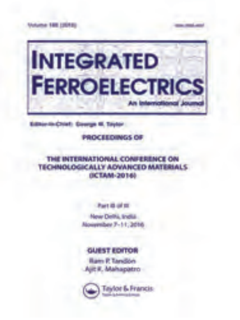

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A review on tungsten bronze ferroelectric ceramics as electrically tunable devices

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ABSTRACT
Ferroelectric ceramics are the most promising material for electrically tunable devices and found its application in microwave devices such as phase shifters, varactors and tunable oscillators and detectors. It has been reported that various non-ferroelectric compound such as carbon nanotubes (CNT), ferrites and microwave dielectrics are used for electrically tunable dielectric materials. This review paper gives overall summary of tungsten bronze ferroelectric ceramics on developing electrically tunable ferroelectric material and improving performance of dielectric material for various applications in microwave devices.

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Introduction

Microwave devices are based on principle either electric field or magnetic field. Tunable microwave devices are paid attention due to their various applications in space based communication and defence etc. Electromagnetic wave travels in space with dielectric constant (ε) and magnetic susceptibility (μ) and its phase speed is $V_p = \sqrt{\varepsilon\mu}$ and intrinsic impedance $z = \sqrt{\mu/\varepsilon}$. For practical applications phase speed and intrinsic impedance are defined by $\sqrt{\varepsilon eff\, \mu\ eff}$ & $\sqrt{\mu eff/\varepsilon eff}$ and used for fabrication of device in which electric and magnetic field can be changed and device become tunable accordingly.

A ferroelectric material is one which exhibits spontaneous polarization in the absence of electric field, which may be switched in direction by application of electric field. Ferroelectric shows electrical properties like a magnetic properties in ferromagnetic materials. Barium titanate, lead titanate (PT), titanate zirconate of lead (PZT), etc. are widely used and scrutinized as ferroelectric materials [1]. For instance, Safari presented a review of the basic concepts on ferroelectricity and various materials which possess electric and magnetic properties [2]. Ferroelectric materials have unique dielectric, pyroelectric, piezoelectric and electro-optic

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properties. These properties have various applications in capacitors, dielectric resonators, sensors, transducers, actuators, and ferroelectric non-volatile memories, dielectric memories, optical waveguides, displays, micro electro mechanical systems (MEMS), miniaturized mechanical and electro-mechanical elements [3–8].

Fundamental knowledge about ferroelectrics

The ferroelectricity is a phenomenon which was first discovered by Valasek in 1921, in the Rochelle salt [9]. Ferroelectricity also goes by "Seignette electricity", as Seignette or Rochelle salt (molecular formula is $KNaC_4H_4O_6.4H_2O$) has a unique property of exhibiting spontaneous polarization when cooled below the Curie temperature. It was observed that in some crystalline materials Curie temperature is less than operating temperature used in practical device applications. As paraelectric phase to ferroelectric phase has low dielectric loss. For many years, Rochelle salt was the only crystal to give ferroelectric property [10]. There was enormous improvement in the research on ferroelectric materials in the 1950's which led to the widespread use of barium titanate ($BaTiO_3$) based ceramics in the domain of capacitors and piezoelectric transducer devices. It has been observed that in some materials, the existence of polar axis in a crystal allows the appearance of spontaneous electrical polarization and these materials are Pyroelectric. A restricted group of pyroelectrics have the further property of being ferroelectric. Thus all ferroelectric are pyroelectric and piezoelectric. All pyroelectric are piezoelectric, but the converse is not true.

Most ferroelectric materials barium titanate $BaTiO_3$, lead zirconate titanate $Pb(Ti,Zr)O_3$ (PZT), lead titanate ($PbTiO_3$), lead lanthanum zirconate titanate (PLZT), $LiNbO_3$, $KNbO_3$, $LiTaO_3$, $Pb(ZnNb)O_3$ and lead magnesium niobate (PMN) which have been developed are used for variety of applications. These materials have a high dielectric constant, piezoelectric, pyroelectric and electro-optic effects. Based on their distinctive properties, ferroelectric materials have been used to produce active elements of various devices [11, 12].

Fundamental knowledge about piezoelectrics

Piezoelectricity is the ability of certain crystalline materials to develop an electrical charge proportional to a mechanical stress. Conversely, crystalline structure changes its shape when these materials are in the presence of applied electric field and also creates dimensional changes in the material. Piezoelectric materials also show a converse effect, whereby the application of voltage deformation occurs. Piezoelectric effect was discovered by the Curie brothers in 1880 [13–14]. D.A. Hall overviewed the nonlinear dielectric, elastic and piezoelectric relationships in piezoelectric ceramics under extreme operating conditions, as there has been increasing recognition in recent years of such materials for electromechanical actuators and high power acoustic transducers. Since the "piezo" effect exhibited by natural materials such as quartz, tourmaline, Rochelle salts is very negligible, materials with improved properties have been developed like polycrystalline ferroelectric ceramic materials such as barium titanate and lead zirconate titanate (PZT). Electric piezoceramics are for actuator applications. The spontaneous polarization can be expressed as the charge per unit area on the surface perpendicular to the axis of spontaneous polarization. The axis of spontaneous polarization is the same as crystal axis. Although, a crystal with polar axes (20 non- centro symmetric point groups) shows the piezoelectric effect. It need not necessarily have a spontaneous polarization vector. It could be due to the cancellation of the electric moments along the different polar axes to give a net zero polarization. Only crystals with a unique polar axis (10 out of 21 non centro symmetric point groups) show a spontaneous polarization vector P_s along this axis. The magnitude of the spontaneous polarization depends on the temperature. This effect is called the pyroelectric. Pyroelectricity was discovered by Teophrast in tourmaline in 314 B.C. [15].

Piezoelectric ceramics belong to the group of ferroelectric materials. The reversibility of the polarization and the coupling between electrical and mechanical effects are of great importance for the utilization of piezoceramics on a wide scale. Various applications have become more significant with the discovery of barium titanate. The dielectric and piezoelectric properties of $BaTiO_3$ have been dependent on the grain size [16, 17]. Piezoceramics $PbTiO_3$–$PbZrO_3$ is synthesized from lead oxides, titanium and zirconium, synthesis by conventional method. Substitution of different ions in PZT is used for piezoelectric and dielectric parameters [18].

Variation of the relative permittivity ε_r with temperature in $BaTiO_3$ from its paraelectric cubic phase to the ferroelectric was given by Safari [2]. Thermodynamic near Curie temperature properties like dielectric, elastic, optical, and thermal constants show an abnormal behaviour. As the phase structure changes, there will be distortion in the crystal. This is the reason for the abnormal behaviour. The temperature dependence of the dielectric constant above the Curie point ($T > T_c$) in ferroelectric crystals is governed by the Curie–Weiss law:

$$\varepsilon = \varepsilon_0 + \frac{\mathbf{C}}{\mathbf{T} - \mathbf{T}_0}$$

where ε is the permittivity of the material, ε_0 is the permittivity of vacuum, C is the Curie constant and T_0 is the Curie temperature. The Curie temperature T_0 is different from the Curie point T_c. T_0 is a formula constant obtained by extrapolation, while T_c is the actual temperature where the crystal structure changes. For first order transitions $T_0 < T_c$ while for second order phase transitions $T_0 = T_c$ [14].

The representation of dielectric, electromechanical and piezoelectric properties were presented in the literature by Jaffe [14]. Pyroelectric materials are widely used for thermal infrared detectors due to characteristics such as good sensitivity, room temperature operation, and low cost. In the recent years, the research in the domain of pyroelectricity has been concentrated on innovation of new materials with better properties.

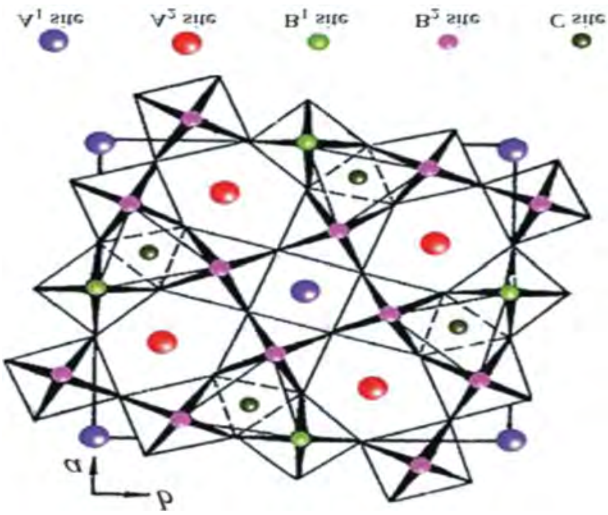

Figure 1. Polyhedral structure of tungsten bronze ferroelectric ceramics along c axis.

Ferroelectric ceramics with tungsten bronze structure

Tungsten bronze ferroelectric ceramics compose the largest dielectric constant which belongs to perovskites. As shown in Figure 1, the tungsten bronze structure is composed of 10 distorted octahedral sharing corners in such a way that these different interstices (A_1, A_2 and C) are available for cation occupy in the general formula $(A_1)_4$ $(A_2)_2$ $(C)_4$ $(B_1)_2$ $(B_2)_8$ O_{30} [19] (where A-sites are occupied by mono to trivalent cations, B-sites are occupied by tetra-hexavalent ions and C-sites is often empty), are complex and disordered. It has been found very useful for many device applications. The properties of these types of materials can be tailored by making suitable modifications/ substitutions at A, B or C sites. TB formula consists of A_1, A_2, C and B is 15, 12, 9 and 6-fold Oxygen coordinated sites in the crystal.

Tetragonal or orthorhombic structures with slight distortion of multiple perovskites are exhibited by Tungsten bronze materials. A few tungsten bronze ferroelectric ceramics are observed to be stable at room temperature with diffuse phase transition and relaxor behavior. Structural flexibility and chemical versatility of these materials make them adaptable for various applications. The tetragonal tungsten bronze structure has been discussed by Magneli [20] and Blomberg [21], Wadsley [22], Francombe [23] and by Jamieson et al [24].

For practical applications of ferroelectric ceramics it has a serious issue for the minimization of dielectric loss to improve the performance of microwave device. Substitution of oxides in ferroelectric materials decreases dielectric loss. From literature it was found that addition of material like Li_2CO_3 and low firing glasses can better the tunable performance of dielectric ferroelectric materials. Composites and epoxy resin is alternative material for tunable device. Outstanding review for tunable microwave device application can be found in open literature [25]. Now it is declared that microwave tungsten bronze ferroelectric ceramics are suitable for resonators with low dielectric loss tangent at microwave frequencies and utterly they are non-tunable in absence of electric field.

Material fabrication and characterization techniques

Generally bulk materials are considered into two categories i.e. single crystal and ceramics. Single crystal is solid in which entire sample in form of crystal lattice and uninterrupted at the edges without grain boundaries. These single crystals are fabricated by hydrothermal synthesis, sublimation or Czochralski process depending on physical characteristics of the crystal [26].

Polycrystalline ceramic materials are generally synthesized by double step processing method by using oxides and carbonates as starting material. In this process two steps are involved (1) Calcination (2) Sintering. In calcination process sample formed with desired phase composition and phase formation in sintering process includes dense microstructure having high enactment of electrical properties.

XRD is used to determine lattice constant and phase formation of material. SEM is used for Grain size & structural morphology. TEM is also used to determine the flaws of bulk materials.

Dielectric properties measurement

Dielectric characteristics of ferroelectric materials are important parameters to determine dielectric tunability, dielectric constant, dielectric loss tangent, and temperature stability. Ferroelectric materials have high dielectric constant for Para electric and ferroelectric phase. Dielectric constant is maximum at Curie temperature (T_c). Dielectric loss is determined by $D = \tan\delta$ $(\varepsilon''/\varepsilon')$ ratio of imaginary part to real part of complex permittivity at given frequency. It is important parameter to study the performance of tunable device. Dielectric tunability is defined as $T = (\frac{\varepsilon ro - \varepsilon rv}{\varepsilon r0} * 100)$ where ε_{r0} and ε_{rv} are dielectric constant at 0 and V applied field. Microwave properties of tunable device are defined by Figure of Merit. It is the ratio of low frequency tunability to microwave loss i.e., $K = (\frac{\varepsilon ro - \varepsilon rv}{\varepsilon r0 \tan\delta})$ where ε_{r0} and ε_{rv} is relative dielectric constant at zero and maximum electric field at low frequency and $\tan\delta$ is loss at microwave frequency.

Dielectric properties of sample are directly measured by impedance analyzer.

Electrically tunable ferroelectric ceramics

In literature it has been reported that various ferrites, semiconductor are fabricated for tunable device application but in comparison of ferroelectric ceramics they have certain drawbacks. For example PIN device has high loss and slow response at microwave frequency and ferrites have high power consumption and are electrically slow and physically heavy and large in size. Although ferroelectric materials are light in weight, small in size and have high dielectric constant. So, these materials are suitable for microwave tunable applications. This review focus on modification of dielectric properties for electric tunable devices by doping of various oxides in present tungsten bronze ferroelectric ceramics.

Tungsten bronze ferroelectric ceramics

Tungsten bronze (TB) ceramics belong to non-perovskite structure. Non perovskite structure is further divided into lead containing and lead free ferroelectric ceramics. The most extensively used tungsten bronze ferroelectric ceramics as tunable device are lead free non perovskite. e.g.

$Ca_6Ti_2Ta_8O_{30}$, Ba_6 $Ti_2Ta_8O_{30}$ and Sr_6 $Ti_2Ta_8O_{30}$

$Ca_6Ti_2Ta_8O_{30}$ is temperature stable dielectric ceramics and show unstable structure in comparison of composition Ba_6 $Ti_2Ta_8O_{30}$ and Sr_6 $Ti_2Ta_8O_{30}$. as ionic radii decreases Ba to Ca. In composition $Ca_6Ti_2Ta_8O_{30}$ cubic $CaTaO_6$ major phase merge with minor amount $CaTiO_3$. TB ceramics show low loss at 1 MHz. It is used as tunable device for high frequency applications and temperature compensated capacitors [27].

$Ba_5LaTi_3Ta_7O_{30}$

In $Ba_5LaTi_3Ta_7O_{30}$ ceramic Y.N.Sun analyzed the effect of Ca and Zr dopent. With Zr doping sample $Ba_5La(Zr_xTi_{1-x})_3Ta_7O_{30}$ show filled tungsten bronze structure but the sample with Ca doping $(Ca_xBa_{1-x})_5$ $LaTi_3Ta_7O_{30}$ show additional X-ray reflection beyond $x = 0.25$. Additional peak of CaTa2O6 show major phase of Ca rich composition. So Ca substitution system is less stable substitution than Zr substitution [28]. At 1MHZ frequency by increasing Zr content dielectric constant decrease 148 to 106 but with increase of Ca content increase 148 to 106.Thus Ca doped ceramics are import materials for tunable devices.

$K_2Sr_4Nb_{10}O_{30}$

In KSN ceramics by doping of MgO at small concentration there is distortion of the octahedral of TTB structure and with increase of MgO content dielectric losses decrease [29]. Thus this ceramic can improve dielectric tunability and dielectric loss characteristic.

$Sr_4M_2Ti_4Ta_6O_{30}$ (M = Pr and Eu)

Polycrystalline ceramics $Sr_4Pr_2Ti_4Ta_6O_{30}$ and $Sr_4Eu_2Ti_4Ta_6O_{30}$ are fabricated by high temperature solid-state reaction technique. $Sr_4Eu_2Ti_4Ta_6O_{30}$ (SETT) has ferroelectric phase at room temperature is filled tetragonal tungsten bronze (TB) structure and sustains a diffuse type ferroelectric–paraelectric phase transition around 90°C with relaxor properties [30]. While $Sr_4Pr_2Ti_4Ta_6O_{30}$ belongs to paraelectric phase with TB structure at room temperature. Dielectric constant observed around 181. Thus in combination with $Sr_4Sm_2Ti_4Ta_6O_{30}$ with T_C around 30°C [16], it is observed that T_C of $Sr_4M_2Ti_4Ta_6O_{30}$ (M = Pr, Sm and Eu) decreases with the increase of the ionic radius of the M^{3+} ion, and these results agree with the work of Bhanumathi et al. [27]. Since SPTT has a negative temperature coefficient of resistance and SETT has a positive temperature coefficient of permittivity at room temperature. These materials are used for multilayer capacitor applications for microwave frequency.

$(Sr_{0.6}Ba_{0.4})4Na_2Nb_{10}O_{30}$

Calcium-doped sodium strontium barium niobate (SBNN), (Sr0.6Ba0.4)4Na-2Nb10O30 ceramics are another microwave dielectric material prepared by two step conventional solid-state reaction method. SBNN showed 'filled' tetragonal tungsten-bronze structure. Tangent loss is reduced with Ca doping at 1MHZ frequency [31]. Thus Ca doped SBNN dielectric material has better performance for electrically tunable devices.

Conclusion

Ferroelectric ceramics have made very significant progress in manufacturing of electrically tunable devices. But main focus on ferroelectric materials as compared to non-ferroelectric materials is due to their compact size and high dielectric constant. Researcher impulse on minimization of dielectric loss by adding various oxides such as MgO, ZrO_2, Al_2O_2, TiO_2, $LaAlO_3$ etc for practical applications. BSTN is dominant prospect for microwave tunable device applications, due to its outstanding dielectric properties over other ferroelectric materials. Now it is necessary to pay more attention to established more complex theories to model simulate or predict better performance of tunable dielectric material, so specific materials are designed for exact application.

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