



Phase, Micro structural Evaluation and Microwave Dielectric Properties of a Ceramics in the MgO-CeO₂-TiO₂ Ternary System

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Abstract: The ceramics along MgO-CeO₂-TiO₂ ternary system for a stoichiometric ratio of Mg₂Ce₂Ti₅O₁₆ was fabricated through solid state sintering route. The phase, microstructure and dielectric properties were analyzed. The XRD analysis revealed that CeO₂ formed as the major phase and another phase identical to MgTi₂O₅ was formed as minor phase. CeO₂ has high sintering temperature about 1650°C and high Q_{uf0} as report in the literature. $Q_{uf0} \sim 22450$ GHz, $\epsilon_r \sim 23.1$ and $\tau_f \sim 30.4$ ppm/°C was obtained for the sample sintered at 1250°C for 4h.

Keywords: Sintering, CeO₂, density, Phase, Microstructure

1. INTRODUCTION

Dielectric resonator is the key component in any wireless telecommunication devices. A dielectric resonator with $\epsilon_r > 20$, a temperature stable resonant frequency (i.e. $\tau_f \sim \pm 3$ ppm/°C) and a high Q-factor ($Q_{uf0} > 30,000$ GHz) need for commercial applications (Bamberger, *et al.* 1994). However, the Q_{uf0} and τ_f can be compromised to be $\sim 10,000$ GHz and ± 10 ppm/°C for certain applications, such as antennas respectively (Belous *et al.* 2010). $A_nB_nO_{3n+2}$ ceramics have recently got considerable attention due of their low dielectric loss and thermal stability. These properties made the materials promising candidates for antenna applications (Freer, and Azough, 2008). (Iqbal *et al.* 2012). The unique dielectric properties of $A_nB_nO_{3n+2}$ ceramics are related to their structure consists of BO₆ octahedra, that share their corners, where n is integer denoting the number of octahedral layers in the perovskite slab. (Sabastian, 2008).

High relative permittivity (ϵ_r), high unloaded quality factor Q_u and a near zero τ_f are the three basic requirements for a ceramic puck to act as resonator (Freer *et al.* 2009). Barium-lanthanide titanates ($Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ (Ln = La-Gd)) satisfactorily meets the above mentioned requirements because of high $\epsilon_r \approx 80-100$. However, the cost of such materials is high (Belous *et al.* 2010). Thus new low loss high and low cost materials are desirable (Iqbal *et al.* 2012).

Bamberger *et al.* firstly reported Sr₂Ce₂Ti₅O₁₆ with pseudo cubic structure (Bamberger *et al.*, 1994). $\epsilon_r \sim 113$, high $Q_{uf0} \sim 8000$ GHz and $\tau_f \sim 306$ ppm/°C has been reported for Sr₂Ce₂Ti₅O₁₆ (Subodh *et al.*, 2013). The

high positive $\tau_f \sim 306$ ppm/°C of Sr₂Ce₂Ti₅O₁₆ needs to be tuned through zero along with a further improvement in Q_{uf0} for possible microwave applications. Manan *et al.* investigated Ca₂Ce₂Ti₅O₁₆ to have $\epsilon_r \sim 87.2$, $Q_{uf0} \sim 5915$ GHz and $\tau_f \sim 219$ ppm/°C (Manan, *et al.*, 2014). The aim of this study was to tailor the τ_f of Ca₂Ce₂Ti₅O₁₆ through substitution like Mg by processing a ceramic along MgO-CeO₂-TiO₂ ternary system for a stoichiometric ratio of the chemical formula of Mg₂Ce₂Ti₅O₁₆.

2. EXPERIMENTAL PROCEDURES

High purity raw materials of MgO, CeO₂ and TiO₂ were weighed in stoichiometric ratios for the fabrication of Mg₂Ce₂Ti₅O₁₆ ceramics followed by ball milling for 18 h. The slurry so obtained was dried and the resulting powder was calcined for 5 h at 1150°C. The powder was then reground after calcination in a pestle and mortar for about an hour. Cylindrical pellets were made from the powder by pressing them at 100 MPa. Sintering of the cylindrical pellets was done in a range of 1250°C to 1350°C for 4 h. The Analysis of the phase(s) of both calcined and sintered the samples were carried out using XRD diffraction technique. X-ray diffractometer (JEOL JDX 3500) operating at 40 mA and 30 kV was used. Archimedes principle was employed measurement of the observed densities of the samples.

The finally polished were thermally etched and carbon coated for microstructural investigation. Using SEM (JEOL 6400 SEM). Cavity method was employed for the measurement of dielectric properties at microwave frequencies. The τ_f was measured by noting the resonant frequencies with at 20°C and 80°C respectively using equation (1);

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$$\tau_f = (f_2 - f_1)/f_1 \Delta T \quad (1)$$

Where f_1 denote the resonant frequency at initial temperature (20 °C) and f_2 denote the resonant frequency at final temperature (80 °C) are the resonant frequencies and ΔT is the difference between the initial and final temperatures.

3. RESULTS AND DISCUSSION

3.1. Identification of Phase(s)

The XRD patterns of calcined and sintered samples are shown in (Fig. 1). The major peak was indexed according to PDF#65-5923 for CeO_2 phase. [Sorensen, 1976]. Few extra peaks of low intensity indexed for MgTi_2O_5 (PDF#82-1125) in the XRD pattern of calcined sample (Fig.1a). This shows that $\text{Mg}_2\text{Ce}_2\text{Ti}_5\text{O}_{16}$ phase could not developed because of the larger difference in ionic size of Mg^{2+} and Ce^{4+} (Shannan, 1976). The peaks intensities of the secondary phase MgTi_2O_5 like phase increases while intensities of the peaks from CeO_2 phase decreased with increase in the sintering temperature (Fig.1.b-c). CeO_2 adopt cubic structure having theoretical density of 7.23 g/cm^3 (Sorensen, 1976).

With increase in sintering temperature was increased from 1250 °C to 1300 °C the bulk density of the sintered samples is observed to decrease from 4.35 g/cm^3 to 4.0 g/cm^3 as given in Table I. The decrease in density might be may related to the abnormal grain growth that leads to porosity and reduction to CeO_2 phase. The lower density of the sample shows that the density of the phase identical to MgTi_2O_5 might have lower density affecting the density of the final sintered ceramic sample.

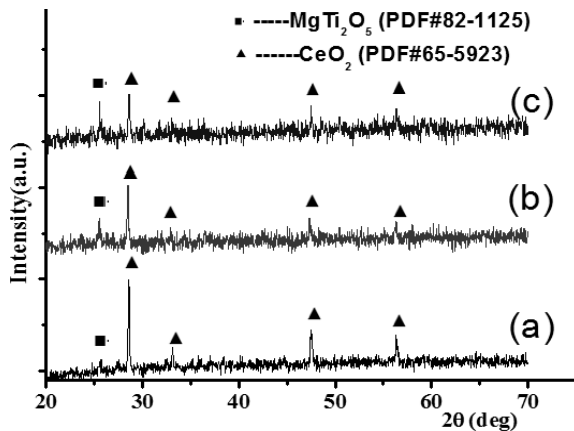


Fig.1. XRD patterns from a) calcined and b-c) sintered samples of $\text{MgCeTi}_5\text{O}_{16}$ ceramic, showing the formation CeO_2 and MgTi_2O_5 phases.

3.2 Microstructure

Backscattered electron images of sintered ceramic are shown in (Fig.3). Bright and dark grain morphologies are observed in microstructure showing the existence of two phases. The grain size increased with increasing sintering temperature from 1250°C to 1300°C. Melting of the sample is observed at 1350°C (Fig.3b). The elemental composition (Table I) of the grains labeled as “A” and “B” in figure 3 (a) showed that these grains are of CeO_2 and MgTi_2O_5 like phase respectively. Small amount of other impurities like that might be contribution from carbon coatings. The EDS (Table 1) of the grains labeled as “C” and “D” shows that such type of grains are that of CeO_2 and MgTi_2O_5 like phase respectively as confirmed by X-ray Diffraction analysis.

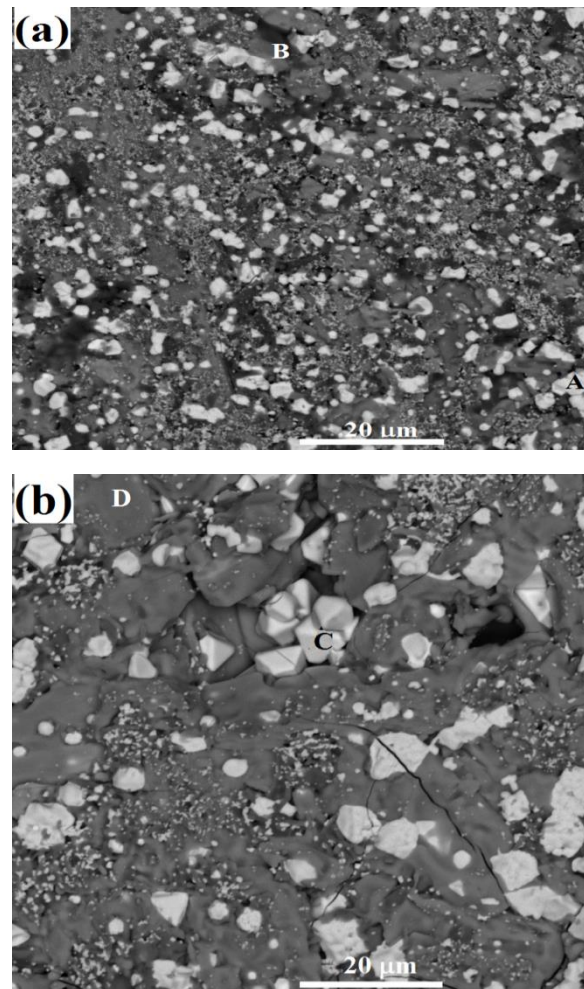


Fig.2. Backscattered electron Images from sintered samples of a) 1250°C b) 1300°C of $\text{Mg}_2\text{Ce}_2\text{Ti}_5\text{O}_{16}$ ceramics, showing bright and dark grain morphologies

Table I. Elemental composition (in moles) calculated from semi-quantitative EDS data of the grains labelled in Fig. 2.

Grain	Mg (Atomic %)	Ce (Atomic %)	Ti (Atomic %)	O (Atomic %)	C (Atomic %)
A	0	24	1.4	60	13.62
B	10.17	1.54	20.88	62.33	5.07
C	0	20.84	2.11	63.39	13.66
D	5.66	2.49	15.83	68.87	7.14

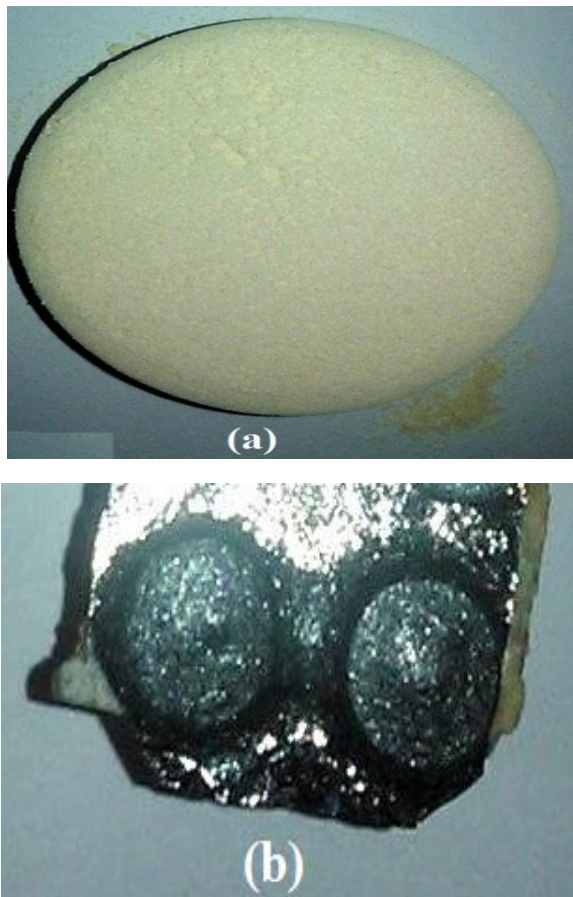


Fig.3. Images (a) Calcined powder (1150°C/6h) (b) melted pellets sintered at 1350°C/4h.

3.3 Analysis of the microwave dielectric properties

The dielectric constant (ϵ_r) of the sintered $\text{Mg}_2\text{Ce}_2\text{Ti}_5\text{O}_{16}$ ceramic with increase in sintering temperature is given in the (Table 2). The variation of ϵ_r with sintering temperature follows density. The Q_{uf_0} values of $\text{Mg}_2\text{Ce}_2\text{Ti}_5\text{O}_{16}$ based ceramic sintered at 1250 °C to 1300 °C are given in Table 2. The intrinsic and extrinsic factors affect the Q_{uf_0} value or the dielectric losses in the microwave region. The intrinsic losses are related to the crystal structure while the extrinsic losses are caused by various defects such as grain boundaries, porosity, micro cracks, and secondary phase(s). In the present study $Q_{uf_0} \sim 22450$ GHz has been achieved for the sample sintered at 1250°C/4h. The τ_f values of the ceramics were calculated from the variation of resonant frequency (f_0) with temperature. The τ_f changes from -30.4 ppm/°C to -26.7 ppm/°C with increase in sintering temperature from 1250°C to 1300 °C. reported CeO_2 to have $\epsilon_r = 24$, $Q_{uf_0} \sim 65000$ GHz and $\tau_f \sim -53$ ppm/°C sintered at 1650°C for 2 hours (Santha *et al.*, 2004). The lower sintering temperature of samples in the present study having CeO_2 as the major phase shows that the observed minor MgTi_2O_5 like phase might have lower sintering temperature, theoretical density, ϵ_r , Q_{uf_0} and τ_f values than CeO_2 that lowered the sintering temperature, observed density, Q_{uf_0} , ϵ_r , and τ_f of the final ceramic. $Q_{uf_0} \sim 22450$ GHz, $\epsilon_r \sim 23.1$, and $\tau_f \sim -30.4$ ppm/°C was obtained for the sample sintered at 1250°C/4h in this study. However, to tune the τ_f through zero, further work is in progress..

Table 2. Preparation conditions, experimental density and microwave dielectric properties of $\text{MgCeTi}_5\text{O}_{16}$ ceramic

ST (°C)	ρ_{exp} (g/cm ³)	ρ_{th}	Q_{uf_0} (GHz)	$\tan \delta$	τ_f (ppm/°C)
1250	4.35	23.1	22450	0.0000044	-30.4
1300	4.08	20.2	20375	0.0000049	-26.7

4. CONCLUSION

A ceramics in the $\text{MgO-CeO}_2\text{-TiO}_2$ ternary system processed via mix oxide route was investigated. The greater ionic size difference between Mg^{2+} and Ce^{4+} did not allow the parent $\text{Mg}_2\text{Ce}_2\text{Ti}_5\text{O}_{16}$ phase. CeO_2 formed as the major phase while another phase identical to MgTi_2O_5 formed as a minor phase. In this study, $Q_{uf_0} \sim 22450$ GHz, $\epsilon_r \sim 23.1$ and $\tau_f \sim -30.4$ ppm/°C was obtained for the sample sintered at 1250 °C.

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