Dielectric Properties of BaZr$_{0.2}$[Ti$_{(1-x)}$Mg$_{x/3}$Ta$_{2x/3}$]$_{0.8}$O$_3$ Solid Solution

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BaZr$_{0.2}$[Ti$_{(1-x)}$Mg$_{x/3}$Ta$_{2x/3}$]$_{0.8}$O$_3$ (x = 0.0, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0) (BZTMT) ceramics were prepared through conventional solid state ceramic route. The crystal structure and microstructure of the compounds were investigated respectively using XRD and SEM. The dielectric properties were measured in the frequency range of 100 Hz–1 MHz. The ferroelectric Curie temperature of BaZr$_{0.2}$Ti$_{0.8}$O$_3$ (x = 0) shifted from 21°C to -10°C with the addition of minute amount of dopant (x = 0.025) and the paraelectric transition temperature is diffusive in nature. The relative permittivity and dielectric loss of BZTMT at 1 MHz varies from 5205 to 24 and 1.8×10^{-2} to 2.0×10^{-5} respectively, as the value of x increases from 0 to 1.

Keywords: ferroelectrics, paraelectrics, solid solution, barium zirconium titanate, ceramics

INTRODUCTION

BaTiO$_3$ based ferroelectric materials have received a great deal of attention from scientific community as an alternative for lead free materials for extensive applications in capacitors, piezoelectric devices and transducers(Wang et al., 2012; Chen et al., 2014; Magnone et al., 2016; Li et al., 2017; Co et al., 2020; Venkatachalam et al., 2020). The high curie temperature (128°C) and intrinsically low relative permittivity in pure BaTiO$_3$ make it unsuitable in practical device applications(Hennigs and Schnell, 1982). Electrical properties of BaTiO$_3$ can be tailored by chemically substituting both dodecahedral Ba^{2+} sites and the octahedral Ti^{4+} sites(Hennigs and Schnell, 1982; Sangwan et al., 2018). Ti^{4+} site is generally substituted by Zr^{4+}, which is more chemically stable than that of Ti^{4+}. The resulting material, BaZr$_x$Ti$_{1-x}$O$_3$ (BZT) generally exhibits very high and broad curie maxima and are often found application as relaxor ferroelectrics(Li et al., 2014). As in the case of BaTiO$_3$, three ferroelectric phase transitions are observed in BZT solid solution for x < 0.13. On increasing the Zr content the three transition points and the corresponding dielectric maxima move closer together and finally coalesce in to single broad maxima(Hennigs and Schnell, 1982). For composition 0.26 < x < 0.42, the temperature dependence of the real part of dielectric constant at transition temperature is broad and frequency dependent (Maiti et al., 2008; Li et al., 2014). Until now many researchers have studied the dielectric properties of BZT system(Buscaglia et al., 2000; Weber et al., 2001; Maiti et al., 2008).

Substitution for both isovalent and aliovalent cation in the host BZT perovskite lattice plays a very important role in the modification of dielectric properties. Buscaglia et al. had reported that the aliovalent cation substitution in perovskite lattice can serve either as donors or as acceptors, which will affect the electrical characteristics greatly(Buscaglia et al., 2000). Many aliovalent compositional alterations in BZT have been studied either with higher valance substitution (donors), or with lower

valance ions (acceptors). Donor dopants induce cationic defects while occupying octahedral site of perovskite lattice(Ravez and Simon, 2000; Surendran and Sebastian, 2005). Rout et al. observed a decrease in Curie temperature (T$_c$) by substituting small amount of Mg^{2+} in place of Ba^{2+} in BZT, which was ascribed to decrease in the grain size(Rout et al., 2007). The cation ordering and dielectric properties of Ba(Mg$_{1/3}$Ta$_{2/3}$)$_{1-x}$Ti$_x$O$_3$ system was reported by Surendran et al (Surendran and Sebastian, 2005) They found that as the concentration of Ti^{4+} is x > 0.2, the cation ordering shifted to disordered state. Moreover the microwave resonance character of Ba(Mg$_{1/3}$Ta$_{2/3}$)O$_3$ vanishes completely when the concentration exceeds x = 0.6(Penn and McN Alford, 2000).

In the present investigation Ti^{4+} octahedral site in ferroelectric BaZr$_{0.2}$Ti$_{0.8}$O$_3$ is systematically replaced with (Mg$_{1/3}$Ta$_{2/3}$)$^{4+}$ ions. The dielectric properties of the materials were investigated both in low frequency and microwave regions. The effect of (Mg$_{1/3}$Ta$_{2/3}$)$^{4+}$ substitution on the curie temperature of the materials were also investigated. To the best of our knowledge no useful work has been done on the aspect of simultaneous substitution of Mg and Ta in the Ti site of BZT. The present paper describe the variation of microwave dielectric properties of BaZr$_{0.2}$ [Ti$_{(1-x)}$Mg$_{x/3}$Ta$_{2x/3}$]$_{0.8}$O$_3$ as a function of x.

MATERIALS AND METHODS

Materials Synthesis

The BaZr$_{0.2}$ [Ti$_{(1-x)}$Mg$_{x/3}$Ta$_{2x/3}$]$_{0.8}$O$_3$ [x = 0.0, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0] solid solution by varying the concentrations of (MgTa)$^{4+}$ were prepared by the conventional solid state ceramic route. High-purity (>99.9%) powders of barium carbonate (BaCO$_3$), magnesium carbonate hydroxide penta hydrate (MgCO$_3$Mg(OH)$_2$-5H$_2$O), titanium dioxide (TiO$_2$), zirconium dioxide (ZrO$_2$) (Aldrich Chemicals), and tantalum pentoxide (Ta$_2$O$_5$) (NFC, Hyderabad) were used as the starting materials. Stoichiometric proportions of these chemicals were mixed from a ball milling unit for 24 h. The slurry obtained was dried in a hot air oven at 100°C for12 h and then calcined at 1,200°C for 8 h at a heating rate of 5°C/min. The calcined powders were ground well and mixed with 4 wt% aqueous solution of Poly vinyl alcohol. The powder was uniaxially pressed into cylindrical pellets having diameter 11 mm and thickness 1.5 mm under a pressure of 100 MPa. These sample pellets were fired to 600°C at a rate of 5°C/min, kept at 600°C for 30 min to expel binder and then sintered at 1,600°C for 2 h in air. The samples were then cooled to 800°C at a slow rate of 3.5°C/min. The bulk densities of the sintered samples were measured using dimensional method.

Characterization Techniques

The phase purity of the as synthesized BZTMT solutions was analyzed by X-ray diffraction technique using Cu-Kα radiation (Philips X'pert Prro diffractometer). The sintered samples were thermally etched, and their surface morphology and grain sizes were studied using a scanning electron microscope (JEOL-JSM 5600 LV, Japan). The sintered and polished thin pellets were electroded by coating silver paste on both sides and the dielectric
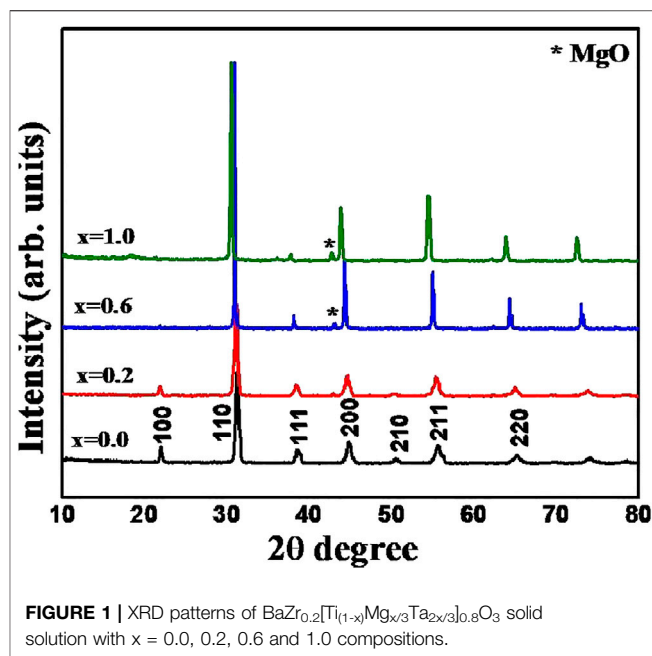

FIGURE 1 | XRD patterns of BaZr$_{0.2}$[Ti$_{(1-x)}$Mg$_{x/3}$Ta$_{2x/3}$]$_{0.8}$O$_3$ solid solution with x = 0.0, 0.2, 0.6 and 1.0 compositions.

properties in low frequency regions (500 Hz–1 MHz) were measured using an LCR meter (HIOKI 3532-50 LCR HiTESTER). The temperature dependence of relative permittivity in the range of -25–70°C was also determined from the same instrument at 1 MHz frequency. The dielectric properties of the materials in the microwave frequency range were measured by the resonance method using a Vector Network Analyzer (Agilent 8753 ET, Palo Alto, CA). TE$_{01\delta}$ mode of resonance is used for the measurements(Krupka et al., 1998). The cavity method is ideal for measuring the Q factor since the electric field is symmetrical with geometry of the cavity and the dielectric(Krupka et al., 1998). The temperature coefficient of resonant frequency (τ$_f$) was measured in the temperature range 25–70°C. The resonance frequency was measured at regular time intervals of temperature ramping and the τ$_f$ was measured by the expression,

$$\tau_f = \frac{f_2 - f_1}{f_1 (T_2 - T_1)}$$

where f$_1$isthe resonant frequency at temperature T$_1$ and f$_2$ is the resonant frequency at temperature T$_2$.

RESULTS AND DISCUSSION

X-Ray Diffraction

The room temperature powder X-ray diffraction patterns of BZTMT solid solution (x = 0, 0.2, 0.6, 1.0) are shown in **Figure 1**. The crystal structure of pure BaZr$_{0.2}$Ti$_{0.8}$O$_3$ (x = 0) is indexed to the cubic symmetry phase (00360019), due to the fact that above 21°C (Curie temperature) the BZT changes from the non-centro symmetric tetragonal phase to the centro-symmetric cubic phase. Unit cell parameter of pure BZT

TABLE 1 | Unit cell parameter and dielectric properties of $BaZr_{0.2}[Ti_{(1-x)}Mg_{x/3}Ta_{2x/3}]_{0.8}O_3$ solid solution phase.

x	Unit cell parameter, a (Å)	Tolerance factor	Low frequency (1 MHz)		Microwave (GHz)	
			ε_r	Tanδ	Quxf	τ_f
0.0	4.04	1.046	5160	1.8×10^{-2}	NR	—
0.2	4.05	1.041	201	7.5×10^{-4}	NR	—
0.4	4.07	1.036	71	6.7×10^{-4}	NR	—
0.6	4.08	1.031	41	6.2×10^{-4}	4900	93
0.8	4.10	1.026	28	2.0×10^{-5}	24000	35
1.0	4.10	1.021	23	9.0×10^{-5}	66500	15
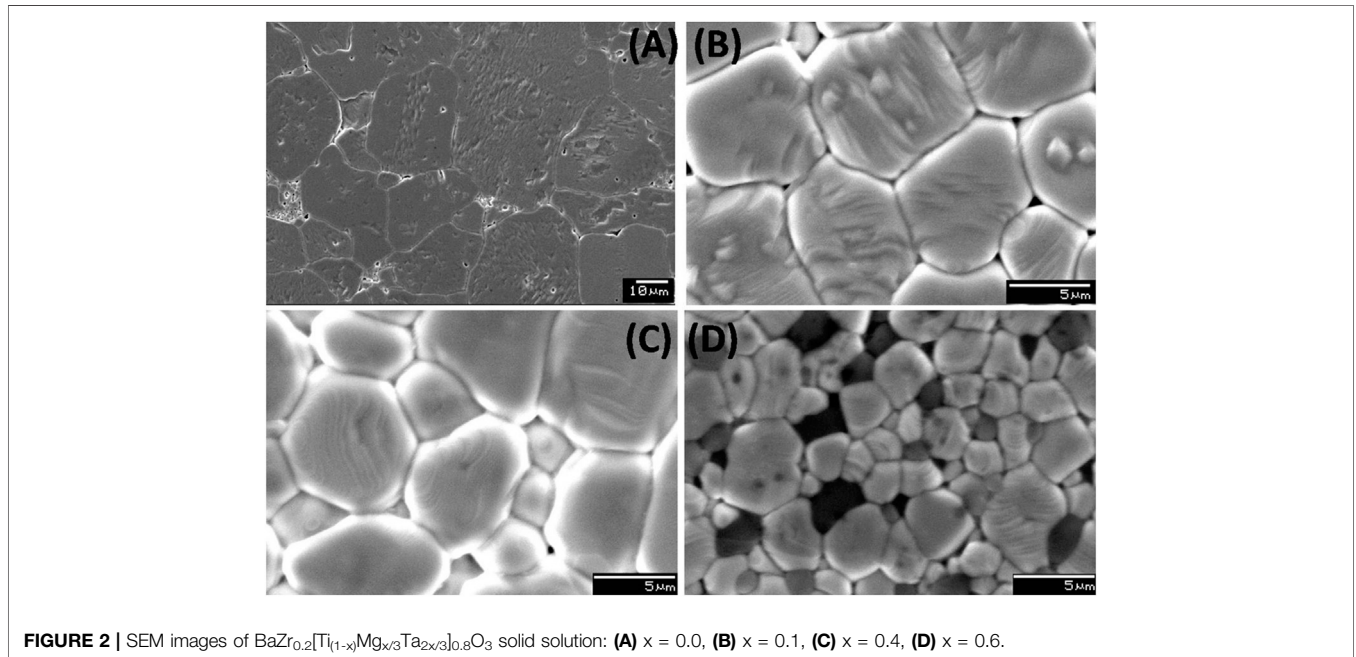
FIGURE 2 | SEM images of $BaZr_{0.2}[Ti_{(1-x)}Mg_{x/3}Ta_{2x/3}]_{0.8}O_3$ solid solution: **(A)** x = 0.0, **(B)** x = 0.1, **(C)** x = 0.4, **(D)** x = 0.6.
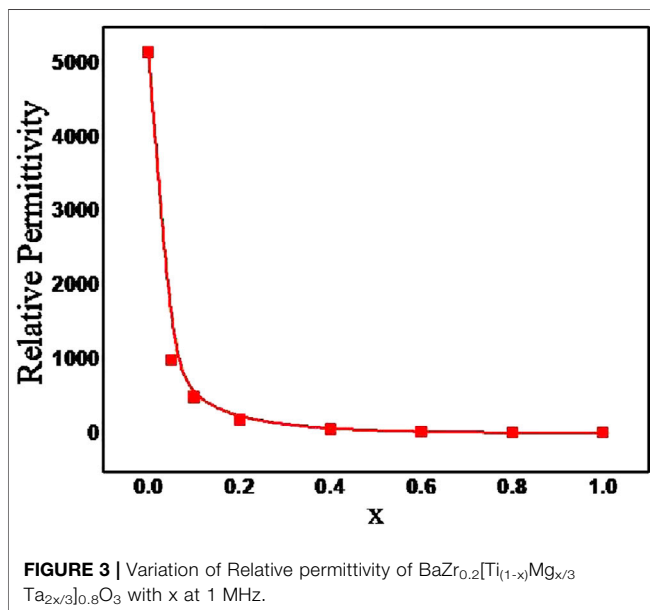
FIGURE 3 | Variation of Relative permittivity of $BaZr_{0.2}[Ti_{(1-x)}Mg_{x/3}Ta_{2x/3}]_{0.8}O_3$ with x at 1 MHz.

calculated from diffraction studies is a = 4.04 Å. As the concentration of $(MgTa)^{4+}$ increases unit cell parameter increases and reaches a maximum of 4.10 Å at x = 1 (**Table 1**).

SEM Analysis

The SEM micrographs of polished and thermally etched surfaces of the sintered $BaZr_{0.2}[Ti_{(1-x)}Mg_{x/3}Ta_{2x/3}]_{0.8}O_3$ (x = 0, 0.1, 0.4, 0.6) is shown in **Figure 2**. The average grain size of pure BZT (x = 0) is about 25–30 µm. It is interestingly noted that as the concentration of Mg and Ta increases, the grain size decreases. The average grain size of x = 0.6 composition was found to be 4–6 µm. For BZTMT compositions with x ≥ 0.6, the presence of unreacted MgO phase is clearly visible from the SEM image (**Figure 2D**) as evidenced from the XRD studies.

Dielectric Measurements

Hard pellets with bulk density above 85% were used for dielectric measurements. **Figure 3** show the variation of relative permittivity of BZTMT solid solution at a frequency of 1 MHz. The relative permittivity of the $BaZr_{0.2}[Ti_{(1-x)}Mg_{x/}$

FIGURE 4 | Variation of Relative Permittivity of $BaZr_{0.2}[Ti_{(1-x)}Mg_{x/3}Ta_{2x/3}]_{0.8}O_3$ for $0.0 < x < 0.4$ with frequency.

FIGURE 6 | Variation of Relative permittivity and Quality factor with tolerance factor of $BaZr_{0.2}[Ti_{(1-x)}Mg_{x/3}Ta_{2x/3}]_{0.8}O_3$ solid solution phases.
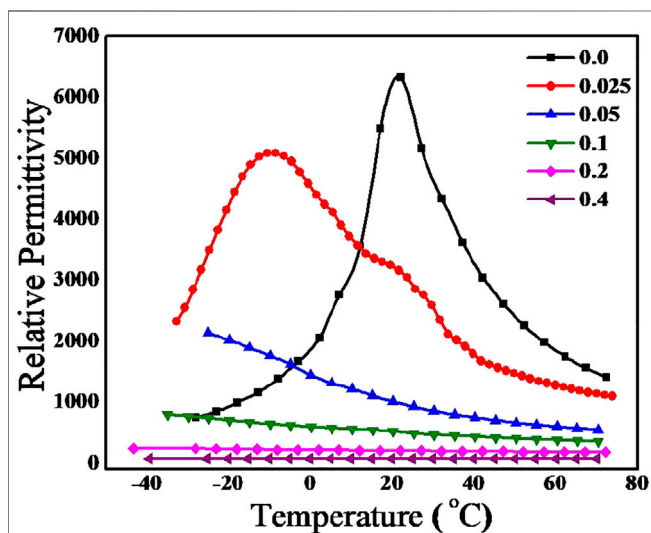

FIGURE 5 | Variation of relative permittivity of $BaZr_{0.2}[Ti_{(1-x)}Mg_{x/3}Ta_{2x/3}]_{0.8}O_3$ for $0.0 < x < 0.4$ with temperature at 1 MHz.

paraelectric phases. However, as the concentration of $(MgTa)^{4+}$ increases the material shows appreciable resonance and the $x = 1.0$ composition shows an excellent quality factor, Q_uxf of 66,500 GHz.

The dependence of frequency on the relative permittivity of BZTMT solid solutions were recorded for compositions $x = 0, 0.05, 0.1, 0.2, 0.4$ and depicted as **Figure 4**. All the compositions of $BaZr_{0.2}[Ti_{(1-x)}Mg_{x/3}Ta_{2x/3}]_{0.8}O_3$ ceramics shows frequency dependent relative permittivity, however the variation of relative permittivity with frequency is very small in with $x = 0.4$ composition. At low frequency region, all the polarization mechanisms such as interfacial, dipolar, ionic and electronic polarizations are active and results in high relative permittivity; as the frequency increases to 1 MHz the permittivity of all the samples decreases due to suppression of interfacial and dipolar polarization mechanisms(Mollá et al., 1999).

The temperature dependence of relative permittivity of $BaZr_{0.2}[Ti_{(1-x)}Mg_{x/3}Ta_{2x/3}]_{0.8}O_3$ at various $(MgTa)^{4+}$ concentrations were recorded at a frequency of 1 MHz and plotted as **Figure 5**. In $BaZr_{0.2}Ti_{0.8}O_3$ ($x = 0$), the relative permittivity value increases with increase in temperature and reaches a maximum of 6,521 at 21°C and thereafter decreases. The temperature corresponding to this maximum value of relative permittivity is the Curie temperature (21°C) of this material which corresponds to the transition from tetragonal (ferroelectric) to cubic (paraelectric) phase of the material. However, it is seen that as the $(MgTa)^{4+}$ concentration increases curie temperature has shifted to lower temperature region and the corresponding relative permittivity value decreases. The relative permittivity at Curie temperature, -10°C for $x = 0.025$ was found to be 5,086. Instead of getting a single sharp Curie peak a broad maxima is observed for both composition which is due to the inhomogeneous distribution of M^{4+} ions in Ti^{4+} octahedral sites and the corresponding mechanical stresses created in the grains(Xu and Li, 2020). The ferroelectric to paraelectric phase transition for $x = 0.05$ composition has shifted to very low temperature region, thus the

$_3Ta_{2x/3}]_{0.8}O_3$ solid solution decreases with increase in $(MgTa)^{4+}$ content. The room temperature relative permittivity of bare BZT was found to be 5,160 which decreases to 23 when the entire Ti^{4+} is replaced by $(MgTa)^{4+}$ ions ($x = 1.0$). As the Ti^{4+} is replaced by $(MgTa)^{4+}$ ions in $BaZr_{0.2}[Ti_{(1-x)}Mg_{x/3}Ta_{2x/3}]_{0.8}O_3$ the solid solution finally shifted to $BaZr_{0.2}[Mg_{x/3}Ta_{2x/3}]_{0.8}O_3$ phase with very low relative permittivity value(Xu and Li, 2020). The microwave dielectric properties of the BZTMT solid solutions were recorded and tabulated in **Table 1**. The compositions from $x = 0.0$ to 0.04, which contains lower concentration of $(MgTa)^{4+}$, does not show any resonance in the microwave region (marked as NR) due to the very high dielectric loss contribution from these

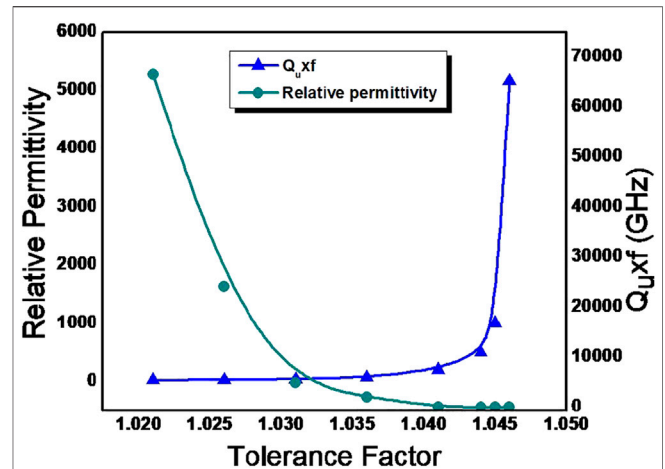paraelectric phase is only visible at experimental temperature range (-50–80°C). The temperature dependence of relative permittivity is visible only upto x = 0.1 composition and above this concentration the material shows any temperature dependence.

The stability of complex perovskite depends on the tolerance factor (t_f) and is given by

$$t_f = \frac{R_O + R_A}{\sqrt{2}\,(R_O + R_B)}$$

Where, R$_o$ is the radius of oxygen anion, R$_A$ and R$_B$ is the radius of A site and B site cation in ABO$_3$ perovskite structure (Tejuca and Fierro, 1993; Reaney and Iddles, 2006) The tolerance factor calculated using Shannon's ionic radii for all the compounds investigated in the present study are in the range of a stable perovskite (1.02< t_f <1.05) (Shannon, 1976) The tolerance factors of all compositions are close to unity which is the characteristics of cubic perovskite structures. **Figure 6** shows the variation of relative permittivity and quality factor of solid solution phases in BZTMT as a function of tolerance factors. It is evident from the figure that as the tolerance factor increases the quality factor gradually decreases. The composition with tolerance factors greater than 1.036 have high dielectric loss and do not resonate. It is evident that quality factor of the specimen increases with increase in concentration of Mg and Ta in BaZr$_{0.2}$[Ti$_{(1-x)}$Mg$_{x/3}$Ta$_{2x/3}$]$_{0.8}$O$_3$.

CONCLUSION

The effect of (MgTa)$^{4+}$ substitution on the ferroelectric to paraelectric transition and the microwave dielectric properties were investigated in BaZr$_{0.2}$[Ti$_{(1-x)}$Mg$_{x/3}$Ta$_{2x/3}$]$_{0.8}$O$_3$ [x = 0.0, 0.025, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0] solid solutions. The ferroelectric Curie temperature of BaZr$_{0.2}$Ti$_{0.8}$O$_3$ (x = 0) has shifted from 21°C to -10°C on the addition of a small amount of dopant (x = 0.025). As the concentration of (MgTa)$^{4+}$ increases the material changes from a lossy ferroelectric phase to a low loss dielectric phase. The microwave dielectric properties show that the temperature variation of resonant frequency (tf) and the quality factor (Quxf) of the composition with x = 1 are 15.8 and 66,500 GHz respectively.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

AUTHOR CONTRIBUTIONS

JK: Material synthesis, Investigation, Writing. GK: Conceptualization, Writing, Review. JV: Microwave characterization and analysis.

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