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Sintering behavior and dielectric properties of ultra-low temperature glass/ceramic composites

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ABSTRACT

Na_2O-K_2O-SiO_2-B_2O_3-Al_2O_3-P_2O_5 (NKAP) glasses with low melting temperatures were obtained by melting. NKAP glass/ceramic composite ULTCC (ultralow temperature co-fired ceramic) materials were prepared at sintering temperature (< 700 °C) by mixing traditional ceramic materials (alumina, quartz and zirconia) and low melting NKAP glasses. Quartz and monolithic zirconia can form stable composites with low melting NKAP glasses. Thus, we prepared ULTCC composite materials containing high amounts of quartz and zirconia. However, alumina and NKAP glasses partially reacted during sintering. Sintering temperature of NKAP glass/ceramic ULTCC composite was lower than 680 °C with the minimum sintering temperature of ˜ 550 °C. All samples containing NKAP glass/quartz ULTCC composites demonstrated excellent dielectric permittivity (equal to 6.51 with loss ˜8×10^{-3}) and mechanical bending strength equal to 82 MPa. Our results can be used for fabrication of multilayer ULTCC packaging structures with tailored physical properties.

1. Introduction

Low temperature co-fired Ceramic (LTCC) technology is very useful in a wide range of applications [1,2]. One of the obvious features of LTCC technology is that passive components can be buried between the LTCC tape layers, minimizing the length of interconnections, improving integration and robustness and further reducing circuit sizes. Currently, many commercial LTCC materials are composed of glass-ceramics and glass/ceramic composites [3,4]. Typically, reliable interface connection between metal layers and glass-ceramic substrates in electronic devices requires sintering temperatures that match melting temperatures of metal electrodes (e.g. silver and copper with melting point at 961 and 1083 °C, respectively). Ultralow temperature co-fired ceramic technologies (ULTCC) recently attracted significant attention to match ultralow-melting metallic electrode materials (e.g. Al with melting point at 660 °C). This will allow ULTCC technology to be expanded to microwave components and device packaging and to become more economical. ULTCC materials can usually be obtained using ultralow temperature sintering processes involving glass-ceramics or glass/ceramic composites [5–7]. Glass materials used as sintering aids during ULTCC preparation must have extremely low softening temperatures to assist in sintering of glass/ceramic composite materials below melting points of ultralow melting metals.

Preparations of such glasses are the key factors for successful preparation of ULTCC composite materials with excellent dielectric properties. Most ULTCC related studies focus on their microwave dielectric properties rather than on those related to packaging materials [3,4]. Very little attention is paid to ultralow melting glass/ceramics ULTCC composites for packaging applications. Preparation of ULTCC glass/ceramic packaging materials needs to be developed to be paired with more economical aluminum electrodes.

Currently, phosphate glasses are widely used in bio- and in high temperature sealing technologies [8–11]. Most phosphate glasses have relatively low softening temperatures and, thus, represent an important research direction towards the search of low melting point glasses [12,13]. In this work, we designed Na_2O-K_2O-SiO_2-B_2O_3-Al_2O_3-P_2O_5 (NKAP) glasses with ultralow softening temperature and then used as a matrix to prepare ULTCC packaging materials. Our ULTCC composites contained alumina, zirconia and quartz as fillers for control and adjustment of dielectric and mechanical properties. Our goal was to develop optimum ULTCC materials for device packaging applications by studying their sintering behavior and physical properties as well as chemical relationship between NKAP glasses and ceramic fillers.

2. Experimental

Reagent-grade NaOH, KOH, H_3BO_3, $Al(OH)_3$, $NaH_2PO_4{\cdot}2H_2O$, ZrO_2 and quartz (all with purity > 99%) were used as starting materials at

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Table 1
Chemical compositions and characteristics of Na_2O-K_2O-SiO_2-B_2O_3-Al_2O_3-P_2O_5 glass[a].

Glass	Chemical composition (wt. %)						T_g(°C) Transition temperature	T_s (°C) Soften temperature	T_f (°C) Melting temperature
NKAP	Na_2O 19	K_2O 10	B_2O_3 5	SiO_2 3	Al_2O_3 28	P_2O_5 35	377	430	520

[a] Na_2O-K_2O-SiO_2-B_2O_3-Al_2O_3-P_2O_5 glass is expressed by an abbreviated form of NKAP.

Table 2
Chemical compositions of ULTCC NKAP glass/ceramic composites.

sample	Glass (wt.%)	Ceramic filler (wt.%)			Sintering temperature
	NKAP	alumina	zirconia	quartz	°C
ZA-1	60	40	–	–	590
ZA-2	50	50	–	–	680
ZZ-1	50	–	50	–	550
ZZ-2	40	–	60	–	630
ZQ-1	50	–	–	50	550
ZQ-2	40	–	–	60	620

the ratios listed in Table 1. Ingredients were weighed, mixed and ball-milled with distilled water (at the water: solid ratio equal to 3:1) for 3 h. After the ball-milling, the slurries were dried overnight at 90 °C, after which the powders were calcined at 700 °C for 3 h. The resulting powders, which had particle sizes of 2–50 μm, were then melted for 2 h at 1100 °C followed by quenching. Compositions of NKAP glass/ceramic ULTCC samples are listed in Table 2.

To prepare ULTCC composites, powders were first prepared by aqueous milling. After drying, the powders were molded into green bodies at ˜320 MPa. Finally, ULTCC composite samples were sintered using the following steps. First, green sample bodies were sintered at 400 °C for 3 h to remove volatile binder components and then sintered for 2 h. (Sintering temperatures for each sample are given in Table 2). NKAP glass powders and aluminum powders were sintered in vacuum at 470 °C to test chemical compatibility between aluminum and NKAP glass.

Microstructures and phase compositions of the ceramic samples were characterized using scanning electron microscopy (JEOL, JSM-7001, Japan) and X-ray powder diffraction (XRD), respectively. XRD patterns were recorded on a D/Max-IIIA (Rigaku Industrial Corporation, Japan) using Cu Kα radiation (at 40 kV and 30 mA) with $2°{\cdot}min^{-1}$ scanning rate. Dielectric properties were measured using an impedance analyzer Kesight E4991B (USA). Bulk densities of the samples were determined using the Archimedes method.

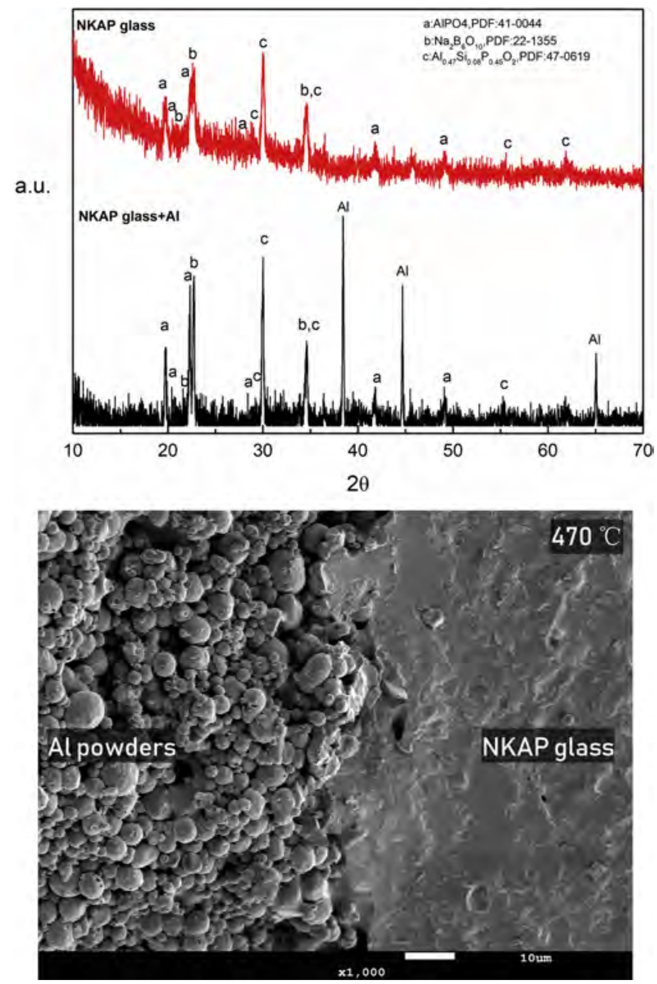

Fig. 1. XRD diffraction patterns of NKAP glass bulk and Aluminum/NKAP glass composites that were sintered in vacuum at 470 °C for 2 h; SEM micrograph of interface layer between Aluminum powders and NKAP glass.

3. Results and discussion

XRD pattern of NKAP glass sintered at 470 °C revealed $AlPO_4$, $Na_2B_6O_{10}$ and $Al_{0.47}Si_{0.08}P_{0.45}O_2$ compounds (see Fig. 1). Glass transition temperature (T_g) of NKAP glass was ˜377 °C according to the DSC analysis (see Fig. 2). Softening temperature (T_s) of NKAP glass determined by thermal expansion analysis was ˜ 430 °C. Melting temperature (T_m) of NKAP glass was ˜520 °C. We investigated chemical compatibility of NKAP glass with aluminum to ensure that no chemical reaction between ULTCC and aluminum occurs. XRD patterns of NKAP glass sintered with metallic Al (shown in Fig. 1) only demonstrated peaks belonging to Al and bulk NKAP glass. Additionally, as shown in SEM image (see Fig. 1) of interface layer between Al powders and NKAP glass, which had been sintered at 470°C, there are chemical stability between Al powders and NKAP glass.Thus, no chemical reaction between aluminum and NKAP glass occurred during sintering. Therefore, aluminum is chemically compatible with the NKAP glasses at elevated temperatures, which is beneficial for further development of NKAP glass/ceramic ULTCC materials. To ensure densification during sintering, ˜40-60 wt.% of ceramic powders (alumina, quartz and zirconia) were mixed with NKAP glass and then sintered below 680 °C for 2 h (see Table 2 for specific sintering conditions). Among these ceramic fillers, alumina addition to glass/ceramic composites was the least: because alumina and NKAP glasses reacted during sintering, fraction of the liquid phases decreased, therefore sintering of ULTCC composites became difficult at relatively low temperatures. Thus, it was necessary to reduce alumina content in ULTCC composites to achieve ultra-low temperature sintering.

Major phases of glass/quartz (ZQ-1 and ZQ-2) and glass/zirconia composites (ZZ-1 and ZZ-2) were quartz and monoclinic zirconia, respectively (see Fig. 3). Secondary phases such as $K_4P_2O_8$ and other SiO_2 crystal were also observed in XRD patterns. Thus, quartz and zirconia are chemically compatibility with NKAP glasses at elevated temperature. Contents of ceramic fillers quartz and zirconia in ULTCC

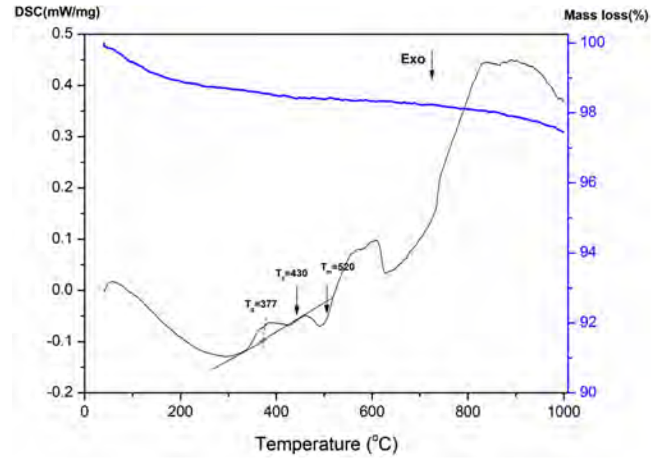

Fig. 2. DSC-TG curves of NKAP glass powders.

composites were increased up to 60 wt%. However, alumina addition to NKAP glasses resulted in chemical reaction, thus, maximum amount of alumina addition to the ULTCC composites is limited. Major phases of NKAP glass/alumina composites were $Na_7(Al_2O_7)_4PO_4$, $K_4P_2O_8$ and $AlPO_4$ (see Fig. 3) indicating that alumina was completely consumed by its chemical reaction with the glass during sintering. In general, reaction between glasses and ceramics can bring uncertainty into their sintering behavior expectations as well as to the design of physical properties of glass/ceramic ULTCC composites.

Because glasses can induce certain liquid-phase sintering properties to obtain denser microstructures, glasses are widely used in device packaging. NKAP glasses represent unique phosphate-based systems with low dispersibility and high refractive characteristics, all of which are extremely useful for optical applications [12]. Low-temperature melting glasses, such as phosphate glasses [13], can assist in achieving ultra-low temperature sintering to prepare ULTCC materials by liquid phase sintering process. SEM analysis of NKAP glass/ceramic ULTCC composites demonstrates very compact microstructures (see Fig. 4). Thus, NKAP glasses, as liquid phase media, can form composites with ceramic powders and provide sintering assistance for densification of ULTCC composites during sintering. Even though contents of quartz and zirconia in ULTCC samples was high (up to 60 wt%), these UTLCC samples still showed dense microstructures, indicating that NKAP glasses can offer sufficient amount of liquid phase for sintering to proceed. Sintering mechanism of the composite ceramics can be explained using liquid phase sintering theory [14]: liquid phases gradually form from NKAP glasses at elevated temperatures. At the same time, through the liquid-phase flow, densification occurs simultaneously with crystal particle dispersion, rearrangement and solid-state sintering. However, alumina addition to NKAP glasses resulted in its reaction with the glass. Thus, chemical reaction at the interface between the liquid phase and ceramic particles significantly decreased liquid phases, which resulted in decreased alumina content in the glass/ceramic composites as well as in poor sintering behavior.

Sintering temperatures for samples ZQ-1 and ZQ-2 were close to those of samples ZZ-1 and ZZ-2 (see Table 2). NKAP glass, acting as a liquid phase flow during sintering, showed similar effect on sintering behavior of the NKAP glass/ceramic ULTCC composites. However, sintering temperature of NKAP glass/alumina ULTCC composites were higher than that of quartz and zirconia composites. Because reaction between alumina and NKAP glass resulted in less liquid phase during sintering, higher sintering temperature were required to obtain more liquid phase to ensure densification.

Chemical reactions of ceramic fillers with glasses can lead to unwanted secondary phases, which might worsen material performance or deviate from the intended properties. Properties of chemically stable glass/ceramic composites can be tailored and designed using empirical formulas such as Maxwell-Wagner equation [15]:

$$\varepsilon_f = \varepsilon_h \frac{2\varepsilon_h + \varepsilon_l + 2V_l(\varepsilon_l - \varepsilon_h)}{2\varepsilon_h + \varepsilon_l - V_h(\varepsilon_l - \varepsilon_h)}$$

where ε is permittivity, V is volume and h and l are phases with high and low permittivity, respectively.

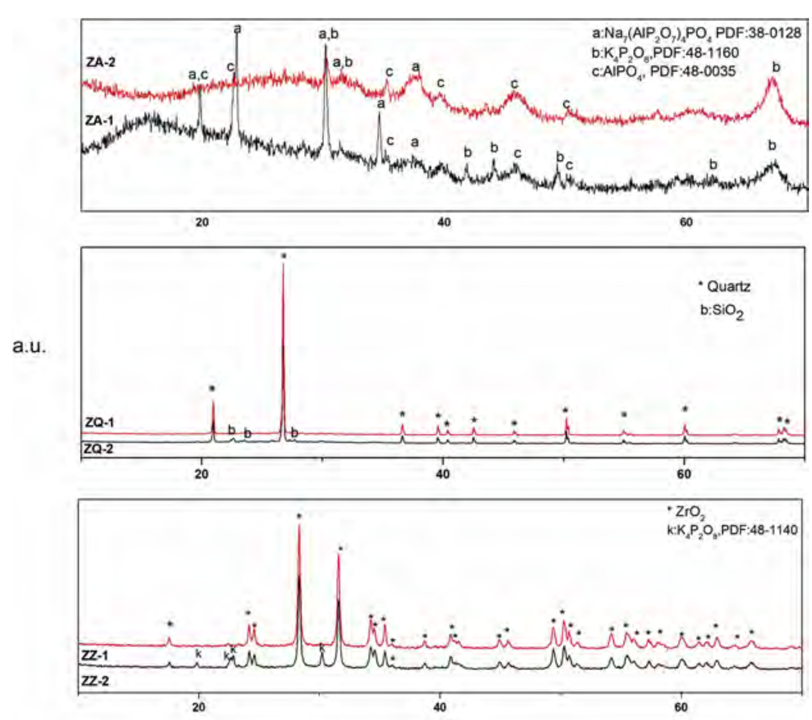

Fig. 3. XRD diffraction patterns of NKAP glass/ceramic ULTCC composite samples (sintering temperature: ZA-1:590 ℃; ZA-2:680 ℃;ZZ-1:550℃; ZZ-2:630℃; ZQ-1:550℃; ZQ-2:620℃).

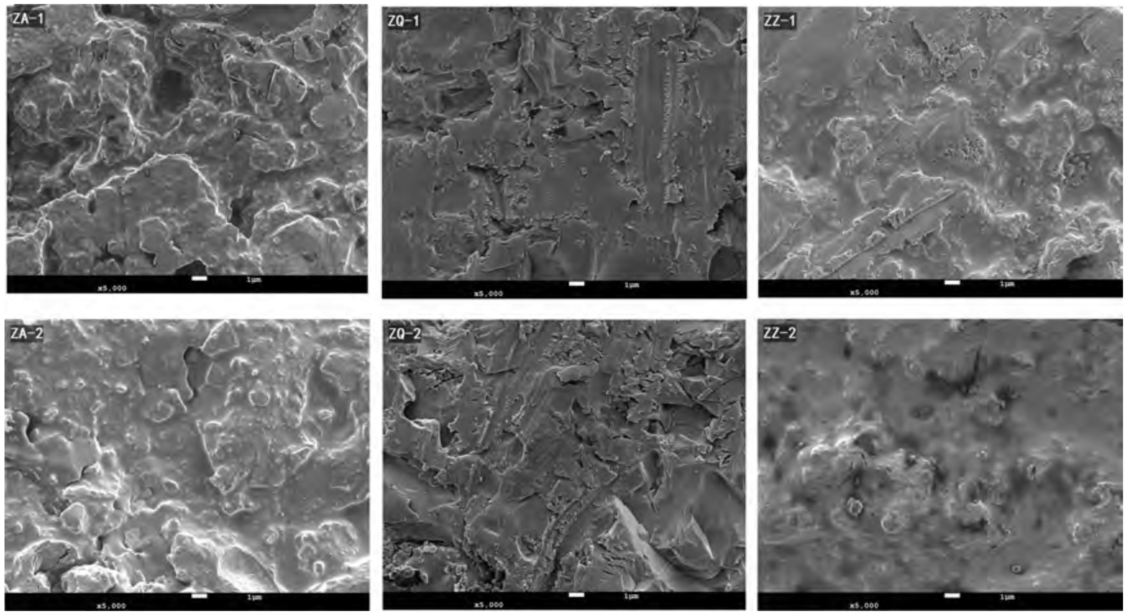

Fig. 4. SEM micrographs of NKAP glass/ceramic ULTCC composite samples (sintering temperature: ZA-1:590 °C; ZA-2:680 °C; ZZ-1:550°C; ZZ-2:630°C; ZQ-1:550°C; ZQ-2:620°C).

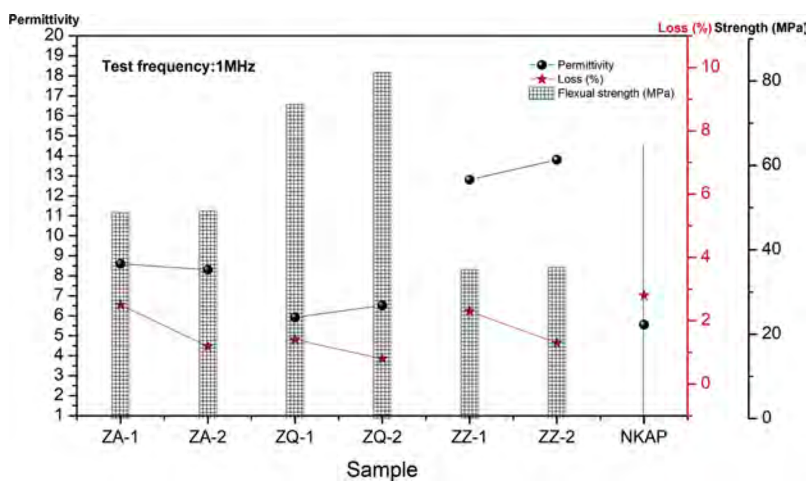

Fig. 5. Physical properties of NKAP glass ULTCC composite materials.

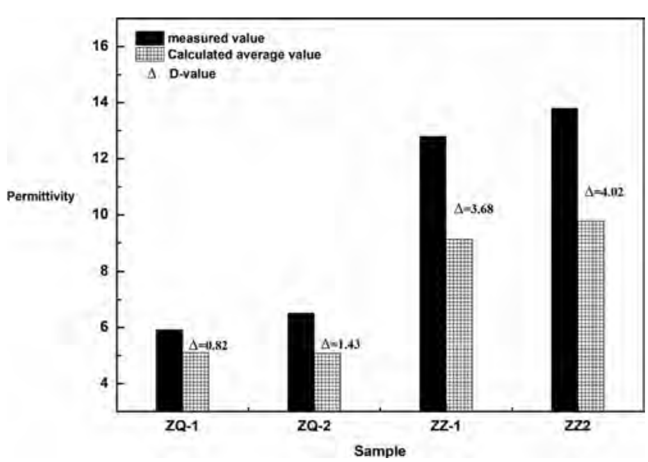

Fig. 6. Comparisons of average calculated values and average measured values for permittivity of ULTCC composite materials.

This equation expresses permittivity of a composite with two phases. Usually, physical properties of ceramics with multi-phases depend on their corresponding major phases. Therefore, UTLCC composite permittivity will be controlled by physical characteristics of ceramic fillers (e.g., quartz or zirconia) and their content in the composite. Quartz-based ULTCC composites exhibited relatively low dielectric constants and losses (see Fig. 5), whereas dielectric constant of zirconia-based ULTCC composite were the highest. Quartz has excellent dielectric properties with permittivity equal to 4.3–4.6 [16,17]. Thus, we expected that quartz addition to ULTCC glass/ceramic composites would improve their dielectric properties. Dielectric constant of ULTCC composite containing 60 wt% quartz (sample ZQ-2) was lower than for the samples with 50 wt% of quartz (sample ZQ-1). Thus, quartz can be used not only to improve but also to tailor dielectric properties of ULTCC or LTCC materials. Another ceramic filler used in ULTCC composite materials, monoclinic zirconia, also has high dielectric constant. So, high dielectric constants of ULTCC samples ZZ-1 and ZZ-2 can be attributed to influence of zirconia. ULTCC composite with alumina showed dielectric constant of ˜8. We believe that dielectric property of alumina ULTCC composite is affected by combination of factors such as microstructure, multiple phases and residual NKAP glasses. In fact, correlations between glass/ceramic ULTCC composite materials and dielectric properties can roughly be expressed using Maxwell-Wagner equation. Thus, using reference permittivity of quartz (4.5), zirconia (˜ 20–22) and of NKAP glass (˜ 6 for the sample sintered at 470°)C, we calculated average values of permittivity for ZQ-1, ZQ-2, ZZ-1 and ZZ-2 samples using *Maxwell-Wagner* equation. Fig. 6 shows some obvious discrepancies between calculated and experimentally obtained values, and this discrepancy increases as ceramic filler content in ULTCC composites increase. We believe that the difference between experimental and calculated permittivity values correlates with microstructures and formation of secondary phases. Thus, to design and to obtain materials with excellent dielectric performance, chemical reactions between glasses and ceramic fillers must be minimized or avoided.

Flexural strength of quartz ULTCC composites was better than for the other ones. Both microstructure of ULTCC composites and mechanical properties of the corresponding ceramic fillers significantly affect mechanical properties of ULTCC composites. Because of excellent mechanical properties of zirconia, its ULTCC composites should demonstrate good flexural strengths. However, flexural strengths of zirconia ULTCC (samples ZZ-1 and ZZ-2) were lower than that of quartz ULTCC samples. Toughness of monoclinic zirconia is weaker relative to other zirconia polymorphs [18], thus, weaker mechanical properties of zirconia ULTCC composites were because we used monoclinic zirconia. Alumina also has excellent mechanical properties; however, alumina ULTCC composites did not demonstrate good flexural strength due to alumina chemical reaction with NKAP glasses during sintering.

Thus, we proposed a convenient method to fabricate ULTCC composite materials by combining ceramic particles with specific properties and basic glasses with low melting temperatures. Physical properties of ULTCC composites can be designed and tailored using specific physical characteristics of the corresponding ceramic components. Ultra-low temperature sintering can be achieved by adding low-melting glasses.

4. Conclusions

(1) We used low-melting Na_2O-K_2O-SiO_2-B_2O_3-Al_2O_3-P_2O_5 (NKAP) glass as a matrix to synthesize NKAP glass/ceramic ULTCC composite materials at ultralow sintering temperature (< 700 °C). Sintering temperatures of quartz and zirconia ULTCC composites were < 630 °C. Their minimum sintering temperatures can be as low as 550 °C. Because of chemical reaction between alumina and NKAP glasses during sintering, alumina addition to the NKAP glass/alumina ULTCC composites are limited to 50 wt%, and their highest sintering temperature is ˜680 °C.

(2) Quartz ULTCC composites showed dielectric constant equal to 5.92 and 6.51 and dielectric losses of 1.4×10^{-2} and 8×10^{-3}. Zirconia ULTCC composites demonstrated dielectric constant equal to 12.8 and 13.8 and dielectric losses of 2.3×10^{-2} and 1.3×10^{-2}. Dielectric constant of NKAP glass was 5.55 and its dielectric loss was 2.8×10^{-2}. Among all ULTCC samples, quartz ULTCC composites demonstrated best mechanical properties. XRD and SEM analyses confirmed chemical compatibility between NKAP glass and aluminum, implying that NKAP glass/ceramic ULTCC composites will be compatible with aluminum electrodes.

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