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Microwave dielectric properties of CeO_2–0.5AO–0.5TiO_2 (A = Ca, Mg, Zn, Mn, Co, Ni, W) ceramics

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Abstract

Microwave dielectric ceramic materials based on cerium [CeO_2–0.5AO–0.5TiO_2 (A = Mg, Zn, Ca, Mn, Co, Ni, W)] have been prepared by a conventional solid state ceramic route. The crystal structure was studied by X-ray diffraction, microstructure by scanning electron microscopy (SEM) techniques and the phase composition was studied using energy dispersive X-ray analysis (EDXA). The sintered ceramics had a relative dielectric constant (ε_r) in the range 17–65 and quality factor $Q_u xf$ up to 50,000 GHz and a temperature variation of resonant frequency (τ_f) ranging from a negative value (−62 ppm/°C) to a high positive value (+399 ppm/°C). The majority of the synthesized ceramics were of a two phase composite consisting of a fluorite CeO_2 and perovskite $ATiO_3$ phase. The microwave dielectric properties were further tailored by adding various amounts of dopants of different valencies to the calcined powder. This made it possible to either tune τ_f to zero or improved the quality factor further.

Keywords: Powders-solid state reaction; Dielectric properties; CeO_2; Microwave dielectrics

1. Introduction

The recent growth in wireless communication systems has caused an increasing demand for temperature stable low loss dielectric materials. Considerable attention has also been paid to the miniaturization of devices in telecommunication infrastructure. A dielectric resonator (DR) is a ceramic puck with high dielectric constant ($\varepsilon_r > 20$), low dielectric loss or high quality factor ($Q_u > 2000$) where Q_u is the unloaded quality factor of the ceramic and a near zero temperature coefficient of resonant frequency ($\tau_f < \pm 20$ ppm/°C) at microwave frequencies.[1] Although a large number of microwave ceramics have been developed,[2] the search continues for new materials with optimum properties. Reference 2 gives a list of dielectric resonator materials with properties reported in the literature. The important applications of ceria-based materials include use in oxygen-permeation membrane systems, fuel cells and catalytic wet oxidation and exhaust combustion catalysts.[3–5] Ceria is a good dielectric resonator material with $\varepsilon_r = 23$, quality factor ($Q_u xf$) of about 60,000 GHz and τ_f of −53 ppm/°C.[6] However, it has a relatively high negative τ_f, which precludes its immediate practical application. It is possible to tailor the properties of CeO_2 by suitable substitution and by the formation of mixed phases having opposite τ_f. Cerium oxide has three phases: CeO_2 with the CaF_2 structure and hexagonal and cubic Ce_2O_3 categorized as the A-type and C-type structures, respectively in rare earth oxides.[7] CeO_2 easily forms solid solutions with other rare-earth elements and with elements belonging to the transition-metal series. Among rare-earth elements, CeO_2–Ln_2O_3 (Ln = La, Pr, Sm, Gd and Tb) systems have been extensively investigated and their effects have been closely monitored.[8,9] Regarding transition/non-transition elements, CeO_2 easily forms solid solutions with ZrO_2,[10] PbO_2,[11] CuO,[12] MnO,[13] TiO_2,[14,15] Al_2O_3[16] and SiO_2[17,18] and each has its own uniqueness. Sebastian et al. reported[19] that CeO_2 also forms solid solution with Sm_2O_3. The ability to substitute one cation for another in a particular structure

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is dependent on several factors, such as ionic size of the host/guest cation and the crystallographic structural features of the materials.[20,21] In the present paper we examine the dielectric properties of CeO_2 together with another flexible and interesting dielectric ceramic, TiO_2, in a novel group of ceria-titania based mixed system such as CeO_2–0.5CaO–0.5TiO_2 (CCaT), CeO_2–0.5MgO–0.5TiO_2 (CMgT), CeO_2–0.5ZnO–0.5TiO_2 (CZnT), CeO_2–0.5MnO–0.5TiO_2 (CMnT), CeO_2–0.5CoO–0.5TiO_2 (CCoT), CeO_2–0.5NiO–0.5TiO_2 (CNiT) and CeO_2–0.5WO_3–0.5TiO_2 (CWT). To further optimize the dielectric properties, small amount of dopants were added to the calcined powder before sintering.

2. Experimental

The samples of CeO_2–0.5AO–0.5TiO_2 (A = Mg, Zn, Ca, Mn, Co, Ni, W) were prepared by the conventional solid-state ceramic route. High purity chemicals CeO_2 (IRE, 99.99%), TiO_2 (Aldrich, 99.9%), $CaCO_3$ (Aldrich, 99+%), $Mg(CO_3)_4Mg(OH)_2\cdot 5H_2O$ (Aldrich, 99%), ZnO (Aldrich, 99.9%), $MnCO_3$ (Aldrich, 99.9+%), Co_3O_4 (Aldrich), NiO (Aldrich, 99%), WO_3 (Aldrich, 99+%) were used as starting powders. Stoichiometric proportions of the chemicals were weighed and ball milled for 24 h using zirconia balls in distilled water media. The slurry was dried and then calcined for 10 h at 1150 °C for Ca, Mg and Zn based and at 1050 °C for Mn, Co, Ni and W based ceramics respectively. The calcined powders were then ball milled for 3 days. Depending on the A site atom, suitable dopants of various valencies were added and again ground well in an agate mortar. The fine powder is then pressed into disc shaped pucks of 14 mm diameter and about 7 mm height at a pressure of about 120 MPa using a WC coated die. The green compacts were fired at a rate of 5 °C/min up to 800 °C and soaked at 800 °C for 30 min to expel the binder. The pellets were sintered in air at temperatures in the range between 1130 and 1550 °C depending on the A site atom and the dwell time was 2 h. 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 noting the mass and the dimensions. X-ray diffraction patterns were recorded from powdered samples using Cu Kα radiation (Philips) and SEM micrographs recorded from the surface of thermally etched samples (Hitachi SEM S-4300). Raman spectra from the sintered pucks were recorded using a Renishaw system 2000 microprobe with a 488 nm line of an Ar^+ laser as exciting radiation with nominally <4 mW power incident on the sample surface. The laser line was focused onto the sample by a cylindrical microscope lens of 50× magnification with a spot diameter of 3 ± 1 μm. Dielectric properties at microwave frequencies were measured by resonance method using a Network Analyzer (Agilent 8753 ET). The specimen was placed on a low loss quartz spacer of height 8 mm inside a copper cavity of inner diameter 40 mm and height 22 mm whose inner side was silver plated. The use of low loss single crystal quartz spacer reduces the effect of losses due to the surface resistivity of the cavity. The $TE_{01\delta}$ mode was used for the microwave measurements.[22] The coefficient of temperature variation of resonant frequency was measured by noting the temperature variation of $TE_{01\delta}$ resonant mode in the temperature range 25–70 °C. Dielectric properties in the range of −253 to 37 °C were measured by placing the copper cavity on the cold head of a closed cycle Gifford McMahon cryocooler ("workhorse", Cryophysics, Abingdon, UK) were an in-house made software calculated permittivity, unloaded Q and resonance frequency over temperature.

3. Results and discussion

The CeO_2–0.5AO–0.5TiO_2 (A = Mg, Zn, Ca, Mn, Co, Ni, W) green compacts were sintered into dense ceramics except those based on tungsten, which were difficult to sinter. Fig. 1 shows the X-ray diffraction pattern recorded from CeO_2–0.5AO–0.5TiO_2 (A = Mg, Zn, Ca, Mn, Co, Ni, W) dielectric ceramics using Cu Kα radiation. The powder diffraction pattern confirm that majority of the CeO_2–0.5AO–0.5TiO_2 (A = Mg, Zn, Ca, Mn, Co, Ni) ceramics consists of two phases namely fluorite CeO_2 and perovskite $ATiO_3$. Careful analysis of the X-ray diffraction pattern show that CeO_2 peaks nearly coincide with some of the peaks of $ATiO_3$ (A = Mg, Zn, Ca, Mn, Co, Ni). In the ceramic with tungsten, CWT, several phases were formed such as CeO_2, Ce_2WO_6 and $Ce_2Ti_2O_7$. Bijumon et al.[23] reported that in the case of $Ce(Ti_{0.5}W_{0.5})O_4$, which can be related to the ratio of atoms used here, a multiphase composite containing $Ce_2Ti_2O_7$, Ce_2WO_6, TiO_2 and CeO_2 was formed. Fig. 2 shows the SEM micrographs of sintered and polished CeO_2–0.5AO–0.5TiO_2 (A = Ca, Mg, Zn, Mn, Co) ceramics revealing a highly dense product. The microstructure changes with change in the 'A' atom in CeO_2–0.5AO–0.5TiO_2 (A = Ca, Mg, Zn, Mn, Co) and it shows clearly two types of grains which were later proven to belong to CeO_2 and $ATiO_3$. The average grain size of sintered pure CeO_2 is rather large (>10 μm). In these CeO_2–$ATiO_3$ composites we found much smaller CeO_2 grain sizes varying from 2 μm in the CCaT (Fig. 2a) to 10 μm in CMgT (Fig. 2b). In all cases, the formed perovskite phase had smaller grain size then CeO_2. The

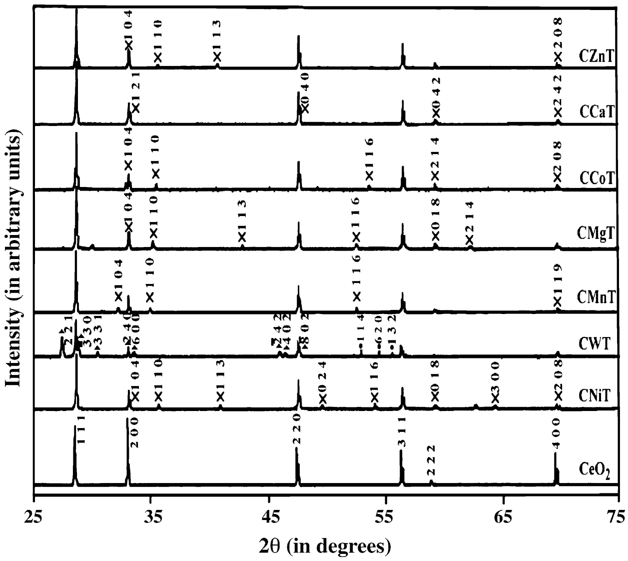


Fig. 1. XRD pattern of CeO_2–0.5AO–0.5TiO_2 (A = Mg, Zn, Ca, Mn, Co, Ni, W) ceramics. ×, $ATiO_3$ (A = Mg, Zn, Ca, Mn, Co, Ni); ▲, Ce_2WO_6; ●, $Ce_2Ti_2O_7$.

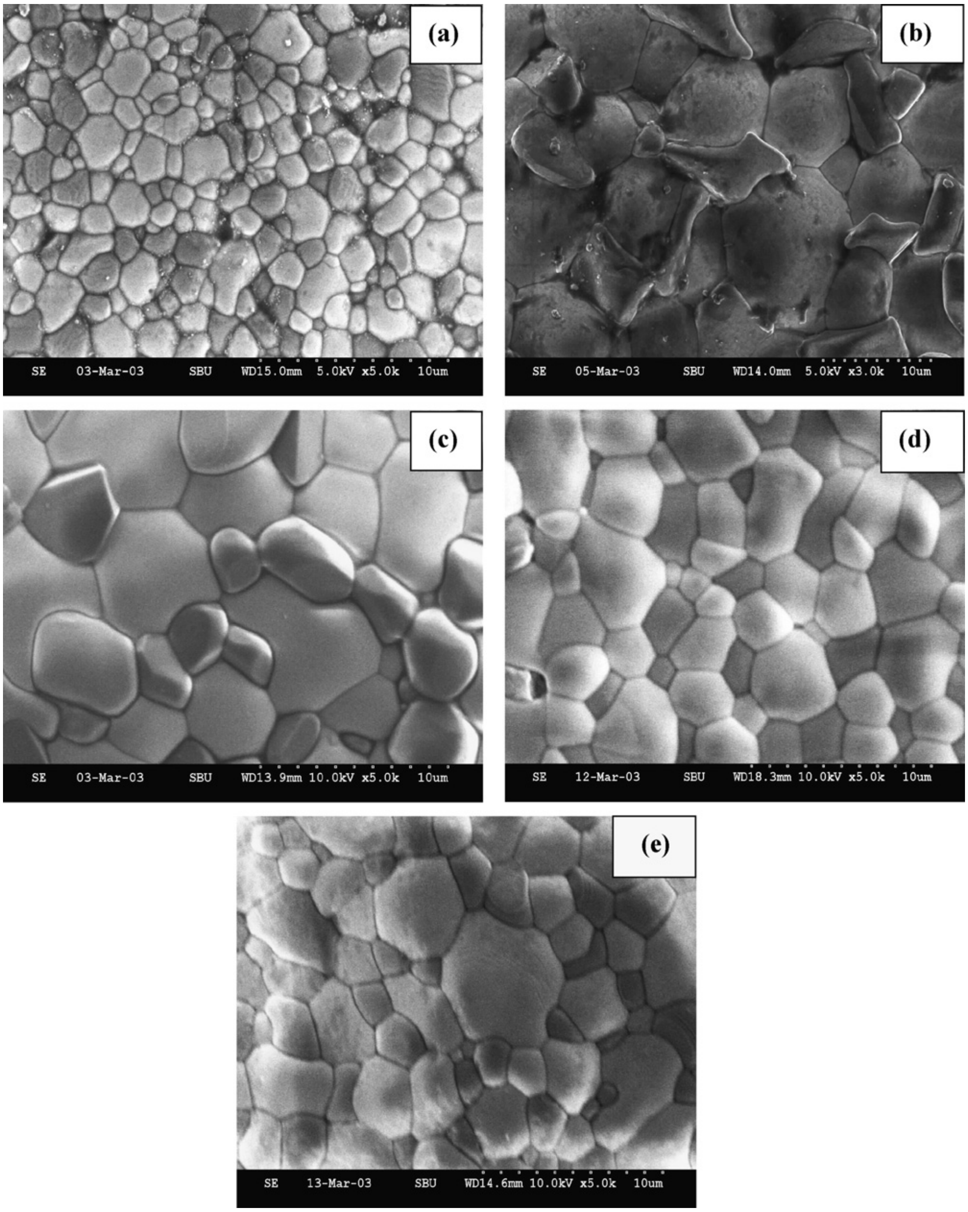
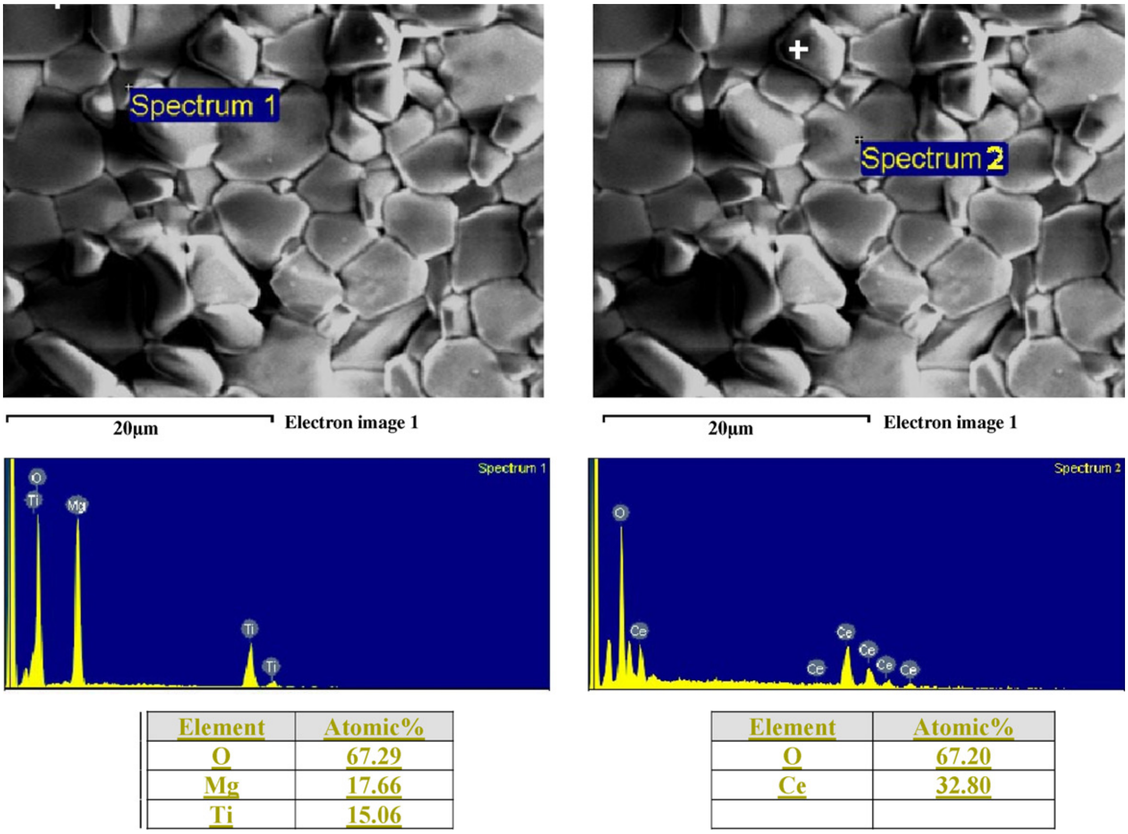


Fig. 2. SEM micrographs of (a) CeO_2–0.5CaO–0.5TiO_2, (b) CeO_2–0.5MgO–0.5TiO_2, (c) CeO_2–0.5ZnO–0.5TiO_2, (d) CeO_2–0.5MnO–0.5TiO_2, and (e) CeO_2–0.5CoO–0.5TiO_2.

CeO_2 grains are polygonal shaped with bright contrast and the smaller $ATiO_3$ (A = Mg, Zn, Ca, Mn, Co) grains with dark contrast and have well defined grain boundaries. An example of EDXA analysis in Fig. 3 confirms the earlier XRD results that there are two major phases of $ATiO_3$ and CeO_2. This result was dominating in all seven ceramic systems. Fig. 4 shows the Raman spectrum of CeO_2–0.5AO–0.5TiO_2 (A = Mg, Zn, Ca, Mn, Co, Ni, W). The mode at 463 cm^{-1} is the characteristic CeO_2 mode which is linked to the Ce–O8 vibration. If ions are substituted into the fluorite structure the line width (FWHM) of the mode and a mode shift will be observed.[19] Here we see clearly that there is no such change. This is yet another confirmation that the CeO_2 is intact as one of the phases. Where possible, $ATiO_3$ standards where compared with the CAT to prove the existence of the perovskite phase.

Table 1 gives the sintering temperature, microwave dielectric properties (ε_r, $Q_u xf$, τ_f) of CeO_2–0.5AO–0.5TiO_2 ceramics. The different ceramics possess fairly high dielectric constant in the range 17.0–65.5 and quality factor $Q_u xf$ from 9500 to 50,000 GHz. The CCaT has the highest dielectric constant of $\varepsilon_r = 65.5$ and CWT has the lowest at $\varepsilon_r = 17$. The CCaT has a high τ_f of +399 ppm/°C which is due to the high positive τ_f of $CaTiO_3$ (+800 ppm/°C) compared with the other $ATiO_3$ (A = Mg, Zn, Co, Ni, Mn) ceramics, which have negative τ_f. CCaT and CWT have a positive τ_f while CMgT, CZnT, CCoT, CNiT and CMnT have negative τ_f. The sintering temperature of the CeO_2–$ATiO_3$ composite ceramics are in the range from 1130 to 1550 °C which is lower than pure CeO_2 and pure $ATiO_3$. The low sintering temperature of CWT though is due to the formation of low melting Ce_2WO_6 phase.



Element	Atomic%
O	67.29
Mg	17.66
Ti	15.06

Element	Atomic%
O	67.20
Ce	32.80

Fig. 3. EDXA of CMgT composite proving two separate phases of CeO_2 and $MgTiO_3$.

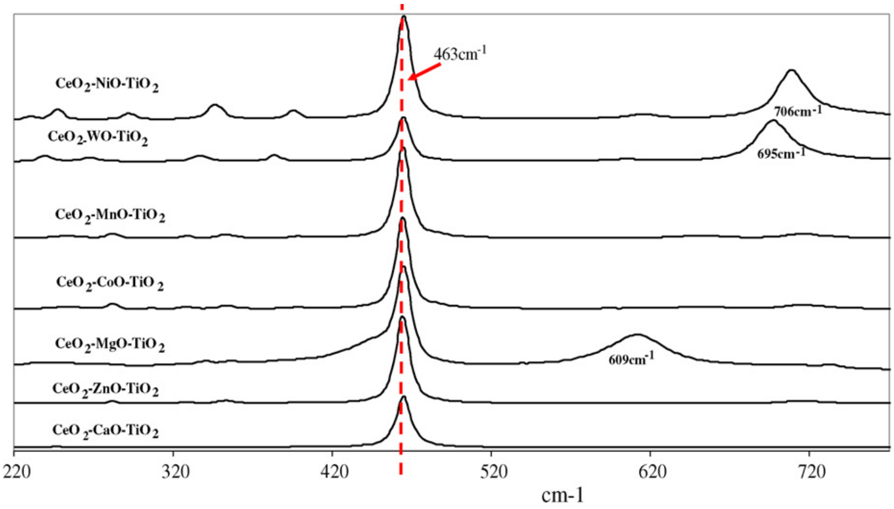


Fig. 4. Raman spectra of CeO_2–0.5AO–0.5TiO_2 (A = Ca, Mg, Mn, Zn, Co, Ni, W) ceramics.

Table 1
The dielectric properties of CeO_2–0.5AO–0.5TiO_2 (A = Ca, Mg, Mn, Zn, Co, Ni, W) ceramics

Material	Sintering temperature (°C)	Density (g/cm^3)	ε_r	$Q_u xf$ (GHz)	τ_f (ppm/°C)
CeO_2–0.5CaO–0.5TiO_2	1550	5.81	65.5	9,500	399
CeO_2–0.5MgO–0.5TiO_2	1400	5.73	22.4	17,500	−62
CeO_2–0.5ZnO–0.5TiO_2	1250	6.19	26.1	24,100	−43
CeO_2–0.5MnO–0.5TiO_2	1200	6.07	26.3	17,100	−30
CeO_2–0.5CoO–0.5TiO_2	1200	6.20	22	50,000	−47
CeO_2–0.5NiO–0.5TiO_2	1200	5.39	18	25,300	−58
CeO_2–0.5WO_3–0.5TiO_2	1130	5.45	17	45,500	7

The density of a mixture of two phases can be calculated using the equation:

$$\rho_{\text{mixture}} = V_1\rho_1 + V_2\rho_2 \tag{1}$$

where V_1 and V_2 are the volume fraction, ρ_{mixture} the calculated theoretical density and ρ_1 and ρ_2 are the densities of the two components. The empirical model proposed for predicting dielectric constant of mixtures is as follows:[24]

$$\ln \varepsilon_{\text{r,mixture}} = V_1 \ln \varepsilon_{\text{r}1} + V_2 \ln \varepsilon_{\text{r}2} \tag{2}$$

where $\varepsilon_{\text{r}1}$ and $\varepsilon_{\text{r}2}$ are the dielectric constant of two materials and $\varepsilon_{\text{r,mixture}}$ is the dielectric constant of the mixed phase ceramic. To calculate the τ_{f} of mixtures, an empirical model was proposed as follows:[25]

$$\tau_{\text{f,mixture}} = V_1\tau_{f1} + V_2\tau_{f2} \tag{3}$$

where $\tau_{\text{f}1}$ and $\tau_{\text{f}2}$ are the temperature coefficient of resonant frequencies of the two components and $\tau_{\text{f,mixture}}$ is the resultant temperature coefficient of resonant frequency of the mixture. Table 2 shows the dielectric properties of the perovskite $ATiO_3$ (A = Ca, Mg, Zn, Mn, Co, Ni) ceramics that we are suggesting as the secondary phase here.[2,26]

By using the Eqs. (1)–(3) and CeO_2 and $ATiO_3$ as the two phases, values of density, ε_{r} and τ_{f} were calculated and compared with experimental results, see Fig. 5. The experimental values of bulk density do not show much variation from the values calculated using mixture relation. The dielectric constant and τ_{f} shows very good agreement between experimental and values derived from mixture rule except in the case of CCaT ceramics. This is yet another confirmation that CeO_2–0.5AO–0.5TiO_2 (A = Ca, Mg, Zn, Mn, Co, Ni) ceramics is a mixture of CeO_2 and $ATiO_3$ phases.

When the seven initial CeO_2–0.5AO–0.5TiO_2 mixtures were microscopically analyzed, dopants such as WO_3, MoO_3, Nb_2O_5, Sb_2O_3, La_2O_3, Nd_2O_3, Bi_2O_3, SnO_2, MnO, CeO_2, Cr_2O_3 and Fe_2O_3 were added to tune their dielectric properties. In the CCaT (CeO_2–$CaTiO_3$) system, addition of 0.5 mol% Fe_2O_3 and 0.5 mol% CeO_2 slightly improved the quality factor of CCaT from 9500 to 10,500 GHz but no other major changes. However, small addition of Cr_2O_3, Fe_2O_3 and MnO tuned the τ_{f} to 0, +22 and +35 ppm/°C from the originally 399 ppm/°C, respectively. The ionic radius of Cr^{3+} (0.615 Å), Fe^{3+} (0.55 Å) and Mn^{2+} (0.67 Å) are comparable to the ionic radius of Ti^{4+} (0.605 Å).[27] Hence Cr^{3+}, Fe^{3+} and Mn^{2+} may diffuse into the Ti^{4+} site. Fig. 6 shows the variation of τ_{f} with concentration of Cr_2O_3, Fe_2O_3 and MnO dopants in the CCaT composite.

Table 2
Microwave dielectric properties of $ATiO_3$ (A = Ca, Mg, Zn, Mn, Co, Ni) and CeO_2

Material	Theoretical density (g/cm^3)	ε_{r}	$Q_{\text{u}}xf$ (GHz)	τ_{f} (ppm/°C)
$CaTiO_3$	4.04	170	12,900	800
$MgTiO_3$	3.89	17	20,780	−50
$ZnTiO_3$	5.17	21	19,000	−50
$MnTiO_3$	4.60	24.3	15,200	−56
$CoTiO_3$	4.52	19.8	37,500	−49
$NiTiO_3$	5.10	19.7	13,900	−51
CeO_2	7.2	23	60,000	−53

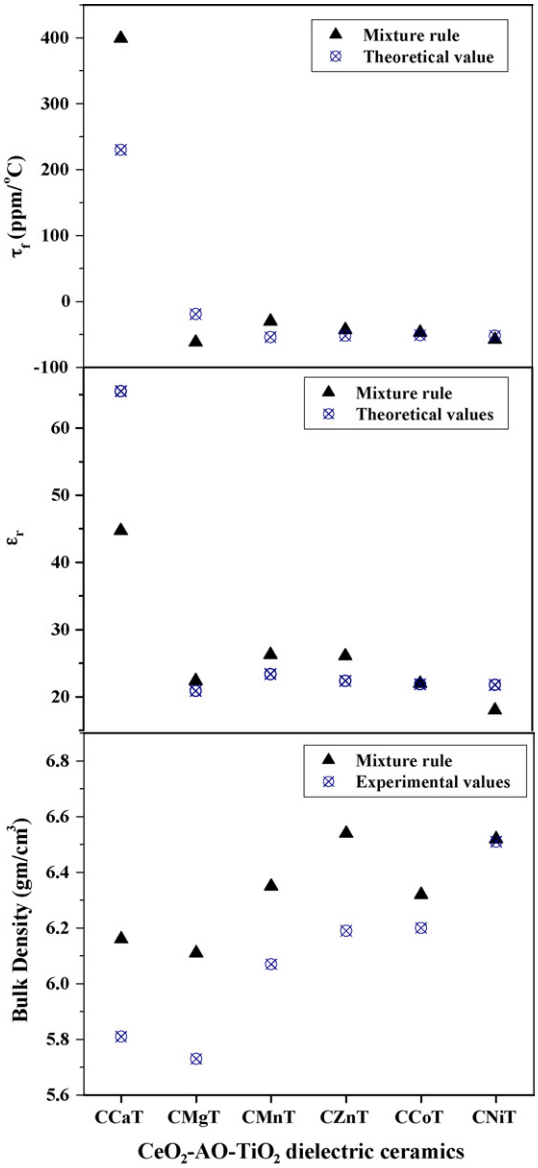


Fig. 5. Calculated and measured values of density, permittivity (ε_{r}) and temperature coefficient of frequency (τ_{f}) for suggested CeO_2–$ATiO_3$ (A = Mg, Zn, Ca, Mn, Co, Ni) composites.

Next we examined the CeO_2–0.5MgO–0.5TiO_2 (CMgT). The CMgT ceramics has $\varepsilon_{\text{r}} = 22.4$, $Q_{\text{u}}xf = 17{,}500$ GHz and $\tau_{\text{f}} = -62$ ppm/°C. Small addition of WO_3, MoO_3, Sb_2O_3, Fe_2O_3 and MnO (all under 4 mol%) increased the quality factor. Titanium based ceramics have a Ti^{4+} oxidation state. It has been reported[28] that heating at high temperatures in air will lead to a reduction of Ti^{4+} to Ti^{3+}. This reduction is well known to increase the dielectric loss.[29] Hence the addition of oxidizing agents such as WO_3, MoO_3, Sb_2O_3, Fe_2O_3 and MnO might be expected to maintain a high quality factor. A quality factor $Q_{\text{u}}xf = 90{,}000$ GHz was found for the addition of only 1 mol% WO_3 to the CMgT composite with a $\varepsilon_{\text{r}} = 21.4$ and $\tau_{\text{f}} = -50$ ppm/°C. By adding another 1 mol% TiO_2 to this system a $Q_{\text{u}}xf$ of 87,700 GHz with $\varepsilon_{\text{r}} = 21.3$ and slightly improved

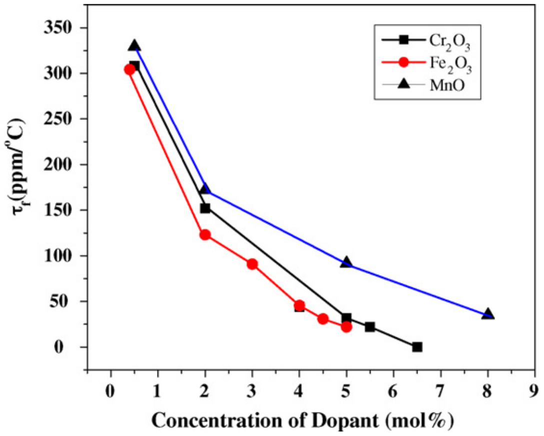


Fig. 6. Tuning of τ_f towards zero in the CeO_2–$CaTiO_3$ composite using different amount of Cr_2O_3, Fe_2O_3 and MnO dopant.

$\tau_f = -48$ ppm/°C was produced. Similarly, addition of 1 mol% MoO_3 and 2 mol% TiO_2 gave a $Q_uxf = 60{,}250$ GHz. Although the quality factor is considerably improved by small amount of dopants there is not much improvement in either the dielectric constant or τ_f.

The CeO_2–0.5ZnO–0.5TiO_2 (CZnT) has $Q_uxf = 24{,}100$ GHz, $\varepsilon_r = 26.1$ and $\tau_f = -43$ ppm/°C. Additions of 4 mol% Co_3O_4 improve the quality factor of CZnT ceramics to 33,100 GHz but there is a decrease in ε_r and τ_f. Co^{2+} (0.65 Å) is having an ionic radius comparable to that of Ti^{4+} (0.605 Å) and hence partial substitution of Co in Ti site may be the reason for the increase in quality factor. All other dopants such as WO_3, MoO_3, Sb_2O_3, Fe_2O_3, MnO, Nb_2O_5, V_2O_5, Nd_2O_3, Cr_2O_3, ZrO_2, Ta_2O_5, La_2O_3, Bi_2O_3, SnO_2 deteriorate the properties of CZnT ceramics. None of the dopants increased the dielectric constant or tuned the τ_f.

CMnT ceramics have originally $\varepsilon_r = 26.3$, $Q_uxf = 17{,}100$ GHz and $\tau_f = -30$ ppm/°C. In the case of CMnT ceramics only an excess addition of MnO improved the quality factor to 20,350 GHz. The enhancement in quality factor with Mn^{2+} doping may be due to a charge compensation mechanism that takes place in dielectric materials involving Ti ($Mn^{2+} + Ti^{4+} \Leftrightarrow Mn^{3+} + Ti^{3+}$).[30] However addition of WO_3, MoO_3, Sb_2O_3, Nd_2O_3, Nb_2O_5 and Ta_2O_5 considerably improved the τ_f. By the addition of 2 mol% WO_3 and 2 mol% Nd_2O_3 the dielectric constant increased from 26.3 to 40.6 and 37.9, respectively. The τ_f is improved from −30 to +2 ppm/°C by the addition of only 0.5 mol% Sb_2O_3, −14 ppm/°C by the addition of 0.5 mol% Nd_2O_3 and −5 ppm/°C by 1 mol% MoO_3. In all three cases the Q_uxf decreased by more than half.

For the CCoT system with starting values of $\varepsilon_r = 22$, $Q_uxf = 50{,}000$ GHz and τ_f of −47 ppm/°C an addition of 0.6 mol% of WO_3 increased the Q_uxf to as high as 70,000 GHz with an improvement in τ_f (from −47 to −30 ppm/°C). In a similar way, addition of TiO_2 tuned the τ_f to positive value. Addition of 8 mol% TiO_2 increased Q_uxf to 62,550 GHz. By combining these two dopants, 0.3 mol% WO_3 and 16 mol% TiO_2, a Q_uxf of 58,150 GHz, $\varepsilon_r = 21.2$ and $\tau_f = +5$ ppm/°C was obtained. Ionic radius of W^{6+} (0.6 Å) and Ti^{4+} (0.605 Å) are similar to that of Co^{2+} (0.65 Å). Hence substitution of W^{6+} may improved the quality factor of CCoT ceramics by stabilizing the oxidation states of both Ce and Ti.

In CNiT the dielectric properties are $\varepsilon_r = 18$, $Q_uxf = 25{,}300$ GHz and $\tau_f = -58$ ppm/°C. Addition of WO_3, MoO_3, Cr_2O_3 and Sm_2O_3 improve Q_uxf slightly and addition of Ta_2O_5, Bi_2O_3, Fe_2O_3 and WO_3 increased ε_r slightly. Addition of 0.9 mol% MoO_3 tuned τ_f from −58 to −21 ppm/°C.

The effect of dopants in CWT system showed promising dielectric properties even before addition of dopants with $\varepsilon_r = 17$, $Q_uxf = 45{,}500$ GHz and $\tau_f = 7$ ppm/°C. This system turned out to be the most complex composite. In all cases, undoped or doped, the CWT system has a low sintering temperature around 1130 °C.

From the doping study, summarized in Table 3, it is clear that CCaT system can be tuned to a $\tau_f = 0$ ppm/°C with 6.5 mol% Cr_2O_3, CMgTi can be optimized to a high $Q_uxf = 90{,}000$ GHz with 1 mol% WO_3, CMnTi can be tuned to $\tau_f = +5$ ppm/°C and CCoTi system shows a great flexibility with W/Ti dopants which makes it possible to improve both Q_uxf and τ_f. The CWT system which initially showed promising dielectric properties but turned out to be of a complex multi phase structure, showed interesting properties with extra amount of CeO_2.

Fig. 7 shows the variation of Q_uxf as a function of temperature in the range 30–310 K. The quality factor increased considerably on cooling for CMgT and at 20 K the Q_u was as high as 98,000 ($Q_uxf = 539{,}000$ GHz) which is comparable with undoped CeO_2, which has a Q_uxf of 580,000 GHz at 20 K[19]. In all samples, the quality factor increased initially on cooling and then on further cooling it decreased at different temperatures depending on the AO material, as shown in Fig. 7. These points occurred at different temperatures in all materials and are also observed in undoped CeO_2 where this anomaly point is at 190 K. The increase in the quality factor at low temperatures is due to many factors, one being the decrease of the damping of lattice vibrations (phonons). This reduces the direct interaction of the incoming dielectric wave with the phonon vibrations. The decrease in quality factor and appearance of anomaly points of some of the CeO_2–0.5AO–0.5TiO_2 (A = Mg, Zn, Ca, Mn, Co,

Table 3
Summary of dielectric properties of CAT composites and their most promising dopants

CAT—dopant	Dopant level (mol%)	Q_uxf (GHz)	$(_r$	τ_f (ppm/°C)
CCaT	–	9,500	65.5	+399
Cr_2O_3	6.5	4,315	35	0
CMgT	–	17,500	22.4	−62
WO_3	1	90,000	21.4	−50
CZnT	–	24,100	26.1	−43
Co_3O_4	4	33,100	22	−48
CMnT	–	17,100	26.3	−30
MoO_3	1	5,980	28	−5
CCoT	–	50,000	22	−47
WO_3	0.6	70,000	21	−30
WO_3/TiO_2	0.3/16	58,200	21.2	+5
CNiT	–	25,300	18	−58
MoO_3	0.9	27,300	10	−21
CWT	–	45,500	17	+7
CeO_2	10	53,000	16	+5

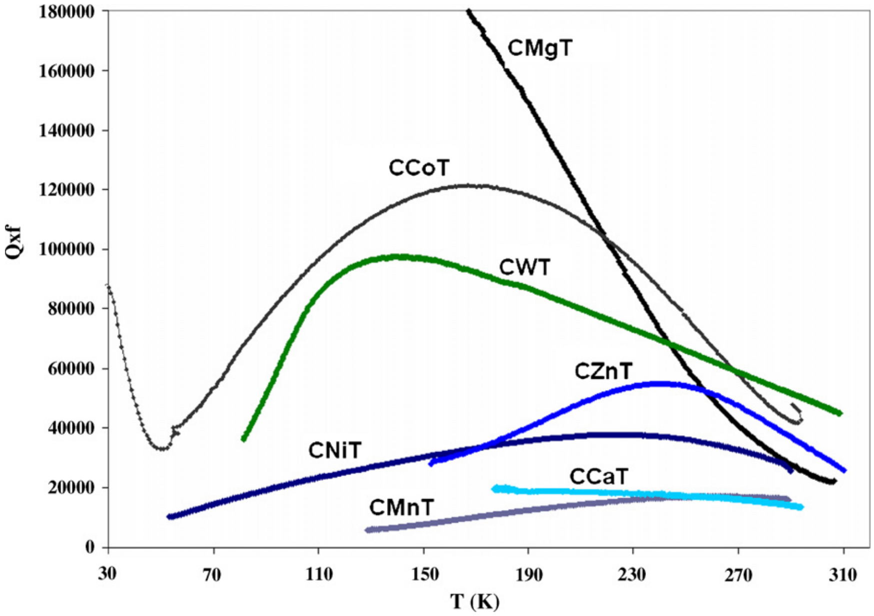


Fig. 7. Variation of $Q_u xf$ (GHz) over cryogenic temperatures of the CeO_2–0.5AO–$0.5TiO_2$ (A = Ca, Mg, Mn, Zn, Co, Ni, W) ceramics.

Ni, W) ceramics may attributed to factors such as oxygen vacancies and other charge defects in the composites, depending on the AO. In one of the cases, CeO_2–0.5CoO–$0.5TiO_2$, the anomaly corresponds to an anomaly of the permittivity which increases at 60 K when cooling, indicates a low temperature phase change.

4. Conclusion

Microwave dielectric ceramics based on a cerium–titania based system [CeO_2–0.5AO–$0.5TiO_2$ (A = Mg, Zn, Ca, Mn, Co, Ni, W)] were prepared by solid-state reaction method. In the majority of the seven ceramic systems it turned out to be a composite consisting of fluorite CeO_2 and perovskite $ATiO_3$ with high density and interesting individual dielectric properties depending on the coexisting perovskite being formed. The ceramics have dielectric constants (ε_r) in the range 17.0–65.5 and quality factor $Q_u xf$ up to 50,000 GHz. The τ_f ranges from +399 to −62 ppm/°C. X-ray diffraction studies indicated that the CeO_2–0.5AO–$0.5TiO_2$ (A = Mg, Zn, Ca, Mn, Co, Ni) ceramics consists of two types of grains, namely CeO_2 and $ATiO_3$ in all cases except for CeO_2–$0.5WO_3$–$0.5TiO_2$ SEM and EDXA analysis confirms this result. The CeO_2–$0.5WO_3$–$0.5TiO_2$ ceramics consists of more than two types of phases—CeO_2, Ce_2WO_6 and $Ce_2Ti_2O_7$. Suitable dopants of various valencies were added to tune the microwave dielectric properties. It was found that only small amounts of dopants could dramatically alter the dielectric properties such as the CeO_2–0.5CaO–$0.5TiO_2$ composite doped with 6.5 mol% Cr_2O_3 tuned the τ_f from +399 to 0 ppm/°C. CeO_2–0.5MgO–$0.5TiO_2$ doped with 1 mol% WO_3 gives a very high $Q_u xf$ of 90,000 GHz. The quality factor increased considerably on cooling for CeO_2–0.5AO–$0.5TiO_2$ (A = Mg, Zn, Ca, Mn, Co, Ni, W) ceramics in a manner which is similar to pure CeO_2. Highest $Q_u xf$ was observed for the CeO_2–0.5MgO–$0.5TiO_2$ system and at 20 K reach as high as 98,000 ($Q_u xf$ = 539,000 GHz).

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