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High k of $Ba(Sm_{1/2}Ta_{1/2})O_3$ Perovskite with the addition of cation

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ABSTRACT

Double perovskite type $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic was prepared in the conventional ceramic route. Dielectric properties were determined with the addition of dopants such as Nb_2O_5, CuO, ZnO, MgO and TiO_2. Addition of MgO and ZnO increased the quality factor of the ceramic to a great extent, while the τ_f could be tuned to nearly zero value with the addition of CuO and TiO_2. Addition of TiO2 increased the dielectric constant of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic to a high k group.

KEYWORDS

Dielectric resonators;
Microwaves;
Complex perovskites;
Cations.

INTRODUCTION

Microwave communication industry is experiencing a remarkable change after the development of ceramic materials that could be used as dielectric resonators and filters to store and transfer microwave communication signals[1,2]. Prominent DR materials family reported in the literature are the complex perovskites of 1:2 ordered type $A(B_{1/3}B'_{2/3})O_3$ and 1:1 ordered type $A(B_{1/2}B'_{1/2})O3$-- ceramics[4-11]. Dielectric properties of complex perovskites can be tuned by suitable substitutions at A or B sites.[3,4,5-7] Among the 1:2 type ordered ceramics $Ba(Zn_{1/3}Ta_{2/3})O_3$ and $Ba(Mg_{1/3}Ta_{2/3})O_3$ were found to have high quality factor and low temperature coefficient of resonant frequency[8-10]. Addition of CuO, NaF, B_2O_3 and $PbO\text{-}B_2O_3\text{-}SiO_2$ glasses[11-14] enhance the liquid phase sintering. In this report, the variation in the dielectric properties of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic with the addition of different dopants were studied.

EXPERIMENTAL

Perovskite type $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic was prepared in the conventional ceramic route. High purity $BaCO_3$ (99.9%, Aldrich Chemicals), Ta_2O_5 (99.9%, Nuclear Fuel Complex), and rare earth oxides (99.9%, Indian Rare Earths) were weighed in the stoichiometric ratio 4:1:1 and ball milled using zirconium balls in distilled water medium for 24 hours. The slurries were dried and calcined at 1375°C for 4 hours. The addition of binder and powder compaction were carried. The obtained compounds were sintered in air at 1575°C, for 4 hours. Addition of different dopants in 0-5 wt.% were added to $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic and sintered at 1625°C. The bulk densities of the sintered samples were measured by Archimedes method. Well-polished samples were used for all the measurements.

RESULTS AND DISCUSSION

Calcination and sintering temperatures of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramics were optimized as 1375°C/4h and 1575°C/4h for better dielectric properties. The cell parameters were calculated by indexing $Ba(Sm_{1/2}Ta_{1/2})O_3$ as tetragonal structure. X-ray diffraction pattern of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic is shown in Figure 1. The

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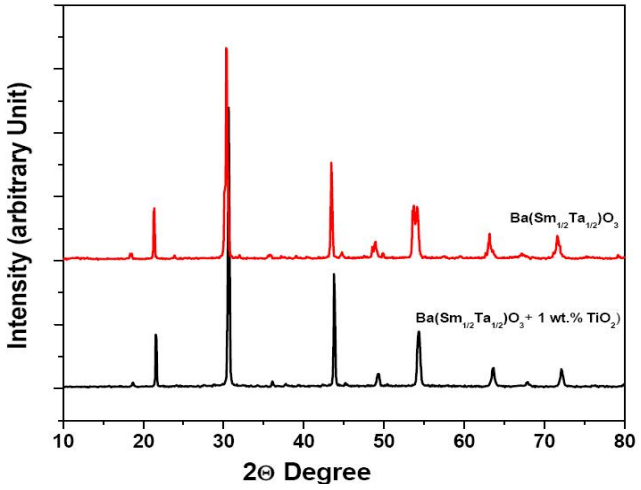

Figure 1: Shows (1) pure $Ba(Sm_{1/2}Ta_{1/2})O_3$ and (2) TiO_2 added $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic

dielectric responses of the $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic sample was measured in the range 4 to 6 GHz range and are shown in TABLE 1. Different valence dopants such as Nb_2O_5, CuO, ZnO, MgO and TiO_2 in 0-5 wt% were added separately to $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramics. Figure 2 shows the variations in the dielectric properties of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramics with the addition of 0-5 wt.% of different valence dopants at the same sintering temperature (1575°C/4h). The ionic radii of B-site elements in the $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic are r_{Sm} = 0.958 ú, r_{Ta} = 0.64 ú and the average ionic radius of Sm and Ta is 0.799 ú. Dopant addition changed the dielectric properties of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic. Dielectric properties of $Ba(Sm_{1/2}Ta_{1/2})O_3$ has been improved with the dopants independent of their valency. Thus the divalent dopants such as MgO, CuO, ZnO; tetravalent dopants such as TiO_2; and pentavalent dopants such as Nb_2O_5 appreciably changed the Q-factor, ε_r and τ_f of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramics. The variation of ε_r with these dopants is in the range 36.6 – 38.2. Further addition of TiO_2 increases the ε_r of $Ba(Sm_{1/2}Ta_{1/2})O_3$ whereas Q-factor decreases. Figure 2a shows the variation of $Q_u \times f$ of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramics with 0-5 wt.% addition of dopants. TiO_2 addition steeply decreases the Q-factor of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramics. Quality factor of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramics showed an increase with a small amount of Nb_2O_5 and CuO and then decreased with further additions as shown in Figure 2a. The additions of MgO and ZnO in 0-5 wt.% showed a trend of increase in Q-factor of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic though the relative densities of the samples were decreased to nearly 95% of the theoretical density. With the rise in sintering temperature of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramics by 25°C per each 1 wt.% addition of MgO and ZnO, the Q-factor of the samples have been increased appreciably as shown. Additional peaks of $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $Ba(Zn_{1/3}Ta_{2/3})O_3$ phases were observed in the XRD pattern of MgO and ZnO added samples (Figure 3). Increase in Q-factor with the addition of MgO and ZnO may be due to the formation of $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $Ba(Zn_{1/3}Ta_{2/3})O_3$ phases along with $Ba(Sm_{1/2}Ta_{1/2})O_3$.

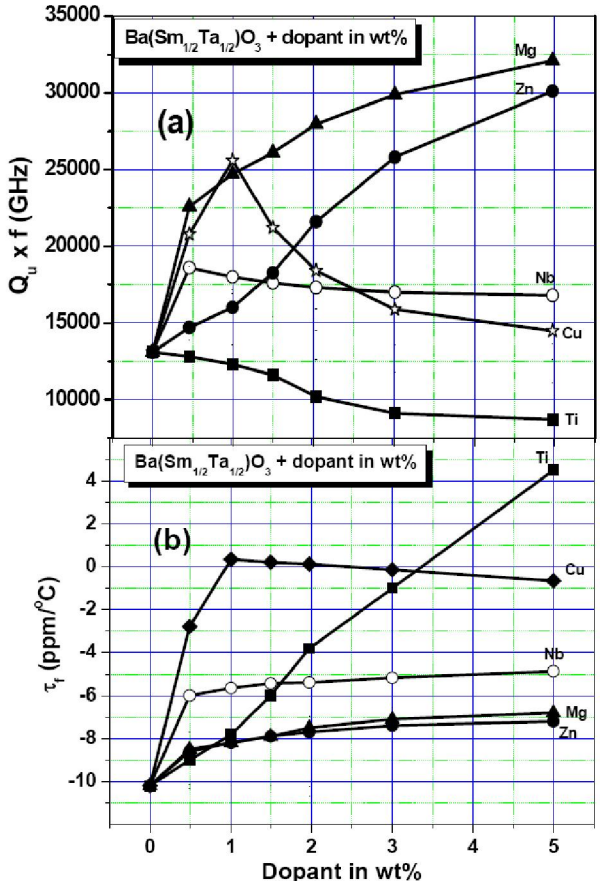

Figure 2 : Shows the variation in (a) Q-factor and (b) τ_f of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic with the addition of dopants in different wt.%.

The variation of τ_f of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramics with the addition of dopants in 0-5 wt.% is shown in Figure 2b. $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic shows a shift in τ_f towards the +ve value with TiO_2 addition. The steep variations in the dielectric properties with the addition of TiO_2 may be due to the TiO_2 secondary phase in the $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic. Similar behaviours with TiO_2 additions were reported for $Sr(B'_{1/2}Ta_{1/2})O_3$ and $Ca(B'_{1/2}Nb_{1/2})O_3$ ceramics. 1 wt.% addition of CuO decreased the $|\tau_f|$ of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic to zero

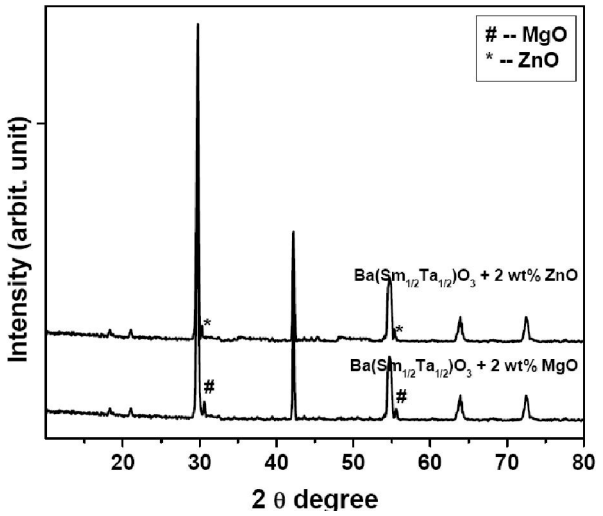

Figure 3: Shows the XRD peaks of cation added $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic.

value and then again increased to –ve value with further additions. 0.5 wt.% addition of Nb_2O_5 lowered the τ_f to -3 ppm/°C and remains nearly steady value with further additions. MgO and ZnO additions to $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic showed an improvement in τ_f to -7 ppm/°C with 0.5 wt.% addition and it remains nearly a constant with further additions. These investigations indicate that, the improvement in the dielectric properties of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramics is more dependent of the dopant's ionic size than their valency. The improvement in dielectric properties of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic with up to 1 wt.% CuO addition was due to the liquid phase sintering. More addition of CuO lowered the dielectric properties of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic due to the liquid phase formation with CuO. Addition of more TiO_2 appreciably increased the ε_r value and hence $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic approaches the high k group.

A combined (1:1 combination) effect of these dopants in 0-6 wt.% were also tried to study the variations in the dielectric properties of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic. These ceramics were sintered at 1600°C/4h. $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic has obtained a maximum ε_r of 37.5 with the addition of 1 wt.% of Nb_2O_5 + CuO and then it was decreased with the further additions. Similarly, MgO + CuO and ZnO + CuO combinations showed slight increase in ε_r with 1 wt.% addition as shown in Figure 4a. The Q-factors of $Ba(Sm_{1/2}Ta_{1/2})O_3$ with MgO + CuO (1:1 ratio) and ZnO + CuO (1:1 ratio) have increased linearly up to 1 wt.% addition and then decreased with further additions. Nb_2O_5 + CuO also slightly increased the Q-factor of $Ba(Sm_{1/2}Ta_{1/2})O_3$

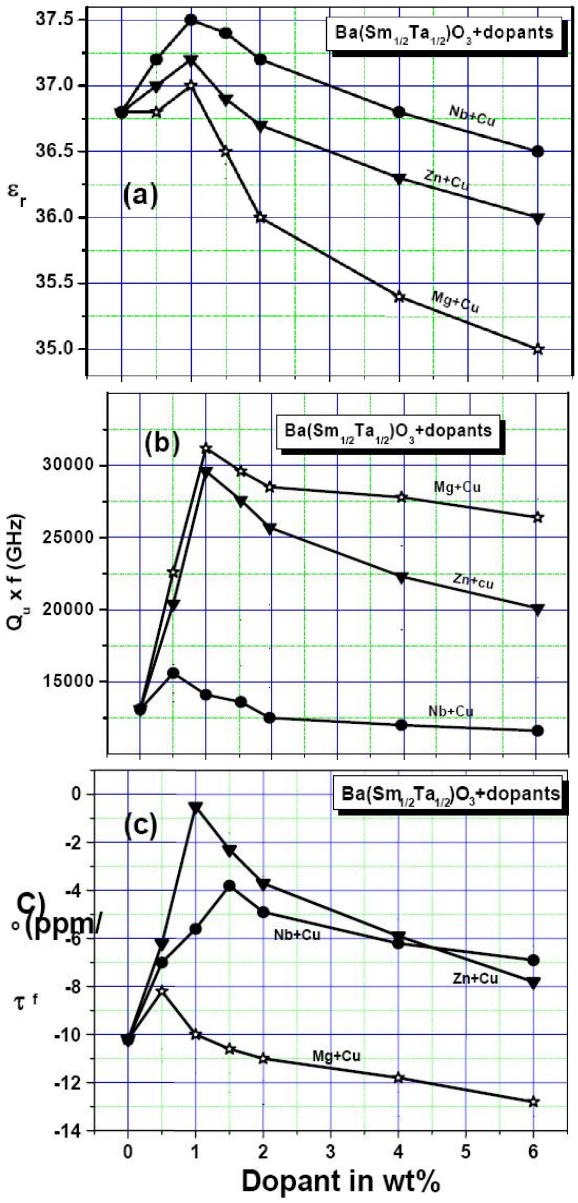

Figure 4: Shows the variation in (a) ε_r (b) Q-factor and (c) τ_f of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic with the addition of multiple dopants in different wt.%.

ceramics up to 0.5 wt.% addition and then decreased with further additions as shown in Figure 4b. The decrease in Q-factors of CuO added samples may be due to the liquid phase formation with the melted CuO.

Figure 4c shows the variation of τ_f of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramics with the addition of dopants in the ratio 1:1. Additions of 1 wt.% of ZnO + CuO and Nb_2O_5 + CuO lowered the τ_f of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic to close to zero value (-0.5 ppm/°C and -3.5 ppm/°C). 1 wt.% addition of MgO + CuO also lowered the τ_f of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic to -8.2 ppm/°C. Any addi-

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tion of TiO_2 to any combination of dopants results decrease in Q-factor, increase in ε_r value and shifts the τ_f to positive side due to the unreacted TiO_2 phase in the $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic.

Effect of dopant (rutile-TiO_2) on $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramics

Generally Ba based double perovskites have –ve τ_f[15-18]. The TiO_2 has high dielectric constant, large positive τ_f and has size (r_{Ti} = 0.645Å) and charge (z_{Ti} = 4^+) close to the average of Sm^{3+} and Ta^{5+}. Hence small wt% of TiO_2 was added to B-site of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramics to tune ε_r and τ_f. $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramics has ε_r = 37.6, Q_u x f = 13100 GHz and τ_f = -10.2 ppm/°C while TiO_2 has ε_r H" 100, Q_u x f H" 45000 GHz and τ_f H" 400 ppm/°C. $Ba(Sm_{1/2}Ta_{1/2})O_3$ + *x* wt.% TiO_2 ceramics for *x* = 0 to 10 were sintered at 1600-1300°C for 4 hours. The sintering temperatures of the compounds decreases by 25°C with each 1 wt.% addition of TiO_2. XRD pattern of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramics with and without the addition of TiO_2 is shown in Figure 1. The tetragonal splitting in the reflection peaks have disappeared and instead sharp peaks of cubic structure appeared with the addition of TiO_2. With the addition of 1 wt.% TiO_2, the difference between the lattice parameters a and b has found decreased and the tetragonal structure transformed to pseudo cubic. Density of the ceramic has increased with a small amount (up to 0.5 wt.%) of TiO_2 addition. Addition of more wt.% of TiO_2 decreases the density of the ceramic but increases the ε_r with TiO_2 content as shown in TABLE 1. Rutile has lower density H" 4 g/cm^3. Addition of 0.5 wt.% TiO_2 has not affected the Q-factor (13000 GHz) of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic. Improvements in ε_r and τ_f with the addition of TiO_2 to $La_{2/3}(Mg_{1/2}W_{1/2})O_3$ was reported by Bian et al.[19]. More than 0.5 wt.% TiO_2 addition to $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramics decreased the density and Q-factor while increased the ε_r value steeply (shows in Figure 5). The continuous increase in ε_r with more addition of TiO_2 is due to the unreacted TiO2 content in the $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic. This type of temperature stable and high k materials opens a window to high k group. The variations in the dielectric properties of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic with the addition of 0-10 wt.% of TiO_2 at 1600-1300°C/4 h are shown in TABLE 1.

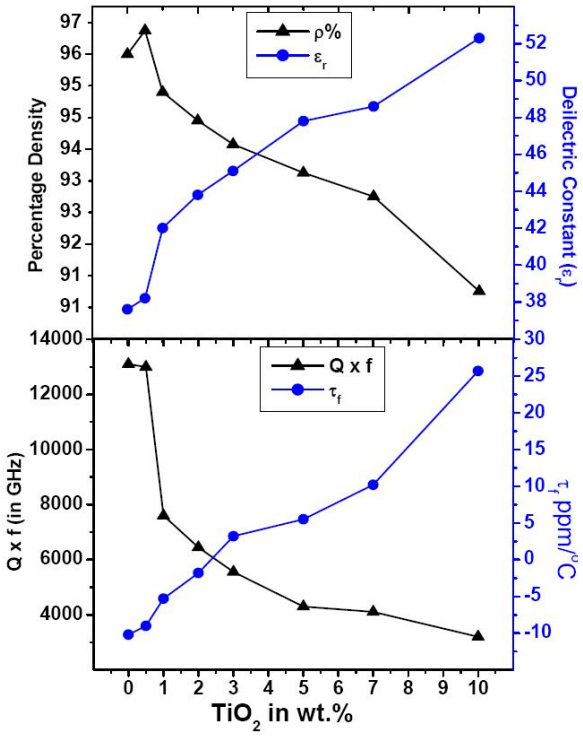

Figure 5 : Shows the variation in the dielectric properties of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic with the addition of TiO_2 in different wt.%

TABLE 1: Shows the dielectric properties of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic with cation addition

Dopant (0.5 wt.%)	r_{dopant} (Å)	% ρ	ε_r	Q_u x f (GHz)	τ_f (ppm/°C)
Pure $Ba(Sm_{1/2}Ta_{1/2})O_3$	---	96.00	37.60	13100	-10.20
+ 0.5 wt% Nb_2O_5	0.64	95.4	37.67	16000	-7.2
+ 0.5 wt% MgO	0.72	95.5	36.60	24000	-7.7
+0.5 wt% CuO	0.73	95.9	36.81	17350	0.0
+0.5 wt% ZnO	0.74	97.5	37.20	16850	-8.4
+0.5 wt% TiO_2	0.645	96.5	38.20	13000	-9.0
+ 1.0 wt% TiO_2	"	95.2	42.00	7600	-5.3
+ 2.0 wt% TiO_2	"	94.6	43.80	6450	-1.8
+ 3.0 wt% TiO_2	"	94.1	45.10	5560	3.2
+ 5.0 wt% TiO_2	"	93.5	47.80	4300	5.5
+ 7.0 wt% TiO_2	"	93.0	48.60	4100	10.2
+ 10.0 wt% TiO_2	"	91.0	52.30	3200	25.7

CONCLUSIONS

The quality factor of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic was increased with the addition of MgO, CuO, ZnO, and Nb_2O_5 separately. But the dielectric constant was least affected by them. τ_f of the ceramic could be

tuned to nearly zero value with a small amount of CuO and TiO_2 and then τ_f was shifted to positive value with further addition of TiO_2. The dielectric properties of $Ba(Sm_{1/2}Ta_{1/2})O_3$ ceramic was increased with a 1:1 combination of Mg & Cu, ZnO & CuO and Nb_2O_5 & CuO up to 1 wt.% addition and then the dielectric properties were deteriorated with further additions. This effect of increase in Dielectric constant of the material with the addition of TiO_2 can add the material in to high k group.

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