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Processing and microwave dielectric properties of $Sr_5Ta_4TiO_{17}$ ceramics

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$Sr_5Ta_4TiO_{17}$ ceramics was processed via solid state mixed oxide sintering route. X-ray diffraction revealed single phase formation of $Sr_5Ta_4TiO_{17}$ ceramics that crystallized into an orthorhombic crystal structure with a space group Pnnm with lattice parameters of a = 5.681 Å, b = 32.542 Å and c = 3.968 Å, refined by the least squares method. The unit cell density (ρ_{th}) was 6.71 g/cm^3. The microstructure consisted of plate-like grains and the average size was increased from 2 µm to 5 µm with an increase in sintering temperature from 1450 °C to 1575 °C. Optimum microwave dielectric properties, i.e. $\epsilon_r \sim 66$, $Q_uf_o \sim 8500$ GHz and $\tau_f \sim 180$ ppm/°C, were achieved for Sr_5TaTiO_{17} ceramics sintered at 1550 °C for 4 h.

Keywords: *electron microscopy; sintering; microwave ceramics*

1. Introduction

Dielectric resonator (DR) is a key component in wireless telecommunication systems and it greatly reduces the size of the microwave components due to its high relative permittivity, $\epsilon_r > 24$, $Q_uf_o > 30{,}000$ GHz and $|\tau_f| \leqslant 3$ ppm/°C, which are the necessary requirements for a material to be commercially used as DR [1]. However, the requirements for low τ_f and high Q_uf_o are flexible for certain applications such as antennas [2].

$A_5B_5O_{17}$ family of layered perovskites has attracted great attention due to their good performance for patch antennas applications [3–5]. $\epsilon_r = 53$, $\tau_f = -20$ ppm/°C and $Q_uf_o = 17359$ GHz was reported by Jawahar et al. [6] for $CaLa_4Ti_5O_{17}$ ceramics. Partial Zn substitution for Ca improved the microwave dielectric properties of $CaLa_4Ti_5O_{17}$ ceramics [7]. $\epsilon_r = 57$, $Q_uf_o = 15{,}000$ GHz, and $\tau_f = -8.16$ ppm/°C were obtained for $Ca_{0.99}Zn_{0.01}La_4Ti_5O_{17}$ ceramics with 0.5 wt.% CuO additive that were sintered at 1450 °C for 4 h [8]. Isupov et al. [9] firstly reported $Sr_5Nb_4TiO_{17}$ within $SrO–Nb_2O_5–TiO_2$ ternary system. $Sr_5Nb_4TiO_{17}$ adopt the centrosymmetric orthorhombic crystal structure with space group Pnnm, No. 58. Iqbal et al. reported [10] $\epsilon_r \sim 80$ for $Sr_5Nb_4TiO_{17}$ ceramics. Iqbal et al. investigated [11] the microwave dielectric properties and reported $\epsilon_r \sim 74$, $Q_uf_o \sim 1303$ GHz and $\tau_f \sim 332$ ppm/°C for $Sr_5Nb_4TiO_{17}$. The high positive τ_f of $Sr_5Nb_4TiO_{17}$ precluded its application as DR. It has been reported that substitution of Nb with Ta reduced the value of τ_f and improved the properties of microwave dielectric ceramics such as $Ba_3LiNb_{3-x}Ta_xTi_5O_{21}$, $Sr_2La_3Nb_{1-x}Ta_xTi_4O_{17}$, $Ca_5Nb_{2-x}Ta_xTiO_{12}$, and $Mg_4Nb_{2-x}Ta_xO_9$ [12–15], however, as per my understanding and knowledge the effect of Ta substitution for Nb on microwave dielectric properties of $Sr_5Nb_4TiO_{17}$ has not been investigated. Therefore, in this paper, the microwave dielectric properties of $Sr_5Ta_4TiO_{17}$ were investigated.

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2. Experimental

The initial ingredients: $SrCO_3$ (Aldrich, 99+ %), Ta_2O_5 (Aldrich, 99.95 %), and TiO_2 (Anatas, Aldrich, 99+ %) were dried to remove the moisture before weighing in order to ensure the correct initial stoichiometry of the final ceramics. The dried carbonates and oxides were milled in polyethylene mill jars using Y-toughened ZrO_2 balls as grinding media and 2-isopropanol as a lubricant to make freely flowing slurries for 24 h. The slurry was dried by the evaporation of 2-isoprapanol from the slurry at 95 °C. The powder was then sieved before calcination at 1400 °C for 6 h, with a heating/cooling rate of 5 °C/min. The calcined powder was ground in a mortar with a pestle for about 45 min to dissociate the agglomerates. This fine powder was pressed into 10 mm diameter and from 4 mm to 5 mm heigh pellets at 100 MPa. The pellets were placed on platinum foils and sintered in a range of temperature of 1450 °C to 1575 °C for 4 h. Phase analysis of the sintered crushed pellets was carried using a Philips X-ray diffractometer operating at 30 kV and 30 mA at 1°/min at $2\theta = 10°$ to 70° with a step size of 0.02°. A STOE PSD X-ray diffractometer with CuKα radiation ($\lambda = 1.540598$ Å) was used for the measurement of lattice parameters. The bulk apparent densities of the sintered pellets were measured using Archimedes method. The percentage relative densities were then calculated by taking the ratio of unit cell density to the apparent densities for each sintered sample.

Each sintered pellet was cut and finely polished before thermal etching for 30 min at temperatures ~10 % less than its corresponding sintering temperature at a heating/cooling rate of 5 °C/min for microstructural examination. The etched surfaces of the samples were gold-coated to avoid charging effects and a JEOL 6400 SEM operating at 20 kV was used.

The faces of the optimally sintered pellet were coated with gold paste and heated to 800 °C for 2 h at heating/cooling rates of 10 °C/min. The dielectric properties were measured in the range of 1 kHz to 1 MHz using HP 4384 A LCR meter.

The microwave dielectric properties were measured using Advantest R3767CH Network Analyzer employing cavity method by placing the cylindrical pellets on a low loss quartz single crystal at the center of Au-coated brass cavity. The τ_f was measured by noting the temperature variation of $TE_{01\delta}$ resonance mode in the temperature range of 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 temperatures.

3. Results and discussion

The room temperature XRD pattern of the highest density sample of $Sr_5Ta_4TiO_{17}$ ceramics is shown in Fig. 1. The reflections were indexed according to PDF Card No. 87-1170 of $Sr_5Nb_4TiO_{17}$. Within the in-house XRD detection limit, the sample was formed as a single phase having orthorhombic crystal structure with a space group Pnnm. The red line pattern is the PDF Card No. 87-1170 and the green is our XRD pattern. The unit cell parameters were calculated from the XRD data using least squares method and are a = 5.681 Å, b = 32.542 Å and c = 3.968 Å. Although Nb^{5+} and Ta^{5+} ions are of almost the same size [16], however, a small increase in the lattice parameters is observed for Ta based composition in comparison to Nb counterpart [11]. This slight increase in lattice parameter increased the cell volume and was found to be 733.6 $Å^3$.

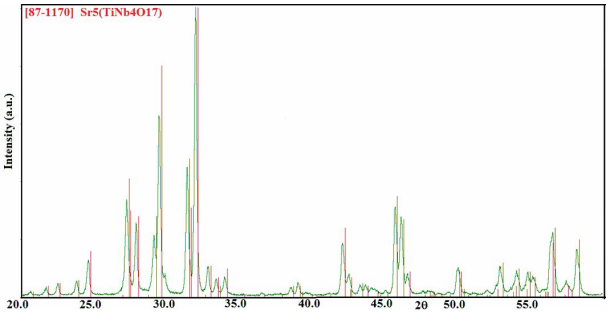

Fig. 1. XRD pattern of $Sr_5Ta_4Ti_4O_{17}$ ceramics sintered at 1550 °C for 4 h.

The theoretical density ρ_{th} was calculated from the unit cell data using equation 2:

$$\rho_{th} = ZM/VA_g \quad (2)$$

where Z is the formula unit, M is the molecular weight, V is the volume of the unit cell and A_g is the Avogadro number. The ρ_{th} was obtained to be 6.71 g/cm^3 which is larger than that of Nb counterpart ($Sr_5Nb_4TiO_{17}$) for which 5.15 g/cm^3 was reported [11]. The increase in ρ_{th} is due to the greater atomic weight to unit cell volume (MW/V) ratio for $SrTa_4TiO_{17}$ than for $SrNb_4TiO_{17}$.

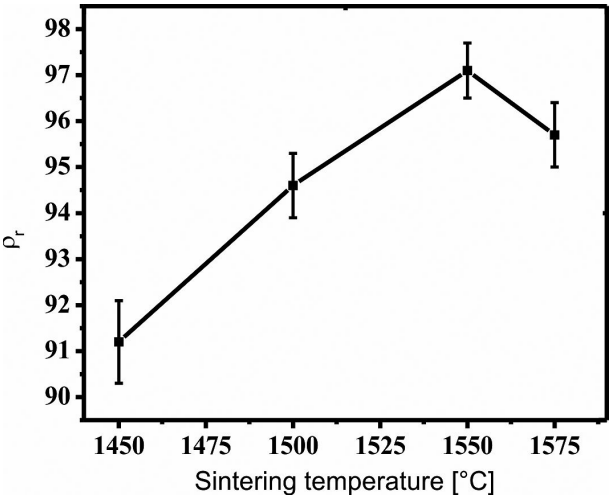

Fig. 2. Variation in ρ_r of $Sr_5Ta_4Ti_4O_{17}$ ceramics with sintering temperature.

The variation in relative density ρ_r of $Sr_5Ta_4TiO_{17}$ ceramics as a function of increasing sintering temperature is shown in Fig. 2. The ρ_r initially increased as the sintering temperature was increased from 1450 °C to 1550 °C and then slightly decreased with further increase in sintering temperature to 1575 °C. The density reached to a maximum value at 1550 °C. The initial increase in density of the ceramics may be due to the elimination of the pores under the mechanism of grain growth. Generally, at higher temperatures abnormal grain growth occurs which causes inhomogeneous microstructure, leading to porosity. Therefore, the final decrease in density above 1550 °C could be attributed to the abnormal grain growth.

The secondary electron microscopy (SEM) images of thermally etched Au-coated surfaces of $Sr_5Ta_4TiO_{17}$ ceramics sintered at 1450 °C to 1575 °C for 4 h are shown in Fig. 3. The microstructure is comprised of plate-like grains whose average grain size increased from 2 μm to 5 μm with the increase in sintering temperature from 1450 °C to 1575 °C. Some abnormal grain growth can also be seen at sintering temperature of 1575 °C which is consistent with relative density data. The relative permittivity ϵ_r of $Sr_5Ta_4TiO_{17}$ ceramics sintered at 1550 °C, measured in the frequency range of 1 kHz to 1 MHz is shown in Fig. 4. ϵ_r significantly decreased with an increase in frequency due to the reduction of active polarization mechanism at higher frequencies. At lower frequencies, the electronic, ionic, dipolar and interfacial/surface polarizations contribute to ϵ_r, however, above 100 kHz, the contribution from the interfacial/surface polarization can no longer follow the field, resulting in a decrease in ϵ_r from 75 to 67 [17].

The variation in microwave dielectric properties of $Sr_5Ta_4TiO_{17}$ ceramics with sintering temperature is shown in Fig. 5. ϵ_r and Q_uf_o show the same trend with sintering temperature (Fig. 5a and Fig. 5b) as the relative density (Fig. 2). It is generally accepted that ϵ_r of a material depends on the ionic polarizability α_D of ions constituting the composition, secondary phase(s), and its density. $\epsilon_r \sim 66$ was obtained for the sample sintered at 1550 °C. The ϵ_r of $Sr_5Ta_4TiO_{17}$ is lower and its Q_uf_o is higher than those of its Nb counterpart ($Sr_5Nb_4TiO_{17}$) for which $\epsilon_r \sim 74$ and $Q_uf_o \sim 1303$ GHz were reported in a previous study [11]. Since ionic dielectric polarizability of Ta^{5+} (4.73 Å^3) is larger than that of Nb^{5+} (3.93 Å^3) [18], therefore, the substitution of Ta for Nb should increase ϵ_r and reduce Q_uf_o value but the trend was opposite. The same trend for ϵ_r and Q_uf_o value with Ta substitution for Nb was also observed in $Ca_5Nb_{2-x}Ta_xTiO_{12}$ ($x = 0$ to 2) [14] and $Ba_4LaTiNb_{3-x}Ta_xO_{15}$ ceramics [12]. Ratheesh et al. [19] suggested that the larger short range interaction parameter in O–Ta–O bond in comparison to O–Nb–O results in higher quality

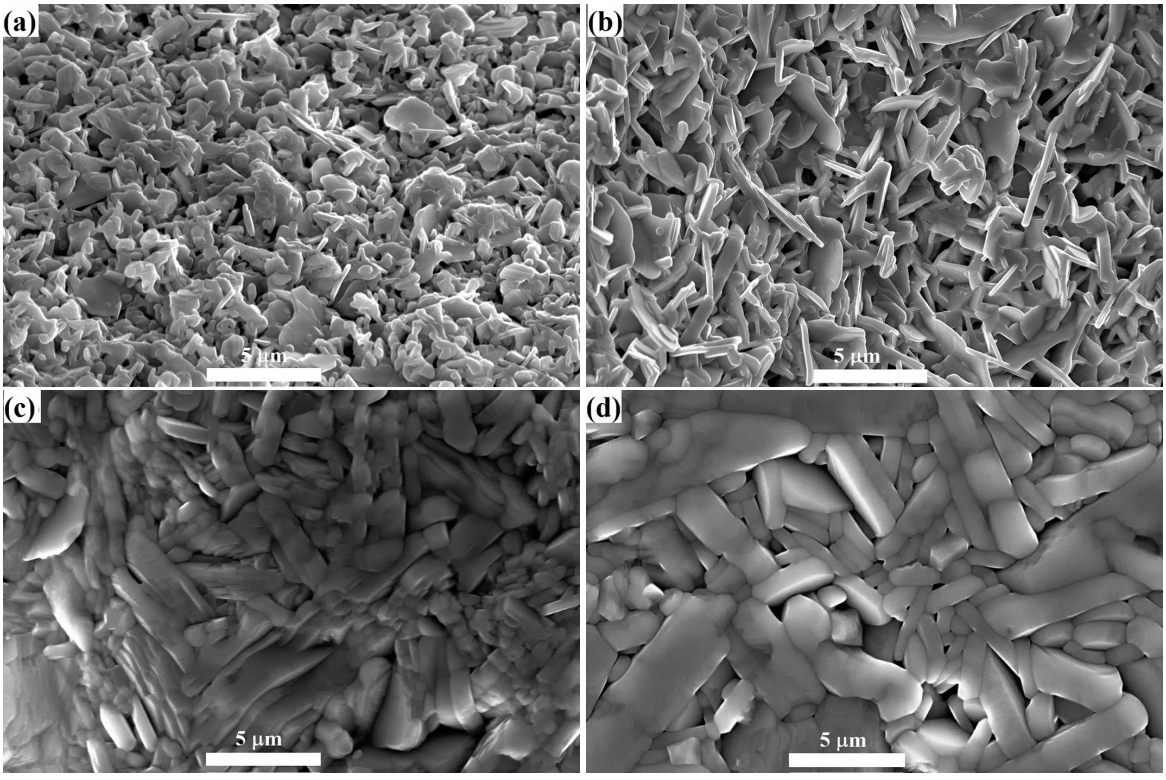

Fig. 3. Scanning electron microscopy (SEM) images of sintered and thermally etched surface of $Sr_5Ta_4Ti_4O_{17}$ ceramics prepared at (a) 1450 °C, (b) 1500 °C, (c) 1550 °C and (d) 1575 °C.

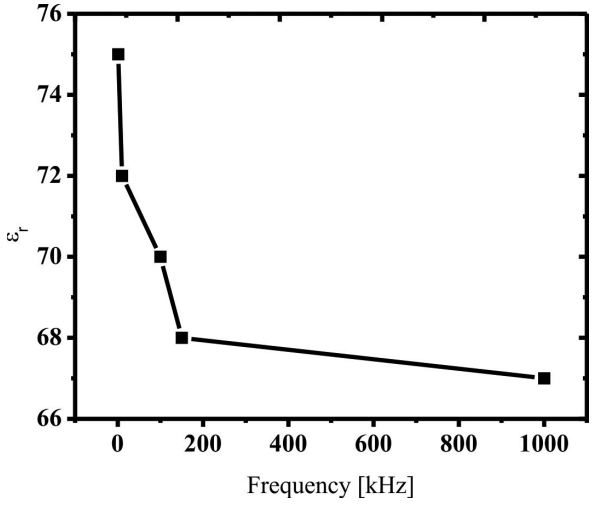

Fig. 4. Variation in ϵ_r of $Sr_5Ta_4Ti_4O_{17}$ ceramics as a function of frequency.

factor and lower ϵ_r and therefore, this suggestion could explain the results in the present study. The quality factor Q or its inverse – the dielectric loss – is considered as the figure of merit for measuring the performance or quality of a resonator. Intrinsic and extrinsic losses contribute to the total dielectric loss of a material. The intrinsic losses are the losses that originate from the interaction of AC electric field with the phonon of the lattice which totally depends on the crystal structure. During this process, the AC electric field modifies the equilibrium state of the lattice phonons leading to energy dissipation and hence dielectric loss. The intrinsic loss is caused by defects such as grain boundaries, stacking faults, chemical or structural disorders, point defects, planar defects, line defects, inclusions, secondary phases, twinning, porosity, etc. [20]. $\tau_f \sim 180$ ppm/°C was obtained for $Sr_5Ta_4TiO_{17}$ ceramics (Fig. 5c) sintered at 1550 °C which is lower than that of $Sr_5Nb_4TiO_{17}$ (∼332 ppm/°C) [11]. Since Nb^{5+} and Ta^{5+} have the same ionic radii (0.64 Å) [17], therefore, they will have the same tolerance factor. Thus, the effect of tolerance factor on the variation in τ_f can

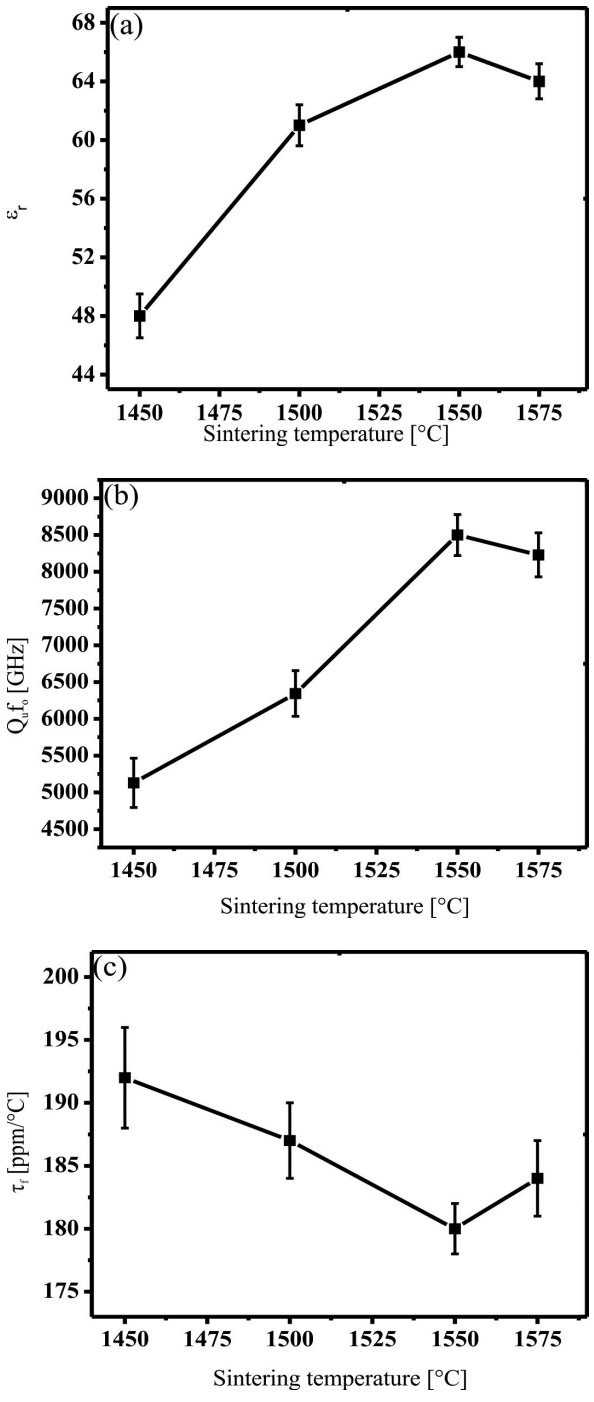

Fig. 5. Variation in (a) ϵ_r, (b) Q_uf_o, and (c) τ_f of $Sr_5Ta_4Ti_4O_{17}$ ceramics as a function of sintering temperature.

be ignored as suggested by Reaney et al. [21]. The lower value of τ_f of $Sr_5Ta_4TiO_{17}$ than that of $Sr_5Nb_4TiO_{17}$ could be the result of relationship between τ_c and τ_f [22]. The processing conditions and the properties of $Sr_5Ta_4TiO_{17}$ are also summarized in Table 1. Further work to reduce the τ_f is in progress and hence, improvement in the Q_uf_o values of $Sr_5Ta_4TiO_{17}$ ceramics for possible microwave applications can be expected.

Table 1. Preparation conditions, relative densities and microwave dielectric properties of $Sr_5Ta_4TiO_{17}$ ceramics sintered at different temperatures.

S.T [°C]	ρ_r	ϵ_r	Q_uf_o [GHz]	τ_f [ppm/°C]
1450	91.2±0.9	48±1.5	5130±345	192±8.0
1500	94.6±0.7	61±1.4	6345±310	187±6
1550	97.1±0.6	66±1.0	8500±280	180±5
1575	95.7±0.7	64±1.2	8230±300	184±6

4. Conclusions

Single phase, >95 % dense $Sr_5Ta_4TiO_{17}$ ceramics was prepared by sintering at 1550 °C for 4 h. Optimum microwave dielectric properties i.e. $\epsilon_r \sim 66$, $Q_uf_o \sim 8500$ GHz and $\tau_f \sim 180$ ppm/°C were achieved for $Sr_5Ta_4TiO_{17}$ ceramics sintered at 1550 °C for 4 h. Further work is in progress to tune the τ_f to zero to further improve the Q_uf_o values of $Sr_5Ta_4TiO_{17}$ ceramics by some suitable cation substitution.

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