This chapter reports three ceria based composites. The first section discusses the effect of glass additives on the microstructure, densification and microwave dielectric properties of cerium oxide. The results of this research established low temperature synthesis of CeO$_2$ ceramics with improved microwave dielectric properties for dielectric resonator and possible Low Temperature Cofired Ceramics (LTCC) applications. Cerium oxide filled polytetrafluoroethylene (PTFE) composites prepared by powder processing technique and high density polyethylene (HDPE) composites prepared by melt mixing method for microwave substrate applications are discussed in the second section of this chapter. The variation of dielectric, thermal and mechanical properties with volume fraction of filler loading is also described. The last section of the chapter discusses the CeO$_2$-La$_{0.5}$Sr$_{0.5}$CoO$_{3-δ}$ composites for electromechanical applications.
7.1 CERIA-GLASS COMPOSITES FOR LOW TEMPERATURE COFIRED CERAMIC APPLICATIONS

7.1.1 Introduction

Recently, the development of low temperature co-fired ceramics (LTCC) has been getting much interest due to the application of multilayer integrated circuit (MLIC), such as chip LC filters and antennas. The most important parameter for the LTCC technology is the low sintering temperature, and it enables the advantageous utilization for today’s packaging concepts in microelectronic and microwave modules. Since the LTCC tapes can be sintered at low temperatures (< 950°C), the embedded microwave components and transmission lines can be fabricated using highly conductive and inexpensive metals such as silver, gold or copper with low conductor loss and low electrical resistance at high-frequencies. This is an advantage over other ceramic technologies. The LTCC is widely used for substrate, semiconductor package, passive integrated device and module applications in wireless communication. A low dielectric loss or high quality factor ($Q\omega$) and a small temperature coefficient of resonant frequency ($\tau_f$) are essential for practical applications. In addition, a low relative permittivity ($\varepsilon_r < 15$) material is needed for substrate applications to avoid signal delay whereas a high relative permittivity ($\varepsilon_r > 20$) is preferred for miniaturization. The sintering temperature must be less than the melting point of the electrode material such that the ceramics can be cofired with the electrode. This is an important requirement for LTCC technology. A number of strategies have been reported to lower the sintering temperature of ceramics (a) addition of low melting point glass or low melting point materials such as CuO, V$_2$O$_5$, B$_2$O$_3$ (b) using starting materials with smaller particle size and (c) development of novel glass free low-sintering dielectric ceramics. Recent research trend suggests that, liquid phase sintering using low loss glass additives is widely employed since it is the least expensive.

Most of the known commercial ceramic materials like BaMg$_{1/3}$Ta$_{2/3}$O$_3$, BaZn$_{1/3}$Ta$_{2/3}$O$_3$, (Zr,Sn)TiO$_4$ etc. need sintering temperatures above 1300°C, which limits their use in LTCC applications. Many attempts were made to reduce the firing
temperature by the addition of various low melting and low loss glasses.\textsuperscript{12,13,14,15} CuO and V$_2$O$_5$ are well-known liquid-phase sintering promoters. But there are reports that multi-component glasses are more effective than single component glasses to lower the sintering temperature of ceramics without much degradation in the physical and dielectric properties of the matrix.\textsuperscript{1,16} Wu et al.\textsuperscript{17} reported the microwave dielectric properties of various borosilicate glasses. After conducting a detailed investigation on the dielectric properties of glasses at ultra-high frequencies, Navias et al.\textsuperscript{18} noted that the dielectric losses of borosilicate glasses are comparatively lower than alkali containing glasses. This is due to the fact that in the latter, alkali ions which are weakly held in the glassy network, absorb energy and eventually give rise to dielectric loss. On the other hand, borosilicate glasses\textsuperscript{18,19} having continuous atomic structures, with SiO$_4$ and BO$_3$ configurations joined to form (-Si-O-B-O-) linkages, will have high electrical resistance and low dielectric loss. The microwave dielectric properties of a few borosilicate glasses (BaO-B$_2$O$_3$-SiO$_2$, PbO-B$_2$O$_3$-SiO$_2$ and ZnO-B$_2$O$_3$-SiO$_2$) have been reported\textsuperscript{18} recently in which it was observed that the $\varepsilon_r$ of all these glasses are negative. Several authors reported the lowering of sintering temperature of ceramics such as MgAl$_2$O$_4$ and CaZrO$_3$-CaTiO$_3$ by adding lithium based glasses such as Li$_2$O-MgO-ZnO-B$_2$O$_3$-SiO$_2$ and Li$_2$O-B$_2$O$_3$-SiO$_2$ respectively.\textsuperscript{20,21} Studies were also conducted on Bi$_2$O$_3$-ZnO-B$_2$O$_3$-SiO$_2$ glass for making it a suitable additive for LTCC applications.\textsuperscript{22,23}

Cerium oxide has been widely used as a substrate or buffer layer for superconducting microwave devices because of its low dielectric loss, excellent lattice matching and a good matching for thermal expansion.\textsuperscript{24} The microwave dielectric properties of ceria have been discussed in section 3.2 of Chapter 3. But ceria requires high sintering temperature of above 1600°C which is time and energy consuming for industrial production.\textsuperscript{25} A considerable amount of work has been done to prepare ceria by chemical methods like urea-based hydrogenous precipitation,\textsuperscript{26,27} solvothermal synthesis,\textsuperscript{28} electrochemical synthesis,\textsuperscript{29} hydrothermal synthesis\textsuperscript{30} etc. The section 4.4.3.3 of Chapter 4 discusses the variation of microwave dielectric properties of B$_2$O$_3$ and CuO added 0.5CeO$_2$-0.5BaTi$_4$O$_9$ ceramics. Hsu et al.\textsuperscript{31} reported the dielectric properties of
B₂O₃ doped 0.98CeO₂-0.02CaTiO₃ ceramics. A considerable number of research has been done on the interaction of glasses with low loss microwave dielectrics. However, the vitreous phase densification and dielectric loss of silicate/borate or borosilicate glasses in cerium oxide for LTCC materials, has not been reported before. This has drawn our attention and provided motivation to study the effect of glass flux on the sintering behaviour and microwave dielectric properties of ceria for LTCC applications.

7.1.2 Experimental

The glass powders used in this investigation were B₂O₃ (abbreviated as B), B₂O₃-SiO₂ (BS), ZnO-B₂O₃ (ZB), Al₂O₃-SiO₂ (AS), BaO-B₂O₃-SiO₂ (BBS), MgO-B₂O₃-SiO₂ (MBS), PbO-B₂O₃-SiO₂ (PBS), ZnO-B₂O₃-SiO₂ (ZBS), 2MgO-Al₂O₃-5SiO₂ (MAS), Li₂O-B₂O₃-SiO₂ (LBS), Bi₂O₃-ZnO-B₂O₃-SiO₂ (BZBS) and Li₂O-MgO-ZnO-B₂O₃-SiO₂ (LMZBS). For synthesizing glasses, high purity (Aldrich Chemical Co., Milwaukee, WI, USA, >99.9 %) oxides/carbonates were weighed stoichiometrically and mixed for two hours in an agate mortar with pestle using distilled water as the medium. It was then melted in a platinum crucible above their softening temperature (see Table 1.2 of Chapter 1), quenched and powdered.

High purity CeO₂ powder (Treibacher Industries, Althofen, Austria, 99.9%) used in the present investigation was initially heated at 1000°C/4h to remove any volatile impurities and then mixed with different weight percentages of the glasses for 2 hours. 4 wt% aqueous solution of polyvinyl alchohol (PVA) was added as a binder. The powder was uniaxially pressed into cylindrical compacts of 20 mm diameter and 9-10 mm in thickness under a pressure of about 130 MPa in tungsten carbide die. These compacts were heated at a rate of 5°C/min up to 600°C and soaked at 600°C for 30 minutes to expel the binder. They were then sintered in the temperature range 900-1650°C for 4 hours in
air at a heating rate of 10°C/min and the samples were then cooled to 1000°C at a rate of 3°C per minute. The sintering temperature was optimized for the best density of each glass ceramic composition. The polished ceramic pellets with an aspect ratio (diameter to height) of 1.8 to 2.2 which is ideal for maximum separation of the modes, were used for microwave measurements.

The bulk densities of the sintered samples were measured using Archimedes method. The powdered samples were used for analyzing the X-ray diffraction patterns using CuKα radiation and the surface morphology was studied using SEM methods. EDXA was used for elemental analysis. The coefficient of thermal contraction of the samples was measured using a thermo mechanical analyzer (TMA-60H Shimadzu, Kyoto, Japan) in the temperature range 30°-1000°C. The dielectric properties \( \varepsilon_r, Q_{v, f} \) and \( \tau_f \) of the materials were measured in the microwave frequency range using resonance technique\(^{32,33,34} \) as described in Chapter 2, sections 2.4.2 to 2.4.5.

7.1.3 Results and Discussion

7.1.3.1 Sintering of Glass Fluxed Ceria

The synthesizing conditions such as sintering temperature and their durations are optimized for glass added CeO\(_2\) ceramics to obtain the best density and dielectric properties. There is no change in density, dielectric properties or in XRD pattern when sintered glass added CeO\(_2\) samples are boiled in water indicating excellent chemical and thermal stability of the material.

Table 1.2 in Chapter 1 gives the physical and electrical properties of the glasses used. Twelve different glasses are added to CeO\(_2\) initially and the variation of sintering temperature, density and microwave dielectric properties with different weight percentage of glasses (up to 5 wt\%) are studied. Table 7.1 gives the sintering temperature, density and microwave dielectric properties of CeO\(_2\) fluxed with different weight percentage of BS, AS, BBS, MBS, LBS, MAS and LMZBS glass frits. The
sintering temperature decreases with the addition of increasing amount of glass frits in ceria. The 5 wt% addition of AS and MAS glass does not further decrease the sintering temperature from 1425 and 1400°C respectively. The 0.5 wt% of glass fluxed CeO$_2$ gives the maximum density and best microwave dielectric properties. With higher amount of glass addition, density is decreased and microwave dielectric properties get deteriorated. Hence we did not study the effect of higher amount of BS, AS, BBS, MBS, LBS, MAS and LMZBS glass frits on the microwave dielectric properties of CeO$_2$. Five glasses (B$_2$O$_3$, ZB, ZBS, PBS and BZBS) were selected for further study since they showed reasonably high $Q$ factor and decreased the sintering temperature.

Fig. 7.1 shows the variation of sintering temperature as a function of weight percentage of B$_2$O$_3$, ZB, ZBS, PBS and BZBS glass. The undoped ceria has a sintering temperature of 1650°C. The sintering temperature of ceria decreases with the addition of glasses, which becomes significant for glass content greater than 5 wt%. Addition of 0.2 wt% of B$_2$O$_3$, ZB, ZBS, PBS and BZBS, lowers the sintering temperature to 1625, 1600, 1575, 1600 and 1550°C respectively. Addition of 20 wt% of B$_2$O$_3$, ZB and PBS and 12 wt% of ZBS lowers the sintering temperature to about 900°C whereas addition of 10 wt% BZBS lowers the sintering temperature to 950°C. Thus the sintering temperature is significantly decreased by the addition of the above glasses. Further increase in the glass content had no effect on the sintering temperature. It is known$^3$ that boron based glasses are more effective in lowering the sintering temperature and this is due to the low softening temperature of B$_2$O$_3$ (450°C). The lowering of sintering temperature of ceria by the addition of ZB, ZBS and PBS glass is due to their low softening temperatures (610, 582 and 442°C respectively). The sintering temperature of BZBS glass added CeO$_2$ could not be decreased below 950°C since the melting point of BZBS glass is 950°C.
Table 7.1 Table showing the sintering temperature, density and microwave dielectric properties of pure and glass fluxed CeO₂ ceramics

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<th>Amount of glass (wt%)</th>
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<th>Density (g/cm³)</th>
<th>εr</th>
<th>Qₑff (GHz)</th>
<th>γ (ppm/°C)</th>
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Fig. 7.2 (a) and (b) shows the shrinkage of CeO₂+20 wt% B₂O₃ and CeO₂+10 wt% BZBS respectively. The sample sintered with B₂O₃ shrinks at a slightly lower temperature than that added with BZBS glass. The onset of shrinkage occurs below 700 and 800°C for B₂O₃ and BZBS added CeO₂ samples respectively. The shrinkage is complete only beyond 1000°C for B₂O₃ and BZBS added CeO₂ samples.
Fig. 7.1 Variation of sintering temperature as a function of weight percentage of B, ZB, ZBS, PBS and BZBS glass additives.

Fig. 7.2 The shrinkage curves of CeO₂ fluxed with (a) 20 wt% B₂O₃ and (b) 10 wt% BZBS.

7.1.3.2 Phase Analysis

![Phase Analysis Diagram]

Fig. 7.3 Powder X-ray diffraction patterns of (a) 1 wt% (b) 5 wt% (c) 10 wt% BZBS and (d) 20 wt% B₂O₃ added CeO₂ ceramic, C- CeO₂, ▲- CeBO₃, ■- Ce(BO₂)₃.

Fig. 7.4 Powder X-ray diffraction patterns of (a) 15 wt% ZBS (b) 10 wt% PBS and (c) 15 wt% ZB added CeO₂ ceramic, C- CeO₂, ×- CeZnB₂O₆, •- PbB₄O₇.

Figs. 7.3 (a)-(c) show the XRD patterns of 1, 5 and 10 wt% BZBS added CeO₂ ceramics. The XRD pattern of 1 wt% BZBS added CeO₂ ceramic did not show any additional peak. New peaks of CeBO₃ [JCPDS Card No. 21-0177] are found in the XRD.
pattern when further amount of BZBS (≥5 wt%) is added to CeO₂. The amount of CeBO₃ has increased with increasing amount of BZBS in CeO₂. Ce(BO₂)₃ phase [JCPDS Card No. 23-0877] coexists with the CeO₂ phase in the XRD pattern of 20 wt% B₂O₃ added CeO₂ ceramic (Fig. 7.3(d)). Figs. 7.4(a)-(c) show the XRD pattern of 15 wt% ZBS, 10 wt% PBS and 15 wt% ZB added CeO₂ ceramic. The new peaks corresponding to CeZnB₂O₅ [JCPDS Card No. 86-1884] are found in the XRD pattern of 10 wt% ZB and 15 wt% ZBS added ceramic whereas peaks of PbB₄O₇ [JCPDS Card No. 15-078] are found in the XRD profile of 10 wt% PBS added CeO₂ ceramic.

7.1.3.3 Microstructural Analysis

The variation in microstructures of different compositions of BZBS and B₂O₃ added CeO₂ ceramic sintered at different temperatures could be observed from SEM photographs. Pure CeO₂ ceramic sintered at 1650°C/4h exhibits a dense microstructure and has faceted grains of large size up to 40 μm (Fig. 7.5(a)). SEM micrographs of 0.5, 5 and 10 wt% BZBS added CeO₂ ceramic sintered at 1550, 1050 and 950°C respectively are shown in Figs. 7.5(b)-(d). Figs. 7.5(e) and (f) illustrate the SEM micrographs of 0.5 and 20 wt% B₂O₃ added CeO₂ ceramic sintered at 1600 and 900°C respectively. 0.5 wt% BZBS and B₂O₃ doped CeO₂ ceramic shows a relatively dense microstructure with no secondary phases. At 5 and 10 wt% BZBS additions, elongated BZBS phase appeared in the SEM micrograph. Many of these elongated grains are found to be hollow. At the end of these tubular grains, they have hexagonal shape, hollow core with a diameter of 2-3 μm, length of about 12-25 μm and wall thickness of 0.5-1 μm. Microstructure of 10 wt% BZBS added CeO₂ ceramic shows typical characteristics of LTCC, where ceramics are distributed in the matrix of dense glass. Presence of Ce(BO₂)₃ secondary phase is confirmed from the SEM picture of 20 wt% B₂O₃ added CeO₂. Flake like grains seen in the SEM picture are of Ce(BO₂)₃. The main requirement for liquid phase sintering to occur is that the liquid phase should wet the grains of the ceramics. Generally, the chemical reaction between sintering aids and ceramics can provide the best wetting condition, with the formation of secondary phase. The addition of 10 and 20 wt% BZBS
and $\text{B}_2\text{O}_3$ to $\text{CeO}_2$ enhanced the porosity and the relatively large pores seem to result from the coalescence of originally small pores. $^{37}$ As the weight percentage of BZBS and $\text{B}_2\text{O}_3$
increases, the size of ceria grain decreases. The size of CeO₂ grain is about 10-20 μm, 2-4.5 μm and 0.5-1.5 μm for 0.5, 5 and 10 wt% BZBS addition respectively. Similar trend of reduction in grain size from 20-33 μm (for 0.5 wt%) to 1-1.8 μm (for 20 wt%) is observed for B₂O₃ added ceramic. These results are in agreement with the report of Corker et al. indicating that a liquid phase sintering produces a smaller grain size than a solid-state sintering process. This decrease in size of the grains with the addition of glass is also due to the low sintering temperature of glass added ceramic compared to that of pure specimen.

Fig. 7.6 shows the EDXA spectrum of 5 wt% BZBS added CeO₂ sintered at 1050°C/4h.

Fig. 7.6 shows the EDXA spectrum of 5 wt% BZBS added CeO₂ ceramic. The EDXA data of elongated grain show that the cation composition is close to 5.64% Bi, 31.8% B, 10.87% Si and 31.4% Zn (the ideal is 35%, 27%, 6%, 32%). Elongated grains are of BZBS phase with some Bi²⁺ (Melting point of Bi₂O₃ is 825°C) evaporated due to the high sintering temperature of 5 wt% BZBS added CeO₂ (1050°C). Fig. 7.6(b) shows the enlarged portion of the hexagonal shaped grains. The EDXA data of small round
shaped grains confirms the presence of CeBO$_3$ phase which is evident from XRD. Similarly, Fig. 7.7 shows the EDXA spectrum of 20 wt% B$_2$O$_3$ added CeO$_2$ ceramic sintered at 900°C/4h. The EDXA data shows that the cationic composition of CeO$_2$ grain is Ce (47.15 %) and that of flake like Ce(BO$_2$)$_3$ grain is Ce (20.31 %) and B (59.12 %).

![Fig. 7.7 EDXA Spectrum of 20 wt% B$_2$O$_3$ added CeO$_2$ sintered at 900°C/4h](image)

<table>
<thead>
<tr>
<th>Grain 1</th>
<th>Grain 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elements</td>
<td>Atomic%</td>
</tr>
<tr>
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<tr>
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</tr>
<tr>
<td>BK</td>
<td>59.12</td>
</tr>
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</table>

**7.1.3.4 Density and Microwave Dielectric Properties**

The low temperature sintering of low loss CeO$_2$ ceramic is important for cosintering with electrodes and also for lowering the cost of production. This can be achieved through vitreous phase sintering by the addition of glasses. But excess addition of glass has been proven to degrade the dielectric properties of the ceramic although the sintering temperature is lowered. Introducing a glassy material into matrix plays a pivotal role in controlling the phase evolution and densification phenomena. As a typical case, the behavior of percentage density and microwave quality factors of CeO$_2$ mixed with 0.5 wt% BZBS glass as a function of sintering temperature is shown in Fig. 7.8. The density increases with sintering temperature, reaches a maximum (6.48 g/cm$^3$) at 1550°C and then decreases with further increase in temperature. This variation in density is due to the evaporation of the glass and the resulting trapped porosity associated with
grain growth at higher temperatures.\textsuperscript{41} The relationship between quality factor and sintering temperature shows the similar trend as the relationship between density and sintering temperature. Maximum quality factor of 69500 GHz (at 5.92 GHz) is obtained at a sintering temperature of 1550°C. At low sintering temperatures, the microwave quality factors are low due to the poor densification. The samples sintered at temperatures higher than 1550°C show a decrease in quality factor and is attributed to the lowering of density and associated porosity.

![Graph](image)

**Fig. 7.9 Variation of bulk density as a function of B, ZB, ZBS, PBS and BZBS glass additives**

The densities of various glass added CeO$_2$ at different compositions is shown in Fig. 7.9. Density of CeO$_2$ increases for addition of glasses up to 0.5 wt%. The density decreases as the weight percentage of glasses increases beyond 0.5 wt%. This is due to the relatively low density of the glasses as given in Table 1.2 of Chapter 1. B$_2$O$_3$ has the lowest density of 2.46 g/cm$^3$ and BZBS has a density of 4.34 g/cm$^3$. Low contact angle, low dihedral angle and high solubility of the solid in the liquid are essential for achieving high sintered density in glass added ceramics. In such cases, the transient glassy phase formed at a lower temperature would act as a short circuit medium for grain to grain materials transport.\textsuperscript{42} The primary glass B$_2$O$_3$ is regarded as a typical glass network...
former that has a lower glass transition temperature.\textsuperscript{43} The density then starts increasing at 10, 15, 10 and 5 wt% for ZB, ZBS, PBS and BZBS glasses respectively. This increase in density is due to the formation of high density secondary phases as a result of higher weight percentage of glass addition. Maximum density of 6.92 g/cm\textsuperscript{3} is obtained for 12 wt% BZBS added CeO\textsubscript{2} ceramic. Moreover, the density of Ce(BO\textsubscript{2})\textsubscript{3}, CeZnB\textsubscript{2}O\textsubscript{5}, PbB\textsubscript{4}O\textsubscript{7} and CeBO\textsubscript{3} phases formed due to the addition of B\textsubscript{2}O\textsubscript{3}, ZB, ZBS, PBS and BZBS glasses are respectively 4.43, 4.41, 5.87 and 5.46 g/cm\textsuperscript{3}.\textsuperscript{44} The densities of the secondary phases formed are higher than the respective glasses used (see Table 1.2 in Chapter 1).

The undoped CeO\textsubscript{2} sintered at 1650°C has $\varepsilon_r = 23$, $\sigma_f = 60200$ GHz and $\gamma = -51$ ppm/°C. Fig. 7.10 shows the variation of relative permittivity with different wt% of glass added CeO\textsubscript{2}. The relative permittivity depends on the density and phase constituents.\textsuperscript{45} The relative permittivity shows a maximum value for 0.5 wt% of glass added CeO\textsubscript{2}. The increase of the relative permittivity is attributed to improved densification due to liquid phase sintering.\textsuperscript{46} The relative permittivity decreases with the addition of higher amount of glass frits due to the lower permittivity of glass flux compared to pure CeO\textsubscript{2} (see Table 1.2 in Chapter 1). The low relative permittivity of secondary phases formed due to B\textsubscript{2}O\textsubscript{3}, ZB, ZBS, PBS and BZBS addition may also attribute to the decrease in permittivity. It is
generally agreed that a non wetting glassy network leads to porosity and hence the
densification will be lower if the solubility of the ceramic in the liquid phase is poor. The
relative permittivity of 20 wt% ZB, 12 wt% ZBS and 20 wt% PBS added ceramic
sintered at 925, 900 and 900°C are 16.1, 15.9 and 16 respectively. Maximum relative
permittivity (22.4) is obtained for 10 wt% BZBS added ceramic sintered at 950°C and
minimum value (13.2) for 20 wt% B₂O₃ added CeO₂ ceramic sintered at 900°C. The
glass forming oxide B₂O₃ have the lowest relative permittivity and most additional oxides
produce increase in $\varepsilon_r$.²

![Graph showing Q vs Weight Percentage of Glass](image)

Fig. 7.11 Variation of $Q_{xf}$ as a function of B, ZB, ZBS, PBS and BZBS glass additives

The microwave dielectric properties of glass added ceramics depend on their
density and presence of secondary phases.¹¹ ¹⁷ Fig. 7.11 shows the variation of quality
factor as a function of different amount of glass additives. The maximum quality factor
for the glasses at 0.5 wt% is due to the good densification obtained for this composition. ⁰. ⁵ wt% BZBS glass added CeO₂ ceramic shows the highest quality factor of 69500 GHz. Small amount of glass addition increases the density and improve the microwave
dielectric properties of the host material, because the liquid forming composition enables
better pore elimination by enhancing the material transport.⁴⁸ The addition of more than
0.5 wt% of all glasses considerably degrades the quality factor. The addition of excess
glass to a ceramic lowers the sintering temperature accompanied by significant
deterioration in the microwave dielectric properties.\textsuperscript{49,38} The quality factor is decreased with higher percentage of glass additives due to the formation of secondary phases. The network formers contained in the glass materials may absorb the microwave power profoundly in high frequency region, degrading the quality factor of the material.\textsuperscript{18} Moreover, the grain size of the CeO$_2$ ceramic decreases with the amount of B$_2$O$_3$ and BZBS glass (Figs. 7.5(a)-(f)) and hence the effective grain boundary area increases. Wersing has reported that grain boundaries, secondary phases and dislocations cause losses in real inhomogeneous ceramics.\textsuperscript{50} These losses are caused by either dipole relaxation of impurities concentrated at the interfaces (grain boundaries) or relaxation of space charge polarization present at the interfaces.\textsuperscript{51} The quality factor of CeO$_2$ ceramic with 20 wt\% ZB (sintered at 925\degree C), 12 wt\% ZBS (900\degree C) and 20 wt\% PBS (900\degree C) addition are 6200, 15500 and 5850 GHz respectively. The quality factor for 20 wt\% B$_2$O$_3$ and 10 wt\% BZBS added CeO$_2$ ceramic sintered at 900 and 950\degree C are respectively 24200 and 12000 GHz.

![Graph showing variation of \( \tau_f \) as a function of different amount of glass additives](image)

**Fig. 7.12 Variation of \( \tau_f \) as a function of B, ZB, ZBS, PBS and BZBS glass additives**

The variation of \( \tau_f \) as a function of different amount of glass additives is shown in Fig. 7.12. The \( \tau_f \) of glass added CeO$_2$ is increasing to the negative side with the addition of glasses except B$_2$O$_3$. This increase in \( \tau_f \) to the negative side is due to the negative \( \tau_f \) of
these glasses. With the addition of 5 wt% B$_2$O$_3$ to CeO$_2$, $\tau_f$ shifts to a less negative value $-40.8$ ppm/°C from $-53$ ppm/°C for pure CeO$_2$. A similar variation in $\tau_f$ value is observed for B$_2$O$_3$ doped 0.98CeO$_2$-0.02CaTiO$_3$ ceramics. The increase in $\tau_f$ with the addition of ZB, ZBS, PBS and BZBS glasses are due to the formation of glass based secondary phases. The $\tau_f$ of 20 wt% ZB sintered at 925°C, 12 wt% ZBS and 20 wt% PBS added CeO$_2$ sintered at 900°C are $-61$, $-59$ and $-61$ ppm/°C respectively. The $\tau_f$ of 20 wt% B$_2$O$_3$ and 10 wt% BZBS added CeO$_2$ ceramic sintered at 900°C and 950°C respectively are $-46$ and $-57$ ppm/°C. There is no significant improvement in $\tau_f$ with the addition of glass frits to CeO$_2$ ceramic.

For co-firing applications, the glass ceramic composite should not react with the common electrode materials such as silver. Figs. 7.13 and 7.14 show the XRD patterns and SEM micrographs of 20 wt% silver added CeO$_2$ with 10 wt% BZBS and 20 wt%
B₂O₃ sintered at 950°C and 900°C for 4 h respectively. The powder diffraction patterns of Ag were indexed based on JCPDS File Card Number 4-0783. Fig. 7.15 shows the EDXA spectrum of 20 wt% Ag added CeO₂ fluxed with 20 wt% B₂O₃ sintered at 900°C/2hrs (Ag marked in Fig. 7.14 (b)). The EDXA data of 20 wt% silver added CeO₂ with 10 wt% BZBS (Ag marked in Fig. 7.14 (a)) is Ag (93.34 at%). It is worth to note from these figures that silver remains unreacted with the ceramic-glass composites, which is one of the requirements for LTCC.

![Fig. 7.14 SEM Micrographs of 20 wt% silver added (a) CeO₂ fluxed with 10 wt% BBSZ (sintered at 950°C/4h) and (b) CeO₂ fluxed with 20 wt% B₂O₃ (sintered at 900°C/4h)]

![Fig. 7.15 EDXA Spectrum of 20 wt% silver added CeO₂ fluxed with 20 wt% B₂O₃ (sintered at 900°C/4h)]
Addition of BS, AS, BBS, MBS, LBS, MAS and LMZBS glass frits although lowered the sintering temperature of CeO₂ ceramics, the dielectric properties are very much degraded. From the above analysis made on the glass added CeO₂ ceramics, it is concluded that 10 wt% BZBS and 20 wt% B₂O₃ added CeO₂ are good candidates for low temperature cofired ceramic applications.

7.2 POLYMER-CERIA COMPOSITES FOR MICROWAVE SUBSTRATE APPLICATIONS

7.2.1 Introduction

High density large scale integrated packaging technologies have been developed for high performance and high functionality of communication electronic devices such as cellular phones and wireless personal digital assistants (PDAs). The microelectronics industry is driven by advances in integrated circuit (IC) technology and hence electronic packaging has advanced in all aspects to meet the interconnection needs of ICs. Materials used in microelectronic packaging have to simultaneously fulfill diverse requirements, like low dielectric loss, low relative permittivity, moderate moisture absorption resistance, a low coefficient of thermal expansion, high dimensional stability and mechanical stiffness. Electrical characteristics of the microelectronic devices such as signal attenuation, propagation velocity and cross talk, are influenced by the dielectric properties of the package substrate and encapsulation material. A low dielectric constant minimizes capacitive coupling as well as signal delay and low dielectric loss reduces signal attenuation along with better device performance.

Thermal considerations in the electronic package have become increasingly important because integration of transistors has resulted in the escalation of power dissipation as well as an increase in heat flux at the devices. Hence the desire for improving thermal properties of materials for electronic component parts is getting stronger and the material performance has become a critical design consideration for packages. Historically, metal components in integrated circuit packages have provided thermal paths for the removal of heat; however, this mechanism has reached its maximum
potential. As a result, the polymeric materials in the components are increasingly important as thermal paths for the removal of excess heat that builds up. Unfortunately, polymeric materials are inherently poor thermal conductors, and they must be modified to assist in heat removal from electronics.\textsuperscript{58,59,60}

Ceramic powder reinforced polymer materials have been extensively used as packaging substrates.\textsuperscript{61,62} These are generally comprised of micron-scale inorganic particulate fillers mixed with a polymer matrix. Polymers and ceramics represent the extremes in electrical and thermal performance of packaging materials. Button \textit{et al.}\textsuperscript{63} proposed composite strategies combining ceramic and polymer matrices to achieve a superior property balance. Fillers can improve the mechanical,\textsuperscript{64,65} thermal,\textsuperscript{66,67,68} optical and electrical properties\textsuperscript{69,70,71} of a polymeric material. Ceramic-polymer composites form a potential material group suitable for producing demanding and functional packages that combine the electrical properties of ceramic and the mechanical flexibility, chemical stability and low temperature processing possibilities of polymers.\textsuperscript{72,73,74} Moreover, the relative permittivities of filled composites can be varied over a wide range by the choice of the shape, size and connectivity of the constituents in the polymeric matrix.\textsuperscript{75,76}

Fluoropolymeric materials are the most desirable polymer matrix for flexible substrate fabrication due to their superior high frequency electrical properties and excellent temperature and solvent resistance. Among fluropolymers polytetrafluoroethylene (PTFE) is the most preferred host matrix for packaging and substrate applications because of its very low relative permittivity ($\varepsilon_r \sim 2.3$), extremely low loss ($\tan \delta \sim 10^{-4}$ at 1 MHz), excellent chemical resistance, easy machinability and good dimensional stability.\textsuperscript{77} PTFE has a high virgin crystalline melting point (342°C), and extremely high shear viscosity ($10^{11}$ Poise at 380°C) in the melt.\textsuperscript{78} However, disadvantages of PTFE substrate include a high linear coefficient of thermal expansion (> 100 ppm/°C) and low surface energy.\textsuperscript{79} The other disadvantages are the difficulty in processing PTFE-based laminates and the relatively high filler loading required for preparing dimensionally stable PTFE composites.\textsuperscript{80,81} A substantial amount of work has
been reported to modify the dielectric and thermal properties of various polymer/ceramic composites for packaging applications.\textsuperscript{82,83,84} Recently, Chen \textit{et al.}\textsuperscript{85} reported the microwave dielectric properties of PTFE-SiO\textsubscript{2} composite and due to its low dielectric constant ($\varepsilon_r = 4$) it cannot be used for the miniaturization of microwave devices. Price \textit{et al.}\textsuperscript{78} reported the thermal conductivity of PTFE and PTFE composites. PTFE based composites involving high dielectric constant ($\sim 100$) low loss ceramics are reported earlier.\textsuperscript{86}

The use of high density polyethylene (HDPE) by the communications industry as the dielectric in submarine cables encouraged us to investigate the effect of CeO\textsubscript{2} filler loading on the microwave dielectric properties of HDPE-CeO\textsubscript{2} composites. Polyethylene is a non-polar polymer which has a melting temperature of approximately 160°C.\textsuperscript{77} Due to its excellent characteristics such as very low dielectric constant ($\varepsilon_r \sim 2.6$), low dielectric loss ($\tan \delta \sim 10^{-4}$ at 1 MHz) better chemical resistance and insulating properties, HDPE has significant applications as an engineering material. Krupa \textit{et al.}\textsuperscript{87} studied the thermal and mechanical properties of polyethylene-graphite composites. The effects of boron nitride content, particle size of HDPE and temperature on the thermal conductivity of HDPE-boron nitride composites have been investigated.\textsuperscript{88} There are reports on the processing and mechanical properties of multiwalled nanotube (MWNT)-HDPE composites.\textsuperscript{89} The effect of material parameters and processing conditions on the foam morphologies and mechanical properties of HDPE-clay nanocomposites have been studied by Jo \textit{et al.}\textsuperscript{90} Even though the mechanical properties of HDPE composites are well studied, less attention has been paid to its electrical and thermal properties.

For electronic packaging and substrate applications, low $\varepsilon_r (<25)$ ceramics having low dielectric loss are preferred. TeO\textsubscript{2} has a relative permittivity of 19 but it is very expensive and hence not cost-effective.\textsuperscript{91} The Sr\textsubscript{2}Ce\textsubscript{2}Ti\textsubscript{5}O\textsubscript{16} composite based on PTFE has a high dielectric loss of 0.01-0.15 (for 0.1-0.6 $V_j$) at 7 GHz and is not suitable for substrate applications.\textsuperscript{92} Ceria possess good dielectric and thermal properties. It has a relative permittivity of 23, dielectric loss of $\sim 10^{-4}$ at 7 GHz, thermal conductivity of 12 W/m°C and thermal expansion coefficient of 109 ppm/°C.\textsuperscript{24,93} The present work
investigates the dielectric and thermo-physical properties of PTFE-CeO$_2$ and HDPE-CeO$_2$ composites at room temperature for the first time to understand the electrical performance, thermal stability and heat transport performance. The study also discusses the comparison of experimental results with theoretical predictions from well-known models in literature.

### 7.2.2 Experimental

CeO$_2$ (99.9%, Indian Rare Earth Ltd., Udyogamandal, India)-PTFE (Hindustan Fluorocarbons, Hyderabad, India) composites were prepared by powder processing technology as explained in section 2.2.1 of Chapter 2. In order to create an active surface for binding with polymer, the fine powder of CeO$_2$ was mixed with acrylic acid solution for 1 hour and then dried. The dried powder was again treated with 2 wt% tetra butyl titanate. The volume fraction of the filler for a given weight fraction is calculated using the equation

\[ V_f = \frac{V_f}{V_f + V_m} = \frac{W_f}{W_f + (\rho_f / \rho_m)(1-W_f)} \]  

(7.1)

where $V_f$ and $V_m$ are the volume of filler and matrix respectively. $W_f$, $\rho_f$ and $\rho_m$ are the weight fraction of filler, density of filler and density of matrix respectively.

Different volume fractions (0 to 0.6) of treated ceramics (CeO$_2$) and PTFE powders were dispersed in ethyl alcohol using ultrasonic mixer for about 30 minutes. A dry powder mixture was obtained by removing the solvent at 70°C under stirring. This led to the formation of thoroughly mixed PTFE-CeO$_2$ powders. These homogeneously mixed composite powders were then compacted using a tungsten carbide die under a uniaxial pressure of 50 MPa for 1 minute. The cylindrical (dimensions: 11x1 mm$^2$) and rectangular pellets (dimensions: 25x3x1 mm$^3$) thus obtained were kept at 310°C for 2h.

The HDPE-CeO$_2$ composites were prepared by sigma-blend technique as explained in section 2.2.2 of Chapter 2. The HDPE is first melted in kneading machine
having sigma blades at 150°C/15 min. Different volume fractions (0 to 0.5) of CeO₂
ceramics were added to the melted polyethylene and blended at 150°C for 30 minutes.
Thus obtained composites were thermo laminated using suitable die under a pressure of
200 MPa and 150°C for 15 min using a die. After thermolamination, the composites with
desired shapes were polished for characterization.

The density of the composites (ρ) was determined using Archimedes method. The
water absorption measurements were conducted following ASTM D570 using disk-'
shaped specimens having diameter 11 mm and thickness 3 mm. The samples were
weighed and submerged in distilled water at 25°C for 24 h. The samples were removed,
wiped dry and the amount of water absorbed was calculated based on the weight gain of
the samples.

The composites were characterized by X-ray diffraction technique using CuKα
radiation and the surface morphology of the composites was studied by Scanning
Electron Microscope. The low frequency dielectric properties were measured using an
LCR meter. In order to investigate the temperature variation of relative permittivity,
these samples were heated in a uniform temperature enclosure from 25–70°C and the
corresponding relative permittivities were measured at 1 MHz. The microwave dielectric
properties of the sample at the frequency 7 GHz were measured using the cavity
perturbation technique using HP 8510 C Network Analyzer as described in section
2.4 of Chapter 2.

The DSC analysis was done by Perkin Elmer DSC 7, Massachusetts, USA. The
instrument was computer controlled and calculations were done using Pyris software. 5-
10 mg of samples were sealed in aluminum pans and heated from 25°C to 600°C at rate
of 5°C/min. and cooled to 25°C at the same rate. Heat treated cylindrical samples of
dimensions (diameter = 8 mm and height = 10 mm) were used to measure the coefficient
of thermal expansion (CTE) of the PTFE-CeO₂ composites using a thermo-mechanical
analyzer in the temperature range 25°C to 270°C. A photopyroelectric (PPE)
technique as discussed in section 2.5.4 of Chapter 2 was used to determine the
thermal conductivity of the PTFE-CeO₂ composites. Thermal diffusivity (α) and thermal
effusivity ($e$) were also measured from PPE signal phase and amplitude. From the values of $\alpha$ and $e$ the thermal conductivity and specific heat capacity of the samples were obtained.

The micromechanical properties of PTFE-CeO$_2$ composites were measured using micro hardness tester (Clemex Model 4, Germany). Both the surfaces of the samples were polished to have optically flat surface for indentation. The specimen was subjected to a load of 50 g and dwell time of 10 s. For pure ceramic sample the load was increased to 400 g. A total of 8 readings were taken to get the average hardness.

### 7.2.3 Theoretical Modeling

**(a) Relative permittivity**

Precise prediction of effective relative permittivity of polymer-ceramic composites is very important for the engineering applications. Composite dielectric is chaotic or is a statistical mixture of several components. The simple volumetric law of mixing for two component system is given by

$$
\varepsilon_{\text{eff}} = V_f \varepsilon_f + V_m \varepsilon_m
$$

(7.2)

where $V_f$ and $V_m$ are the volume fractions and $\varepsilon_f$ and $\varepsilon_m$ are the permittivities of ceramic filler and polymer matrix respectively and $\varepsilon_{\text{eff}}$ is the effective permittivity of the composite.

Several quantitative rules and simulation techniques predict the dielectric behaviour of a composite system based on experimental results and theoretical derivation. In the present study, following equations were used to calculate the effective relative permittivity of low filler content composites:

1. **Lichtenecker equation:**

   $$
   \ln \varepsilon_{\text{eff}} = V_m \ln \varepsilon_m + (1-V_f) \ln \varepsilon_f
   $$

   (7.3)

2. **Serial mixing rule:**

   $$
   \frac{1}{\varepsilon_{\text{eff}}} = \frac{V_f}{\varepsilon_f} + \frac{V_m}{\varepsilon_m}
   $$

   (7.4)
3. Effective Medium Theory:  

\[ \varepsilon_{\text{eff}} = \varepsilon_m \left[1 + \frac{V_f (\varepsilon_f - \varepsilon_m)}{\varepsilon_m + n(1-V_f)(\varepsilon_f - \varepsilon_m)} \right] \]  

\[ (7.5) \]

4. Jayasundare-Smith Equation:  

\[ \varepsilon_{\text{eff}} = \frac{\varepsilon_m (1-V_f) + \varepsilon_f V_f \left[ \frac{3\varepsilon_m}{\varepsilon_f + 2\varepsilon_m} \left( 1 + \frac{3V_f(\varepsilon_f - \varepsilon_m)}{\varepsilon_f + 2\varepsilon_m} \right) \right]}{(1-V_f) + V_f \left[ \frac{3\varepsilon_m}{\varepsilon_f + 2\varepsilon_m} \left( 1 + \frac{3V_f(\varepsilon_f - \varepsilon_m)}{\varepsilon_f + 2\varepsilon_m} \right) \right]} \]  

\[ (7.6) \]

5. Maxwell-Garnett Equation:  

\[ \frac{\varepsilon_{\text{eff}} - \varepsilon_m}{\varepsilon_{\text{eff}} + 2\varepsilon_m} = V_f \frac{\varepsilon_f - \varepsilon_m}{\varepsilon_f + 2\varepsilon_m} \]  

\[ (7.7) \]

where \( \varepsilon_{\text{eff}}, \varepsilon_f, \varepsilon_m \) are the relative permittivities of composite, filler and matrix respectively and \( V_f \) is the volume fraction of the filler.

In the Effective Medium Theory (EMT) proposed by Rao et al., composites can be treated as an effective medium whose relative permittivity is obtained by averaging over the relative permittivity of the constituents. In EMT model equation (7.5) is used to calculate the effective relative permittivity of the composites. The value of \( n \) is determined empirically which is found to be 0.38 for the PTFE-CeO₂ composites. Earlier reports showed an \( n \) value of 0.35 for well-dispersed polymer ceramic composites.

(b) Thermal Conductivity

Determining the thermal conductivity of composite materials is crucial in a number of industrial processes. The effective thermal conductivity of a heterogeneous material is strongly affected by its composition, crystal structure, distribution within the medium and contact between the particles. Numerous theoretical and experimental approaches have been developed to determine the precise value of thermal conductivity.
Comprehensive review articles have discussed the applicability of several models that appear to be more promising.\textsuperscript{108,109,110}

For a two component composite, the simplest model would be with the materials arranged in either parallel or series with respect to heat flow, which gives the upper or lower bounds (also referred to as Weiner bounds) of effective thermal conductivity.\textsuperscript{111}

In the present study, following models were used to calculate the effective thermal conductivity of polymer-ceramic composites:

1. **Geometric Mean Model:**
   \[ k_c = k_f^{V_f} k_m^{1-V_f} \]  \hspace{2cm} (7.8)
   where \( k_c \), \( k_f \) and \( k_m \) are the thermal conductivities of composite, filler and matrix respectively and \( V_f \) is the volume fraction of the filler in the composite.

2. **Effective-Medium Theory (EMT) Model**

   The Effective-medium theory (EMT) assumes that the composite system is a homogeneous medium and the EMT equation for thermal conductivity can be derived through the Laplace equation for thermal transfer, which can be expressed as\textsuperscript{112,113}
   \[ V_m \frac{k_m-k_c}{k_m+2k_c} + V_f \frac{k_f-k_c}{k_f+2k_c} = 0 \]  \hspace{2cm} (7.9)
   where \( V_m \) is the volume fraction of polymer in the composite and \( k_c, k_f, k_m, V_f \) same as in eqn (7.5).

3. **Maxwell - Eucken Model**

   Maxwell, using potential theory\textsuperscript{114}, obtained an exact solution for the conductivity of randomly distributed and non interacting homogeneous spheres in a homogeneous medium and is given by
   \[ k_c = k_m \left[ \frac{k_f + 2k_m + 2V_f(k_f-k_m)}{k_f + 2k_m - V_f(k_f-k_m)} \right] \]  \hspace{2cm} (7.10)
4. Cheng - Vachon Model

Based on Tsao's model which gives the thermal conductivity of two phase solid mixture\textsuperscript{115}, Cheng and Vachon assumed a parabolic distribution of the discontinuous phase in the continuous phase. The constants of this parabolic distribution were determined by analysis and presented as a function of the discontinuous phase volume fraction. Thus, the equivalent thermal conductivity of the two phase solid mixture was derived in terms of the distribution function, and the thermal conductivity of the constituents. For $k_f > k_m$,

\[
\frac{1}{k_c} = \frac{1}{\sqrt{C(k_f - k_m)[k_m + B(k_f - k_m)]}} \ln \left[ \frac{[k_m + B(k_f - k_m)] + \frac{B}{2} \sqrt{C(k_f - k_m)}}{[k_m + B(k_f - k_m)] - \frac{B}{2} \sqrt{C(k_f - k_m)}} + 1 - B \right]
\]

(7.11)

where

\[
B = \sqrt{\frac{3V_f}{2}} \quad C = -4 \sqrt{\frac{2}{3V_f}}
\]

(c) Coefficient of Thermal Expansion (CTE)

Thermal expansion coefficients of composites are very important in relation to the dimensional stability and the mechanical compatibility when used with other materials. A considerable amount of work has been done to predict the thermal expansion coefficients of composites.\textsuperscript{116,117,118} The rule of mixtures serves as the first-order approximation to the overall calculation of the co-efficient of thermal expansion of the composite.\textsuperscript{119} This can be expressed as

\[
\alpha_c = V_f \alpha_f + (1 - V_f) \alpha_m
\]

(7.12)

where $\alpha_c$, $\alpha_m$ and $\alpha_f$ are coefficient of thermal expansion of the composite, matrix and filler respectively. Turner developed a model that takes into account the mechanical interaction between different materials in the composite.\textsuperscript{120} Based on the assumption that all phases in the composite have the same dimension change with temperature, he derived a relationship which is expressed as
where $B_f, B_m$ are Bulk Modulus of filler and matrix respectively. Schapery developed a model to predict the upper and lower bounds of the CTE of a composite. The two bounds are given by

\begin{align}
\alpha'_c &= \alpha_m + \frac{B_f}{B'^u_c} \frac{(B_m - B'^u_c)(\alpha_f - \alpha_m)}{(B_m - B_f)} \\
\alpha''_c &= \alpha_m + \frac{B_f}{B'^l_c} \frac{(B_m - B'^l_c)(\alpha_f - \alpha_m)}{(B_m - B_f)}
\end{align}

where superscript "u" and "l" refer to the upper and lower bounds, respectively. It can be seen that the upper and lower bounds as calculated from the Hashin-Shtrikman model are used to calculate the lower and upper bounds in the Schapery model. Hashin and Shtrikman model assumes a homogeneous and isotropic reference material in which the constituents are dispersed. Depending on whether the stiffness of the reference material is more or less than that of the reinforcement, the lower and upper bounds are calculated as:

\begin{align}
B'^u_c &= B_f + \frac{1 - V_f}{B_m - B_f + \frac{3V_f}{3B_f + 4G_f}} \\
B'^l_c &= B_m + \frac{V_f}{B_f - B_m + \frac{3(1-V_f)}{3B_m + 4G_m}}
\end{align}

where $G_f$ and $G_m$ represents the Shear Modulus of filler and polymer respectively.

### 7.2.4 Results and Discussion

#### 7.2.4.1 Densification and Microstructural Analysis

The density of a two-component mixture should depend on the densities of the ingredients and also on their volume percentage. Fig. 7.16 (a) and (b) depicts the
measured and theoretical densities of PTFE-CeO₂ and HDPE-CeO₂ composites respectively as a function of volume fraction. The density is measured using Archimedes method and compared with the mixing rule

$$\rho_{\text{eff}} = V_f \rho_f + V_m \rho_m$$  \hspace{1cm} (7.18)$$

where $\rho_{\text{eff}}, \rho_f, \rho_m$ are the densities of composite, filler and matrix respectively. The experimental values for lower volume fractions agree well with the theoretical values for PTFE-CeO₂ composites.

In the case of HDPE-CeO₂ composites, the experimental and theoretical values agree well for all volume fractions. The measured densities of both cylindrical pellet and rectangular sheet increase with filler content due to the higher density of CeO₂. The deviation of measured densities from theoretical values increases with the filler content for both PTFE and HDPE composites. For cylindrical pellets of PTFE-CeO₂ composites, the deviation of 0.29% for 0.1 $V_f$ suddenly increases from 0.2 $V_f$ onwards and reaches a maximum value of 19% for 0.6 $V_f$. This may be due to the increase in void formation inside the composite for higher filler content. In HDPE-CeO₂ composites, the deviation increases from 0.44% for 0.1 $V_f$ to 2.4% for 0.5 $V_f$. The densification of PTFE-CeO₂ composites is found to be 96.6% for 0.1 $V_f$ filler loading which decreases with filler content.
content and reaches a value of 71% with 0.6 $V_f$ filler. The percentage deviation of relative density is less for HDPE composites compared to PTFE composites. This may be due to the difference in the method of preparation of composites. The relative density varies from 99.4 to 97.5% as the volume fraction of HDPE-CeO$_2$ increases from 0.1 to 0.5 $V_f$ CeO$_2$ loading. For cylindrical samples, a maximum deviation of 2.5% is obtained for 0.5 $V_f$ of HDPE based composites.

Table 7.2 The theoretical, experimental density and volume of air in PTFE-CeO$_2$ and HDPE-CeO$_2$ composites

<table>
<thead>
<tr>
<th>$V_f$ of CeO$_2$</th>
<th>PTFE</th>
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<th></th>
<th></th>
<th>HDPE</th>
<th></th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>$\rho_{\text{eff}}$ (g/cm$^3$)</td>
<td>$\rho_{\text{exp}}$ (g/cm$^3$)</td>
<td>$V_{\text{CeO}_2}$ (vol%)</td>
<td>$V_{\text{PTFE}}$ (vol%)</td>
<td>Porosity (%)</td>
<td>$\rho_{\text{exp}}$ (g/cm$^3$)</td>
<td>$\rho_{\text{exp}}$ (g/cm$^3$)</td>
<td>$V_{\text{CeO}_2}$ (vol%)</td>
</tr>
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<td>2.57</td>
<td>9.68</td>
<td>87.12</td>
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<td>1.58</td>
<td>1.57</td>
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<td>0.3</td>
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<td>2.83</td>
<td>2.79</td>
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<td>3.45</td>
<td>36.90</td>
<td>36.90</td>
<td>26.3</td>
<td>4.08</td>
<td>3.98</td>
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<td>3.69</td>
<td>42.60</td>
<td>28.40</td>
<td>29.0</td>
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</table>

Assuming that there are three phases in the composite- matrix, filler and air, volume fraction of air in the composite can be calculated by equation $^{124}$

$$\rho_{\text{eff}} (1 - V) + \rho_{\text{air}} V = \rho_{\text{exp}}$$ (7.19)

where $V$ is the volume fraction of air in the composites, $\rho_{\text{eff}}, \rho_{\text{air}}, \rho_{\text{exp}}$ are the theoretical densities of composite, density of air and experimental densities of composites respectively. Table 7.2 shows the theoretical density, experimental density and porosity, of the composites with varying filler content for PTFE and HDPE based composites. It can be seen that the porosity of the composites increases with the volume fraction of CeO$_2$ in both types of composites. A similar variation of porosity is reported by Xiang et al. $^{125}$ for SrTiO$_3$-POE composites.

Table 7.3 and 7.4 gives the water absorption values of PTFE and HDPE composites respectively. The water absorption values of PTFE based composites are higher than that of HDPE based composites. A maximum value of 1.55% is obtained for 0.6 $V_f$ PTFE-CeO$_2$ and 0.52% for HDPE-CeO$_2$ composites respectively.
Fig. 7.17 SEM micrographs of (a) CeO$_2$ powder (b) 0.1 $V_f$ (c) 0.3 $V_f$ (d) 0.6 $V_f$ PTFE-CeO$_2$ composites and (e) 0.1 $V_f$ (f) 0.3 $V_f$ (g) 0.5 $V_f$ (h) fractured surface of 0.3 $V_f$ HDPE-CeO$_2$ composites
Fig. 7.17 (a) shows the microstructure of heat treated and ground CeO₂ powder used in the present study. The size of the CeO₂ powder is approximately 2-5 μm. The surface morphology and filler distribution are studied using Scanning Electron Microscope and the results of PTFE composites (ψf = 0.1, 0.3, 0.6) are shown in Figs. 7.17(b)-(d) and of HDPE composites (ψf = 0.1, 0.3, 0.5) are shown in Figs. 7.17(e)-(g). The micrographs reveal that the CeO₂ particles are uniformly distributed throughout the PTFE and HDPE matrix. For higher volume fractions (ψf = 0.3, 0.5) of the composites, there is aggregation of CeO₂ particles. With the increase of filler content, the aggregation of ceramic particles increases (Fig. 7.17(d)) in both PTFE and HDPE composites. The increase in porosity of the composite with the volume fraction of CeO₂ is due to the aggregation of ceramic particles in the continuous PTFE matrix. For higher mixing ratios the connectivity among the ceramic particles increases, which in turn improves the properties. The connectivity of the individual components is important since it controls the electric flux pattern as well as mechanical and thermal properties. Comparison of SEM micrographs of similar volume fractions of PTFE and HDPE composites confirm that the porosity is higher for PTFE based composites. Fig. 7.17(h) shows the fractured surface of 0.3 ψf HDPE-CeO₂ composite. The higher densification of HDPE-CeO₂ composite is confirmed from the microstructure of 0.3 ψf HDPE-CeO₂ composite.

7.2.4.2 Thermal Analysis

The TGA measurements of PTFE-CeO₂ composites show that the heat resistance of PTFE is very good. The polymer begins to decompose around 530°C and a residue is observed at 600°C which corresponds to the CeO₂ content as shown in Fig. 7.18(a). Table 7.3 lists the decomposition temperature (Td) of PTFE-CeO₂ composites for different filler contents of CeO₂. It shows that the total mass loss values are in good agreement with the amount of CeO₂ originally mixed into the different volume fractions of PTFE-CeO₂ samples and the decomposition temperature was not affected by the CeO₂ content. This is due to the unreactive nature of PTFE matrix with CeO₂. Fig. 7.18 (b) shows the TGA measurements of HDPE-CeO₂ composites. The TGA measurement of
virgin HDPE shows that it starts decomposing around 280°C and decomposition is complete around 500°C. The decomposition temperature of pure HDPE is around 347°C, which increases with CeO₂ loading and reaches 453°C for 0.5 \( V_f \) i.e., the thermal stability is improved with filler concentration. The total mass loss values obtained from TGA are in agreement with the amount of CeO₂ originally mixed into HDPE-CeO₂ samples and are given in Table 7.4.

A typical DSC thermogram of 0.3 \( V_f \) CeO₂ - reinforced PTFE is shown in Fig. 7.19 (a) in which two peaks appear at 19.9°C and 327.3°C, respectively, in the heating mode. The melting point of PTFE is around 325-335°C and it has several first or second order transition temperatures ranging from -110 to 140°C.\(^{126}\) PTFE shows low-temperature phase transitions at about 19 and 30°C at atmospheric pressure.\(^{127}\) The crystal structure of PTFE is triclinic at temperatures below 19°C and above that temperature the unit cell changes to hexagonal. The three-dimensional register of chain segments gets lost in the temperature range of 19-30°C and the preferred crystallographic orientation disappears.\(^{128}\) Therefore, the result suggests that the CeO₂ filled PTFE composites absorb heat to change the crystal formation at 19.9°C and melt at 327.3°C.\(^{126}\) The sample also get re-cratyctallized by cooling from the molten state so as to observe the crystallization temperature \( T_c \). The crystallization behavior of materials is characterized using
crystallization temperature, $T_c$ and the onset crystallization temperature, $T_o$. Filler induced changes in $T_t$, $T_m$, $T_o$ and $T_c$ of virgin PTFE and PTFE-CeO$_2$ composites are determined using DSC in the temperature range 0-350°C (see Table 7.3). Both endothermic and exothermic curves of PTFE-CeO$_2$ composites are similar to those of pure PTFE. $T_t$, $T_m$, $T_o$ and $T_c$ of the PTFE-CeO$_2$ composites are very similar to those of pure PTFE, which implies that the existence of the CeO$_2$ filler has no effect on the melting and crystallization behavior of PTFE. This is due to the chemical inertness of the PTFE matrix with CeO$_2$ and the resultant very weak interface between the matrix and the filler.

Table 7.3 Summary of data obtained via TGA and DSC measurements for virgin PTFE and PTFE-CeO$_2$ composites

<table>
<thead>
<tr>
<th>Composition of PTFE-CeO$_2$</th>
<th>CeO$_2$ content$^a$ $W_f^a$</th>
<th>CeO$_2$ content$^b$ $W_f^b$</th>
<th>$T_d$ ($°C$)</th>
<th>$T_i$ ($°C$)</th>
<th>$T_m$ ($°C$)</th>
<th>$T_o$ ($°C$)</th>
<th>$T_c$ ($°C$)</th>
<th>Water absorption (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100-0</td>
<td>0.0</td>
<td>0.0</td>
<td>529</td>
<td>20.1</td>
<td>328.5</td>
<td>316.2</td>
<td>312.5</td>
<td>0.53</td>
</tr>
<tr>
<td>90-10</td>
<td>27.0</td>
<td>25.0</td>
<td>528</td>
<td>19.2</td>
<td>326.4</td>
<td>317.4</td>
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<td>80-20</td>
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<td>530</td>
<td>19.8</td>
<td>327.2</td>
<td>316.8</td>
<td>312.8</td>
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<tr>
<td>70-30</td>
<td>59.0</td>
<td>59.0</td>
<td>529</td>
<td>19.9</td>
<td>327.3</td>
<td>316.7</td>
<td>312.5</td>
<td>0.95</td>
</tr>
<tr>
<td>60-40</td>
<td>69.0</td>
<td>68.5</td>
<td>528</td>
<td>19.6</td>
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<td>40-60</td>
<td>83.0</td>
<td>80.0</td>
<td>527</td>
<td>19.0</td>
<td>326.2</td>
<td>316.9</td>
<td>312.1</td>
<td>1.55</td>
</tr>
</tbody>
</table>

$T_d$ is the temperature at which 10 wt% of the sample is lost after heating in nitrogen atmosphere by TGA, $T_i$ is the first order transition temperature, $T_m$ is the melting temperature, $T_o$ is the temperature of crystallization, $T_c$ is the onset crystallization temperature. $W_f^a$ is the weight fraction of CeO$_2$ content in the PTFE-CeO$_2$ composite, $W_f^b$ is the weight fraction of CeO$_2$ content in the PTFE-CeO$_2$ composite by TGA.

Table 7.4 Summary of data obtained via TGA and DSC measurements for virgin HDPE and HDPE-CeO$_2$ composites

<table>
<thead>
<tr>
<th>Composition of HDPE-CeO$_2$</th>
<th>CeO$_2$ content$^a$ $W_f^a$</th>
<th>CeO$_2$ content$^b$ $W_f^b$</th>
<th>$T_d$ ($°C$)</th>
<th>$T_m$ ($°C$)</th>
<th>$T_o$ ($°C$)</th>
<th>$T_c$ ($°C$)</th>
<th>Water absorption (%)</th>
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<td>0</td>
<td>347</td>
<td>130.1</td>
<td>119.2</td>
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<td>90-10</td>
<td>45.7</td>
<td>47.9</td>
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<td>130.8</td>
<td>119.2</td>
<td>115.6</td>
<td>0.21</td>
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<td>65.5</td>
<td>44.8</td>
<td>438</td>
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<td>118.9</td>
<td>115.4</td>
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<td>70-30</td>
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<td>76.6</td>
<td>450</td>
<td>130.1</td>
<td>118.6</td>
<td>115.5</td>
<td>0.33</td>
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<tr>
<td>60-40</td>
<td>83.5</td>
<td>68.5</td>
<td>452</td>
<td>129.8</td>
<td>118.9</td>
<td>115.3</td>
<td>0.47</td>
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<tr>
<td>50-50</td>
<td>88.4</td>
<td>88.7</td>
<td>453</td>
<td>129.7</td>
<td>118.6</td>
<td>115.2</td>
<td>0.52</td>
</tr>
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</table>
Fig. 7.19 (b) shows the DSC curves of different filler loaded HDPE composites in the temperature range 0-300°C. The melting temperature of pure HDPE is 130.1°C and the addition of CeO₂ to virgin HDPE showed no significant effect on the melting point of polymer (Table 7.4). There is no significant change in the $T_o$ and $T_c$ of HDPE composites with filler loading and are given in Table 7.4.

![DSC curves of different filler loaded HDPE composites](image)

Figure 7.20 shows the X-ray diffraction of PTFE and 0.3 volume fraction ($V_f$) PTFE-CeO₂ composite. PTFE is a semi crystalline polymer. The XRD pattern of PTFE shows a strong crystalline peak superimposed over an amorphous halo as reported. The strong crystalline peak of PTFE is observed at $2\theta = 18^\circ$. The composite (0.3 $V_f$) was examined with XRD to study any possible interactions with CeO₂ (Fig. 7.20(b)). The
XRD peaks corresponding to CeO₂ are indexed based on JCPDS file no. 34-0394. No unidentified or undesired secondary phases were observed in CeO₂ filler added PTFE.

7.2.4.3 Dielectric Properties

The frequency dependence of relative permittivity of the PTFE and HDPE composites with the different volume fraction of CeO₂ filler is shown in Fig. 7.21 (a) and (b) respectively. CeO₂ and PTFE have relative permittivities of 23 and 2.3 respectively at 1 MHz. In the PTFE-CeO₂ composites of all volume fractions, permittivity remained almost constant in the frequency range 0.5 KHz to 3 MHz. It reveals the good frequency stability of CeO₂-PTFE composites over a wide frequency range. Devaraju et al.¹³⁰ reported a similar observation in BaTiO₃-polyimide nanocomposite films. In HDPE-CeO₂ composites, at the lower frequency range the relative permittivity decreases with frequency for all volume fractions. It is believed that a decrease in the dipolar polarization of the matrix and the accumulation of charges at the interface between ceramic particles and polymers results in a large scale field distortion.¹³¹ After about 100 kHz, the changes become smaller. Cheng et al.¹³² reported similar variation of relative permittivity with frequency for BaTiO₃-epoxy-resin. The plots of both PTFE and HDPE composites further exhibit that the relative permittivity increases with CeO₂ content.

Fig. 7.22(a) and (b) shows the variation of dielectric loss with frequency for different compositions of PTFE and HDPE composites in the range 0.5 KHz to 3 MHz. For both PTFE and HDPE based composites, at each frequency dielectric loss increases as the concentration of CeO₂ is increased. The increase in dielectric loss for higher volume fraction of the filler is due to the increase in porosity.¹³³ For each volume fraction, the dielectric loss shows a sharp decrease with frequency up to 1 MHz and thereafter the decrease is small and gradual. This means the extent of interfacial polarization is substantially augmented as the frequency is gradually reduced and the CeO₂ is increased, yielding quite a high value of loss at each composition. In polymer composite materials, interfacial polarization is always present because of additives, fillers or even impurities having masses larger than low molecular weight dipoles that make
these systems heterogeneous. It is known that both relative permittivity and dielectric loss depend on electronic, ionic, dipole-orientation and space charge polarizations. The present system of compact is a biphase mixture of two dielectrically different materials, where ceria is ionic and polycrystalline and PTFE is semi crystalline and non-polar. Such a mixture with a distinct interphase should be appreciably lossy at low frequencies; it has displayed a large space-charge effect owing to Maxwell-Wagner polarization. The dispersion regions become somewhat broader as the amount of CeO₂ is increased for both
PTFE and HDPE composites. Khastgir et al.\textsuperscript{135} reported a similar broadening of dispersion curve with titania addition for polystyrene-titania composite.

Fig. 7.23 Variation of relative permittivity ($\varepsilon_{\text{eff}}$) and dielectric loss with volume fraction at 1 MHz and 7 GHz for both PTFE and HDPE composites. The relative permittivity and dielectric loss increase with the increasing amount of CeO$_2$ addition both at 1 MHz and 7 GHz. The increase in relative permittivity is expected as the CeO$_2$ ceramic has higher relative permittivity compared to that of polymer matrix. The dipole-dipole interaction increases and contributes to higher relative permittivities as CeO$_2$ fillers come closer at higher filler loading (see Fig. 7.17 (c), (d) of PTFE composites and (f), (g) of HDPE composites). The relative permittivity and dielectric loss of HDPE composites are higher than that of PTFE composites. When the CeO$_2$ is minor and forms a dispersed phase in a
CeO$_2$-PTFE composite, the relative permittivities of composites are determined mainly by the continuous matrix ($\varepsilon_r$ of PTFE and HDPE are 2.3 and 2.6 respectively) instead of the minor filler.$^{136}$ The relative permittivity of CeO$_2$-PTFE composites at 7 GHz (2.1 - 5) is less than that at 1 MHz (3.3 - 6.4) ($\pm$0.2). The dielectric loss of the CeO$_2$-PTFE composites (0.1 - 0.6 $\varepsilon_f$) at 7 GHz (0.0022-0.0064) is higher than that at 1 MHz (0.0012 - 0.0036) ($\pm 1\times10^{-4}$). Similarly, the $\varepsilon_{eff}$ of CeO$_2$-HDPE (0.1 - 0.5 $\varepsilon_f$) composites at 7 GHz and 1 MHz are in the range 2.8-6.9 and 3.2-7.3 respectively. The dielectric loss of these composites is 0.0036-0.0085 (at 7 GHz) and 0.0022-0.0076 (at 1 MHz). The pellets used for low frequency measurements (dimensions: 11x1 mm$^2$) have relatively higher density than the rectangular sheet (dimensions: 25x3x1 mm$^3$) used for microwave measurements. Hence the relative permittivity of samples at microwave frequency is smaller in addition to the difference in the polarization mechanisms. The dielectric loss which is the main factor affecting the frequency selectivity of a material is influenced by many factors such as porosity, microstructure and defects.$^{133}$ There are defects such as porosity and the interface phase between CeO$_2$ and PTFE in the composite materials, which can influence the relative permittivity and dielectric loss of composites.$^{137}$ In addition, the increase of CeO$_2$ amount causes the increase of interphase between CeO$_2$ and PTFE and hence the influence of interface polarization on the dielectric loss becomes more significant.$^{138}$ Yutao et al.$^{139}$ reported that interphase introduced in a polymer matrix by inorganic filler is clear compared to that by polymer blends and interfacial relaxation occurs under field around 50 Hz and cause increased tan $\delta$. The interphase region is comprised of polymer molecules that are bonded or otherwise oriented at the filler particle interface resulting in unique physical and electrical properties.$^{140,141,142}$ Vo and Shi$^{143}$ model predicts that the effective relative permittivity of a polymer-filled composite material is dependent not only on the relative permittivity of the polymer and filler phases and the concentration of the filler, but also on the relative permittivity of the interphase region and the volume of the interphase region. The interface characteristics that change the relative permittivity of the composite are affected by a change in the filler particle size and/or surface area or by a change in the chemical structure of the interphase region. Since the chemical
structure of the interphase region is a function of the polymer and its interaction with the surface of the filler particles, a change of the bonding between these two phases will alter the molecular polarizibility and hence a change in the effective relative permittivity of the composite.\textsuperscript{144} The relative permittivity values of the interphase regions are less than the relative permittivity of either the filler or matrix phases themselves. Polymer orientation or bonding at the surface of the filler eliminates one or more degrees of freedom for movement and alignment of the polymer chains under an applied electric field, which restricts the dipole polarization of the polymer molecules within the interphase region and hence a reduction in the relative permittivity.\textsuperscript{145} Todd \textit{et al.}\textsuperscript{144} reported that if the relative permittivity of the polymer is less than the relative permittivity of the filler, the effective relative permittivity decreases with decreasing interphase relative permittivity. The volume fraction of the interphase region is dependent upon the volume fraction of the filler which increases as the particle size of the filler decreases due to the increase in surface area of the smaller filler. The chemical structure of the interphase region may be the predominant factor, which affects the relative permittivity of PTFE-CeO\textsubscript{2} system.

The variation in relative permittivity with temperature of the PTFE and HDPE based composites is shown in Fig. 7.24(a) and (b) respectively. It should be noted that the variation in relative permittivity of both PTFE and HDPE based composites are very small. As the temperature increases the relative permittivity decreases. A negative deviation of 0.6 \% from the room temperature is observed for 0.1 \textit{V}_f of PTFE-CeO\textsubscript{2} system. However, as the volume fraction of CeO\textsubscript{2} increases the change in relative permittivity with temperature increases and reaches a maximum value of 1.5 \% for 0.6 \textit{V}_f. In HDPE-CeO\textsubscript{2} system, a percentage deviation of 0.8-2.6 is observed as the volume fraction increases from 0.1-0.5. This slow decrease in relative permittivity with temperature for both the composite systems is due to the large difference in thermal expansion coefficient of polymer (CTE of PTFE is 109 ppm/°C and that of HDPE is 230 ppm/°C)\textsuperscript{85} and CeO\textsubscript{2} filler (12.7 ppm/°C)\textsuperscript{146}, which would disturb the aggregation of polar components causing a decrease in relative permittivity.\textsuperscript{147,148}
The predicted values of relative permittivities using equations (7.3)-(7.7) are compared with the experimental results at 7 GHz for PTFE and HDPE based composites and is shown in Fig. 7.25 (a) and (b). In PTFE-CeO\(_2\) composites, it is seen that for lower volume fractions (up to 0.3 \(V_f\)), Serial Mixing Model and Maxwell-Garnett Equation holds good and thereafter it deviates from the experimental values. Predicted permittivity using EMT model deviates from the experimental values for PTFE-CeO\(_2\) composites. In HDPE-CeO\(_2\) composites, Litchnecker and Jayasundare-Smith equations are valid up to 0.4 \(V_f\). Maxwell-Garnett and EMT model equations agree with the experimental values for lower volume fractions only. Generally all theoretical predictions are valid for low
filler contents.\textsuperscript{149,150,151,152} This is due to the imperfect dispersion of ceramic particles at higher filler contents and also to the air enclosed by the composites. The complex effective permittivity will depend on the permittivity of each phase in the mixture, their volume fraction, shape and size of the ceramic particle, porosity and interface between components and eventually on the spatial arrangement in the mixture.\textsuperscript{153} Inclusion of all these parameters makes the calculations tedious.

Fig. 7.25 Experimental and predicted $\varepsilon_{\text{eff}}$ of (a) PTFE-CeO$_2$ composites (b) HDPE-CeO$_2$ composites at 7 GHz

Fig. 7.26 Experimental and predicted $k_c$ of (a) PTFE-CeO$_2$ composites (b) HDPE-CeO$_2$ composites

Fig. 7.26(a) and (b) shows comparison of experimental and predicted values of thermal conductivities using equations (7.8)-(7.11) of PTFE-CeO$_2$ and HDPE-CeO$_2$ composites with varying filler contents. For both PTFE and HDPE based composites, thermal conductivity increases gradually with CeO$_2$ filler loading due to the higher
thermal conductivity of CeO\textsubscript{2} (12 W/m°C). Thermal conductivity is improved to 1.85 W/m°C (standard deviation ± 0.01 W/m°C) for 0.6 \( V_f \) from 0.265 W/m°C for pure PTFE. In HDPE composites, thermal conductivity increases from 0.54 to 3.22 W/m°C as CeO\textsubscript{2} loading increases from \( V_f = 0 \) to 0.5. This is due to the presence of more connecting path between filler without disturbing the matrix. A similar observation of variation of thermal conductivity was reported by Kim \textit{et al.}\textsuperscript{154} in AlN-epoxy composites. Experimental results of PTFE-CeO\textsubscript{2} composites are close to the predictions of Geometric Mean Model and Chen-Vachon Model while for HDPE-CeO\textsubscript{2} composites, EMT model holds good with the experimental values. Predicted thermal conductivity using EMT model holds good for lower volume fractions (up to 0.2 \( V_f \)) of PTFE-CeO\textsubscript{2} composites and thereafter it deviates from the experimental values. The EMT model considers the composite system to be homogeneous with an ideal interface. As the volume fraction of the filler increases, the mismatch between the matrix and the filler in the form of interfacial gap becomes serious which is bad for heat conduction.\textsuperscript{155} Generally, all theoretical predictions are valid for low filler contents.\textsuperscript{154,156} Agari \textit{et al.}\textsuperscript{157} reported that in thermal conduction systems containing a high volume of fillers, particles interact with each other and affect the position of particles in a composite. Hence it is considered that the powder properties of particles (the ease of forming an aggregate of particles, limit of packing etc.) greatly affect the thermal conductivity of the composite. Maxwell-Eucken model predicts values significantly higher than the experimental data in PTFE-CeO\textsubscript{2} composites while in HDPE-CeO\textsubscript{2} composites the values are below experimental data. This difference in values with experimental data is due to the fact that it does not account for differences in morphology or the effects of chain formation. Theoretical models account for variations in the size, shape, intrinsic thermal conductivity and state of dispersion of the filler. The wide variation in filler geometry, orientation and dispersion makes it difficult to compare composites filled with different compounds. Moreover, the interfacial boundary thermal resistance between the filler particles and the matrix referred to as Kapitza resistance\textsuperscript{158} is not taken into account while calculating the thermal conductivity of PTFE and HDPE based CeO\textsubscript{2} composites. It is not possible to measure it on the molecular level where it
Moreover in the theoretical models explained above porosity of the composites is not accounted. As a result, experimental and theoretical thermal conductivity data are often not in agreement.

Fig. 7.27 Experimental and predicted thermal expansion coefficients (CTE) of in (a) PTFE-CeO₂ composites (b) HDPE-CeO₂ composite

Fig. 7.28 Variation of Vicker's microhardness with volume fraction in (a) PTFE-CeO₂ and (b) HDPE-CeO₂ composites

Fig. 7.27(a) and (b) shows the comparison between the experimental data and theoretical models (equations (7.12)-(7.17)) for coefficient of thermal expansion (CTE) of PTFE-CeO₂ and HDPE-CeO₂ composites with varying filler fractions. The CTE decreases with the increasing amount of CeO₂ content for both PTFE and HDPE composites. CeO₂ has CTE of 12.5 ppm/°C (Standard deviation, 0.04 ppm/°C) in the temperature range 25 to 270°C. If a composite is heated, the polymer matrix will expand more than the ceramic fillers. However, if the inter-phases are capable of transmitting
stresses the expansion of the matrix will get reduced.\textsuperscript{161} CTE is improved to 22.9 ppm/°C from 99.3 ppm/°C (for PTFE) for a filler loading of 0.6 $V_f$. As $V_f$ increases from 0 to 0.5, CTE varies from 230 to 78.5 ppm/°C. The parameters used for the prediction of CTE are $\alpha_m$ ($\alpha_{PTFE} = 99.3$ ppm/°C and $\alpha_{HDPE} = 230$ ppm/°C), $\alpha_f = 12.58$ ppm/°C, $B_f = 220$ GPa, $B_m$ ($B_{PTFE} = 0.4$ GPa and $B_{HDPE} = 1.46$ GPa), $K_f = 149$ GPa and $K_m$ ($K_{PTFE} = 0.55$ GPa and $K_{HDPE} = 0.30$ GPa). The CTE values calculated using rule of mixtures (equation (7.11)) are slightly higher than the corresponding experimental values for both PTFE and HDPE based composites. This may due to difference in microstructure, bulk modulus and thermal softening of the components in the composites, which are not accounted in this relation.\textsuperscript{162} The values of CTE calculated using Turner equation (7.12) also shows a large deviation from the experimental values for both PTFE and HDPE based composites. It can be seen that in both the composites and for all volume fractions, the CTE obtained lies in between Schapery’s upper and lower bounds (equations (7.14) & (7.15)). The deviation from experimental data is smaller for Schapery’s upper bound than the lower bounds. Similar variation of CTE is reported by Wong \textit{et al.}\textsuperscript{120} while calculating the CTE values for epoxy resins filled with silica, alumina and aluminum nitride.

Micro indentation with a point indenter involving a deformation on a very small scale is one of the simplest ways to measure the mechanical properties of a polymer composite. Fig. 7.28(a) and (b) shows the variation of micro hardness with CeO$_2$ filler loading in PTFE and HDPE based composites. Vickers microhardness tests are performed for a range of indentation diagonals. Micro hardness of 700 kg/mm$^2$ is obtained for the sintered and dense CeO$_2$ for a load of 400g. An average Vickers’s hardness of 7 and 9 kg/mm$^2$ are obtained for virgin PTFE and HDPE respectively. As the volume fraction of CeO$_2$ loading increases, the hardness also increases in PTFE and HDPE based composites. An increase in hardness to 17 kg/mm$^2$ is obtained for 0.6 $V_f$ in PTFE-CeO$_2$ composite. In HDPE-CeO$_2$ composite the microhardness obtained is 28 kg/mm$^2$ for 0.5$V_f$. Optical microscopic images of PTFE and HDPE based composites after indentation are shown in Fig. 7.29(a)-(f).
Fig. 7.29 Optical microscopic images of (a) virgin PTFE (b) 0.1 $V_f$ and (c) 0.3 $V_f$ of PTFE-CeO$_2$ composites (d) virgin HDPE (e) 0.1 $V_f$ (f) 0.3 $V_f$ of HDPE-CeO$_2$ composites after indentation

Micro hardness determination using the imaging method is a promising technique for the morphology–mechanical property correlations in heterophase systems of known composition. It is worth to note from the optical micrographs of the composites that CeO$_2$ particles are well dispersed in the PTFE and HDPE matrix.
Though the dielectric loss and CTE is slightly high for HDPE-CeO₂ composite, it has reasonably good relative permittivity, thermal conductivity and mechanical properties compared to PTFE based composites.

7.3 CERIA-La0.5Sr0.5CoO₃-δ COMPOSITES FOR GIANT PERMITTIVITY APPLICATIONS

7.3.1 Introduction

The electronic packaging industry is continuously seeking ways to increase the integration density of printed circuit boards (PCBs) as part of an effort to miniaturize electronic equipments. Towards this goal recent years have witnessed an increasing demand on high relative permittivity materials for its potential application in electrostrictive and embedded passive devices. It is widely known that several high permittivity materials such as Pb(ZrTi)O₃ (PZT), Pb(Mg₁/₃Nb₂/₃)O₃-PbTiO₃ (PMNT), 50Pb(Ni₁/₃Nb₂/₃)O₃-35PbTiO₃-15PbZrO₃ (PNN-PT-PZ), are indispensable to modern electronic devices. Lead based ceramics are not environmental friendly and have high dielectric loss compared to low loss ceramics. Moreover, these materials are ferroelectric and have strong temperature dependent properties. A very high relative permittivity with weak temperature and frequency dependency is observed in polycrystalline CuO, which is comparable to those of recently, discovered non-ferroelectric CaCu₃Ti₄O₁₂ and Li and Ti doped NiO ceramics. Almost all the investigated materials for passive embedded technology are composites.

Electrically percolative composites have attracted much attention because they can possess a high relative permittivity at a critical concentration of fillers and thus can have potential applications as dielectrics for energy storage capacitors and electrostrictive devices. The conductor-insulator composites of several kinds were extensively studied to understand the insulator-conductor transition in percolative networks. There are reports that a certain kind of two-phase composite could improve the dielectric properties. Composites with conducting phases dispersed in an insulating matrix exhibit high permittivity near the percolation limit of the conducting phase. In the
context of high \( \varepsilon_r \) composites several polymer-ceramic,\textsuperscript{176} polymer-metal\textsuperscript{167,177} and ceramic-metal composites\textsuperscript{178,179} have been extensively studied. Polymer based composites are flexible and have low processing temperature. However, its permittivity is low compared to ceramic metal composites. Commonly used metallic powders in ceramic metal composites are Al, Ni, Cu, Ag, Pt, Pd. Among these Al, Ni, Cu have oxidation problem and need inert atmosphere at higher sintering temperature. Pt and Pd are too expensive and silver is one of the few metals that can be fired in air at higher temperature without oxidation. But it melts above 960°C and cannot be used at sintering temperatures above 950°C. Generally, ceramic metal composites (cermets) are sintered at the sintering temperature of ceramic. Reports\textsuperscript{180,181} show that silver can diffuse along the open pores and escapes at higher sintering temperature. It is reported that in ceramic silver composite, the sintering temperature has a crucial role in determining the percolation threshold. Hence the sintering temperature of the ceramics should be reduced below the melting point of silver. Another difficulty with cermet composite is that it shows a narrow smearing region and hence difficult to obtain a filler loading close to percolation threshold.

Reports shows that the cubic crystalline \( \text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3-\delta \) (LSCO) ceramic has conductivity (200 S/cm) comparable to that of metals\textsuperscript{182,183,184,185} and avoids the oxidation problems of metal. This motivated us to study the effect of conducting phase \( \text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3-\delta \) (LSCO) on the insulating matrix \( \text{CeO}_2 \). As the strontium content of \( \text{La}_1-x\text{Sr}_x\text{CoO}_3-\delta \) perovskite increases, its crystal structure shifts from rhombohedral to cubic (for \( x > 0.4 \)). Cerium oxide has been chosen as the insulating phase due to its good dielectric properties.\textsuperscript{24} In the present work the electrical properties of \( \text{CeO}_2\text{-LSCO} \) composites are investigated. The present study reports for the first time the giant permittivity of ceramic-ceramic two phase composite in which one phase is insulating and the other conducting.

### 7.3.2 Experimental

The samples of \( \text{CeO}_2\text{-LSCO} \) composites were prepared by the conventional solid-state ceramic route. High purity \( \text{CeO}_2 \) powder (IRE, 99.9 %) used in the present
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investigation was initially heated at 1000°C to remove any volatile impurities. La$_{1-x}$Sr$_x$CoO$_{3-\delta}$, $x=0.5$ (LSCO) ceramics were prepared by the conventional solid-state ceramic route as described in section 2.1.2 of Chapter 2. High purity chemicals La$_2$O$_3$ (Aldrich, 99.9%), SrCO$_3$ (Aldrich, 99+%) and Co$_3$O$_4$ (Aldrich, 99%) were used as starting powders. Stoichiometric proportions of the chemicals were weighed and ball milled for 24 hours using zirconia balls in distilled water media. The slurry was dried and then calcined for 5 hours at 1100°C. The calcined powder was then ball milled for 24 hours. Different volume fraction of fine LSCO powder were added to the CeO$_2$ powder and mixed again in distilled water medium. 4 wt % Poly vinyl alcohol solution was then added to the powder, mixed, dried and ground well. The powder was uniaxially pressed into disc shaped pucks of 11 mm diameter and about 1 mm thickness at a pressure of about 100 MPa using a tungsten carbide die. The green compacts were fired at a rate of 5°C/min up to 600°C and soaked at 600°C for 30 minutes to expel the binder. The pellets were sintered in air at temperatures in the range 1050-1250°C and the dwell time was 2 hours. After sintering, the samples were allowed to cool down to room temperature at the rate of 3°C/min. The samples were then polished to remove surface irregularities.

The densities of the samples were measured by the Archimedes method. The powdered samples were used for analyzing the X-ray diffraction patterns using CuK$_\alpha$ radiation and the surface morphology of sintered samples were studied using a scanning electron microscope. The polished thin pellets were electroded by coating silver on both sides in the form of ceramic capacitors and were used for dielectric measurements using LCR meter (HIOKI 3532-50 LCR Hi TESTER, Japan).

7.3.3 Results and Discussion

7.3.3.1 Densification of CeO$_2$-LSCO composites

The synthesizing conditions such as sintering temperature and their durations were optimized for LSCO added CeO$_2$ ceramics to obtain the best density and dielectric properties. The samples are having good thermal and chemical stability as explained in section 3.3.4 of Chapter 3. The theoretical density of CeO$_2$-LSCO composites is
calculated using equation (7.18), section 7.2.4.1. Fig. 7.30 shows the variation of bulk density with sintering temperature for all volume fractions of LSCO added CeO₂ ceramic. The density increases with increase in sintering temperature. The variation in percentage densification with different volume fraction of LSCO added CeO₂ ceramic sintered at 1150 and 1250°C respectively is shown in Fig. 7.31. The percentage densification increases with volume fraction and reaches a maximum value at \( V_f = 0.4 \) and then decreases. The percentage densification of samples sintered at 1250°C is higher than that sintered at 1150°C. This is due to the increase in grain size and simultaneous reduction in porosity with increase in sintering temperature. The densification of CeO₂-LSCO composite increases and reaches a maximum at 0.4 \( V_f \) and then decreases for samples sintered at 1150 and 1250°C.

7.3.3.2 Phase and Microstructural Analysis

The XRD patterns of LSCO added CeO₂ is shown in Fig. 7.32. The XRD patterns of 0.40 volume fraction \((V_f)\) LSCO added CeO₂ samples sintered at 1150 and 1250°C show that it is a mixture of CeO₂ and LSCO. The XRD patterns of CeO₂ and LSCO are indexed according to ICDD File Nos. 34-0394 and 36-1394 respectively. It is clearly
evident from the XRD pattern of CeO$_2$-LSCO samples sintered at 1150 and 1250°C that no additional phases are present.

![XRD Patterns](image)

**Fig. 7.32** XRD patterns of (a) pure CeO$_2$ (b) 0.40 V$_f$CeO$_2$ -LSCO composite sintered at 1150°C (c) 0.40 V$_f$CeO$_2$ -LSCO composite sintered at 1250°C (d) pure LSCO

SEM micrographs of 0.40 volume fraction LSCO added CeO$_2$ samples sintered at 1150 and 1250°C are shown in Figs. 7.33(a) and (b) respectively. Both the microstructures show two types of grains - brighter contrast is of CeO$_2$ and darker contrast is of LSCO. The 0.40 V$_f$ LSCO added CeO$_2$ ceramic sintered at 1150°C shows that the ceramic has a porous microstructure. This is due to the low densification of ceramic at 1150°C (see Fig. 7.31). The grain growth of the sample is observed with increase in the sintering temperature, resulting in the decrease of porosity (Fig. 7.33(b)). The LSCO grain starts melting for the sample sintered at 1250°C. The grain size of pure CeO$_2$ ceramic sintered at 1650°C/2h is approximately 40 μm (see Fig. 7.5 (a), section 7.1.3.3). For the sample sintered at 1150°C, both CeO$_2$ and LSCO grains have approximately 0.4-1 μm size and that sintered at 1250°C grain size is approximately 1-3 and 5-10 μm respectively. The reduction in size of CeO$_2$ grain from 40 to 5-10 μm for sample sintered at 1650 and 1250°C respectively is due to the lower sintering
temperature. The LSCO aids liquid phase sintering and lowers the sintering temperature of CeO$_2$-LSCO composite.

![SEM Micrographs](image)

**Fig. 7.33** SEM Micrographs of 0.40 volume fraction of CeO$_2$-LSCO composite sintered at (a) 1150°C (b) 1250°C

### 7.3.3.3 Dielectric Properties

The variation of relative permittivity with sintering temperature for different volume fractions of LSCO added CeO$_2$ samples is shown in Fig. 7.34. For all volume fractions except 0.1 and 0.2, the relative permittivity increases with sintering temperature, reaches a maximum at 1150°C and then on further the increase in permittivity is small. The variation in the relative permittivity with sintering temperature is more prominent for those composites with LSCO content greater than 0.2 volume fraction. For composites containing LSCO less than 0.3 $V_f$, the variation is much more gradual. At sintering temperatures below 1250°C, the LSCO particles are distributed in the CeO$_2$ matrix. The size of LSCO grains below 1250°C is small compared to that at higher temperature (see Fig. 7.33). Hence the surface area increases, the number of particles at a particular volume fraction of composite increases, and the interparticle distance decreases$^{176}$ When the LSCO particles come closer, at a particular interparticle distance, an overlapping of diffused double layer charged clouds around the conducting particles can occur$^{186}$ The resulting electromagnetic coupling between the neighboring particles increases the local field, and thereby enhances the dipole moment of individual particles in the composite.
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This, in turn, can lead to multipolar interaction between the particles. The net effect of this multipolar interaction between all the particles can account for the rapid increase in relative permittivity and conductivity of the composites at the percolation threshold. As the sintering temperature increases, agglomeration of LSCO particles occurs. Hence, the size of the LSCO particles increases with the sintering temperature and results in an increase in interparticle distance and decrease in number of LSCO particles. This can lead to a decrease in the relative permittivity with an increase in sintering temperature. Another reason for the decrease of relative permittivity at higher sintering temperature may be due to the reduction of Ce$^{4+}$ to Ce$^{3+}$ at temperatures greater than 1200°C. The high electrical conductivity of LSCO depends on the strontium content ($x$), oxygen deficiency ($\delta$) and temperature. According to Jonker, in La$_{1-x}$Sr$_x$CoO$_3$, when a Sr$^{2+}$ ion occupies La$^{3+}$ site and if $x > 0.4$, the charge compensation is accomplished by the formation of O$^{2-}$ vacancy. The ionic radius of Ce$^{3+}$ and Ce$^{4+}$ are 1.34 and 1.14 Å respectively. The ionic radius of Ce$^{3+}$ is comparable to that of La$^{3+}$ (1.36 Å) and Sr$^{2+}$ (1.44 Å) and hence Ce$^{3+}$ will be substituted in the La/Sr site of LSCO. The value of $\delta$ (oxygen vacancy) decreases only when Ce$^{3+}$ is substituted in the Sr$^{2+}$ site. The reduction of Ce$^{4+}$ to Ce$^{3+}$ occurs at temperatures greater than 1200°C. XPS analysis is required to confirm the valence state of Ce in CeO$_2$-LSCO composite at 1150 and 1250°C. Thus the optimum sintering temperature of the composite is found to be 1150°C as far as the relative permittivity is concerned.

Fig. 7.34 Variation of relative permittivity ($\varepsilon_r$) with sintering temperature for different volume fraction of LSCO added CeO$_2$ ceramic
The variation in relative permittivity and conductivity with different volume fractions of LSCO sintered at 1150 and 1250°C are as shown in Figs. 7.35 and 7.36. An abrupt increase in the relative permittivity ($\varepsilon_r \approx 10^5$) is obtained at 0.40 $\nu_f$ of LSCO, and this is taken as the percolation threshold. The sharp increase of relative permittivity can be explained by two mechanisms: the generation of a dielectric field around conducting particles and the formation of microcapacitors through isolation of LSCO with thin dielectric layers. It is reported that a dielectric field develops around the conducting particles dispersed in insulating materials$^{194,195}$ The sharp increase in relative permittivity is a result of an interfacial polarization phenomenon that occurs at the interface of the dissimilar materials$^{196}$. The charge carriers in the different phases of the composite are trapped at the interfaces within the dielectrics. These charges are unable to discharge freely and give rise to an overall field distortion, which results in an increase in capacitance and relative permittivity. In CeO$_2$-LSCO composite, the dielectric field developed around the LSCO particle can result in an increase in the effective relative permittivity. The LSCO conducting particles in the composites act as internal electrodes.
of a unit micro-capacitor. Such regions contribute to an extremely large capacitance, which adds up macroscopically and results in a large relative permittivity. The variation of conductivity with volume fraction follows the same trend as that of relative permittivity and volume fraction of LSCO and it is shown in Fig. 7.36. As the volume fraction of LSCO increases, the LSCO particles merges and at the percolation limit, there is a continuous path of adjacent allowed sites across the system and this leads to the sudden increase in conductivity. In composites, the conduction occurs either by the transfer of electrons between the particles in intimate contact or by the tunneling of electrons between the grains whose distance is less than 100 Å.\textsuperscript{197} At 1150°C, due to large number of LSCO particles in a particular region, the increased carrier concentration increases the probability of electron hopping and hence higher conductivity than at 1250°C.

![Graph](image)

**Fig. 7.37** Variation of relative permittivity ($\varepsilon_r$) with frequency for different volume fraction of CeO$_2$-LSCO composites sintered at 1150°C

The variation of relative permittivity with frequency for different volume fractions of CeO$_2$-LSCO composites sintered at 1150°C are shown in Fig. 7.37. The relative permittivity increases gradually with the LSCO content up to $V_f = 0.2$ and beyond that the relative permittivity increases by several orders of magnitude. The decrease in relative permittivity with frequency is slightly higher than that below $V_f = 0.3$. Due to the direct
relation with polarization, relative permittivity has a strong frequency variation as different polarization mechanisms become active. Fig. 7.38 shows the temperature dependence of relative permittivity of CeO$_2$-LSCO composites with different volume fraction of LSCO measured at 1 MHz. It is clear that for all the volume fractions of LSCO, the relative permittivity is almost independent of temperature in the range -30 to 70°C.

Enhanced electrostriction is related to an enhanced relative permittivity. This suggests that the electrostriction can be enhanced by increasing the relative permittivity of the composite so that the same electric field can induce a higher polarization and thus a higher electrostriction. The present ceramic-ceramic composite overcomes the disadvantages of cermets such as oxidation problem and evaporation of metals at high sintering temperatures. CeO$_2$-LSCO composites can replace the present cermets used in electromechanical and embedded passive devices.

### 7.4 CONCLUSIONS

#### Ceria-Glass Composites

- Effect of B$_2$O$_3$, B$_2$O$_3$-SiO$_2$, Al$_2$O$_3$-SiO$_2$, ZnO-B$_2$O$_3$, BaO-B$_2$O$_3$-SiO$_2$, MgO-B$_2$O$_3$-SiO$_2$, PbO-B$_2$O$_3$-SiO$_2$, ZnO-B$_2$O$_3$-SiO$_2$, 2MgO-Al$_2$O$_3$-5SiO$_2$, Li$_2$O-B$_2$O$_3$-SiO$_2$, Bi$_2$O$_3$-ZnO-B$_2$O$_3$-SiO$_2$ and Li$_2$O-MgO-ZnO-B$_2$O$_3$-SiO$_2$ glass addition on the structure, density and microwave dielectric properties of CeO$_2$ ceramics have been investigated.

- The X-ray Diffraction studies indicate the presence of Ce(BO$_2$)$_3$, CeZnB$_2$O$_5$, CeZnB$_2$O$_5$, PbB$_2$O$_4$ and CeBO$_3$ phases with the addition of higher weight percentage of B$_2$O$_3$, ZnO-B$_2$O$_3$, ZnO-B$_2$O$_3$-SiO$_2$, PbO-B$_2$O$_3$-SiO$_2$ and Bi$_2$O$_3$-ZnO-B$_2$O$_3$-SiO$_2$ respectively.

- Maximum quality factor of 69500 GHz (at 5.92 GHz) is obtained for 0.5 wt% Bi$_2$O$_3$-ZnO-B$_2$O$_3$-SiO$_2$ added CeO$_2$ ceramic at a sintering temperature of 1550°C which also showed the best densification
Addition of BS, AS, BBS, MBS, LBS, MAS and LMSZB glass frits although lowered the sintering temperature of CeO₂ ceramics, the dielectric properties are very much degraded.

The microwave dielectric properties of CeO₂ added with 20 wt% B₂O₃ (sintered at 900°C) are $Q_{uf} = 24200$ GHz, $\varepsilon_r = 13.2$, $\tau_f = -46$ ppm/°C and that of CeO₂ added with 10 wt% BBSZ (sintered at 950°C) are $Q_{uf} = 12000$ GHz, $\varepsilon_r = 22.4$, $\tau_f = -57$ ppm/°C.

XRD, SEM and EDX analysis revealed that there is no reaction of 20 wt% B₂O₃ and 10 wt% BBSZ added CeO₂ ceramic with silver.

From the analysis of above results it is obvious that CeO₂ + 20 wt% B₂O₃ and CeO₂ + 10 wt% Bi₂O₃-ZnO-B₂O₃-SiO₂ are promising materials for low temperature cofired ceramic applications.

**Ceria-Polymer Composites**

- PTFE-CeO₂ composites are prepared by powder processing method and HDPE-CeO₂ composites by sigma-blend technique.
- SEM micrographs show that with the increase of filler content, the packing of particles grew denser and indicated the excellent compatibility between polymer and CeO₂ particles.
- The dielectric, thermal and mechanical properties of both PTFE and HDPE composites are studied in relation to filler concentration. The relative permittivity ($\varepsilon_{eff}$), dielectric loss (tan δ) and microhardness increased with increase in CeO₂ content. The thermal conductivity ($k_c$) increased and coefficient of thermal expansion ($\alpha_c$) decreased with increase in CeO₂ content for both PTFE and HDPE composites.
- For 0.6 volume fraction loading of the ceramic, the PTFE composite has $\varepsilon_{eff} = 5$ and tan δ = 0.0064 (at 7 GHz), $k_c = 1.85$ W/m°C, $\alpha_c = 22.9$ ppm/°C and Vickers’ microhardness of 17 kg/mm². The 0.5 volume fraction of
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HDPE-CeO₂ composite has $\varepsilon_{\text{eff}} = 6.9$ and $\tan \delta = 0.0085$ (at 7 GHz), $k_c = 3.22 \text{ W/m}^{\circ}\text{C}$, $\alpha_c = 78.5 \text{ ppm}/^{\circ}\text{C}$ and Vickers' microhardness of 28 kg/mm².

- Different theoretical approaches have been employed to predict the effective permittivity, thermal conductivity and coefficient of thermal expansion of composite systems and the results are compared with that of experimental data.
- Due to the reasonably good dielectric, thermal and mechanical properties of HDPE composite (0.5 $V_f$) compared to PTFE composites, 0.5 $V_f$ HDPE-CeO₂ can be considered as a possible candidate for microwave substrate applications.

- Ceria-La$_{0.5}$Sr$_{0.5}$CoO$_{3-\delta}$ composites
  - The samples of CeO₂-LSCO (insulator-conductor) composites are prepared by the conventional solid-state ceramic route. XRD and SEM results show that the composite is a mixture of CeO₂ and LSCO.
  - The variation of relative permittivity with sintering temperature shows that the permittivity is maximum at 1150°C for $V_f = 0.4$. Further increase in sintering temperature decreases the permittivity in CeO₂-LSCO composites.
  - For all volume fractions of LSCO, the relative permittivity of CeO₂-LSCO composites is almost independent of temperature.
  - CeO₂-LSCO composites can replace the present cermets used in electromechanical and embedded passive devices due to its high relative permittivity.

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7.5 REFERENCES


32 B. W. Hakki and P. D. Coleman, IRE Trans. on Microwave Theory Tech., MTT-8, 402 (1960).


44 ICDD Card Nos. 23-0877, 86-1884, 21-0177, 15-078.


155 H. He, R. Fu, Y. Han, Y. Shen and X. Song, J. Mat. Sci., 42, 6749 (2007).


