Development of Novel Nanocomposite Dielectrics for High Voltage, High Energy Density Multilayer Ceramic Capacitors (MLCCs) Applications

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ABSTRACT

Current multilayer ceramic capacitors (MLCCs) suffer from limitations of low energy densities and poor temperature stability. In this study, Aegis Technology developed a novel class of ceramic-glass nanocomposite dielectric materials and the resultant MLCCs. The materials provided: (1) high breakdown strength; (2) moderate dielectric constants; (3) promising material level energy density (~2.84 J/cc); (4) low dielectric losses (tan $\delta \sim 1.0 \times 10^{-3}$); and (5) desirable temperature coefficient of capacitance (TCC) at a wide temperature range and elevated temperature (TCC within ±15% from -55 ℃ to 200 ℃). These results are among the best as reported in the literature. Once fully developed, the resultant MLCCs will provide much better overall performance than those of the state-of-the-art products.

Keywords: MLCC, capacitor, nanocomposite, high energy density, dielectric, dielectric materials, low costs.

1 INTRODUCTION

Presently, there are demanding requirements on high performance MLCC-based power capacitors for the development of more advanced electronics and pulsed power systems for both military and civil applications. For instance, several high voltage capacitors are being utilized in typical multi-point electronic designs. To be more attractive for these applications, MLCCs should provide more promising properties including high energy density, rapid discharge capability, high thermal stability, and long endurance times. However, current MLCCs-based capacitors suffer from limitations of low energy densities, resulting in bulky/heavy pulsed power systems with high costs. For example, state-of-the-art capacitors that are used in current multi-point systems are approximately $440 mm^3$ for a 0.1uF 1500V device, and generally cost ~$50-$100 per capacitor. These capacitors contribute significantly to the size and cost of resultant multi-point systems, preventing wider applications in more advanced systems. These capacitors also exhibit relatively poor temperature stability making them difficult in providing the required performance at elevated temperatures (*e.g.*, >160 ℃). As a result, it is highly desirable to develop new inexpensive, high-energy-density, high-temperature-capable dielectric materials and resultant new-generation MLCCs. Based on these new-generation of MLCCs, enhanced performance of the resultant multi-point systems and other pulse power systems at higher working temperatures (> 160 ℃ or more) can be achieved with smaller volume, lighter weight, and lower costs.

In recently reported studies [1,2], it was suggested that utilization of nanocomposite dielectrics is a promising solution in order to enhance the properties of capacitors. In particular, polymer-based composite or nanocomposite dielectric materials, which consist of high-breakdown-strength polymers and high-dielectric-constant ceramic fillers (micron- or nano-scale particles), have been demonstrated with attractive performance. However, a wide use of these polymer-based capacitors in practical applications is hindered by two major technical challenges: (1) still limited energy densities because of low breakdown strengths as a result of high concentrations of polymer/ ceramic interfacial defects; and (2) degraded performance at elevated temperatures because of the intrinsic limitation of polymers that lead to low use temperatures. On the other hand, MLCCs have received increasing attention for power capacitor applications based on a promising combination of high energy density and high temperature capabilities. In addition, recent progress in new ceramic-glass dielectric nanocomposites is enabling the development and fabrication of high energy density and high temperature MLCCs in a cost-effective and scalable manner.

2 MATERIALS / EXPERIMENTAL

In this study, Aegis (teamed up with Bioenno, Mines, and Novacap) developed a novel class of MLCCs based on innovatively designed ceramic-glass nanocomposite dielectrics, which can provide high energy density, good stability/reliability across a wide range of temperatures, and potentially low costs. In this design, nanoparticles of a high performance linear dielectric based on Mn-doped Ca(Ti, Zr)O_3 (referred to as CTZ+Mn) has been used as the ceramic phase, which offers relatively high dielectric constant (ε_r), high breakdown strength (E_B), and good stability (*i.e.*, low temperature coefficient of capacitance, TCC) [3,4]. A properly selected commercially available glass (SiO_2-Na_2O-B_2O_3-Al_2O_3) from Elan Technology was integrated in the resultant nanocomposites as glass phase, which will allow for high E_B, lower sintering temperatures, higher density, lower defect concentration, thereby resulting in not only enhanced dielectric properties, but also higher mechanical reliability and longer service life.

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3 RESULTS

The obtained nanocomposite dielectrics and the resultant single-layer capacitors (SLCs) and MLCCs prototypes were subjected to microstructural and dielectric characterizations. XRD (X-ray diffraction) was employed to determine whether pure phase structures have been well synthesized. It was also used to identify the influence of the processing procedures on the crystal structure. SEM (Scanning Electron Microscopy) was used to examine the morphologies of the prepared nanocomposite particles, and microstructures of sintered dielectric and electrode layers, with a focus on the sinterability of these layers and the interfacial contacts between them. Dielectric tests were conducted to study the electrical properties of materials and capacitor prototypes. It is noteworthy that for these preliminary SLC/MLCC prototypes, further optimization on processing is still required in order to fully realize the potentials of the developed nanocomposite dielectrics.

3.1 Microstructural Examination

Fig. 1 shows representative XRD results of CTZ+Mn samples processed at ~1250 ℃ with different length of calcination time. XRD results of a similar composition reported in the literature are also showed in Fig. 1 as a reference for comparison. In this study, in order to achieve pure phase CTZ+Mn, a series of samples were fired with a temperature range from ~1150 ℃ to ~1250 ℃, and a time range from ~ 2 hours to ~6 hours. Results indicated that higher calcination temperatures (~1250 ℃) and relatively longer time (~6 hours) were required for the achievement of pure phase samples.

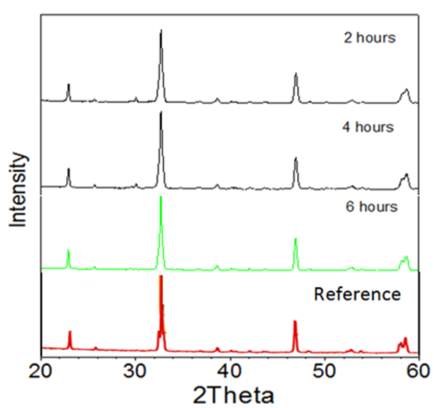

Fig. 1: Representative XRD patterns of CTZ+Mn samples

Fig. 2 shows the comparison of XRD results of a prepared ceramic-glass nanocomposite samples, which were processed with different milling times. From these figures, it can be seen that the glass phases cannot be distinguished from these XRD patterns, despite a high glass weight percentage (>10 wt.%). A major reason can be attributed to the amorphous nature of the glass. Therefore, the milling time has relatively little influence on the phase purity of the nanocomposites.

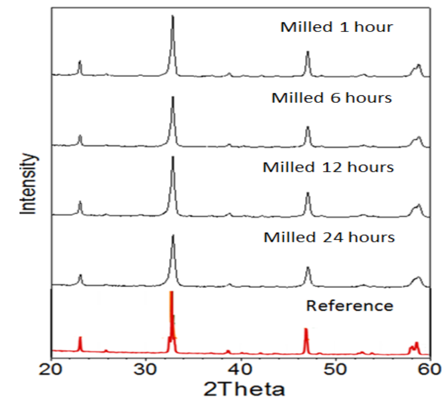

Fig. 2: Representative XRD patterns of nanocomposite dielectric samples.

SEM image of a pure phase CTZ+Mn ceramic sample is shown in Fig. 3. As shown in the image, overall, the obtained ceramic particles have dimensions of ~0.8 - 1 µm with good uniformity. Fig. 4 shows a representative SEM image of an obtained nanocomposite dielectric sample. From the image, it can be seen that obtained nanocomposites consist of both relatively larger particles (~250nm to submicron) of ceramic phase (CTZ+Mn) and smaller particles (< 150 nm) of glass phase. The particles of both phases distribute homogeneously, and there is no obvious aggregation that can be observed.

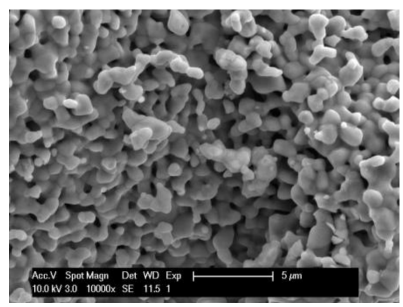

Fig. 3: Representative SEM image of a CTZ+Mn sample.

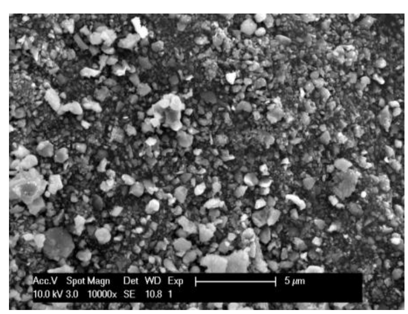

Fig. 4: Representative SEM image of a nanocomposite.

Fig. 5 shows typical SEM images of polished cross-sections of a SLC prototype sample. As shown in the figure, active dielectric layer with a thickness ~50 µm is sandwiched between two Ag/Pd (70/30) electrode layers (with a thickness ~5 µm), which are further buried by inactive dielectric layers. Both active dielectric layer and electrode layers exhibit uniform thicknesses, which is important for estimating the breakdown strengths of ceramic capacitors. It can also be seen that there is an intimate interfacial contact between dielectric and electrodes phases, since there is no obvious defects (such as gaps, voids, and cracks) that can be seen on the interfaces, showing the good compatibility between these two phases. Some voids/cavities can be seen in the dielectric layers, which indicate that the sintering parameters such as temperature and time still need to be optimized. Fig. 6 shows the SEM image of the cross-section near the end/terminal of this SLC, in which the bottom electrode extends to the SLC end and contacts with the outside Ag conducting terminal, just like normal MLCCs. The functionality of the Ag terminal has been confirmed by the results of dielectric tests as discussed below.

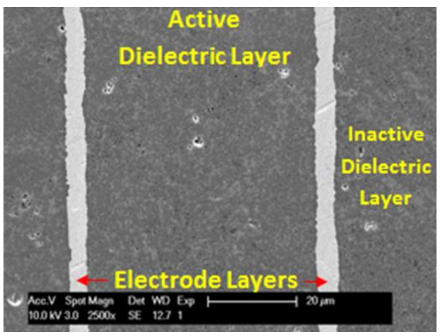

Fig. 5: Typical cross-sectional SEM image of a SLC prototype with dielectric and electrode layers.

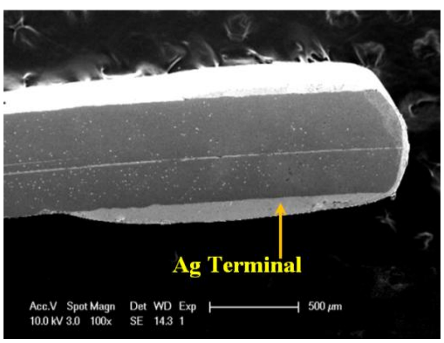

Fig. 6: Cross-sectional SEM image of one end of a SLC.

3.2 Dielectric Tests

Some tests for typical dielectric characterizations were carried out on the prepared SLC and MLCC prototypes. It is important to note that these test results are mainly used to demonstrate the functionality of these samples, and further enhanced performances can be expected based on further optimizations on material composition and device fabrication. Some typical dielectric properties including polarization vs field (P-E), TCC, and dielectric loss (tan δ) have been investigated .

Fig. 7 and 8 shows representative P-E loops tested on two SLCs (SLC-1&2) and two MLCCs (MLC-1&2), in which SLC-1 and MLC-1(SLC-2 and MLC-2) have the same compositions (*e.g.*, in SLC-1/MLC-1, glass phase fraction is ~18 wt.%, while in SLC-2/MLC-2, is ~21 wt.%). From the figures, it can be found that these prototypes exhibit very typical P-E profiles of standard linear dielectrics. These results showed that the established prototyping method has little negative influence on the dielectric properties of the developed dielectric nanocomposites. The measurements also confirm that the electrodes and Ag terminals in these SLC/MLCC prototypes functioned very well.

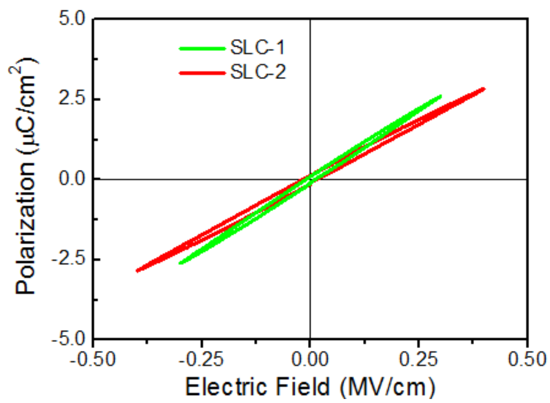

Fig. 7: Representative P-E loops of prepared SLCs.

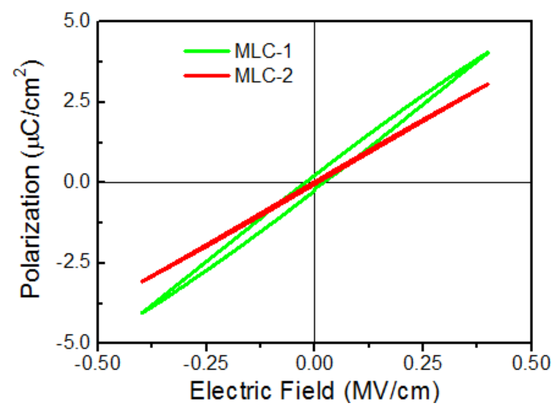

Fig. 8: Representative P-E Loops of prepared MLCCs.

Breakdown strengths (E_B) were also measured on some prepared SLC prototype samples. In this investigation, the highest breakdown strength was ~0.81 MV/cm, which was recorded on a SLC sample with a dielectric layer thickness ~40 µm and a similar composition as that of SLC-2 (*i.e.*, glass fraction ~21 wt.%). Based on this result, it is estimated that a high material level energy density (U_{EB}) can be obtained (*i.e.*, U_{EB} ~2.84 J/cc based on E_B ~0.81 MV/cm). This result also partially confirms the effectiveness of the relationship between the dielectric thickness and the breakdown strength. It is noteworthy that although at this moment E_B is still lower than the projected value (*i.e.*, $E_B \geq 1.1$ MV/cm), it is quite feasible to achieve

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this objective through further optimizations on both material compositions and processing parameters of MLCCs, leading to a resultant material level energy density of U_{EB} > 5 J/cc and a desirable device level of U_{EB} > 2 J/cc.

Figs. 9 and 10 show TCC and Tan δ results measured on two MLCC prototypes (MLC-1 in Fig. 9 and MLC-2 in Fig. 10) respectively. Both these two MLCCs exhibited promising TCC performance (within ±15.0% from -55 ℃ to 200 ℃). Based on the results, the MLCCs should be able to work for high temperature (>160 ℃) applications. These two MLCCs also showed low dielectric losses (Tan δ ~10^{-3}) across a wide temperature range (-55 ℃ to 175 ℃). Even at 200 ℃, Tan δ is still lower than 4 × 10^{-2}, among the best of state-of-the-art products.

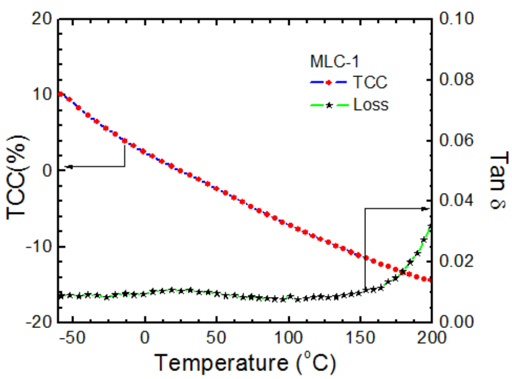

Fig. 9: Representative TCC and Tan δ of MLC-1.

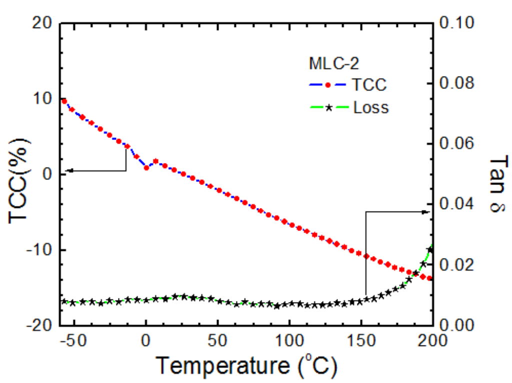

Fig. 10: Representative TCC and Tan δ of MLC-2.

4 DISCUSSION

The conducted research has successfully demonstrated the technical feasibility of the developed technology through material design, processing, characterization, and preliminary prototyping. Microstructural analysis indicated the formation of ceramic-glass nanocomposites with good morphologies. Dielectric characterization results obtained showed very promising properties in the synthesized nanocomposite dielectric materials. They include: 1) high breakdown strength (E_B ~0.81 MV/cm,; it can be easily extended to E_B > 1.10 MV/cm using thinner samples); 2) moderate dielectric constants (ε_r ~43-82); 3) promising material level energy density (~2.84 J/cc); 4) low dielectric losses (tan δ ~1.0 × 10^{-3}, which is among the best of state-of-the-art); and 5) desirable temperature coefficient of capacitance at a wide temperature range and elevated temperature (TCC, within ±15% from -55 ℃ to 200 ℃, which means the resultant MLCCs can be potentially qualified as X9R [EIA specification, requiring TCC (or $\Delta C/C_{25℃}$) varies within ±15% across −55°C and +200°C, where $C_{25℃}$ means the capacitance at 25 ℃], vs. X7R of state-of-the-art within ±15% from -55 ℃ to 125 ℃). These results are among the best as reported in the literature. Based on further optimizations on materials composition and processing, the resultant nanocomposite dielectrics and MLCCs are expected to provide overall much better performances than those of the state-of-the-art products.

5 CONCLUSION

Our research has provided a successful demonstration of the innovatively designed ceramic-glass nanocomposite dielectrics and the resultant MLCC power capacitors with very promising properties. These results are among the best as reported in the latest literature, and are much better than the state-of-the-art products. This research has also set forth the direction for future optimization and scaled-up production that would lead to development of commercially viable MLCC for a number of defense/civil applications.

6 ACKNOLEDGEMENTS

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7 REFERENCE

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