

Processing, dielectric behavior and conductivity of some complex tungsten-bronze dielectric ceramics

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Ceramic samples of a complex structural formula $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$, where R is a rare-earth oxide and R=Sm, Nd and Gd and $x=0.2-0.7$ were prepared by a high temperature solid-state reaction technique. The dielectric properties (i.e. dielectric constant (ϵ'), dielectric loss (ϵ'') and Q-factor) have been measured on the sintered disks with respect to the frequency in the range 0.3 GHz-3.0 GHz at room temperature. The dielectric properties of the synthesized samples have been found out to be a function of the wt.% of rare-earth oxides used. Dielectric conductivity (σ) was derived from the dielectric constant and loss tangent data in the same frequency range. Conductivity calculations were carried out based on this derived formula. The capacitance values have been calculated knowing the geometrical dimensions of the samples synthesized.

Key words: Tungsten-bronze structure, dielectric constant, dielectric loss, dielectric conductivity.

Introduction

Transmission lines for the guided propagation of electromagnetic waves in the microwave frequency range are waveguides and microwave integrated circuits (MICs). The waveguide components and devices are bulky and expensive but can carry high power where as microwave integrated circuits show their versatility in low power, light weight and miniaturized microwave systems. The development of these waveguide-based components and MICs depends upon the availability of materials with specific characteristics. Moreover, the physiochemical, dielectric and electrical properties of such materials have a great impact on microwave technology. The growing demand for microwave products induces the need for new ceramic materials that combine a high dielectric constant or dielectric permittivity, low dielectric loss, high Q-factor and low conductivity. Complex ceramics with the tungsten-bronze structure $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ have been proved to be promising microwave materials because of their favorable dielectric and electrical properties. Significant research has been done on these complex compounds [1-5]. The excellent response of these ceramics has been utilized in a variety of devices, such as, multi-layered capacitors, dielectric resonators, filters, sensors, actuators, etc. $BaTiO_3$ has been the most favorable and key material for microwave devices and it possesses a perovskite structure [7]. But when rare-

earth oxides as dopants were intentionally diffused in this structure, solid-solutions known as Barium Lanthanide Titanates-BLTs with the structural formula $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ were formed [8]. This also made these materials semi-conductive, in some cases, based on the wt.% of rare-earth (RE) oxides doped. The RE ions actually work as the cations in the structure as these consist of 4-f electrons, which is their peculiar property and hence can store charge [9]. The oscillations of atoms in a solid are responsible for different characteristics, basically dielectric and electrical properties. The anharmonicity in solids is very much responsible for the existence of lattice distortions, micro-deformations and structural variations [10]. In dielectrics all these factors are associated with the displacement of a whole sub lattice of ions of one type relative to another sub lattice. Tungsten-bronze dielectrics have different valence cations with large sized: divalent Ba^{2+} and trivalent rare-earth R^{3+} . To maintain electrostatic stability, three Ba^{2+} ions should be replaced with two R^{3+} ions and a vacancy [11]. The impurity ions which replace either Ba or Ti to some extent do show changes in dielectric constant, dielectric loss and Q-factor.

Tungsten-bronze compounds have been best utilized especially for dielectric resonators [12]. Dielectric resonators (DR) are used in (Microwave Integrated Circuits) MICs for frequency control. They are just a ceramic pellet in the form of a parallelepiped or cylindrical disc [13]. When a continuous band of microwaves is passed through a DR, it will resonate at a discrete frequency determined by the geometry and dimensions of the pellet. The dielectric element

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actually functions as a resonator because of the internal reflections of electromagnetic waves at the high dielectric constant material/air boundary. This results in confinement of energy within, and in the vicinity of, the dielectric material which, therefore forms a resonant structure. The material used for making DRs should have a high dielectric constant (> 20) to aid miniaturization and a low tangent loss (< 0.0004) to have high Q values. All these factors strongly depend on the lattice dynamics of the materials and the ceramic processing techniques employed. DRs are used in various types of filters and oscillators and as miniature radiating elements [12] in microwave integrated circuits. Coupling to a DR is easy and can replace bulky cavity resonators in many applications. DRs, which can be made to perform the same functions as waveguide filters and resonant cavities, are, in contrast very small, stable and lightweight. The popularization of advanced dielectric resonators roughly coincides with the miniaturization of many of the other associated elements of most microwave circuits.

Another important aspect regarding these materials is dielectric conductivity. It should be low for dielectrics to show a good response. In general, the defect centres and impurities that could contribute to the conductivity are randomly distributed in dielectrics. Conduction is basically due to a hopping mechanism of various particle species in the dielectric materials. In the case of ionic crystalline solids, the excess electrons in a narrow conduction band (or excess holes in a narrow valence band) due to their interaction with lattice ions distort the surroundings in such a way that a potential well thereby generated is deep enough to introduce localization leading to the existence of conduction although it is very little in the case of dielectrics even less than 10^{-11} mho/cm.

In this paper, we report the frequency dependence of dielectric and electrical properties of $\text{Ba}_{6-3x}\text{R}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ (with $\text{R}=\text{Sm}$, Nd and Gd) ceramics in the frequency range of 0.3 GHz-3.0 GHz at room temperature. Dielectric conductivity and capacitance have also been calculated using the dielectric constant and tangent loss data and geometrical dimensions of the sintered samples. Plots for various responses of dielectric and electrical properties are shown.

Experimental

Dielectrics of composition $\text{Ba}_{6-3x}\text{R}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ with $\text{R}=\text{Sm}$, Nd and Gd ; $x=0.2-0.7$ were synthesized by a high temperature solid-state reaction technique using carbonate and oxides viz. BaCO_3 , TiO_2 , Sm_2O_3 , Nd_2O_3 and Gd_2O_3 . These oxide powders were taken in appropriate molar proportions and thoroughly mixed in an agate mortar for 12 hours to get a homogeneous mixture. The mixture was pre-sintered at 1100°C for 3h followed by grinding. The fine homogeneous

powders were then granulated using an organic binder of PVA (poly vinyl alcohol) to provide strength and flow ability to the granules. This was followed by shaping. For this, the granulated powders were compacted to pellets of rectangular (23 mm by 10 mm) and cylindrical (12 mm diameter and 3 mm thickness) shapes under a pressure of 75 kN. These pellets were finally sintered at 1300°C for 3h in air in a linearly programmable furnace. These sintered pellets were polished with fine emery paper to make the surfaces flat, smooth and parallel for electrical measurements. The dielectric measurements were made using a Network Analyzer from Agilent Technologies, 8714ET. These measurements were carried out as a function of frequency in the range 0.3 GHz-3.0 GHz at room temperature. The dielectric Q-factor serves as the figure of merit and is given by $Q=1/\tan\delta=2\pi \times (\text{average energy stored/energy dissipated})$, where $\tan\delta = \epsilon''/\epsilon'$ and is called the tangent loss. The dielectric conductivity (σ) was obtained from the data of the dielectric constant and loss tangent using the relation:

$$\sigma = \epsilon' \epsilon_0 \omega \tan\delta = \epsilon'' \epsilon_0 \omega$$

where, ' ϵ' ' is the dielectric constant for free-space and ' $\omega = 2\pi f$ ' is the angular frequency.

The capacitance measurements have been made at various frequencies knowing the geometrical dimensions of the pellets, using the formula:

$$C = \epsilon_0 \epsilon' A/d$$

where, ' A ' is the cross-sectional area of the flat surface of the pellet and ' d ' is the thickness of the pellet. Responses of various properties have also been observed with respect to the compositional variations.

Results and Discussion

Dielectric constant (ϵ'), Dielectric loss (ϵ'') and Q-factor

The variation of ϵ' with frequency at room temperature for the three series prepared with $\text{R}=\text{Sm}$, Nd and Gd are shown in the Fig. 1, 2 and 3 respectively. It was observed that in all the three series ϵ' decreased with frequency. A similar response has been observed by

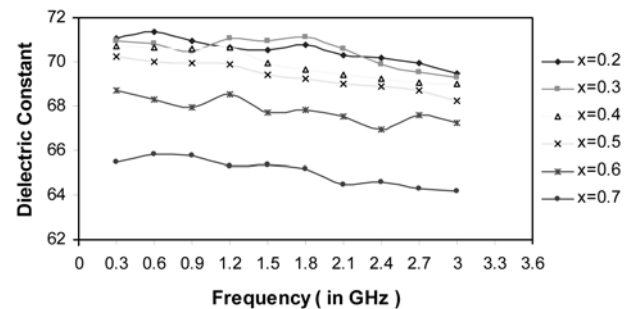


Fig. 1. Variation of Dielectric Constant with frequency for $\text{Ba}_{6-3x}\text{Sm}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ series.

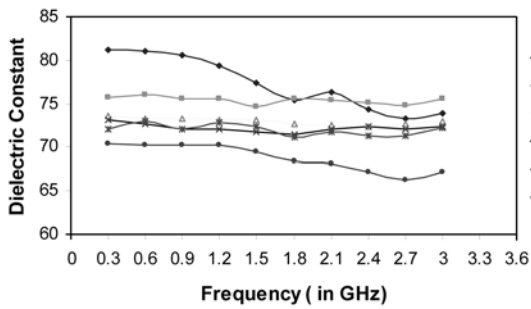


Fig. 2. Variation of Dielectric Constant with frequency for Ba_{6-3x}-Nd_{8+2x}Ti₁₈O₅₄ series.

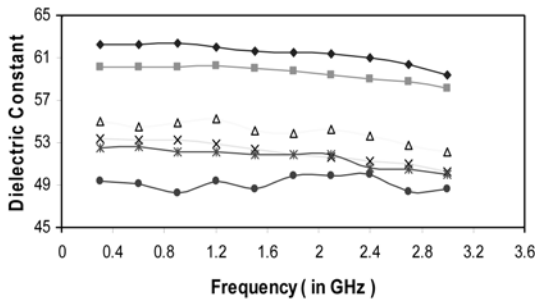


Fig. 3. Variation of Dielectric Constant with frequency for Ba_{6-3x}-Gd_{8+2x}Ti₁₈O₅₄ series.

other researchers [12, 14, 15]. Also it was observed that by varying the composition (x) in the structural formula ϵ' decreased. In the case of R=Sm, the maximum value of ϵ' was observed to be 71 for x=0.2 at 0.3 GHz. For R = Nd and Gd, maximum values have been observed to be 81 and 63 respectively, at the same composition and frequency. The range ϵ' has been observed to be 64-71 for R=Sm, 66-81 for R=Nd and 48-63 for R=Gd respectively. The decrement in ϵ' was greatest in the case of the Nd series. It was nearly 3% up to 1.2 GHz, but after that it was 5%. In the cases of R=Sm and Gd series, this was observed to be 2% and 3% respectively. It was basically due to the difference in the radius of the substituted ions. Also, when the composition varied, the concentration of Ba decreased and rare earth (RE) increased according to the formula. RE ions are middle sized ions and therefore substituted themselves at the large sized Ba sites. But the substitution of RE ions behaved differently in the three cases depending upon their individual properties.

Further, the dielectric loss was observed to increase with frequency and composition in the three series. With R=Sm, ϵ'' increased sharply with composition up to 3 GHz. However, a minimum loss has been obtained at 0.9 GHz for x=0.2. For R=Nd, ϵ'' was observed to be lower than R=Sm. It was a minimum for x=0.2 in the frequency range 0.3 GHz-2.1 GHz, then increased at a frequency of 2.4 GHz to an upper value. For an increased RE concentration, the loss increased almost linearly with frequency up to 3.0 GHz. In the case of R=Gd, ϵ'' decreased with frequency as well as com-

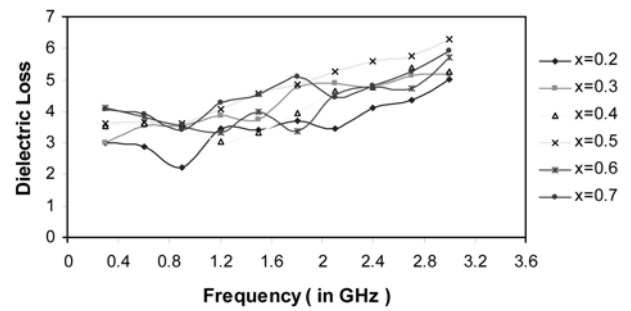


Fig. 4. Variation of Dielectric Loss with frequency for Ba_{6-3x}-Sm_{8+2x}Ti₁₈O₅₄ series.

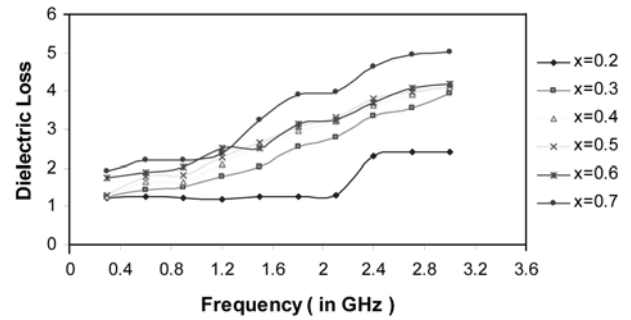


Fig. 5. Variation of Dielectric Loss with frequency for Ba_{6-3x}-Nd_{8+2x}Ti₁₈O₅₄ series.

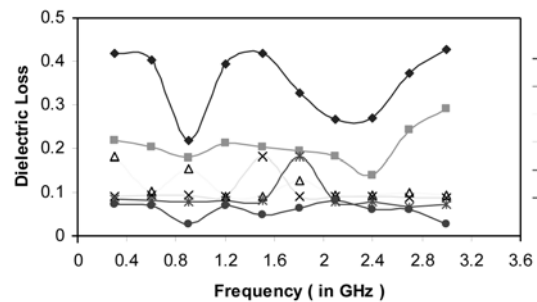


Fig. 6. Variation of Dielectric Loss with frequency for Ba_{6-3x}-Gd_{8+2x}Ti₁₈O₅₄ series.

position. The minimum value was 0.02 at 0.9 GHz for x=0.7. It was observed that the change in the loss with respect to frequency was a minimum in the R=Sm series and a maximum in the R=Nd series. The responses that have been observed are plotted in Fig. 4, 5 and 6 respectively. The minimum loss has been studied in the R=Gd series. This was attributed to the ionic radius of the Gd ions substituted for the Ba sites. The ionic radius of Gd was the smallest of the three rare-earth ions selected for substitution. Also, the atomic size of the Lanthanides decreases with increasing atomic number. There is also a regular decrease in the ionic radii with increasing ionization [9]. Due to the smaller ionic radius it diffused well into most of the Ba sites and vacancies leaving very few defects or voids for the generation of absorption current which results in the dielectric loss.

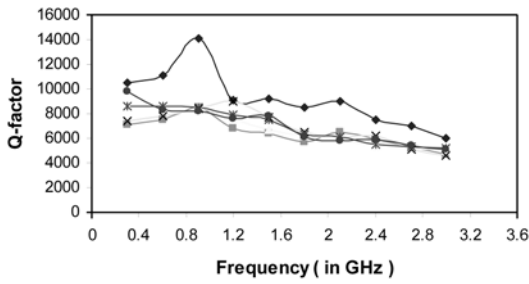


Fig. 7. Variation of Q-factor with frequency for $\text{Ba}_{6-3x}\text{Sm}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ series.

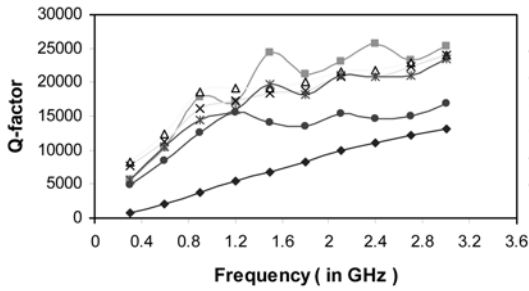


Fig. 8. Variation of Q-factor with frequency for $\text{Ba}_{6-3x}\text{Nd}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ series.

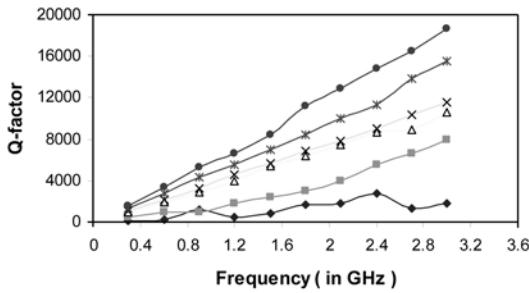


Fig. 9. Variation of Q-factor with frequency for $\text{Ba}_{6-3x}\text{Gd}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ series.

Q-factors for the various series are shown in Figs. 7, 8 and 9. For $R=\text{Sm}$, Q was a maximum at 14250 at $x=0.2$ at 0.9 GHz. It decreased first to 6000, but again increased rapidly with x . With $R=\text{Nd}$, it increased very linearly with frequency for $x=0.2$. It peaked at 25675 for $x=0.3$ at 1.4 GHz, then decreased to 15000. It was a 18650 maximum for $R=\text{Gd}$ for $x=0.7$ at 3.0 GHz. In this series it almost increased linearly with frequency.

In normal behaviour, the ϵ' decreases with increasing frequency due to the fact that beyond a certain frequency of the applied electric field the particle exchange does not follow the alternating field [16]. The low frequency rise in dielectric constant is attributable to the interfacial effects. These take place at the contacts or in the bulk of the material at the grain boundaries. Charge is able to accumulate at these interfacial sites and thereby able to contribute to the total capacity or dielectric permittivity or dielectric constant. As the frequency is raised, eventually the system can no longer follow the time-dependent charge fluctuations and ϵ' tries to settle

down to a value equal to the one without the interfacial charges. This explanation is from the frequency point-of-view only. But the dielectric behaviour is also dependent upon the physics of the materials. As the frequency is increased, the next polarizability is associated with the material rather than interfaces. Actually, tungsten-bronze structures are a distortion in a defective form of or the perovskite structures. These perovskites have oxygen vacancies that will exhibit a dipolar polarization. However, it is possible to control the number of vacancies in the manufacturing process by proper doping. As the frequency is increased again, into the range above 2.0 GHz, there will be contribution due to the ionic separation of the components of a material. Electronic cloud associated with a unit cell is slightly distorted. So, in the octahedron associated with these kind of materials, the unit cell has a dipole moment, which will contribute to the polarization. Eventually, the charges will no longer be able to follow the external field and the polarizability and therefore the ϵ' decreases to a new plateau.

Moreover, in dielectric materials, inhomogeneties like defects, space charge formation, lattice distortions, etc in the interfacial layers together produce an absorption current resulting in a dielectric loss (ϵ''). In the low frequency range, ϵ'' is dominated by the influence of ion conductivity. The variation of ϵ'' in the microwave range is mainly caused by dipolar relaxation and absorption in the above range is mainly due to atomic and electronic polarization [17].

Dielectric conductivity (σ) and Capacitance

The plots for dielectric conductivity are shown for $R=\text{Sm}$, Nd and Gd in Figs. 10, 11 and 12 respectively. Very low conductivity has been observed for the three prepared series. For $R=\text{Sm}$ and Nd it basically decreased with composition, but increased with frequency. With $R=\text{Gd}$, it increased with respect to both frequency as well as composition. This was due to the reason that the atomic size of the Gd element is small compared to Sm and Nd , so it substituted easily with Ba and Ti sites leaving very few vacancies in the structure. The minimum σ has been studied for $R=\text{Nd}$. Its value was $1.12\text{E-}12$ mho/cm for $x=0.4$ at 0.9 GHz. For $R=\text{Sm}$, it was very low again, but increased from $0.8\text{E-}9$ mho/cm

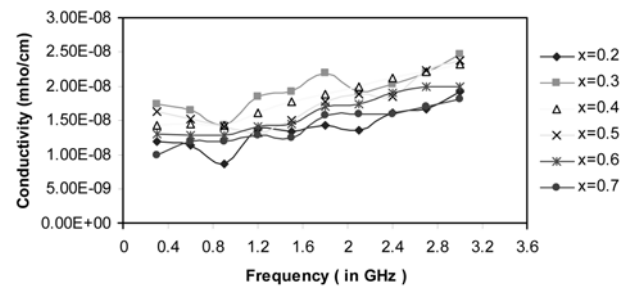


Fig. 10. Variation of Conductivity with frequency for $\text{Ba}_{6-3x}\text{Sm}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ series.

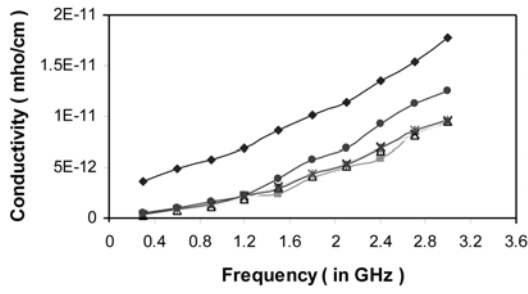


Fig. 11. Variation of Conductivity with frequency for $\text{Ba}_{6-3x}\text{Nd}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ series.

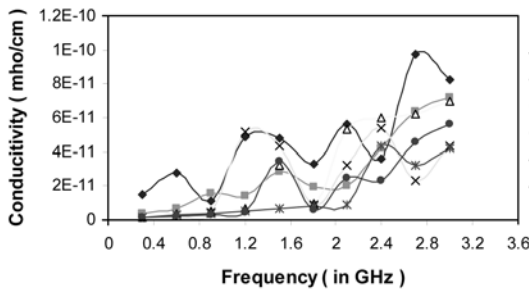


Fig. 12. Variation of Conductivity with frequency for $\text{Ba}_{6-3x}\text{Gd}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ series

to $2.4\text{E}-8$ mho/cm for $x=0.2$ to 0.3 respectively. However, it decreased afterwards with a minimum value at 0.9 GHz again as in $\text{R}=\text{Nd}$. For $\text{R}=\text{Gd}$, it was a minimum at 0.3 GHz for $x=0.7$. Actually, the dielectric conductivity (σ) sums over all the dissipative effects of the material [17]. Conductivity might have originated caused by migrating charge carriers and it may also refer to an energy loss associated with the dispersion of ϵ' , for example, the friction accompanying the orientation of dipoles. Also, the defect centres and impurities could contribute to the conductivity which are generally randomly distributed in dielectrics. Moreover, the excess electrons or excess holes due to their interaction with lattice ions generally distort the surroundings in such a way that the potential well thereby generated is deep enough to introduce localization leading to the existence of conduction. No doubt, its value remains very low in the case of dielectrics but it does exist.

Capacitance, in a real sense, signifies just the di-

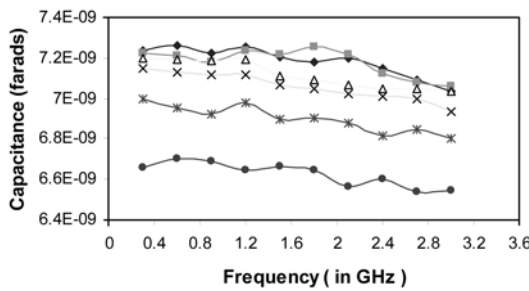


Fig. 13. Response of variation of Capacitance with respect to the frequency for $\text{Ba}_{6-3x}\text{Sm}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ series.

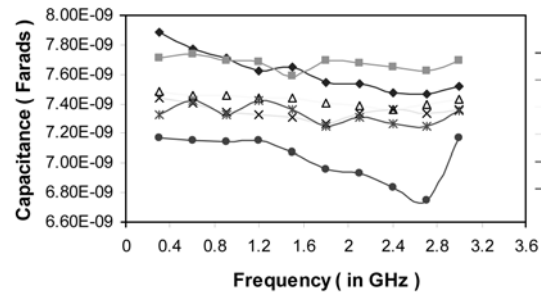


Fig. 14. Response of variation of Capacitance with respect to the frequency for $\text{Ba}_{6-3x}\text{Nd}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ series.

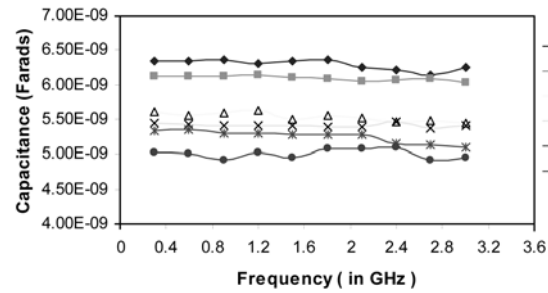


Fig. 15. Response of variation of Capacitance with respect to the frequency for $\text{Ba}_{6-3x}\text{Gd}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ series.

electric constant of a dielectric material. In many cases ϵ' has been defined simply as the capacity of a condenser having the dielectric between charged plates. It is plotted here for $\text{R}=\text{Sm}$, Nd and Gd in Figs. 13 to 15. In all the three cases, it decreased with frequency as well as composition and its value was in pF (picoFarads). With $\text{R}=\text{Sm}$, its value was a maximum $7.28\text{E}-09$ for $x=0.3$ at 1.2 GHz and shifted to $6.45\text{E}-09$ for $x=0.7$ at 3.0 GHz. For $\text{R}=\text{Nd}$, the maximum recorded value was $7.85\text{E}-09$ for $x=0.2$ at 0.3 GHz, then decreased continuously. It was observed from the geometrical dimensions of the pellets and was found that the behavior of capacitance was very similar to that of ϵ' ; in the sense that, it also decreased with frequency just like dielectric constant. The charge storage capability of a capacitor is simply the dielectric permittivity or the dielectric constant itself. Also, according to the relation between capacitance C and ϵ' , it is proportional to ϵ' .

Conclusions

In summary, complex ceramics $\text{Ba}_{6-3x}\text{R}_{8+2x}\text{Ti}_{18}\text{O}_{54}$ with $\text{R}=\text{Sm}$, Nd and Gd ; $x=0.2-0.7$ were synthesized by a high temperature solid-state reaction technique and characterized for their dielectric and electrical properties. Experimental results showed that dopants like rare-earth oxides enhanced the properties. Three series were prepared with tungsten-bronze structure. Of the three series prepared, the one with $\text{R}=\text{Nd}$ had the greatest dielectric constant (ϵ') and the lowest tangent loss (ϵ''). Conductivity was very low in all the materials processed, especially for $\text{R}=\text{Nd}$. Capacitance proved to

be very proportional to the dielectric constant. These could be promising materials for applications in microwave technology.

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