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Tunable $Sr_4Ta_2O_9$-B'_2O_3 [B' = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er and Yb] microwave dielectrics; A novel method of synthesis

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ABSTRACT

The $Sr_4Ta_2O_9$ + (x) B'_2O_3 ceramics, [B' = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er and Yb] for x = 0-15 have been synthesized by a different solid state ceramic route without any sintering aid. $Sr(B'_{1/2}Ta_{1/2})O_3$ perovskites were prepared by $Sr_4Ta_2O_9$: B'_2O_3 = 1:1 method. The microwave dielectric properties of the ceramics were investigated and could be tuned by varying the B'_2O_3 content. The structure and microstructure of the ceramics have been characterized by X-ray diffraction and SEM techniques. The dielectric properties of $Sr(B'_{1/2}Ta_{1/2})O_3$ ceramics depends on RE- ionic radii. Nearly zero τ_f for $Sr_4Ta_2O_9$ + (x)Sm_2O_3 was obtained for x = 13. The $Sr_4Ta_2O_9$ + B'_2O_3 ceramics [B' = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er and Yb] have ε_r = 27.9-33.2, $Q_u \times f$ = 6200-56400 GHz and τ_f = -71 to -35 ppm/°C. A slight deviation from stoichiometry affects the dielectric properties of these ceramics.

KEYWORDS

Electro ceramics;
Microwave dielectrics;
Perovskites;
Dielectric properties;
Microwave communications.

INTRODUCTION

Microwave dielectric materials play a key role in our global society with a wide range of applications, from terrestrial and satellite communication including software radio, GPS, and DBS TV to environmental monitoring via satellite. In the last few decades, a wide range of dielectric materials have been developed for the microwave applications[1-5] especially in the rapid growth of wireless communication industry. A small ceramic component made from a dielectric material is fundamental to the operation of filters and oscillators in several microwave systems. Several types of microwave dielectric materials have been studied to meet the requirements of the microwave applications[6-10]. Some of the complex perovskites had been found to have excellent microwave dielectric properties[11-13]. In microwave communications, dielectric resonator filters are used to discriminate between wanted and unwanted signal frequencies in the transmitted and received signal. For clarity it is also critical that the wanted signal frequencies are not affected by seasonal temperature changes. In order to meet the specifications of current and future systems, improved or new microwave components based on dedicated dielectric materials and new designs are required. The frequency determining component (resonator) used in such a high frequency device must satisfy certain criteria. The three important characteristics required for a dielectric resonator are (a) high dielectric constant which facilitates miniaturiza-

tion (b) high quality factor ($Q_u \times f$) which improves the signal-to-noise ratio, (c) low temperature coefficient of the resonant frequency which determines the stability of the transmitted frequency.

Recently, we have reported[12,14] $Sr(B'_{1/2}Ta_{1/2})O_3$ and $Sr(B'_{1/2}Nb_{1/2})O_3$ [B' = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er and Yb] ceramics with interesting dielectric properties. Proper densification of these ceramics was obtained only with the addition of Nb_2O_5 and CeO_2 as sintering aids. In the present paper we report an alternate concrete method of preparation of phase pure $Sr(B'_{1/2}Ta_{1/2})O_3$ ceramics [B' = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er and Yb] without any sintering aid. The aim of the present work was (i) to adopt a different method in the preparation of $Sr(B'_{1/2}Ta_{1/2})O_3$ ceramics for better dielectric properties without any sintering aid and (ii) to study the variation in the dielectric properties of $Sr(B'_{1/2}Ta_{1/2})O_3$ by off stoichiometry.

EXPERIMENTAL

The strontium-lanthanide-tantulum-oxide ceramics were prepared by conventional solid state ceramic oxide route. The starting reagents $SrCO_3$ (Aldrich Chemical; 99.9%), rare earth oxides (Treibacher; 99.99%) and Ta_2O_5 (Nuclear Fuel Complex, Hyderabad; 99.9%) were weighed in stoichiometric ratio, mixed thoroughly in distilled water by ball milling for 48 hours. We have prepared single phase $Sr_4Ta_2O_9$ by mixing $SrCO_3$ and Ta_2O_5 in the molar ratio 4:1 and heating at 1250°C/4 h. Rare earth oxide powders were separately calcined at 1250°C for 4 hours. The rare earth oxides were separately mixed with $Sr_4Ta_2O_9$ in different ratios, again ground well, mixed with 3 wt.% PVA solution (as binder; molecular wt. ≈ 22000) and dried, pelletized and sintered at 1600°C/4h. It was then pressed in to discs (14 mm in diameter and 7-10 mm in thickness) under a pressure of 150 MPa. The green compacts were sintered at 1600°C/4 h. The bulk densities of the sintered samples were measured by Archimedes method. The crystal structure and phase purity of the sintered samples were examined by X-ray powder diffraction using Cuk_α radiation (Philips X'pert PRO MPD X ray diffractometer; Philips, Eindhoven, The Netherlands). The microstructures of sintered and thermally etched samples were recorded using Scanning Electron Microscopy (JEOL-SEM 560LV, Tokyo, Japan). The samples for SEM were polished and thermally etched at a temperature 50°C below the sintering temperature for 30 minutes. The dielectric constant was obtained by the Hakki and Coleman method[15] using the TE_{011} mode, and the quality factor was calculated from the $TE_{01\delta}$ mode by the cavity method[16]. The τ_f was measured by noting the temperature variation of $TE_{01\delta}$ resonance frequency by heating the sample in the temperature range 25–75°C. The variation of resonant frequency is plotted as a function of temperature and τ_f is evaluated from the slope of the plots using the equation.

$$\tau_f = \frac{1}{f_0}\frac{\Delta f}{\Delta T}$$

Where f_0 is the resonant frequency and Δf is the change in frequency during a temperature interval ΔT.

RESULTS AND DISCUSSION

In a previous work we have synthesized $Sr(B'_{1/2}Ta_{1/2})O_3$ [B' = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er and Yb] ceramics by mixing $SrCO_3$, B'_2O_3 and Ta_2O_5 in the molar ratio 4:1:1. The densification and material formation was incomplete without the addition of Nb_2O_5 as sintering aid even after fired at 1600-1625°C/4h. It was clearly evidenced by the surface morphology (Figure 1) of a representative sample $Sr(Sm_{1/2}Ta_{1/2})O_3$ prepared in the 4:1:1 method at 1600°C without any sintering aid. The secondary phases were completely disappeared and densified to 98% of the theoretical density with the addition of 0.5 wt% Nb_2O_5 as sintering aid[12]. In the present work, we synthesized different compositions of $Sr_4Ta_2O_9 + (x)B'_2O_3$, where x = 0 to 15 and were characterized. The variation in the densities of $Sr_4Ta_2O_9 + B'_2O_3$ compositions was corresponding to the variation in the densities of B'_2 elements (as shown in Figure 2).

The X-ray powder diffraction pattern of $Sr_4Ta_2O_9$ is shown in Figure 3a. It was noted that the structure of $Sr_4Ta_2O_9$ is cubic in agreement with JCPDS file 11-575. Among the rare earth oxides, Sm_2O_3 was selected as a representative for the characterization. X-ray powder diffraction pattern of Sm_2O_3 heated to 1250°C/4h is shown in Figure 3b. It has monoclinic structure in agreement with JCPDS 42-1464. The calcined powders of $Sr_4Ta_2O_9$ and Sm_2O_3 were mixed well in differ-

ent molar ratio (1:x, where x = 0-15) and the compacts were sintered at 1600°C/4h. The XRD patterns of the composition with $Sr_4Ta_2O_9$ and Sm_2O_3 mixed in the molar ratio 1:1 without any sintering aid (Figure 3c) shows tetragonal structure similar to that of the single phase $Sr(Sm_{1/2}Ta_{1/2})O_3$ obtained as in the previous study[12]. Addition of 1 mole of Sm_2O_3 lowered the cubic structure of $Sr_4Ta_2O_9$ to tetragonal with the formation of pure ternary phase $Sr(Sm_{1/2}Ta_{1/2})O_3$. Further addition of more than 1 mole of Sm_2O_3 to 1 mole of $Sr_4Ta_2O_9$ formed a mixture phase of tetragonal $Sr(Sm_{1/2}Ta_{1/2})O_3$ and monoclinic Sm_2O_3. Figure 3d shows the mixture phases of tetragonal $Sr(Sm_{1/2}Ta_{1/2})O_3$ and monoclinic Sm_2O_3 when $Sr_4Ta_2O_9$ and Sm_2O_3 were mixed in the molar ratio 1:1.5 and sintered at 1600°C/4h.

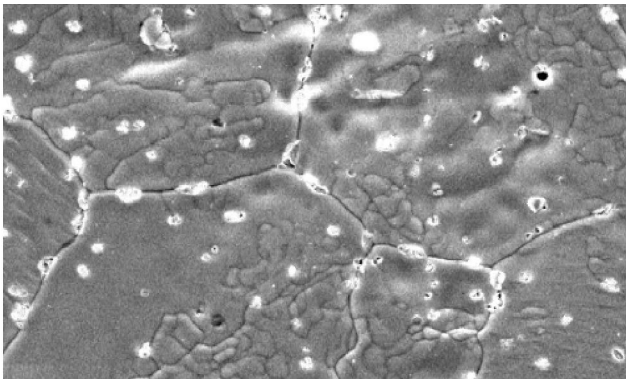

Figure 1 : The microstructure of pure $Sr(Sm_{1/2}Ta_{1/2})O_3$ ceramic prepared in the conventional ceramic route without any sintering aid at 1600°C/4h. The material was under formation.

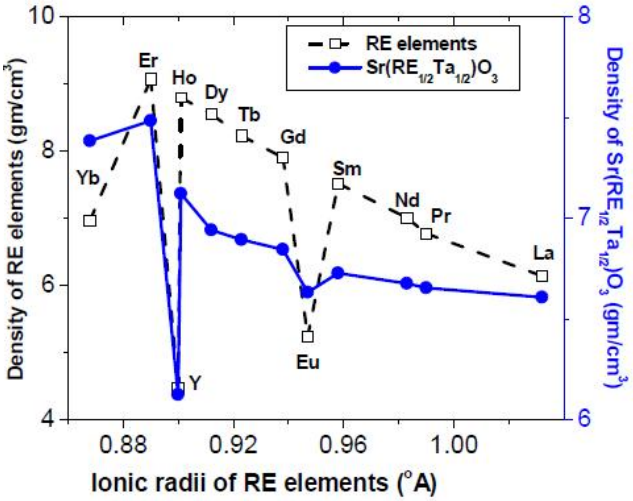

Figure 2 : Shows the corresponding variations in the densities of $Sr_4Ta_2O_9 + B'_2O_3$ compositions and B' elements against the B'-ionic radii.

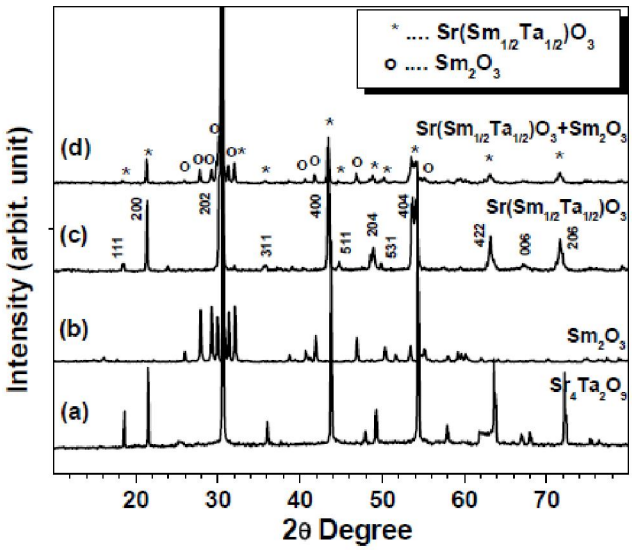

Figure 3 : Shows the XRD patterns of (a) $Sr_4Ta_2O_9$, (b) Sm_2O_3, (c) pure $Sr(Sm_{1/2}Ta_{1/2})O_3$ and (d) mixture of $Sr_4Ta_2O_9$ and Sm_2O_3.

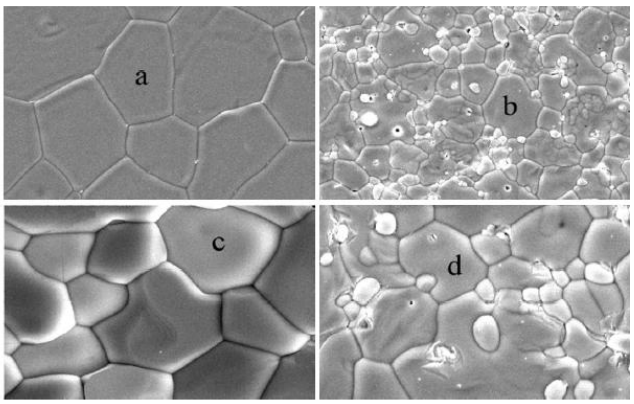

Figure 4 : Shows (a) well packed and phase pure $Sr_4Ta_2O_9$ grains, (b) partial formation of $Sr(Sm_{1/2}Ta_{1/2})O_3$ when sintered at 1550°C, (c) Single phase $Sr(Sm_{1/2}Ta_{1/2})O_3$ when $Sr_4Ta_2O_9$ and Sm_2O_3 were combined in the molar ratio 1:1 and heated at 1600°C/4h and (d) unreacted Sm_2O_3 among the ternary grains when $Sr_4Ta_2O_9$ and Sm_2O_3 were added in the molar ratio 1:1.5 and sintered at 1600°C/4h.

Figure 4a shows the microstructure of well packed and phase pure $Sr_4Ta_2O_9$ grains of size 5-20 μm. The density and dielectric properties of $Sr_4Ta_2O_9$ are given in TABLE 1. The $Sr_4Ta_2O_9$ has $\varepsilon_r = 38$, $\tau_f = -10$ ppm/°C and $Q_u \times f = 5600$ GHz while Sm_2O_3 has $\varepsilon_r = 24$, $\tau_f = 20$ ppm/°C and $Q_u \times f = 36000$ GHz. The role of Sm_2O_3 on $Sr_4Ta_2O_9$ ceramic was investigated by the addition of Sm_2O_3 in 0-15 mole separately to one mole of $Sr_4Ta_2O_9$ and sintered at 1600°C/4h. The variation in the densities and dielectric properties of the compositions were measured and given in TABLE 1. Densities of the compositions increased uniformly with Sm_2O_3

content as shown in Figure 5a. Dielectric constant of $Sr_4Ta_2O_9$ rapidly decreased with the addition of 1 mole Sm_2O_3 (see Figure 5a). The τ_f of $Sr_4Ta_2O_9$ ceramic increased to large negative value due to the formation of $Sr(Sm_{1/2}Ta_{1/2})O_3$ at $Sr_4Ta_2O_9$:Sm_2O_3 = 1:1 as shown in Figure 5b. Further addition of Sm_2O_3 to 1 mole of $Sr_4Ta_2O_9$ decreased the negative value of τ_f and then brought to positive value. Addition of 13 mole of Sm_2O_3 to 1 mole of $Sr_4Ta_2O_9$ could tune the τ_f to nearly zero value (shown in Figure 5b). This composition has ε_r = 28.4, τ_f = -0.5 ppm/°C and $Q_u \times f$ = 28200 GHz. In the previous report[12] dielectric properties of $Sr(Sm_{1/2}Ta_{1/2})O_3$ ceramic was tuned with the addition of TiO_2. Addition of TiO_2 increased the dielectric constant but deteriorated the $Q_u \times f$ to very low value (<10,000 GHz). Unreacted TiO_2 was found shaltered in the terenary grains of $Sr(Sm_{1/2}Ta_{1/2})O_3$ ceramic (see Figure 6). Figure 4b shows the partial formation of the material when sintered at 50°C below the sintering temperature. Single phase $Sr(Sm_{1/2}Ta_{1/2})O_3$ was formed (see Figure 4c) when $Sr_4Ta_2O_9$ and Sm_2O_3 were combined in the molar ratio 1:1 and heated at 1600°C/4h. This 1:1 composition of $Sr(Sm_{1/2}Ta_{1/2})O_3$ ceramic shows good dielectric properties (ε_r = 32, τ_f = -40 ppm/°C and $Q_u \times f$ = 49500 GHz) compared to the previous study results (ε_r = 30.5, τ_f = -61 ppm/°C and $Q_u \times f$ = 45200 GHz)[12]. Any addition of Sm_2O_3 more than 1 mole to 1 mole of $Sr_4Ta_2O_9$ remains as unreacted among the ternary phase $Sr(Sm_{1/2}Ta_{1/2})O_3$. In this report $Q_u \times f$ of $Sr(Sm_{1/2}Ta_{1/2})O_3$ ceramic increased to 54500 GHz when 1.25 mole of Sm_2O_3 was added to 1 mole of $Sr_4Ta_2O_9$ (represented by a dotted line in Figure 5b). It is an off stoichiometry for $Sr(Sm_{1/2}Ta_{1/2})O_3$. Microstructure Figure 4d shows the unreacted Sm_2O_3 among the ternary grains when $Sr_4Ta_2O_9$ and Sm_2O_3 were added in the molar ratio 1:1.5 and sintered at 1600°C/4h. The variation shown (in TABLE 1) in the dielectric properties of $Sr_4Ta_2O_9$-Sm_2O_3 compositions with more than 1.25 mole of Sm_2O_3 is due to the mixture property of $Sr(Sm_{1/2}Ta_{1/2})O_3$ and Sm_2O_3. More Sm_2O_3 content could tune the dielectric properties of $Sr(Sm_{1/2}Ta_{1/2})O_3$ ceramics by mixture method. Detailed study will be reported later. The preparation of $Sr(B'_{1/2}Ta_{1/2})O_3$ ceramics by mixing $Sr_4Ta_2O_9$ and rare earth oxides [B' = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er and Yb] in the molar ratio 1:1 simplified the formation of single phase material without the help of any sintering aid. This compositions show better dielectric properties (see TABLE 2) compared to the samples prepared in the 4:1:1 composition[12] (see Figure 5). In the case of $Sr(Pr_{1/2}Ta_{1/2})O_3$ ceramic $Sr_4Ta_2O_9$ and Pr_6O_{11} were mixed in the molar ratio 1:1/3. The dielectric properties of $Sr(B'_{1/2}Ta_{1/2})O_3$ ceramics in the 1:1 composition were found in the ranges ε_r = 27.9-33.2, $Q_u \times f$ = 6200-56400 GHz and τ_f = -71 to -35 ppm/°C [TABLE 2].

TABLE 1 : The density and dielectric properties of $Sr_4Ta_2O_9$-Sm_2O_3 compositions when $Sr_4Ta_2O_9$ and Sm_2O_3 were mixed in the molar ratio 1:x, where x = 0 to 15.

$Sr_4Ta_2O_9$-(x)Sm_2O_3 when x =	Density of the Material (gm/cm^3)	ε_r	Q_u x f (GHz)	τ_f (ppm/°C)
0.0	6.1	38.0	5600	-10
0.5	6.2	37.2	8800	-19
1.0	6.7	32.0	49500	-40
1.25	6.8	31.8	54500	-37
1.5	6.9	31.3	50300	-34
2.0	7.0	31.1	47300	-33
4.0	7.2	30.0	36750	-31
6.0	7.4	29.0	34500	-20
10.0	7.7	28.5	30700	-8.0
12	7.8	28.4	28300	-3.1
13	7.8	28.4	28200	-0.5
14	7.9	28.2	27500	2.0
15.0	7.9	28.2	26400	4.5
Sm_2O_3	8.35	24.0	36000	20
Nb_2O_5 added $Sr(Sm_{1/2}Ta_{1/2})O_3$ sample[12]	6.6	30.5	45200	-61

TABLE 2 : Dielectric properties of $Sr_4Ta_2O_9$-B'_2O_3 ceramics where B' = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er and Yb ceramics when $Sr_4Ta_2O_9$ and B'_2O_3 were mixed in the molar ratio 1:1 (Pr_6O_{11} in the ratio 1:1/3).

$Sr_4Ta_2O_9$+B'_2O_3	ε_r	Q_u x f(GHz)	τ_f(ppm/°C)
+ La_2O_3	33.2	6200	-35
+(1/3)Pr_6O_{11}	33.0	10500	-37
+ Nd_2O_3	32.6	42300	-38
+ Sm_2O_3	32.0	49500	-40
+ Eu_2O_3	31.6	48200	-51
+ Gd_2O_3	31.2	8600	-58
+ Tb_2O_3	30.2	48300	-59
+ Dy_2O_3	29.9	38200	-61
+ Ho_2O_3	29.0	42100	-64
+ Y_2O_3	28.9	56400	-66
+ Er_2O_3	28.5	29600	-69
+ Yb_2O_3	27.9	40000	-71

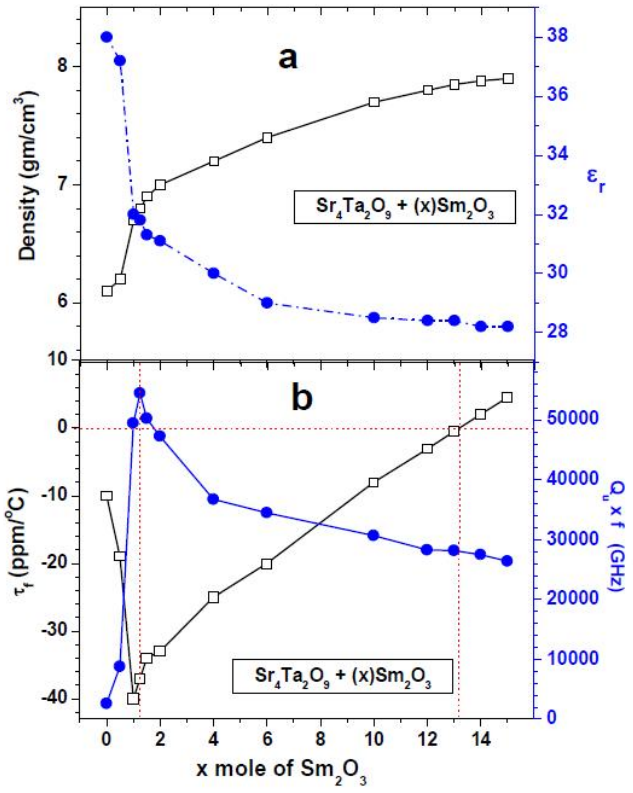

Figure 5 : Shows (a) variations in the density and ε_r of $Sr_4Ta_2O_9$ + (x)Sm_2O_3 ceramics for x = 0-15 and (b) variations in the ε_r and Q_u × f of $Sr_4Ta_2O_9$ + (x)Sm_2O_3 ceramics for x = 0-15.

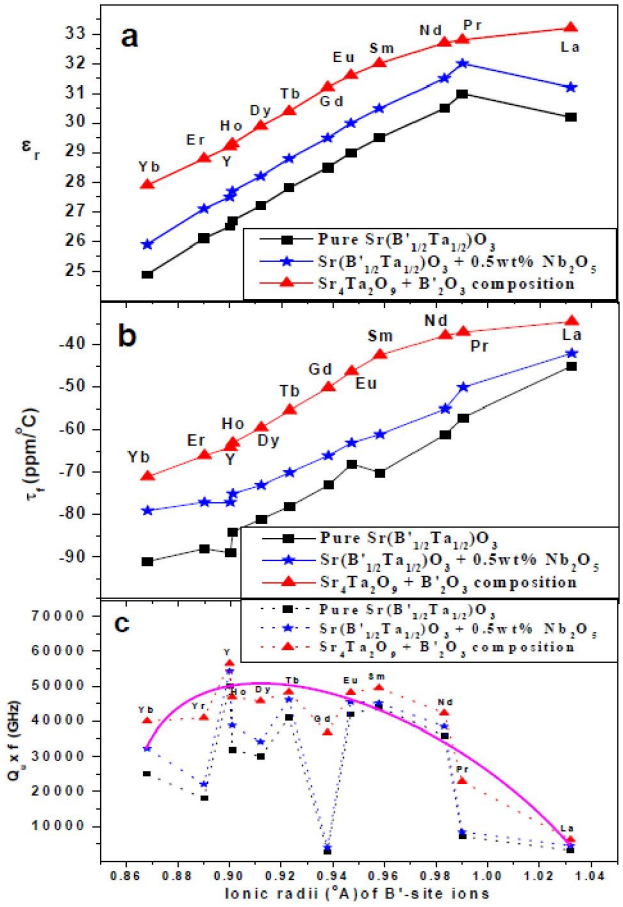

Figure 6 : Shows the unreacted TiO_2 content shaltered in the terenary grains of $Sr(Sm_{1/2}Ta_{1/2})O_3$ ceramic when 1 wt% TiO_2 was added.

The variations in the dielectric properties of $Sr(B'_{1/2}Ta_{1/2})O_3$ [B' = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er and Yb] ceramics synthesized in $Sr_4Ta_2O_9$-B'_2O_3 compositions and prepared in the conventional 4:1:1 method (with and without the sintering aid) are shown in Figure 6. The dielectric values ε_r, Q_u × f and τ_f were found improved in the present study. The $Sr_4Ta_2O_9$-B'_2O_3 compositions show betterment in ε_r compared to other two results. The fall in ε_r for $Sr(La_{1/2}Ta_{1/2})O_3$ ceramic in the 4:1:1 methods is not observed here. The ε_r of $Sr(B'_{1/2}Ta_{1/2})O_3$ ceramics in the $Sr_4Ta_2O_9$-B'_2O_3 composition varies from 27.9 to 33.2 towards the large ionic radius side (Figure 6a). The τ_f of $Sr_4Ta_2O_9$-B'_2O_3 composition shows low negative values compared to other two results. The τ_f of $Sr_4Ta_2O_9$-B'_2O_3 composition varies from -71 ppm/°C to -35 ppm/°C towards the large ionic radius side (Figure 6b). The Q- factor of $Sr_4Ta_2O_9$-B'_2O_3 compositions also found increased compared to other two results. The trend of Q_u × f variation of $Sr(B'_{1/2}Ta_{1/2})O_3$ ceramics is represented by the curved dotted line in Figure 6c.

CONCLUSIONS

Dense and phase pure $Sr(B'_{1/2}Ta_{1/2})O_3$ [B' = La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Y, Er and Yb] ceramics were prepared by mixing the calcined powders of $Sr_4Ta_2O_9$ and B'_2O_3 in the molar ratio 1:1 and when sintered at 1600°C/4h without any sintering aid. The microwave dielectric properties of the ceramics were investigated and found depends on the B'-site ionic radii. Amount of B'_2O_3 content is a determining factor of the dielectric properties of $Sr_4Ta_2O_9$+(x)B'_2O_3 compositions. The τ_f of $Sr_4Ta_2O_9$+(x)Sm_2O_3 has tuned to near zero value for x = 13. Quality factor of $Sr_4Ta_2O_9$+(x)Sm_2O_3 compositions improved up to x = 1.25 and then deteriorated. But τ_f has increased (to -40 ppm/°C) up to x = 1 and then lowered to zero at x = 13 and turned to positive value with further addition Sm_2O_3. The dielectric properties of $Sr_4Ta_2O_9$+(x)B'_2O_3 compositions for x = 1 were found

in the ranges ε_r = 27.9-33.2, $Q_u \times f$ = 6200-56400 GHz and τ_f = -71 to -35 ppm/°C.

REFERENCES

[1] A.Borisevich, P.K.Davies; J.Eur.Ceram.Soc., **21(10-11)**, 1719-22 **(2001)**.

[2] W.S.Kim, K.H.Yoon, E.S.Kim; Mater.Res.Bull., **34(14-15)**, 2309-2317 **(1999)**.

[3] W.Wersing; High frequency ceramic dielectrics and their applications for microwave components in electronic ceramics, B.C.H.Steele (Ed); Elsevier Applied Science, London, U.K., 67-119 **(1991)**.

[4] L.L.Hench, J.K.West; Principles of electronic ceramics, John Wiley and Sons, New York, **202(27)**, **(1990)**.

[5] F.Galasso, L.Katz, R.Ward; J.Amer.Chem.Sot., **820-23(81)**, **(1959)**.

[6] O'Byran, H.M.Thomson, J.K.Plorud; J.Am.Ceram. Soc., **57**, 450-453 **(1974)**.

[7] K.Wakino, T.Nishikawa, Y.Ishikawa, H.Tamura; Br.Ceram., Trans.J., **89**, 39-43 **(1990)**.

[8] S.Kawashima, M.Nishida, I.Ueda, H.Ouchi; J.Amer.Ceram.Soc., **66**, 421-23 **(1983)**.

[9] S.Nomura, K.Toyama, K.Kaneta; Jpn.J.Appl. Phys., **21(10)**, L624- L626 **(1982)**.

[10] W.Wersing; Curr.Opin.Solid State Mater.Sci., **1**, 715-31 **(1996)**.

[11] M.T.Sebastian, K.P.Surendran; J.Eur.Ceram.Soc., **26**, 1791-99 **(2005)**.

[12] L.A.Khalam, M.T.Sebastian; J.Am.Ceram.Soc., **89(12)**, 3689–3695 **(2006)**.

[13] J.Takahashi, K.Kageyamma, T.Fuji, T.Yamada, K.Kodaira; J.Mater.Sci.Elect., **8**, 79-84 **(1997)**.

[14] L.A.Khalam, M.T.Sebastian; J.Appl.Ceram. Technol., **3(5)**, 364-374 **(2006)**.

[15] B.W.Hakki, P.D.Coleman; IRE Trans.Microwave Theory Tech., MTT, **8**, 402–410 **(1960)**.

[16] J.Krupka, K.Derzakowski, B.Riddle, J.B.Jarvis; Meas.Sci.Technol., **9**, 1751–1756 **(1998)**.