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Effect of substitution of neodymium on electrical and dielectric properties of barium titanate (BT) ceramics

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ABSTRACT

Ceramic samples of a complex structural formula $Ba_{2-x}Re_{4+2x/3}Ti_{18}O_{54}$ where Re=Nd(Neodymium) and x=0.0 & x=0.2 were prepared by a high temperature solid state reaction technique. The dielectric properties (ε', tanδand AC Conductivity) were measured on network analyser in the frequency range of 20Hz - 1 MHz at room temperature. The dielectric properties of samples were found out to be a function of weight percentage of rare earth elements used and frequency of applied electric field. Dielectric conductivity was derived from the conductance and geometrical dimension of the samples in the same frequency range. The capacitance values were obtained directly from the network analyser.

KEYWORDS

Dielectric constant;
Los tangent;
AC conductivity and Capacitance.

INTRODUCTION

Due to rapid growth in wireless communication and microwave industry a large number of ceramic dielectric materials have been developed. In order to achieve miniaturization of the dimensions of devices and for them to serve the system with high efficiency and selectivity, the materials for microwave applications are required to display some important dielectric characteristics. First is high Dielectric constant (ε') for miniaturization since high dielectric constant materials confine the electromagnetic field to itself. Due to their high dielectric constant, the alkaline earth titanates having a perovskite structure have been of great interest to the electronics industry for use in microwave applications. Second is high Q-factor which is the inverse of loss tangent (tanδ). It helps in achieving high frequency selectivity in microwave components. Research has proved that when the alkaline earth titanates are combined with rare earth lanthanides, a new family of dielectric materials, which has a tungsten bronze (TB) structure is generated, and has a high dielectric constant (ε) with low loss and are quite temperature stable[1–4].

The TB structure consists of a framework of BO_6octrahedra sharing corners to form three different types of tunnels parallel to the c-axis in the unit cell of a general formula $[(A_1)_2(A_2)_4C_4][(B_1)_2(B_2)_8]O_{30}$[5, 6]. There are 12-coordinated A1 sites and 15-coordinated A2 sites corresponding to four-fold and five-fold tunnels, respectively. The 9-coordinated C-site has the smallest space among all. Hence there is a scope for a variety of cations of different ionic radii and valences to be substituted at the many interstitial sites (i.e., A_1, A_2, C, B_1 and B_2) that can alter physical properties and device parameters. Ceramics based on the $BaO-Re_2O_3$ –TiO_2 ternary system (where Re=rare earth) have been the subject of detailed study in recent years because of their attractive microwave properties such as high dielectric constant and low loss[7-9]. In this system, $Ba_{6-3x}Re_{8+2x}Ti_{18}O_{54}$ solid solutions depicting high dielectric constant were discovered on the tie line joining BaTiO3 and Re_2TiO_5 composition[9, 10]. This structure is made up of corners sharing TiO_6^{-2}octahedra, which extends in the short axis direction and forms a network of rhombic and pentagonal channels. To maintain electrostatic stability, three Ba^{2+} ions should be replaced with two Re^{3+} ions and a vacancy[11]. Ba^{2+}ions occupy the A-site and Ti^{4+}ions occupy the B-site using generic perovskite formula ABO_3. Basically, if a Ln^{3+}dopant occupies the A-site, it behaves as a donor. The RE ions actually work as cations in the structure as they consist of 4-f electrons, which have their peculiar property of storing charge[12]. The tungsten–bronze compounds have been best utilized for dielectric resonators[13]. The dielectricresonators (DR) are used in microwave integrated circuits (MICs) for frequency control. They are just ceramic pellets in the form of a parallelopipes or cylindrical discs[14]. When microwaves are continuously passed through a DR, it resonates at a discrete frequency determined by the geometry and dimensions of the pellet. The dielectric element functions as a resonator because of the internal reflections of electromagnetic waves at the material air interface. This results in confinement of energy in the vicinity of the dielectric material and within the dielectric material which therefore forms a resonant structure. The material used for making DRs should have high dielectric constant (>20) to aid miniaturization and a low tangent loss (<0.005) to have high Q values. DRs can perform the same functions as waveguide filters and resonant cavities and are in contrast very small, stable and lightweight. The foremost reason for popularization of advanced dielectric resonators is the miniaturization of many of the other associated elements of most microwave circuits[15]. Ceramic dielectrics based on $Ba_{6-3x}Re_{8+2x}Ti_{18}O_{54}$ composition are widely used in applications in microwave region.

In this study, the dielectric behaviour of the compounds with a molecular formula of $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ w.r.t frequency has been observed. Microwave dielectric property measurements have been performed at room temperature on already prepared pelletized ceramic samples in the frequency range of 20Hz - 1 MHz using a Wayne Kerr 6500B precision impedance analyzer.

RESULTS AND DISCUSSION

Variation of ε' with frequency and composition

With increase in frequency, net polarisation decreases as a general behaviour of dielectrics. There are four types of polarisation:

1 Space charge polarisation
2 Dipolar polarisation
3 Ionic polarisation
4 Electronic polarisation

When frequency is increased, total polarisation decreases and only electronic polarisation is left. The dielectric constant 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[16-18]. It was observed that with increase in composition the value of ε'decreased as shown in Figure 1. It was due to difference in radius of substituted ions as smaller radius (R^{3+}) ions occupy larger Ba^{2+} vacancies. When the Nd^{3+} ions substituted for the Ba^{2+} ions, not only the vacancies were created to maintain charge neutrality but the lattice parameters changed due to the difference in ionic radius between Nd^{3+} and Ba^{2+}. The difference of ion radius directly affects the length of c-axis, which is an important characteristic of tungsten-bronze type structure. The decrease of the lattice parameters (i.e. change in length of c-axis) promotes the shrinkage of the octahedra that decreases the dielectric constant indirectly[19].

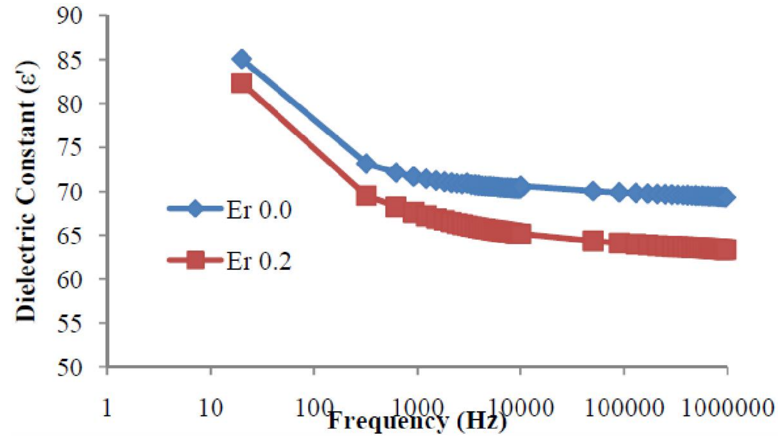

Figure 1 : Variation of dielectric constant with respect to frequency of BNT samples

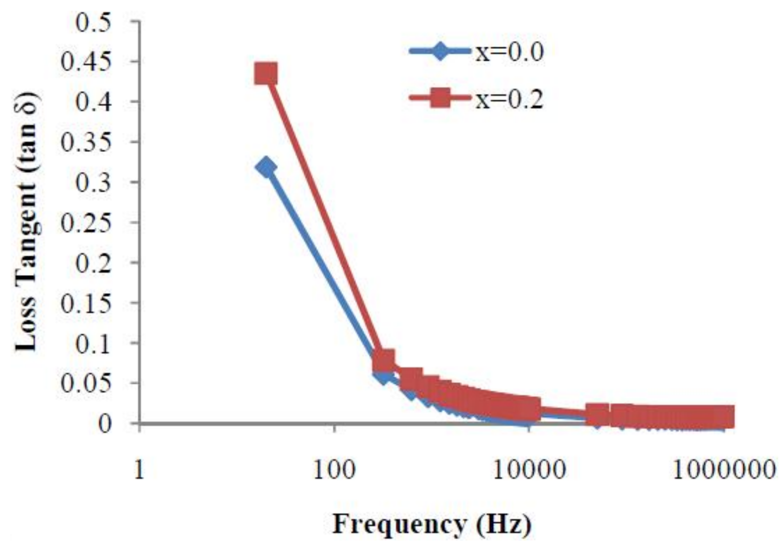

Figure 2 : Variation of loss tangent (tanδ) with frequency and composition

Variation of tan δ with frequency and composition

It was found that the values of loss tangent decreased non-linearly with the increase in frequency. At lower frequencies conduction losses (or ion migration losses) become dominant so that the loss tangent remains high[20]. This could be explained taking ion hopping frequency between two ion positions into account. The maximum energy loss occurs for a frequency equal to the hopping frequency. When the applied alternating frequency is higher than the hopping frequency, the atoms do not have an opportunity to hop at all, and hence the losses are small. It was also noticed that the loss tangent decreased with an increase in composition in theNd substituted samples. It was noticed that the variation of loss tangent was in direct proportion to the internal strain observed for the Nd^{3+} substitutions[5,6]. As the internal strain in the crystal structure was reduced with Re^{3+} concentration, the loss tangent decreased.

Variation of capacitance with frequency and composition

Variation of capacitance with frequency showed the similar trend as the dielectric constant. Capacitance basically signifies the dielectric constant of the material. ε'can be defined as the capacity of a capacitor having dielectric between its charged plates. The capability of a capacitor to store charge is simply the dielectric permittivity or the dielectric constant of the capacitor itself[13].

Variation of ac conductivity with frequency and composition

Conductivity was found to increase non-linearly

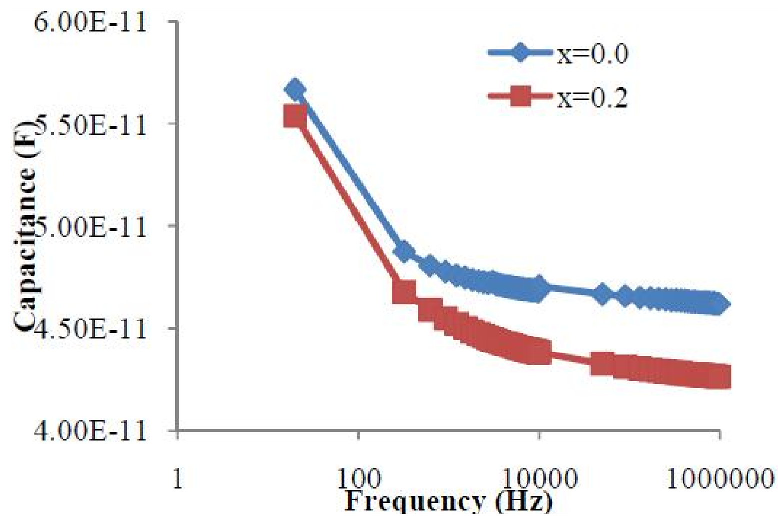

Figure 3 : Variation of capacitance with frequency and composition

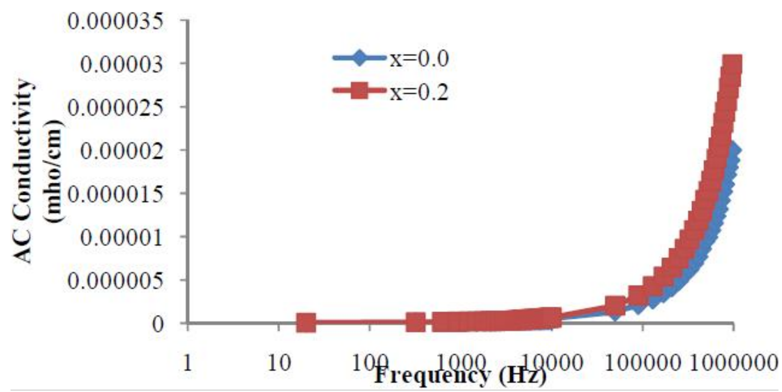

Figure 4 : Variation of AC conductivity with frequency and composition

with frequency as well as with composition. Conductivity could have originated caused by migrating charge carriers or it may 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. Its value remains very low in the case of dielectrics but it does exist. Actually, the dielectric conductivity (σ) sums over all the dissipative effects of the material[17]. Increase in AC conductivity can be justified by the formula $\sigma = \omega\varepsilon'\varepsilon \tan\delta$. Since, AC Conductivity is proportional to frequency of applied field, so we obtain the curve as shown in Figure 4. When we dope Nd in $BaTiO_3$ substitution takes place in the Barium sub-lattice with electronic compensation and formation of Titanium vacancies resulting in increase in conductivity[20].

CONCLUSION

Substitution or doping with rare earth metals improved the dielectric and electrical properties of BT (Barium Titanate) ceramics. The studied samples have a Tungsten Bronze structure and showed a decrement in Dielectric constant with increase in rare earth metal concentration. Loss Tangent (tanδ) decreased with frequency but slightly increased with composition. AC Conductivity increased with frequency as well as with composition. Capacitance was proportional to dielectric constant. These materials are very promising materials in microwave applications.

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