, which is attributed to the significant decrease in residual grain boundary phase containing yttrium by using SPS method [18]. The addition of $\text{CaF}_2$ and increasing temperature also improved the densification, thermal conductivity, and grain boundary purification at the AlN–BN system. As a result, high thermal conductivity of 110 W/mK was obtained when 3 wt% of $\text{CaF}_2$ was added and sintered at 1850°C [19]. In the aluminum oxynitride ($\gamma$-AlON)–BN system that was prepared by the self-propagating high-temperature synthesis (SHS) process, platelet shaped h-BN grains are re-oriented during the hot-pressing process resulting in the anisotropy of thermal conductivities. The thermal conductivity of ($\gamma$-AlON)–BN composites were 14 W/mK for through-plane direction of BN grains and 42.5 W/mK for in-plane direction which is perpendicular to the hot-pressing force [20] (Figure 4).

### Table 3. Thermal conductivities of AlN–BN composites.

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Additives</th>
<th>Thermal conductivity (W/mK)</th>
<th>Sintering temp/method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlN–BN</td>
<td>$\text{Sm}_2\text{O}_3$-$\text{CaF}_2$</td>
<td>40–85</td>
<td>1800/SPS</td>
<td>[17]</td>
</tr>
<tr>
<td>AlN–BN(15%)</td>
<td>$\text{Y}_2\text{O}_3$</td>
<td>141</td>
<td>1800/SPS</td>
<td>[18]</td>
</tr>
<tr>
<td>AlN–BN</td>
<td>$\text{CaF}_2$</td>
<td>110</td>
<td>1850/hot-press</td>
<td>[19]</td>
</tr>
<tr>
<td>(Al-O-N)–BN</td>
<td>$\pm 14, //42.5$</td>
<td>1900/hot-press</td>
<td>[20]</td>
<td></td>
</tr>
</tbody>
</table>

In the AlN–BN composites with 8 wt% $\text{Sm}_2\text{O}_3$-$\text{CaF}_2$ as sintering aid, the highest thermal conductivity of 85 W/mK and lowest loss tangent of $4 \times 10^{-3}$ were achieved at the sintering temperature of 1800°C by the SPS method. The obtained thermal conductivity was lower than that of pure AlN because the platelet BN particles randomly distributed along the AlN matrix hinders direct contact of AlN so that phonon scattering is inhibited [17]. When yttrium oxide ($\text{Y}_2\text{O}_3$) from 3 to 8 wt% is added to the AlN–15%BN composites, the thermal conductivity was increased from 110 to 140 W/mK, which is attributed to the significant decrease in residual grain boundary phase containing yttrium by using SPS method [18]. The addition of $\text{CaF}_2$ and increasing temperature also improved the densification, thermal conductivity, and grain boundary purification at the AlN–BN system. As a result, high thermal conductivity of 110 W/mK was obtained when 3 wt% of $\text{CaF}_2$ was added and sintered at 1850°C [19]. In the aluminum oxynitride ($\gamma$-AlON)–BN system that was prepared by the self-propagating high-temperature synthesis (SHS) process, platelet shaped h-BN grains are re-oriented during the hot-pressing process resulting in the anisotropy of thermal conductivities. The thermal conductivity of ($\gamma$-AlON)–BN composites were 14 W/mK for through-plane direction of BN grains and 42.5 W/mK for in-plane direction which is perpendicular to the hot-pressing force [20] (Figure 4).

#### 2.2. Polymer matrix composites with high thermal conductivity ceramic fillers

Polymer matrix composites for thermal management packaging are usually filled with high thermal conductivity ceramics such as AlN, h-BN, and carbon based fillers like carbon nano-

### Table 4. Physical properties of $\text{Si}_3\text{N}_4$ ceramics with the addition of sintering additives and densification methods.

<table>
<thead>
<tr>
<th>Main element $\text{Si}_3\text{N}_4$</th>
<th>Sintering additives</th>
<th>Thermal conductivity (W/mK)</th>
<th>Mechanical properties</th>
<th>Sintering condition</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{YF}_3$, MgO</td>
<td>52–75</td>
<td>87 MPa/14.8 GPa</td>
<td>1750–1850°C/20 MPa</td>
<td>[9]</td>
<td></td>
</tr>
<tr>
<td>$\text{Yb}_2\text{O}_3$, SiO$_2$</td>
<td>46–100</td>
<td>–</td>
<td>1900°C/0.9 MPa</td>
<td>[10]</td>
<td></td>
</tr>
<tr>
<td>$\text{Y}_2\text{O}_3$, MgO</td>
<td>98.5</td>
<td>–/17.52 GPa</td>
<td>1950°C/GPS</td>
<td>[11]</td>
<td></td>
</tr>
<tr>
<td>$\text{MgO}$-$\text{Y}_2\text{O}_3$, MgSiN$_2$-$\text{Y}_2\text{O}_3$, MgSiN$_2$-$\text{Yb}_2\text{O}_3$, MgSiN$_2$-$\text{Yb}_2\text{O}_3$, and MgSiN$_2$-$\text{YF}_3$</td>
<td>101.5</td>
<td>862 MPa</td>
<td>1800°C/250 MPa</td>
<td>[12]</td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Physical properties of $\text{Si}_3\text{N}_4$ ceramics with the addition of sintering additives and densification methods.
fibers (CNTs), graphite or graphene nanosheets (GNSs), and reduced graphene oxide (rGO). Polymers with AlN and h-BN ceramic filler systems are mostly preferred for high thermal conductivity with electrically insulating heat transfer substrates or thermal interface materials (TIM) due to the high thermal conductivity, low dielectric constant and low loss characteristics of AlN and BN ceramics. On the other hand, carbon based fillers are preferred in TIMs where electrically conducting characteristics are allowed.

2.2.1. Polymer: BN composites

In the hexagonal-boron nitride (h-BN) filled polymer composites, the major issues to enhance heat transfer property are surface treatment of h-BN platelet particles to improve the dispersion of the filler particles in the polymer matrix; to lower the interface thermal resistance; and to increase the alignment of h-BN particles to the preferred orientation in order to achieve high directional thermal conductivity in composites. Table 5 summarizes several technical efforts to enhance the heat transfer properties of polymer–BN composites [13–16, 21–24].

A combined technique that uses mechanical vibration and rotating magnetic field induced high degree of alignment of 10% filler loaded composite exhibited 74% improvement in thermal conductivity compared to the unaligned sample by the formation of conductive network and the reduction of the thermal boundary resistance. The reduction in the thermal boundary resistance between h-BN and bisphenol-A based resin was induced by a high degree of alignment of h-BN platelets via the combined process [13].

The effect of AC and DC electric fields on the anisotropically aligned microstructure in the h-BN filled silicone rubber composites was studied. It was found that the degree of re-orientation of h-BN was more effective under the AC than the DC field during the curing process of the h-BN-silicone composite (Figure 5), and the thermal conductivity of the e-field assisted curing composite was about 250% higher than that cured without E-field [14]. In a recent study, the largest total number of linear densely packed BN nanosheets (LDPBNs) was formed by applying AC field, and thickening of LDPBNs and narrowing of interparticle gaps were achieved by applying a switching DC field (Figure 6). As a result, the thermal conductivity was increased four times that of the composite without LDPBN structure [15].

Figure 4. Compositional dependence of thermal conductivity of the composites in the (γ-AlON)–BN system determined in (a) perpendicular and (b) parallel to the pressing force [20].
A flexible h-BN/poly(vinyl alcohol) composite tape was fabricated by the infiltration of poly(vinyl alcohol) (PVA) solution into the h-BN stack with vacuum filtration to reduce the gap between the h-BN particles and to increase the degree of alignment of h-BN platelets. The in-plane and through-plane thermal conductivities of h-BN/PVA composites thus obtained were 1.63 and 8.44 W/mK, respectively [16]. In the same h-BN/PVA system, the degree of the orientation of h-BN platelet particles can be improved by pressure assisted casting [24], where the degree of orientation of the h-BN particle can be observed by the characteristic peaks in the X-ray diffraction (XRD) data. In order to boost the alignment of h-BN particles, the coating of electric or magnetic field sensitive materials such as TiO$_2$ or Fe$_3$O$_4$ ceramics on to the h-BN

<table>
<thead>
<tr>
<th>Composition</th>
<th>BN %</th>
<th>Thermal conductivity (W/mK)</th>
<th>BN align method</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BN-epoxy</td>
<td>10–20</td>
<td>74% ↑</td>
<td>Mechanical and magnetic</td>
<td>[13]</td>
</tr>
<tr>
<td>BN-silicone</td>
<td>20</td>
<td>250% ↑</td>
<td>E-field(AC, DC)</td>
<td>[14]</td>
</tr>
<tr>
<td>BN-polysiloxane</td>
<td>15 vol%</td>
<td>400% ↑</td>
<td>AC/switching DC</td>
<td>[15]</td>
</tr>
<tr>
<td>BN–PVA</td>
<td>27 vol%</td>
<td>1.63 W/mK ↓/8.44 W/mK/</td>
<td>PVA solution infiltration</td>
<td>[16]</td>
</tr>
<tr>
<td>BN–polyurethane acrylate (PUA)</td>
<td>30 vol%</td>
<td>190%↑(in-plane) 72%(through-plane)</td>
<td>e-field (TiO$_2$-coated BN)</td>
<td>[21]</td>
</tr>
<tr>
<td>BN–PEN(poly(arylene ether nitride))</td>
<td>30 wt%</td>
<td>140%</td>
<td>Magnetic + mussel inspired co-modification (Fe$_3$O$_4$/PDA + KH550)</td>
<td>[22]</td>
</tr>
<tr>
<td>BN</td>
<td></td>
<td>3.49 W/mK(45.4%)</td>
<td>Silane coupling agents with different carbon chain</td>
<td>[23]</td>
</tr>
<tr>
<td>BN–PVA</td>
<td>50 vol%</td>
<td>1.1 W/mK ↓/13 W/mK/</td>
<td>Mechanical exfoliation, compression</td>
<td>[24]</td>
</tr>
</tbody>
</table>

Table 5. Examples of thermal conductivities of polymer–BN composites.
particles are also explored to enhance the thermal conductivity [21, 23]. The h-BN particles coated with TiO$_2$ by the sol–gel process were aligned in a vertical direction to the applied field such that the through-plane thermal conductivity of h-BN/polyurethane acrylate (PUA) composite was increased by 190%, while the in-plane thermal conductivity of the composite was decreased by 72% compared to the untreated h-BN composite [21]. High dielectric constant and high thermal conductivity h-BN/poly(arylene ether nitrile) (PEN) composites were developed by magnetic alignment of h-BN through the coating of magnetic Fe$_3$O$_4$ particles together with an additional surface modification by polydopamine (PDA) and functional monomer KH550: (3-aminopropyl) triethoxy-silan. These surface modifications improved the dispersion of h-BN fillers in PEN matrix and the interfacial adhesion. In the BN/Fe$_3$O$_4$/PDA + KH550/PEN composite system, both dielectric constant and loss tangent were increased significantly with the amount of BN/Fe$_3$O$_4$/PDA + KH550, and the thermal conductivity was increased by 140% compared to the neat PEN film [22]. The enhancement of thermal conductivity in h-BN/epoxy composites through the surface modification of h-BN particles via silane coupling agents with different carbon chain has been investigated. The thermal conductivity of h-BN/epoxy composite was improved by 45.4% due to better dispersion of h-BN in epoxy resin than untreated h-BN, which attributed to the higher interfacial affinity of the composite obtained by using longer carbon chain of silane on the h-BN surface [23] (Figures 7, 8, and 9).

The effects of h-BN particle sizes, exfoliation of BN particles, and compression of h-BN/PVA composites on the thermal conductivity behavior were investigated [24]. Figure 10(a) shows that the thermal conductivity of h-BN/PVA composites was increased to almost two times when the as-received h-BN flakes are exfoliated into a thin h-BN nanosheet. Also, h-BN particles with smaller size exhibited a higher thermal conductivity in the h-BN/PVA composites, as shown in Figure 10(b). Further increase in the thermal conductivity of h-BN/PVA composites were realized by uniaxial thermal compression after solution casting of h-BN/PVA composite film at 90°C which is above the glass transition temperature of the PVA polymer. Figure 11 shows FE-SEM micrographs of the cross-sectional views of 30 vol% h-BN/PVA composites before (a) and after compression, which clearly show the h-BN particles alignment perpendicular to the pressing direction (b). The through (transverse)-plane and in-plane thermal conductivities measured by laser flash method are plotted together with theoretical modeling in Figure 12. Two models, arithmetic and Wiener models are used for the calculation of the two-phase composite system with the following equations.
Figure 7. Thermal conductivity of h-BN/PUA composite and TiO₂-coated h-BN/PUA composite before and after electric field alignment: (a) through-plane and (b) in-plane thermal conductivity [21].

Figure 8. Thermal conductivities of neat PEN and BN/Fe₃O₄/PDA + KH550/PEN composite films with various amounts of filler loading content [22].

Figure 9. Thermal conductivities of h-BN/epoxy composites with untreated BN, MPCB (Al₂O₃/epoxy), silane (C3)/BN, and silane (C16)/BN [23].
Figure 10. Effect of mechanical exfoliation (a) and h-BN particle sizes (b) on the through-plane thermal conductivities of h-BN/PVA composites [24].

Figure 11. Cross-sectional views of 30 vol% h-BN/PVA composite films observed by FE-SEM: (a) uncompressed and (b) compressed [24].

Figure 12. Effect of uniaxial compression on the transverse and in-plane mode thermal conductivities of h-BN/PVA composite films: (a) uncompressed and (b) compressed samples [24].
Arithmetic model:

\[
\lambda = c\lambda_1 + (1 - c)\lambda_2
\]  

(1)

where, \(c\) = proportion of component 1.

\(1 - c\) = proportion of component 2.

\(\lambda_1, \lambda_2\) = thermal conductivity of component 1, 2.

Wiener model:

\[
\frac{\lambda}{\lambda_2} = \frac{(1 - c)((1 - \lambda_1/\lambda_2)/(1 + \alpha \lambda_1/\lambda_2))}{(1 + \alpha c((1 - \lambda_1/\lambda_2)/(1 + \alpha \lambda_1/\lambda_2)))}
\]  

(2)

where, \(\alpha = 0.5\) for dispersion model, \(\lambda_1 < \lambda_2\).

In this calculation, the thermal conductivity of PVA and h-BN was assigned as 0.2 and 33 W/mK, respectively. The in-plane, perpendicular to the compressing direction, thermal conductivities were 5 times higher than those of through-plane at the un-compressed samples, and had 10 times higher values at the compressed samples. The highest thermal conductivity obtained at 50 vol% h-BN loaded PVA composite was 13 W/mK in the in-plane mode, while that of through-plane mode was about 1.1 W/mK, which is lower than that of the uncompressed sample [24]. The decrease in the through-plane mode thermal conductivity at the h-BN/PVA composites is due to the reduction in through-plane particle contact by the alignment of h-BN platelets parallel to the in-plane direction, which results in the increasing in-plane thermal conducting paths and decreasing through-plane thermal conducting paths. The Wiener model seems more close to the experimental data than the arithmetic model but the gap between these theoretical and experimental data is wide indicating that there still remain many factors that should be improved to reach an optimum condition in the fabrication of polymer/ceramic composites with high thermal conductivity.

In summary, several methods were explored to increase the thermal conductivity of h-BN/polymer composites. Examples are (i) surface modification of h-BN particles with functional organics to improve the affinity and dispersion of the h-BN/PVA solution, (ii) coating dielectric and ferrous ceramic materials on the h-BN particle to increase the alignment performance with the application of electric and magnetic field, (iii) exfoliation of h-BN flakes into thin h-BN nanosheets for better particle connection in a given filler loading, and (iv) mechanical compressing to promote particle alignment and inter-particle contact.

2.2.2. Polymer: AlN composites

Aluminum nitride (AlN) is a priority choice for filler material in high thermal conductivity polymer/ceramic composites since it has high thermal conductivity (320 W/mK, theoretical), good insulating (electrical resistivity > $10^{14}$ Ω·cm) characteristic, low dielectric constant (2.2–3.7 at 1 MHz), and low CTE (4.4 ppm/°C) which is close to silicon. In hot-pressed AlN/PMMA (poly-methyl methacrylate) composites, thermal conductivity of 1.87 W/mK was obtained at 70 vol% AlN loaded composite which is about 10 times higher than the PMMA resin (0.18 W/mK) as shown in Figure 13(a). The dielectric constant and loss of the composite were 4.4 (Figure 13(b)) and
In the polypropylene (PP)/AlN composites with 3-D segregated structure made by mechanical grinding of PP and AlN mixture followed by hot-pressing at 190°C, core–shell structured PP/AlN composites were obtained. The comparative results of this 3D core–shell structure composite with conventional solution and melt mixed composites revealed that this mechanically ground composite with 10 vol% AlN showed 23% higher thermal conductivity than the others [26]. Thermal conductivity of aluminum nitride loaded poly(propylene glycol) (PPG) fluidic solution was also studied and the results have shown that the thermal conductivities of AlN/PPG fluids were dependent on the AlN solid loading and molecular weight of PPG [27].

In summary, in spite of efforts to increase thermal conductivity in polymer/ceramic composites, the thermal conductivities obtained in polymer matrix ceramic filled composites are still far below that of the fully ceramic base materials due to the low thermal conductivities in the polymer matrix which is limited in improving thermal conductivity when they are electrically insulating. So, further elaboration is needed in the development of high thermal conductivity polymers with electrical insulation to get the utmost high thermal conductivity in polymer/ceramic composites, since the thermal conductivities of filler ceramics are more likely to depend on their own intrinsic nature and are hardly changed by material science and engineering manipulation.

2.3. LTCC ceramics with high thermal conductivity

Low temperature co-fired ceramics (LTCC) have several benefits in microelectronic packaging. Typical sintering temperature of LTCC is below 1000°C, so they can be co-fired with highly conductive electrodes such as silver (Ag) or copper (Cu) metal. Most of the current LTCC materials are composed of low temperature melting glass matrix and ceramic fillers for functional adjustment such as electrical, mechanical, and thermal properties depending on the requirement of the application. Hence, LTCC is sometimes called glass–ceramics but technically, LTCC is part of glass–ceramic composites. For example, in the field of high frequency (RF, microwave, and mm wave) devices and packaging substrates, low loss and low dielectric constant ceramic powder such as alumina (Al₂O₃) powder is added to the low loss glass matrix. As a result, secondary phases are evolved during the heat treatment process due to part of the alumina filler particles being subjected to react with glass matrix. Interestingly, these secondary phases contribute to the improvement of dielectric properties and mechanical strength when proper filler particle and matrix composition are selected. LTCC has been used for many applications due to energy saving in the low temperature sintering process, excellent dielectric properties,
and ease in 3D integration and miniaturization. Examples are radio frequency-system in-a-package (RF-SiP) module, LED packages, high temperature sensors, microelectromechanical system (MEMS) package, micro-heaters, microfluidics etc. [28–38].

2.3.1. Glass-ceramic base LTCC system

Recently, the use of high thermal conductivity with insulating ceramic substrate is rapidly increasing to enhance the heat transfer property of integrated electronic device and package. Since the conventional LTCCs are based on the glass matrix ceramic composite (GMC) system with low thermal conductivity of the glass phase (1–2 W/mK), the thermal conductivity of most LTCCs are as low as 2–5 W/mK as shown in Table 6 [38–44], which is still higher than FR-4 (typically 0.1–0.2 W/mK) substrate but far lower than high thermal conductivity bulk ceramics such as alumina, AlN, or Si$_3$N$_4$.

Increasing the thermal conductivity in the glass–ceramic system can be realized by recrystallization, addition of high thermal conductivity fillers such as Al$_2$O$_3$, AlN, BN, and Si$_3$N$_4$ particles.

### Table 6. Physical properties of commercial LTCC systems and some of recent research works on high thermal conductivity glass–ceramics.

<table>
<thead>
<tr>
<th>Category</th>
<th>Maker code/ Chemical composition</th>
<th>Sintering temp (°C)</th>
<th>Thermal conductivity (W/mK)</th>
<th>CTE (ppm/°C)</th>
<th>Dielectric constant</th>
<th>Dielectric loss</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial products</td>
<td>ESL41110-70C</td>
<td>—</td>
<td>2.5–3</td>
<td>6.4</td>
<td>4.3</td>
<td>0.004</td>
<td>[37, 38]</td>
</tr>
<tr>
<td></td>
<td>Heraeus CT2000</td>
<td>850</td>
<td>3</td>
<td>5.6</td>
<td>9.1</td>
<td>0.002</td>
<td>[37, 39]</td>
</tr>
<tr>
<td></td>
<td>DuPont 951</td>
<td>850</td>
<td>3.2–3.9</td>
<td>5.8</td>
<td>7.8</td>
<td>0.006</td>
<td>[37, 40]</td>
</tr>
<tr>
<td></td>
<td>DuPont 9K7</td>
<td>850</td>
<td>4.6</td>
<td>4.4</td>
<td>7.1</td>
<td>0.001</td>
<td>[37, 41]</td>
</tr>
<tr>
<td></td>
<td>DuPont 943</td>
<td>850</td>
<td>4.4</td>
<td>6</td>
<td>7.4</td>
<td>0.002</td>
<td>[37, 42]</td>
</tr>
<tr>
<td></td>
<td>Ferro A6</td>
<td>850</td>
<td>2</td>
<td>7</td>
<td>5.9</td>
<td>0.002</td>
<td>[37, 43]</td>
</tr>
<tr>
<td></td>
<td>Murata</td>
<td>850</td>
<td>2.5</td>
<td>5.5</td>
<td>7.7</td>
<td>—</td>
<td>[37, 44]</td>
</tr>
<tr>
<td>Research works</td>
<td>MgO–CaO–Al$_2$O$_3$–SiO$_2$</td>
<td>900</td>
<td>1.95–2.6</td>
<td>8</td>
<td>—</td>
<td>—</td>
<td>[33, 45]</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$–BBSZ glass</td>
<td>850</td>
<td>7.2</td>
<td>6.9</td>
<td>10.9</td>
<td>0.009</td>
<td>[46]</td>
</tr>
<tr>
<td></td>
<td>ZnTiO$_3$–B$_2$O$_3$</td>
<td>900</td>
<td>6.6</td>
<td>—</td>
<td>20</td>
<td>0.001</td>
<td>[47]</td>
</tr>
<tr>
<td></td>
<td>ABS–MWCNT</td>
<td>—</td>
<td>2.2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>[48]</td>
</tr>
<tr>
<td></td>
<td>CAS + β-Si$_3$N$_4$</td>
<td>850</td>
<td>7.9</td>
<td>—</td>
<td>7.1</td>
<td>0.006</td>
<td>[49]</td>
</tr>
<tr>
<td></td>
<td>LZT–LMZBS</td>
<td>900</td>
<td>5.8</td>
<td>—</td>
<td>11.97</td>
<td>—</td>
<td>[50]</td>
</tr>
<tr>
<td></td>
<td>Glass–diamond</td>
<td>750</td>
<td>9.01</td>
<td>4.35</td>
<td>—</td>
<td>—</td>
<td>[51]</td>
</tr>
<tr>
<td></td>
<td>Al$_2$O$_3$/glass+ AlN whisker/carbon fiber/ copper fiber</td>
<td>850</td>
<td>38.9</td>
<td>4.6–6.1</td>
<td>6.6–7.4</td>
<td>—</td>
<td>[52]</td>
</tr>
<tr>
<td></td>
<td>Borosilicate glass–AlN–β-Si$_3$N$_4$</td>
<td>850</td>
<td>18.8</td>
<td>4.2–4.4</td>
<td>6.5</td>
<td>0.0016</td>
<td>[53]</td>
</tr>
</tbody>
</table>

BBSZ: Bi$_2$O$_3$–ZnO–B$_2$O$_3$–SiO$_2$. ABS: Al$_2$O$_3$–B$_2$O$_3$–SiO$_2$. CAS: CaO–Al$_2$O$_3$–SiO$_2$. LZT: Li$_2$ZnTi$_2$O$_7$. LMZBS: Li$_2$O–MgO–ZnO–B$_2$O$_3$–SiO$_2$. 

Table 6. Physical properties of commercial LTCC systems and some of recent research works on high thermal conductivity glass–ceramics.
Various types of filler particle morphologies such as platelet, fibrous types are addressed to improve the inter-particle contact to lower interfacial heat resistance and tailor heat transfer directionality in the substrate. Microstructural manipulations such as filler particle re-orientation, low thermal conductivity, secondary phase removal, and grain boundary control are also explored. Among them, some of key research works are summarized in Table 6 [33, 45–53].

In the alumina (Al$_2$O$_3$) filled glass–ceramic system, MgO–CaO–Al$_2$O$_3$–SiO$_2$, the addition of alumina decreased the thermal conductivity of the glass–ceramic, where diopside or anorthite phase is a major re-crystallized secondary phase as shown in Figure 14. The thermal conductivities of diopside-based and anorthite-based glass–ceramics that sintered at <1000°C are 2.37 and 2.35 W/mK, respectively. It was found that the crystallinity is a more important factor than the ratio of diopside and anorthite such that the highest bending strength and thermal conductivity were obtained at the samples with high crystallinity, since the main peak intensities in the XRD patterns of glass–ceramics is linearly proportional [33, 45]. In the 40 wt% alumina–60 wt% BSSZ (Bi$_2$O$_3$–ZnO–B$_2$O$_3$–SiO$_2$) glass system [46], the reported thermal conductivity of 7.2 W/mK is unusually high compared to that of previously known glass–ceramics [38–44] with a high dielectric constant of 10.9 and low loss of 0.009 at the sintered tape.

Aluminoborosilicate (ABS) glass-ceramics containing ≤15 wt% of multiwalled carbon nanotubes (MWCNTs) exhibited an improvement of electrical conductivity by ~10$^6$ and a thermal conductivity by ~70%. The maximum electrical conductivity of 2.1 S/cm was obtained when 15 wt% MWCNTs was added to an ABS base LTCC, while that of pure ABS was only ~10$^{-6}$ S/cm. The percolation threshold exists at the 2.5–5 wt% MWCNTs added region owing to the uniform dispersion of MWCNTs up to 10 wt%, which is a relatively higher loading rate than others [48] (Figure 15).

In the calcium aluminosilicate (CAS) glass system, the thermal conductivity was increased from 1.6 to 7.9 W/mK when 35 vol% of β-Si$_3$N$_4$ whiskers added to CAS–Si$_3$N$_4$ composites were sintered at 775–850°C in air (Figure 16). This thermal conductivity is much higher than other LTCC systems reported [38–44, 46, 47, 50]. However, the thermal conductivity was decreased when the β-Si$_3$N$_4$ whiskers loading exceed 35 wt%. The dielectric constant and loss measured at 1 MHz were 7.1 and 0.006, respectively [49].
The Li$_2$ZnTi$_3$O$_8$ (LZT) system with 1 wt% of LMZBS (Li$_2$O: MgO: ZnO: B$_2$O$_3$: SiO$_2$ = 1: 1: 1: 1: 1) as a sintering aid, thermal conductivity of 5.8 W/mK, and CTE of 11.97 ppm/°C were obtained at samples sintered at 875°C. High dielectric constant and loss of the LZT–LMZBS system at 1 MHz were 24.14 and 5.1 × 10$^{-4}$, respectively. Microwave dielectric properties of the sintered tape measured by split post dielectric resonator (SPDR) technique were $\varepsilon_r = 21.9$, $\tan\delta = 6 \times 10^{-4}$ at 5 GHz, and $\tau_c$ of −29 ppm/°C [50] (Figure 17).

Glass–ceramics filled with 3–40 μm size monocrystal diamond particles were studied, and the results showed highest thermal conductivity at the glass–diamond composites with 30 μm size diamonds that sintered at 750°C and revealed the lowest CTE, the highest thermal conductivity and bending strength: 4.35 ppm/°C, 9.01 W/mK, and 108.25 MPa [51] (Figure 18).

The Li$_2$ZnTi$_3$O$_8$ (LZT) system with 1 wt% of LMZBS (Li$_2$O: MgO: ZnO: B$_2$O$_3$: SiO$_2$ = 1: 1: 1: 1: 1) as a sintering aid, thermal conductivity of 5.8 W/mK, and CTE of 11.97 ppm/°C were obtained at samples sintered at 875°C. High dielectric constant and loss of the LZT–LMZBS system at 1 MHz were 24.14 and 5.1 × 10$^{-4}$, respectively. Microwave dielectric properties of the sintered tape measured by split post dielectric resonator (SPDR) technique were $\varepsilon_r = 21.9$, $\tan\delta = 6 \times 10^{-4}$ at 5 GHz, and $\tau_c$ of −29 ppm/°C [50] (Figure 17).

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The addition of 1D materials such as AlN whiskers, carbon fibers, and copper fibers to the alumina/30 vol% glass composites was studied. The addition of AlN whiskers did not improve the thermal conductivity compared with AlN powder addition and fibrous fillers was more effective in increasing thermal conductivity of the composites. The highest thermal conductivity obtained in these composites was Al$_2$O$_3$/glass with 30 vol% copper fibers that sintered at 850°C as shown in
The specific resistivity of Al₂O₃/30% glass and Al₂O₃/30% glass/30%AlN-whiskers are 2.0–2.1 × 10¹² Ω·cm while those of 30% carbon fiber and 30% copper fiber added composites were 8.7 × 10⁻³ and 3.4 × 10⁻⁶ Ω cm, respectively. Therefore, these two electrically conductive composites are not applicable to electrically insulating thermal management material, or they can be coated with a insulating glass layer on the surface to improve electrical resistivity [52].

In the borosilicate glass–AlN composite LTCC, the thermal conductivity was increased from 11.9 to 18.8 W/mK by the addition of 14 vol% \( \beta \)-Si₃N₄ whiskers as shown in Figure 20. This enhanced...
thermal conductivity may be due to the formation of a thermal conducting path by bridging the isolated AlN particles through β-Si$_3$N$_4$ whiskers. The dielectric properties of this composites are $\varepsilon_r = 6.5$ and $\tan \delta = 0.0016$ at 1 MHz, and the values are not significantly changed with the amount of whiskers due to their similarity in dielectric properties between AlN and Si$_3$N$_4$ [53].

2.3.2. Glass-free LTCC system

Glass-free or non-glass base LTCC systems have been investigated to reduce the complexity of the LTCC systems due to the multiple phases included such as glass, filler particles, and additional sintering additives. Due to their complexity, several problems occurred during the preparation of LTCC circuits and devices in the integrated electronic module. To overcome this complexity in chemical interaction and inhomogeneous dielectric properties and difficulties in slurry dispersion, LTCC systems with simple phase components were developed [54–60] (Table 7).

In a conventional LTCC system, glass was used as a matrix phase to lower the sintering temperatures below 1000°C because the functional dielectric ceramic materials were mostly fully densified at the high sintering temperatures, over 1200°C, where high electrically conductive
metals such as Ag or Cu cannot be used as a matching electrode. LTCCs containing glass phase matrix generally exhibited low thermal conductivity as we have seen in Table 6. In the glass-free LTCCs, lowering the sintering temperature below 1000°C is a primary requirement without introducing secondary phases except the minor content of the sintering agent. Finding a low temperature synthesis and low temperature melting crystalline phase ceramic compound is a crucial point to develop glass-free LTCCs. Glass-free LTCC compositions applicable in the industry with proven mechanical properties and reliabilities are hardly found, even though several primary research results showing excellent dielectric properties were reported [54–60]. The substantial problems exposed in the previous glass-free LTCC systems are weak mechanical strength, reactive with matching electrode materials during heat treatment, and vulnerable in moisture environment.

In the calcium germinates and silicates system, the dielectric constants were 6.5–10.8, quality factor (Q × f) = 16,000–39,000 (@10 GHz), temperature coefficients of dielectric constant were 70–140 ppm/°C for samples sintered at 1180–1200°C, which are slightly higher temperatures for LTCC processing. These systems did not show any chemical reaction with Ag electrode. On the other hand, in the calcium tellurates system, the dielectric constants were 15.5–23.6, Q × f = 13,400–49,300 (~10 GHz), temperature coefficients of dielectric constant were 130–140 ppm/°C; but this system was vulnerable at Ag electrode. The high temperature coefficients of dielectric constant were suppressed by the addition of 10 mol% of CaTiO₃ [54].

For an AMP₂O₇ (A = Ca, Sr.; B = Zn, Cu) system, all of the compounds reacted with Ag but can be co-fired with Cu under reduced atmosphere. Among them, SrZnP₂O₇, sintered at 950°C exhibited a dielectric constant of 7.06, Q × f = 52,871 GHz, and temperature coefficient of resonance frequency (τf) = −70 ppm/°C; therefore, this compound can be modified into a temperature stable composition if a proper counter dielectric material with negative temperature coefficient is mixed with it. The thermal conductivity of this system was not provided [55].

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>Sintering temp (°C)</th>
<th>Thermal conductivity (W/mK)</th>
<th>CTE (ppm/°C)</th>
<th>Dielectric constant</th>
<th>tan δ/ Q factor</th>
<th>Reactivity with electrode</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO–(GeO₂, SiO₂, TeO₃)</td>
<td>780–1200</td>
<td>−</td>
<td>−</td>
<td>6.5–19.3</td>
<td>2.4 × 10³ –1 × 10⁴ (MHz)</td>
<td>N(Ag: germanates, silicate)</td>
<td>[54]</td>
</tr>
<tr>
<td>AMPO₃O₅ (A = Ca, Sr., M = Zn, Cu)</td>
<td>950</td>
<td>−</td>
<td>−</td>
<td>7.06</td>
<td>52,871 (GHz)</td>
<td>Y(Ag: tellurate)</td>
<td>[55]</td>
</tr>
<tr>
<td>LiMgPO₄</td>
<td>950</td>
<td>7.1</td>
<td>10.5</td>
<td>6.4</td>
<td>0.0002</td>
<td>−</td>
<td>[56]</td>
</tr>
<tr>
<td>Bi₂(SiO₄)₃</td>
<td>900</td>
<td>2.82</td>
<td>7.09</td>
<td>13.3</td>
<td>0.0007</td>
<td>−</td>
<td>[57]</td>
</tr>
<tr>
<td>Li₂Mg,Ti,2O₆</td>
<td>925</td>
<td>−</td>
<td>0.45(τf)</td>
<td>27</td>
<td>58,480 (5.8 GHz)</td>
<td>N(Ag)</td>
<td>[58]</td>
</tr>
<tr>
<td>Li₂Zr,Ti,2O₄·LiF</td>
<td>900</td>
<td>4.75</td>
<td>22.4</td>
<td>22.4</td>
<td>35,490 (GHz)</td>
<td>N(Ag)</td>
<td>[59]</td>
</tr>
<tr>
<td>11ZnO-10MoO₃</td>
<td>850</td>
<td>1.3</td>
<td>4.7</td>
<td>11.1</td>
<td>−</td>
<td>−</td>
<td>[60]</td>
</tr>
</tbody>
</table>

Table 7. Compositions and physical properties of glass-free LTCC systems.
In the LiMgPO$_4$ tape sintered at 950°C, the microwave dielectric properties were, $\varepsilon_r = 6.4$, $\tan \delta = 0.0002$, CTE = 10.5 ppm/°C, and the thermal conductivity was 7.1 W/mK, which is twice as high as that of conventional glass–ceramic based LTCCs. The microwave dielectric properties of sintered tape were measured by using split post dielectric resonator (SPDR) method connected with a vector network analyzer [56].

Bi$_4$(SiO$_4$)$_3$ glass-free LTCC tape system has shown dielectric constant of 13.3, loss ($\tan \delta$) of 0.0007 at 15GHz, and thermal conductivity of 2.82 W/mK [57]. The Li,Mg,TiO$_4$ glass-free ceramics sintered at 925°C exhibited a dielectric constant of 27, Q × f value of 58,480 GHz (at 5.8 GHz), and very stable temperature coefficient of resonance frequency $\tau_f = 0.45$ ppm/°C. This system is compatible with silver electrode [58]. Another Li-base glass-free LTCC is Li$_{20.8}$TiO$_3$–LiF system, where the microwave dielectric properties of $\varepsilon_r = 22.4$, Q × f = 35,490 GHz were obtained at the 900°C sintered tape. The CTE and thermal conductivity of the system were 22.4 ppm/°C and 4.75 W/mK, respectively. The system also is compatible with silver electrode and has a high insulating rate of 50 kV/mm that has a potential in high power application. For the aforementioned glass-free system, the thermal conductivities obtained are 2.28–7.1 W/mK, which is well above that of the most of conventional glass–ceramic base LTCCs [59].

3. Summary and future prospects

In this chapter, recent research and development works on high thermal conductivity ceramics and their composites for thermal management of integrated electronic packages are briefly explored. Key lessons drawn from these prior works can be summarized as follows:

3.1. High thermal conductivity bulk ceramics

Most frequently found HTCC base high thermal conductivity ceramics are alumina and nitride ceramics such as AlN, BN, and Si$_3$N$_4$ materials. Among them, silicon nitride ceramic seems the most frequently used in the power electronic applications these days. In nitrides and nitride based ceramic matrix composites, key parameters that control the thermal property are densification including pore removal, grain size and grain boundary control, impurity, and secondary phase control. Among them, densification is the primary factor to achieve high thermal conductivity due to high thermal resistance of pores. These nitride ceramics are difficult to sinter with high density so that spark plasma sintering and two-step sintering methods together with the addition of small amount of sintering aids should be applied to realize high densification. In nitride ceramics, controlling the oxygen content is a very important factor in addition to the parameters required in oxide materials.
In the LTCC-base materials, there are many research works on the development of high mechanical strength LTCC materials but few works are found in the improvement of thermal conductivity of LTCCs. Some works found in the literature are mainly on re-crystallization and phase control in the matrix and show only minor improvement in thermal properties compared with the noticeable enhancement in mechanical properties. The main reason for this minor change in thermal property in the conventional glass–ceramic type LTCC comes from the glass matrix which comprises more than half the volume of the sintered body. The volume fraction of newly evolved nano-crystalline phases through heat treatment process are so small that the overall apparent thermal conductivity might not change significantly while the mechanical strength can be easily boosted by the inclusion of the nano-crystalline phase in the matrix.

In thermally conductive and electrically conducting ceramics composites, the electrical conductivity was improved with the addition of 2D carbon allotropes like graphene nano sheet/platelet; however, the thermal conductivity was decreased with the involvement of graphene in the AlN matrix, which may be due to the thin interaction layer at the AlN–GNS/GNP interface that would cause thermal resistance. Large difference was observed between the in-plane and through-plane thermal conductivity of the composites as can be observed in the polymer/graphene composites.

### 3.2. Polymer matrix composites with high thermal conductivity

Polymer matrix composites with high thermal conductivity and electrically insulating ceramic filler materials are mostly used for dielectric insulation layers in LED packaging substrate for effective heat dissipation to the metallic heat spreading panels. Most frequently used insulating ceramic filler materials are alumina, BN, and AlN powders. Among them, BN platelet powders are preferred due to the anisotropic thermal conductivity behavior in the 2D structure of the BN crystal. Lots of researches have been focused on the tailored re-orientation of BN nanosheets in the BN/polymer solution into in-plane or through-plane of the BN/polymer composite tape using magnetic and electric field during casting process. Also, there are some efforts to coat ferrous or dielectric nano particles on BN platelet particles to promote the easy alignment of BN platelet particles into the intended direction. Surface modification of BN particles with functional organics such as silane coupling agent, dopamine, and secondary functional monomers are applied to enhance the thermal conductivity of the composites by improving the BN/polymer affinity and interfacial adhesion, thereby lowering interfacial heat resistance.

Polymer matrix composites with high thermal conductivity inorganic fillers such as CNT, graphite flake, and graphene nanosheets exhibited a great improvement in thermal conductivity with a little amount of additions. However, they are mostly electrically conducting so that they cannot be used for electrical circuit substrates. Instead, these composites are mainly used for thermal interface materials. These polymer/carbon allotropes base composites can also be used for flexible device application as well as rigid substrates since the morphology of carbonates filler particles are 1D or 2D.

### 3.3. High thermal conductivity ceramics for LED and IGBT packages

Ceramic materials used for applications in LED packages are typically of two types: dielectric insulating substrates for circuit forming bed and high thermal conductivity fillers for thermal...
interface material. The insulating ceramic substrates for IGBT modules mostly use alumina, AlN ceramics, but recent development moves to Si$_3$N$_4$ and LTCC for high power device due to reliability or low cost.

3.4. Future prospects

Regardless of the aforementioned progresses in the development and commercialization of ceramics, there are several challenges in the high thermal conductivity ceramic based heat transfer materials:

Continuous efforts in lowering costs and cost-effective processing of high temperature sintering HTCCs with high thermal conductivity are required in materials chemistry and innovative processing techniques. Compared to the HTCC based high thermal conductivity ceramics, LTCCs still require further enhancement in both thermal and mechanical characteristics in order to be adopted in thermal management applications. Since the major part of the conventional LTCC formulation consists of glass, the utmost thermal conductivity of the glass–ceramic filler composites thus obtained is limited and far below that of HTCC based high thermal conductivity ceramics. Therefore, first, we need to investigate ways to improve thermal conductivity of the glass phase itself as it is done in many polymer matrix composites. Second, the mechanical strength of LTCC should be further improved even though some results demonstrated enhanced mechanical strength via recrystallization process through the interfacial reaction and nucleation between glass phase and crystalline filler phase. Other challenges in high thermal conductivity LTCCs may be the development of non-glass base LTCCs, which have already been attempted earlier as applications in RF and microwave dielectric materials. The non-glass based LTCCs are exempted from the usage of low thermal conductivity glass matrix phase; they will exhibit higher thermal conductivity than the conventional type.

There are many reports that state the achievement of high thermal conductivities in polymer matrix composites using high thermal conductivity ceramic fillers. As a practical point of view, however, simply increasing thermal conductivity of ceramic filled polymer composites does not ensure the potential use in thermal management application, especially when they are used as thermal interface materials. Other factors, such as adhesion strength to the substrates or heat sink materials for TIM application and tensile strength of thermal tapes or flexible device substrates, also should be considered in addition to thermal and electrical properties since the more filler loading, the less adhesion and tensile strength is provided.

For insulated metal substrates (IMS) using high thermal conductivity ceramics, a reliable solution for CTE mismatch between ceramic and metal joining inducing delamination and crack generation failure in harsh conditions such as cyclic temperature environment is still required. In addition, for highly effective heat transfer performance IMS, we may need an ultra-thin insulation layer with high dielectric breakdown voltage together with high mechanical strength, which enables both low thermal resistance and low package profile of high power device and module.
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Conflict of interest

None.

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References


[26] Hu M, Feng J, Ng KM. Thermally conductive PP/AlN composites with a 3-D segregated structure. Composites Science and Technology. 2015;110:26-34. DOI: 10.1016/j.compscitech.2015.01.019


[38] Golonka LJ. Technology and applications of low temperature co-fired ceramic (LTCC) based sensors and Microsystems. Bulletin of the Polish Academy of Sciences, Technical Sciences. 2006;54:221-231


[40] http://www.dupont.com, DataSheetofDupontTM Green TapeTM 951


