

Influence of sintering temperature on secondary phases formation and microwave dielectric properties of Ca₂Ce₂Ti₅O₁₆ ceramics

Abdul Manan^{1*}, Sami Ullah Khan¹, Ibrahim Qazi²

¹Department of Physics, University of Science and Technology Bannu, 28100 KPK, Pakistan ²Department of Materials Science and Engineering, Institute of Space Technology, Islamabad 44000, Pakistan

Ca₂Ce₂Ti₅O₁₆ dielectric ceramics prepared by conventional solid-state ceramic route was investigated. Phase composition and microwave dielectric properties were measured using XRD and Vector network analyzer, respectively. XRD analysis of the calcined and sintered samples revealed the formation of CeO₂ and another unidentified phase (that vanished at ≥ 1400 °C) as secondary phases along with the parent Ca₂Ce₂Ti₅O₁₆ phase. The amount of the parent Ca₂Ce₂Ti₅O₁₆ phase increased with increasing sintering temperature from 1350 °C to 1450 °C accompanied by a decrease in the apparent density. The density decreased but ε_r and $Q_u f_o$ increased with sintering temperature. An $\varepsilon_r \sim 81.5$, $Q_u f_o \sim 5915$ GHz and $\tau_f \sim 219$ GHz were achieved for the sample sintered at 1450 °C.

Keywords: ceramics; sintering; phase transitions

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1. Introduction

Dielectric oxides have revolutionized the microwave wireless communication industry by reducing the size and cost of filter, oscillator and antenna components in applications ranging from cellular phones to global positioning systems. The importance of miniaturization cannot be overemphasized in any hand-held communication application and can be seen in the dramatic decrease in the size and weight of devices such as cell phones in recent years [1].

Ceramics which could function as dielectric resonator must possess three basic properties:

1. High relative permittivity (ε_r), which insures the reduction in the size of the microwave component because the size of the component is inversely proportional to the square root of the relative permittivity (i.e. $\lambda_d \sim D \sim 1/\sqrt{\varepsilon_r}$), where λ_d is the wavelength of the microwaves in the dielectric

media which is equal to the diameter of the dielectric resonator (DR).

- 2. High unloaded quality factor multiplied by the resonant frequency $(Q_u f_o)$, in order to get high signal to noise ratio or selectivity.
- 3. near zero temperature coefficient of resonant frequency (τ_f) , to insure temperature stability of the component [2].

Depending on the frequency range of modern communication systems, microwave (MW) dielectrics with varying properties are needed. In the decimeter wave band, high relative permittivity values ($\varepsilon \ge 100$) along with the high thermostability of electro-physical properties and high Q_u are required, which enables effective solution of microminiaturization problems. At the present time, solid solutions based on barium-lanthanide titanates (Ba_{6-x}Ln_{8+2x/3}Ti₁₈O₅₄ (Ln = La - Gd)), which have a potassium-tungsten bronze structure and $\varepsilon_r \approx 80 - 100$, satisfactorily meet these requirements, but these materials are costly [3]. Therefore, new low cost materials with high permittivity ($\varepsilon_r \ge 100$) and $Q_u f_o > 10,000$ GHz with

^{*}E-mail: drmanan82@yahoo.com

 $\tau_f \sim 0$ ppm/°C are essential for further miniaturization of the mobile handsets devices.

In 1994, Bamberger et al. [4] reported the existence of a new Sr₂Ce₂Ti₅O₁₆ compound with a pseudo cubic structure in the SrO–CeO₂–TiO₂ system. Its microwave dielectric properties i.e. $\varepsilon_r \sim 113$, high $Q_u f_o \sim 8000$ GHz and $\tau_f \sim 306$ ppm/°C were reported by Subodh et al. [5]. Sr₂Ce₂Ti₅O₁₆ could be a suitable candidate for further miniaturization of the mobile communication devices provided its high $\tau_f \sim 306$ ppm/°C is reduced to zero ppm/°C and if its $Q_u f_o$ could be improved for possible microwave applications. Ca substitutions for Sr in other compounds reduced their τ_f with improved $Q_u f_o$ values [6–8].

The aim of the present study was to investigate the changes in τ_f of Sr₂Ce₂Ti₅O₁₆ through substitutions such as Ca, for possible microwave applications.

2. Experimental procedures

The batch composition was fabricated using a solid-state mixed oxide route. CaCO₃ (Aldrich, 99 + %), CeO₂ (Aldrich, 99 + %) and TiO₂ (Anatase, Aldrich, 99 + %) were dried at ≈ 200 °C for 5 h to remove moisture prior to weighing in order to ensure the correct initial stoichiometry of the compounds. The dried carbonates and oxides were weighed in stoichiometric ratios and wet ballmilled for 4 h in disposable polyethylene mill jars, using Y-toughened ZrO2 balls as grinding medium and 2-isopropanol as lubricant to make freely flowing slurry. The slurry was dried in an oven at \approx 95 °C overnight. The resulting powder was sieved and calcined in air at 1150 °C for 5 h at a heating/cooling rate of 5 °C/min. The calcined powder was ground in a mortar and pestle for ≈ 45 min to dissociate agglomerates (if any). The powder was pressed into 4 mm to 5 mm high and 10 mm diameter pellets at 150 MPa. The green pellets were placed on platinum foils and sintered in air at 1350 °C to 1450 °C for 4 h at a heating/cooling rate of 5 °C/min. Phase analysis of the calcined and sintered crushed pellets was carried out using a Philips X-ray diffractometer operating at 30 kV and 40 mA at a scan speed of 1°/min for $2\theta =$

 $10^{\circ} - 70^{\circ}$ with a step size of 0.02° . Bulk densities of the sintered pellets were measured using the Archimedes method.

Microwave dielectric properties were measured using a R3767CH Agilent network analyzer using cavity method. The cylindrical pellets were placed on a low loss quartz single crystal in the center of an Au-coated brass cavity away from the walls of the cavity. τ_f was measured by noting the temperature variation of the TE_{01 δ} resonance at temperatures ranging from 20 °C to 80 °C using equation (1):

$$\tau_f = (f_2 - f_1)/f_1 \Delta T \tag{1}$$

where f_1 and f_2 are the resonant frequencies at 20 °C and 80 °C respectively, and ΔT is the difference between the initial and final temperature.

3. Result and discussion

3.1. Phase analysis

Fig. 1 shows the XRD patterns recorded for the calcined and sintered samples. The XRD pattern of the calcined sample shows the formation of CeO_2 as the major phase with the peaks indexed according to PDF#34-394 and Ca2Ce2Ti5O16 and an unidentified phase as minor phases respectively. The peaks of the parent $Ca_2Ce_2Ti_5O_{16}$ phase were indexed according to PDF#49-1554 for Sr₂Ce₂Ti₅O₁₆ having cubic structure with the peaks position shifted towards higher diffraction angles i.e. smaller d values due to smaller ionic radius of Ca⁺² (1.34 Å) than Sr⁺² (1.44 Å) [9]. At temperatures ≥ 1350 °C, the parent Ca₂Ce₂Ti₅O₁₆ phase was developed as the major phase accompanied by a decrease in the unidentified as well as CeO_2 phases. The unidentified phase completely vanished at \ge 1400 °C as shown in Fig. 1. The lattice parameter calculated from the XRD data is a = 3.8511 Å and unit cell volume is V = 57.11 Å³.

3.2. Microwave dielectric properties

Fig. 2 shows the experimental density (ρ_{exp}) and relative permittivity (ε_r) of the sintered Ca₂Ce₂Ti₅O₁₆ ceramics with increasing sintering temperature. Generally, the trend in the variation



Fig. 1. XRD patterns from (a) calcined and (b) – (d) sintered samples of $Ca_2Ce_2Ti_5O_{16}$ ceramics, showing the formation of secondary phases along with the parent $Ca_2Ce_2Ti_5O_{16}$ phase.

of ε_r with sintering temperature follows density, but the trend does not hold in the present study. The bulk density decreases while ε_r increases with increasing sintering temperature from 1350 °C to 1450 °C. This contradiction is due to the existence of the CeO₂ and unidentified secondary phase, which disappeared at temperature ≥ 1400 °C, but might have lower ε_r and higher apparent density than the parent Ca₂Ce₂Ti₅O₁₆ phase as observed in XRD pattern (Fig. 1). In the present study, the highest $(\varepsilon_{r(exp)}) \sim 81$ was achieved at 1450 °C. The experimental dielectric constants $(\varepsilon_{r(exp)})$ were corrected for porosity using Rushman and Strivens equation [10] and the highest was to be 87.2 at 1450 °C. The Ca substitution for Sr in Sr₂Ce₂Ti₅O₁₆ ceramics lowers its ε_r from 113 to 81.5 due to lower ionic dielectric polarizability of Ca (3.14 Å^3) than Sr (4.24 Å^3) in the present study [11]. The observed and corrected values of ε_r are also summarized in Table 1.

The $Q_u f_o$ of the Ca₂Ce₂Ti₅O₁₆ ceramics sintered at 1350 °C to 1450 °C is shown in Fig. 3 and also summarized in Table 1. There are various factors that affect the dielectric losses or its inverse $(Q_u f_o)$ in the microwave region. These include defects such as porosity, grain boundaries, microcracks and secondary phase(s). The $Q_u f_o$ increased

with increasing sintering temperature, showing opposite trend to experimental density (ρ_{exp}). The increase in $Q_u f_o$ might be due to the vanishing of the unidentified phase at ≥ 1400 °C and a decrease in the CeO₂ phase as well as an increase in the parent Ca₂Ce₂Ti₅O₁₆ phase (Fig. 1). The temperature coefficient of resonant frequency (τ_f) increased from 172 ppm/°C to 219 ppm/°C with increasing sintering temperature from 1350 °C to 1450 °C. This indicated that the unknown phase had lower τ_f than the parent Ca₂Ce₂Ti₅O₁₆ phase.



Fig. 2. Variation in ρ_{exp} and ε_r of Ca₂Ce₂Ti₅O₁₆ ceramics as a function of sintering temperature.



Fig. 3. Variation in $Q_u f_o$ and τ_f of Ca₂Ce₂Ti₅O₁₆ ceramics as a function of sintering temperature.

4. Conclusion

The density decreased but ε_r and $Q_u f_o$ increased with sintering temperature probably due to

| ST | $ ho_{exp}$ | \mathcal{E}_r | \mathcal{E}_r | $Q_u f_o$ | tan δ | $	au_f$ |
|---------------|-------------|-----------------|-----------------|-----------|--------------|----------|
| $(^{\circ}C)$ | (g/cm^3) | (experimental) | (corrected) | (GHz) | | (ppm/°C) |
| 1350 | 5.01 | 68.07 | 72.8 | 2017 | 0.00049579 | 172 |
| 1400 | 4.95 | 79.77 | 85.4 | 4337 | 0.00023057 | 213 |
| 1450 | 4.85 | 81.52 | 87.2 | 5915 | 0.00016906 | 219 |

Table 1. Preparation conditions, observed density and microwave dielectric properties of Ca2Ce2Ti5O16 ceramics.

the presence of CeO₂ and unidentified phases. An $\varepsilon_r \sim 81.5$, $Q_u f_o \sim 5915$ GHz and $\tau_f \sim 219$ GHz were achieved for the sample sintered at 1450 °C. Further work is in progress to tune the τ_f to zero for possible application.

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References

- SEBASTIAN M.T., Dielectric Materials for Wireless Communication, 1st Ed., Elsevier Science & Technology, GB, 2008.
- [2] FREER R., AZOUGH F., J. Eur. Ceram. Soc., 28 (2008), 1433.

- [3] BELOUS A., OVCHAR O., Acta Phys. Pol. A, 117 (2010), 221.
- [4] BAMBERGER C.E., HAVERLOCK T.J., KOPP O.C., J. *Am. Ceram. Soc.*, 77 (1994), 1659.
- [5] SUBODH G., SEBASTIAN M.T., Mater. Sci. Eng B-Adv., 136 (2007), 50.
- [6] MANAN A., IQBAL Y., QAZI I., J. Mater. Sci., 46 (2011), 3415.
- [7] IQBAL Y., MANAN A., REANEY I.M., Mater. Res. Bull., 46 (2011), 1092.
- [8] BIJUMON P.V., SEBASTIAN M.T., DIAS A., MOREIRA R.L., MOHANAN P., *J. Appl. Phys.*, 97 (2005). 104108.
 [9] GUMMER P. D. A. J. Const. Hep. 1, 22 (1076). 251
- [9] SHANNON R.D., Acta Crystallogr. A, 32 (1976), 751.
- [10] RUSHMAN D.F., STRIVENS M.A., P. Phys. Soc., 59 (1947), 1011.
- [11] SHANNON R.D., J. Appl. Phys., 73 (1993), 348.

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