Review on dielectric study of polycrystalline rare earth substituted Tungsten Bronze electroceramics for high temperature applications

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Abstract: This review paper describes a new era of polycrystalline rare earth substituted tungsten bronze ferroelectric ceramics for high temperature device applications. In the scientific and technological period ferroelectric ceramics are well known due to voltage dependent dielectric constant. But below Curie temperature ferroelectric ceramics exhibits hysteresis and this phase is not suitable for high device applications. Generally for paraelectric state to ferroelectric state particularly thin films have great potential applications including nonvolatile memories, optoelectronics devices and integrated electronics as passive components. To achieve high figure of merits for high temperature applications, low dielectric loss is most important. Tungsten bronze ferroelectric ceramics have capabilities to give higher tunability with low dielectric loss due various cations substitution at various sites. Here, special attention has been paid to the study the effect of composition, dielectric properties, and ferroelectric properties of tungsten bronze ferroelectric ceramics which are important materials for high temperature applications.
Keyword : Ferroelectric; Tungsten Bronze; Dielectric constant; Dielectric loss.

Introduction

Ferroelectric materials are a group of crystalline dielectrics having spontaneous polarization in a certain temperature range. The orientation of this polarization can be switched by an electric field, which varies significantly under the influence of external factors. The electrical properties of ferroelectrics are in many respects similar to the magnetic properties of ferromagnetics. Now a day, several hundred ferroelectrics ceramics are known. Barium titanate, Rochelle salt (which has given its name to an entire group of crystals), lead titanate (PT), titanatezirconate of lead (PZT), etc. are among the most commonly used and thoroughly investigated as ferroelectrics [1]. In 1995 Safari etal.presented a review of the basic principles governing ferroelectricity and some materials showing these properties [2]. Ferroelectric materials display unique dielectric, pyroelectric, piezoelectric and electro-optic properties that are utilized for a variety of applications such as: capacitors, dielectric resonators, sensors, transducers, actuators, ferroelectric non-volatile memories [3,4], dielectric memories, optical waveguides, displays, microelectro mechanical systems (MEMS), miniaturized mechanical and electro-mechanical elements (i.e. devices and structures). These techniques are used for micro fabrication device application [5].
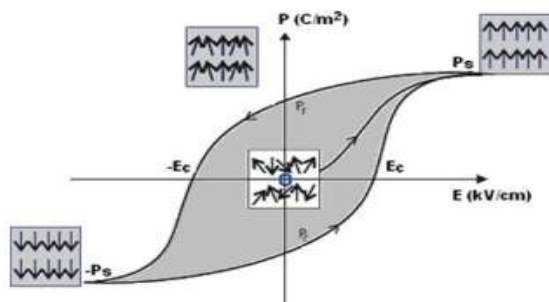
1. Fundamental knowledge about piezoelectrics

Piezoelectricity is the ability of certain crystalline materials to grow an electrical charge proportional to a mechanical stress. Conversely, when an electrical field is applied to one of these materials the crystalline structure changes shape and producing dimensional changes in the material. Piezoelectric materials also show a contrary effect, where a geometric strain (deformation) is produced on the application of a voltage. Piezoelectric effect was exposed by the Curie brothers in 1880. A review of the early history of piezoelectricity could be found in the work of Cady [9]. Cook and Jaffe published the book ''Piezoelectric Ceramics'' [10] that is still one of the most referenced works on piezoelectricity. Also, D.A. Hall overviewed the nonlinear dielectric, elastic and piezoelectric relationships in piezoelectric ceramics under extreme operating conditions, as 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 salt, is very small, polycrystalline ferroelectric ceramic materials such as barium titanate and lead zirconatetitanate (PZT)have been developed to enhance the various properties. The Piezoceramics are available in many variations and most widely used materials for actuator applications. Piezoelectric ceramics (or piezoceramics) belong to the group of ferroelectric materials. The reversibility of the polarization and the coupling between electrical and mechanical effects are of great significance for the wide technological utilization of piezoceramics. Progress in this field for various applications became more significant with the discovery of barium titanate, $BaTiO_3$, in 1947 and the ability to activate it as a piezoelectric material by poling. The dielectric and piezoelectric properties of $BaTiO_3$ have been found to be strongly dependent on the grain size [12, 13]. The main piezoceramics used today, $PbTiO_3$–$PbZrO_3$ are synthesized from oxides of lead, titananium and zirconium, and are prepared by conventional synthesis technologies. Doping of these lead zirconate-titanate ceramics (PZT) by Ni, Bi, Sb, Nb ions , make it possible to enhance their piezoelectric and dielectric parameters as required for various application.

Polycrystalline piezoelectric ceramics must be poled in order to have very high piezoelectric coefficients, because the polarization in the domains is randomly oriented. In cubic perovskites, the crystallites have symmetric cubic unit cells at temperatures above the Curie temperature. Below this, the crystallites become deformed and asymmetric. The unit cells exhibit spontaneous polarization, i.e. the individual crystallites are piezoelectric. Groups of unit cells with the same alignment are called ''Weiss domains''. Because of the random distribution of the domain orientations in the ceramic material no macroscopic piezoelectric conduct is observable.

After poling, many domains are aligned or switched to the direction of the applied electric field resulting in a finite polarization. However, the domains in polycrystalline materials are not easily aligned as in a single crystal, due to the pinning of grain boundaries, and the case of thin films, the clamping of substrates. Applying a strong electric field E, the spontaneous polarization is ferroelectric reoriented to the saturation polarization Ps.

During poling, intense electric field (2,000 V/mm) is applied to the piezoceramic, the material expands along the axis of the field and contracts perpendicular to that axis so the domains line up. When the field is removed, the electric dipoles stay roughly, but not completely, in alignment. The material now has a remnant polarization (Pr), which can be degraded by exceeding the mechanical, thermal and electrical limits of the material. Characteristic of this state is thermo-dynamically stable reversibility of the axis of polarization under the influence of an electric field, described by a hysteresis loop (Fig1)

Fig 1: Hysteresis loop of ferroelectric materials

2. Fundamental knowledge about ferroelectrics

Ferroelectricity is a phenomenon first discovered by Valasek in 1921, in Rochelle salt [6]. The name 'ferroelectricity'similar to magnetic analogies, though has no association with iron (ferrum) at all. Ferroelectricity has also been called ''Seignette electricity'', as Seignette or Rochelle Salt(molecular formula $KNaC_4H_4O_6.4H_2O$) was the first material found to show ferroelectric properties. The spontaneous polarization is given by the value of the dipole moment per unit volume or by the assessment of the charge per unit area on the surface perpendicular to the axis of spontaneous polarization. For many years, Rochelle salt was the only crystal known to as ferroelectric [7]. A vast push in research on ferroelectric materials in the 1950's, leading to the extensive use of barium titanate ($BaTiO_3$) based ceramics in capacitor applications and piezoelectric transducer devices. Ferroelectric material is subgroup of spontaneously polarized pyroelectric crystal. However, polarizationof ferroelectric is similar to the polarization of pyroelectric. The basic difference between two polarizations is, in ferroelectric polarization reversible by external applied electric field.

The morphology and average grain size of powders are very different. As ferroelectrics are not uniformly polarized, and contain domains with different directions of spontaneous polarization. In the absence of external factors the total electric dipole moment (p) of a specimen is equal to zero. The equilibrium domain structure of a ferroelectric is determined by the balance between the decrease in the energy of electrostatic interaction of domains when the crystal is broken down into domains and the increase in energy arising from the formation of new domain walls with excess energy. The number of different domains and the relative orientation of the spontaneous polarization in the domains are determined by the crystal symmetry. The configuration of the domains depends only on the dimensions and shape of the specimen, the distribution of crystal defects in the specimen, internal stresses, and other non-homogeneities invariably occur in real crystals.

The spontaneous polarization is given by the value of the dipole moment per unit volume or by the value of the charge per unit area on the surface perpendicular to the axis of spontaneous polarization. All crystals can be categorized into 32 different types of points groups by using the symmetry elements: (i) centre of symmetry, (ii) axes of rotation, (iii) mirror planes and (iv)several combinations of them. These 32 points groups are subdivisions of seven basic crystal systems according order of ascending symmetry, triclinic, monoclinic, orthorhombic, tetragonal, rhombohedral (trigonal), hexagonal and cubic. 21 classes of the 32 point groups are noncentrosymmetric, which is a necessary condition for piezoelectricity to exist. 20 of them are piezoelectric. Of the 20 piezoelectric crystal classes, 10 crystals are of pyroelectric properties. Within a given temperature range, this group of materials is permanently polarized. Compared to the general piezoelectric polarization produced under stress, the pyroelectric polarization is developed spontaneously and kept as permanent dipoles in the structure. Because this polarization varies with temperature, the response is termed as pyroelectricity, which was first discovered in tourmaline by Teophrast in 314 B.C. and so named by Brewster in 1824 [11].

Ferroelectric crystal can be divided into three-dimensional regions having different directions of polarization, called ferroelectric domains. Depending on the particle size of the polycrystalline ceramic material, the individual crystallites contain only a few domains, bounded by domain walls. . So, large changes of the electric field or mechanical stress, shifting occurs and the polarity of thatregions can be reversed by domain reforming. These processes and the irreversible displacement of domain walls are the reasons for the existence of ferroelectric hysteresis.

Most ferroelectric materials include: barium titanate $BaTiO_3$, lead zirconatetitanatePb(Ti,Zr)O_3 (PZT), lead titanate ($PbTiO_3$), lead lanthanum zirconatetitanate (PLZT), $LiNbO_3$, $KNbO_3$, $LiTaO_3$,Pb(ZnNb)$O_3$and relaxor ferroelectrics like lead magnesium niobate (PMN) which have been developed and used as for a variety of applications. Generally, these materials have a high dielectric constant and are characterized by large piezoelectric, pyroelectric and electro-optic effects as well as nonlinear optical effects. On the basis of these unique properties, ferroelectric materials have been applied to create active elements of various devices [8].

All ferroelectric materials have a transition temperature called the Curie point (Tc), and at T<Tc temperature the crystal does not exhibit ferroelectricity, while for T>Tc it show ferroelectric nature. On decreasing the temperature through the Curie point, a ferroelectric crystal undergoes a phase transition from a non-ferroelectric phase to a ferroelectric phase. If there are more than one ferroelectric phases, the temperature at which the crystal transforms from one ferroelectric phase to another is called the transition temperature (Tc). Early research work on ferroelectric transitions has been summarized by Nettleton [14]. Below the Curie point of the material, the cubic, electrically neutral crystalline form gives the lattice distortions, resulting in the

formation of dipoles and rhombohedra and tetragonal phases, which are of interest. Above Curie temperature there is simply no correlation between the electric dipoles, whereas the dipoles are more or less ordered. The ordering can be described by a Langevin function.

Safari et al. presented the dependence of the relative permittivity £r with temperature, when a BaTiO$_3$ crystal is cooled from its paraelectric cubic phase to the ferroelectric tetragonal, orthorhombic, and rhombohedral phases [2]. Near the Curie point or transition temperatures, thermodynamic properties including dielectric, elastic, optical, and thermal constants show an anomalous behavior. This is due to a distortion in the crystal as the phase structure changes. The temperature dependence of the dielectric constant above the Curie point (T>Tc) in ferroelectric crystals is governed by the Curie–Weiss law:

$$£ = £_0 + \frac{C}{T-T0}$$

Where £ is the permittivity of the material , $£_0$ 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 Tc. 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 $T_0 = T_c$ [10].

The description of the most important dielectric, electromechanical and piezoelectric relationships was presented in the literature by Jaffe [10]. Pyroelectric materials are extensively used for thermal infrared detectors due to their advantages because of good sensitivity, room temperature operation, and low cost. In recent years, the research in the field of pyroelectricity has been concentrated on discovering materials with higher figures of merit.

The pyroelectric effect can be described in terms of the pyroelectriccoefficient(π). A small change in the temperature ΔT in a crystal, leads to a change in the spontaneous polarization vector ΔPs given by the relation,

$$\Delta P_s = \pi \, \Delta T$$

Corner Sharing Octahedra is a larger class of ferroelectric crystals made up of mixed oxides containing corner sharing octahedra of O^{2-} ions [2]. Inside each octahedron is a cation B^{b+} where 'b' varies from 3 to 6. The space between the octahedra is occupied by A^{a+} ions where 'a' varies from 1 to 3. In prototypic forms, the geometric centers of the A^{a+}, B^{b+} and O^{2-} ions coincide, giving rise to a new nonpolar lattice. When polarized, the A and B ions are displaced from their geometric centers with respect to the O^{2-} ions and give a net polarity to the lattice. These displacements occur due to the changes in the lattice structure when phase transitions take place as the temperature is changed. The formation of dipoles by the displacement of ions will not lead to spontaneous polarization if a compensation pattern of these dipoles are formed which give zero net dipole moment. The corner sharing oxygen octahedra includes the perovskite type compounds, tungsten bronze type compounds, bismuth oxide layer structured compounds, and lithium niobate and tantalite.
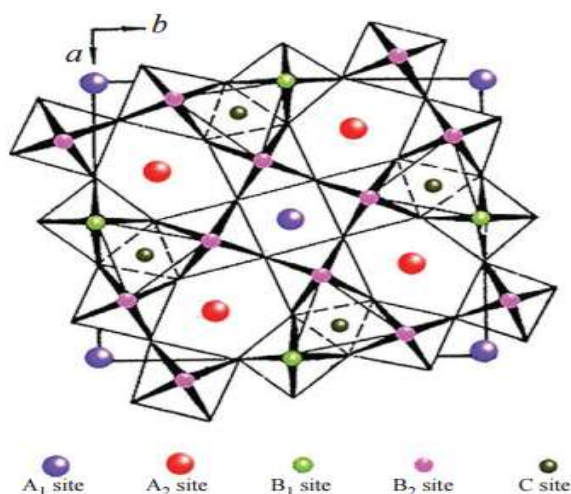
Fig 2: Polyhedral structure of tungsten bronze ferroelectric ceramics along c axis

3. Ferroelectric ceramics with tungsten bronze structure

The TB-type structure shown in Fig2 possess generalized formula$[(A_1)_4(A_2)_2(C)_4][(B_1)_2(B_2)_8]O_{30}$ consists of a complex array of distorted BO_6 octahedral corners sharing by three different types of interstices (A, B and C).Here , A_1 and A_2 sites are commonly filled by divalent or trivalent cations such as (Sr, Ba, Ca, Pb, Na, Mn and rare earth etc.) B_1 and B_2 sites filled by tetravalent or pentavalentcations (Nb, Ta and Ti) and C site often remains empty. Due to open nature structure of tungsten bronze compound there is a scope for substitution by variety of cations at different interstitial sites (i.e., A_1, A_2, B_1, and B_2) which can alter the physical & electrical properties of the materials for various device applications.

These TB structured ferroelectric ceramics exhibit Curie temperature reaching up to 560°C and consists a family containing more than 85 compounds in the most recent survey [16].The interest in tungsten bronze ferroelectrics got renewed in the 1960's because of the large optical non-linearity of these materials. Ferroelectric tungsten bronze niobate materials are classified into three types by the occupation of the metal ion:

(i)   Completely filled tungsten bronze (e.g. KLN ($K_6Li_4Nb_{10}O_{30}$),
(ii) Filled tungsten bronze (e.g. SKN, BNN ($Ba_4Na_2Nb_{10}O_{30}$)
(iii) Partially filled tungsten bronze(e.g. PBN ($Pb_5Nb_{10}O_{30}$) ,SBN).

Mostly, the full-filled tungsten bronzes such as $K_3Li_2Nb_5O_{15}$ have attracted much attention for the nonlinear optic applications, whereas the un- filled tungsten bronzes have been well studied due to their unique ferroelectric and piezoelectric characteristics.

Tungsten bronze materials revelation either tetragonal or orthorhombic structure with small distortion of multiple perovskites. Some tungsten bronze ferroelectric ceramics are found to be stable at room temperature with diffuse phase transition and relaxour behavior. Also, structural flexibility and chemical versatility of these materials make them suitable for various application. The tetragonal tungsten bronze structure has been discussed by Magneli [16] and Blomberg [17], Wadsley [18], Francombe [19] and by Jamieson et al.[20].

In earlier work only two simplest ferroelectric compounds have been known with basis structure, namely lead metaniobate ($PbNb_2O_6$) and lead meta-tantalate ($PbTa_2O_6$) where the lead atoms are located only in the $A_1$and A_2sites between the NbO_6 orTaO_6 octahedra. It is analysed that in these material have small orthorhombic distortion from tetragonal unit cell. At the Curie temperature Tc = 575°C $PbNb_2O_6$ turn out to be tetragonal but $PbTa_2O_6$ remains orthorhombic throughout. In $LiNbO_3$ and $LiTaO_3$ solid solution the replacement of tantalum ion for niobium ions in $PbNb_2O_6$ the Curie temperature decrease from 575°C to 260°C between the end members. It is found that the ferroelectric behavior of these materials could be significantly modified if lead ions are partially replaced by Ca, Sr, Mg and Ba ions, discovery led to a comprehensive study of a large number of alkaline earth niobate solid solutions. H.Ida et.al. observed $BaNb_2O_6$(BN) and $SrNb_2O_6$(SN) crystal, which are the end member of SBN crystals, donot show any ferroelectric properties, because their crystal structure are not the TTB type, but (SBN) $Sr_xBa_{1-x}Nb_2O_6$ show TTB structure that possess various excellent nonlinear optical properties and ferroelectric properties such as large electro-optic coefficients

5. Structure Stability and General Formula of Filled Tungsten Bronzes

The tolerance factor was first suggested by Megaw to determine the stability of the perovskite structure [21]. The tolerance factor for tetragonal tungsten-bronze (TTB) structure has been deliberated by Wakiya et al.[22] According to the general formula, there are two kinds of A sites for TTB: one is the A_1 site with 12-fold harmonization, which is identical to that in perovskite structure; and the other is A_2 site with 15-fold coordination. Therefore two kinds of tolerance factor for A sites can be given by the following equations.

$$t_{A1} = \frac{RA1+R0}{\sqrt{2}(RB+R0)}$$

$$t_{A2} = \frac{RA2+R0}{\sqrt{(\sqrt{23}-12\sqrt{3})(RB+R0)}}$$

Where, R_A, R_B, and R_O are the ionic radii of the A, and B-site ions and the O^{2-} ion, respectively. The combination of these tolerance factors denoted as following gives a general measure to determine the structure stability of tungsten bronzes.

Also from recent literature survey it has been shown that abundant cationic sites of Tungsten Bronze structure result in extended substitution can induce magnetic collaboration. Moreover the magnetic crystal of TB compound is known to reveal incommensurate polar state, which may favour a coupling between magnetic and ferroelectric order. Yan-Qing Tan et al. indicated the relationship between the ferroelectric behaviour in TB structure and modulation of commensurate/incommensurate driven by A_2 cation size. When A_2 cation size less than 1.32A° the compound display ferroelectric phase transition otherwise compound exhibit relaxour behaviour with a incommensurate phase. Most of TTB tantalites are paraelectric at room temperature while the niobate having high temperature tend to display ferroelectric or relaxor ferroelectric nature.

In this review paper we studied compositiona dielectric and ferroelectric behavior of various tungsten bronze ferroelectric niobates, vanadates, tantalates having tungsten bronze (TB) structure. We investigate these TB compound by substitution of rare earth substituted polycrystalline ceramics for high temperature device applications.

6. Study of Dielectric and Ferroelectric properties of Rare Earth substituted tungsten bronze electro ceramics:

Dielectric Study

$Ba_pNd_{6-p}Ti_{8-p}Nb_{2+p}O_{30}$

X.H.Zheng etal.[23] studied Tungsten Bronze compound with composition $Ba_pNd_{6-p}Ti_{8-p}Nb_{2+p}O_{30}$ was $3 < p <= 6$ i.e $Ba_3Nd_3Ti_5Nb_5O_{30}$, $Ba_4Nd_2Ti_4Nb_6O_{30}$, $Ba_5NdTi_3Nb_7O_{30}$. Here $Ba_4Nd_2Ti_4Nb_6O_{30}$ and $Ba_5NdTi_3Nb_7O_{30}$ has filled tetragonal tungsten-bronze structure, and $Ba_3Nd_3Ti_5Nb_5O_{30}$ entailed of the tetragonal tungsten-bronze major phase and a minor amount of secondary phase $BaNd_2Ti_3O_{10}$. All three compounds has significant relaxour behaviours, and the Curie temperatures (at 1 MHz) were 0 and 55 °C for $Ba_3Nd_3Ti_5Nb_5O_{30}$ and $Ba_5NdTi_3Nb_7O_{30}$ ceramics, respectively. A high dielectric constant (213) combined with low dielectric loss (0.004 at 1 MHz) was obtained in $Ba_3Nd_3Ti_5Nb_5O_{30}$ ceramics and a flat peak was measured at 10 KHz below 20 °C for $Ba_4Nd_2Ti_4Nb_6O_{30}$. The peak vanished with increasing measured frequency, and this peak might be due to the rotation reduction at low frequency for compounds with the tungsten-bronze structure [24] and the dielectric constant increased continuous with temperature for $Ba_4Nd_2Ti_4Nb_6O_{30}$ at all measured frequencies, which proposes that the Curie temperature was above 85 °C. Variation of relative dielectric constant (ϵr) and loss tangent (tanδ) as function of temperature at frequency ($100H_Z-1MH_Z$). $Ba_5SmTi_3Nb_7O_{30}$ TB compound show ferroelectric paraelectric phase transition and dielectric analomy exist at 170°C but compound not show relaxour behavior.Hence ,this material have high dielectric constant and low dielectric loss may be suitable for high temperature device applications.

$K_2Pb_2X_2W_2Ti_4Nb_4O_{30}$ (X=Sm)

R.Padhee et al. [25] observed in complex compound $K_2Pb_2X_2W_2Ti_4Nb_4O_{30}$ (X=Sm), show double phase transition. Value of dielectric constant ($\pounds r$) of KSmN increase with rise in temperature uptotransition temperature (Tc) and then decrease to a certain value. The dielectric anamoly exist at two phase transition:

(1) Ferroelastic to Ferroelectric (Tc_1) at 315°C and
(2) Ferroelectric to Paraelectric (Tc_2) at 366° C.

This shows that upper phase transition at Tc_2 is gradually decrease $\pounds r$ at higher temperature and obey curie weiss law and tungsten bronze compound show typical non polar dielectric behaviour of ferroelectrics and this compound not show relaxour properties. Increase in value of $\pounds r$ in sample due to electron –phonon interaction. Similar change in tan δ with temperature pragmatic but above 425°C tan δ increases monotonically due to space charge polarization.

$Ba_{5-x}CaxSmTi_3Nb_7O_{30}$

PrasunGanguly et al. [26] studied samples of the compositions $Ba_{5-x}CaxSmTi_3Nb_7O_{30}$ for (x = 0–5), where Ba has been replaced by Ca. Temperature dependency of dielectric constant($\pounds$) and dielectric loss (tan δ) for all the compounds at different frequencies (1, 10 and 100 kHz). It is observed that the compounds with x = 0, 1, 2, 3, 4 undertake ferroelectric– paraelectric phase transition of diffuse type at the Curie temperature (Tc) ,

whereas the compound with x = 5 does not show any dielectric anomaly as unhurried in temperature range. It is also observed that all the compounds have the same Tc at frequencies (1,10,100 kHz), signifying that the compounds do not show any relaxour behaviour. This result is altered from the results obtained for $Ba_5SmTi_3Nb_7O_{30}$ ceramic reported by Shannigrahi et al.[27]. The dielectric constant decreases as the concentration of calcium increases and this is due to the decrease in the net polarization of the compounds with increase in Ca concentration as the ionic polarizability, (α_I) of Ca is 3.16Åcompared to that of Ba 6.40Å [28].However, Tc increases from 170 °C (in Ca free specimen) to 198 °C in calcium (x = 1) containing specimen. Larger value of tetragonal strain (c/a) on adding Ca indicates that a larger amount of thermal energy is required for the phase transition resulting in an increase in Tc. Another possible reason for the increase in the transition temperature could be attributed to the reduced value of the tolerance factor due to the partial substitution of smaller cationCa at Ba-site [29]. However, for higher concentration of calcium (i.e. x ≥2), Tc decreases sharply upto 85°C. This is due to the formation of the secondary phase at these concentrations. At all the frequencies, the dielectric peak is found to be broadened indicating the existence of diffuse phase transition.

BRTN($Ba_4RETiNb_9O_{30}$)

In BRTN($Ba_4RETiNb_9O_{30}$) R=La,Pr,Nd,Sm,Eu,Gd) unfilled TB ferroelectrics show that dielectric characterization for the La , Pr ,Nd ,Sm doped ceramics showed relaxors behavior with strong diffuse phase transition and frequency dispersion while the Eu, Gd doped sample show only diffuse phase transition. This ceramics have also shown the similar componentt of dielectric constant and dielectric loss with temperature (i.e dielectric constant decrease with the increasing frequency due to reduction of active polarization mechanism.)Also diffuse phase transition, frequency dependent Tm and dielectric scattering observed in BRTN ceramics. As temperature increase broad peak for all compound in dielectric constant suggesting the ferroelectric–paraelectric transition i.e the typical property of TTB ceramics. Generally,tungsten bronze ferroelectric compound $Ba_5LnTi_3Nb_7O_{30}$, such as $Ba_5LaTi_3Nb_7O_{30}$[30]and, $Ba_5NdTi_3Nb_7O_{30}$[31] $Ba_5RTi_3Nb_7O_{30}$ (R = Dy, Sm) [32,33], has shown relaxor ferroelectric due to their disordered distribution of Ba and Ln ions at interstice A_1.

But for the $Ba_4Ln_2Ti_4M_6O_{30}$ compounds, not all the ferroelectric nature, such as $Ba_4La_2Ti_4Nb_6O_{30}$[34,35]. Stennettet al. [36]suggested that due to lack of commensurate periodicity may contribute to the disruption of long range dipolar couplingin these compositions, and show relaxor behavior rather than classic ferroelectricbehavior, which may be due to the effects of the ionic radius ofrare-earth ion at interstice A_1. Zhu concluded that the magnitude of radius difference between A_1 and A_2 ions had important effectson the relaxer behavior of $(Ba_xSr_{1-x})_4Nd_2Ti_4Nb_6O_{30}$ compounds[37,38].Not only A site substitution can tend to be relaxer ferroelectric, but also the substitutions on B site tend to be relaxer ferroelectric. Arnold et al. [39,40] reported the family of B-site substitutions $Ba_6M^{3+}Nb_9O_{30}$relaxer materials and explained the relaxer with the degree of structural distortion, which was governed by tetragonality(c/a). However, attention has been paid to unfilled TB compounds except $Ba_xSr_{1-x}Nb_2O_6$(SBN) [41]. Relaxor behavior of $Sr_{0.3}Ba_{0.7}Nb_2O_6$ is detected and correlated to the cationic disorder in pentagonal and tetragonal sites of the tungsten bronze structure [42]. The effects of Sr/Ba ratio of $Sr_xBa_{1-x}Nb_2O_6$ (with x = 0.50, 0.45, 0.40 and 0.30) ceramics on the relaxer feature of SBN ceramics were also studied [43].Wang et al. reported ferroelectrics based on$Ba_4MNb_xTa_{10-x}O_{30}$ (M = Zn, Mg, Co, Ni), and found that the substitution of Nb for Ta leaded to low-temperature dielectric with a relaxor-type behavior[44].

$Ba_5NdNi_{1.5}Nb_{8.5}O_{30}$

Similarly same behavior observed in $Ba_5NdNi_{1.5}Nb_{8.5}O_{30}$ but due to Ni doping in TB broad dielectric constant peak at 293K is observed and constant peak dwindles down to disappear with increasing frequency. However T_{max} does not exhibit understandable up shift at low frequency which is different characteristics of relaxor ferroelectrics.

S.F.Liu et al. [45] studied the effects of Nb-substitution dielectric,ferroelectric and magnetic properties of $Ba_4Nd_2Fe_2Ta_8O_{30}$ tungsten bronze ceramics.With the increase of x, $Ba_4Nd_2Fe_2(Nb_xTa_{1-x})_8O_{30}$ ceramics transform from para electric to ferroelectric. The compositions x = 9 and 0.95show diffuse-type ferroelectric phase evolution with Tc above room temperature (306 K for x= 0.9 and 320 K for x= 0.95). For x=0 and 0.5, $Ba_4Nd_2Fe_2(Nb_xTa_{1-x})_8O_{30}$ ceramics are paramagnetic at room temperature. From x= 0.7 to x= 0.95, the remnant moment of $Ba_4Nd_2Fe_2(Nb_xTa_{1-x})_8O_{30}$ ceramics increases with increasing x. The $Ba_4Nd_2Fe_2(Nb_xTa_{1-x})_8O_{30}$

ceramics with x=0.9 and 0.95 are single-phase multiferroics at room temperature. Josse etal. reported that $Ba_4Nd_2Fe_2Nb_8O_{30}$ is a normal ferroelectric with Tc= 323 K [46]. It is obvious that the high temperature dielectric abnormality for x=0.95 can be attributed to the ferroelectric transition. For x= 0.9, this ferroelectric transition becomes more diffuse and coexistence of the low temperature and high temperature dielectric aberrations leads to form a flat platform of dielectric constant from 180 K to 310 K with a very small temperature coefficient of dielectric constant of 1.95ppm/1°C at 1MHz. This makes $Ba_4Nd_2Fe_2(Nb_{0.9}Ta_{0.1})_8O_{30}$ ceramics to be a good candidate for high frequency capacitor.

$Ba_2MTi_2X_3O_{15}$

M.C. Stennett et al. [47] has shown a compound $Ba_2MTi_2X_3O_{15}$; M= (La, Pr, Nd, Sm, Eu, Gd, Dy, Bi); X=Nb, Ta show a new family of TTB ferroelectric phase transition. With larger M cation, La, Bi the material exhibit relaxor behaviour with sub ambient transition temperature Tc. With decreasing M size, sharp 1st order ferroelectric phase transition is observed and Tc rises maximum. at 330°C for Gd. For this composition all the phase are TTB with A site order (Ba, M) and non-statistical B- site disorder of (Ti, Nb for M=La). More recent studies on the other M equivalents show that all possess a super lattice with a repetition of c, however , the periodicity parallel to [110] is incommensurate for M=La, Ba but proportionate for smaller rare earth e.g Nd, Sm, Gd. It is probably not coincidental that two phase exhibit relaxor behavior [M=La, Bi] are those where sub lattice is incommensurate parallel to [110]. For this composition confirmation of ferroelectric- paraelectric nature of phase transition at Tc shows hysteresis loop.

$Li_2Pb_2R_2W_2Ti_4Nb_4O_{30}(R=Y,Eu,Gd$)

B.N. Parida et al [48] in polycrystalline complex TB ferroelectric ceramics $Li_2Pb_2Y_2W_2Ti_4V_4O_{30}$, $Li_2Pb_2R_2W_2Ti_4Nb_4O_{30}(R=Y,Eu,Gd)$, $Li_2Pb_2Pr_2W_2Ti_4Ta_4O_{30}$ .Variation of relative dielectric constant and loss tangent with temperature at different frequencies are studies. It is observed by R.Padhee et al. in above complex TB has shown the dielectric constant(£r) and tangent loss (tanδ) increases gradually on increasing temperature upto transition temperature (Tc) and then decreases. Increase in value of (£r) in all above sample due to electron-phonon interaction mainly observed in niobates,tantalates and vandalates. Above transition temperature decrease in (£r) indicate para electric behavior of all sample.

R.Padhee et al. in above sample indicate that above transition temperature (Tc) increase in (£r) due to thermally activated transport property and due to occurrence of space charge. Higher value of dielectric constant at lower frequency is due to charge accumulation at grain boundaries. Here in comparison to (£r) negligible increase in tan δ is observed up to transition temperature (Tc). Above transition temperature (Tc) monotonous increase in tanδ can also attributed due to thermal transport of oxygen vacancies and Nb^{+4} ,Ta^{+4} and V^{+4} act as donor centre initiating extrinsic n type conduction in samples. Also in all samples increase in transition temperature due to increase in ionic radii of rare earth ions and sharp increase in tan δ at higher temperature in sample due to scattering of thermally activated charge carrier and contribution of ferroelectric domain wall to tanδ is less. In all above polycrystalline complex TB ferroelectric ceramics dielectric anomaly assumed related to ferroelectric–paraelectric phase transition and this assumption give confirmation of hyterersis loop at different temperature (below Tc).

$Ba_5NdCu_{1.5}Nb_{8.5}O_{30-\delta}$

Yan-Qing Tan et.al. [49] studied a new type of tungsten bronze ceramic $Ba_5NdCu_{1.5}Nb_{8.5}O_{30-\delta}$.The occupations of sites A and B are quite interesting for this compound. A_1 sites are fully disordered occupied by Ba ions and Nd ions and A_2 sites for Ba ions only, while B-sites are equal for both Cu and Nb ions to occupy. This material exhibits relaxation behavior in the 213–573 K temperature range. The dielectric constants have been fitted by the modified Curie–Weiss law and all the estimated g values are close to 2, confirming the typical relaxour ferroelectric behaviour. The disorders of Ba^{2+} or Nd^{3+} in A_1 sites and Nb^{5+}, Cu^{2+} in B sites induced by the oxygen vacancies may contribute to this dielectric behavior. Little variation of dielectric constant due to extrinsic factors, such as phase purity, porosity and grain boundaries, two dielectric relaxations, marked as I and II with strong frequency dispersion are observed in the BNCN ceramic in the temperature range of 213–573 K. The relaxation I appear in the 450–523 K, where the peaks of dielectric constant shift to higher temperature and the magnitude of dielectric constant decreases with increasing frequency. The relaxation II is weak and appears below 250 K, being similar with that in Ref. [50] which maybe arises from the inhomogeneous structure such as the interfaces between grain boundaries or different phases. However, there are no peaks observed in the

temperature dependence of dielectric loss, this is a typical characteristic of tetragonal tungsten bronze TTB structure ceramics with non-relaxer but high dielectric permittivity. Juan Li et al. [51] has studied in $Ba_4Sm_2Ti_4Ta_6O_{30}$ dielectric ceramics by Sr substitution for Ba on the A-sites and Ti substitution for Ta on the B-sites was investigated. High dielectric constants and low dielectric loss are indicated for all these dense ceramics. The considerable decrease in the dielectric constant of $Ba_2Sr_2Sm_2Ti_{4+x}Ta_{6-x}O_{30-x/2}$ ceramics compared with that of $Ba_4Sm_2Ti_4Ta_6O_{30}$ ceramics is due to the substitution of Sr for Ba on A-sites. Moreover, the dielectric constant slightly decreases with increasing content of Sr.

In compound $Na_2Pb_2Nd_2W_2Ti_4Nb_4O_{30}$ same behaviour of tan δ increases slowly at low temperature, but at the higher temperature it increases rapidly as $K_2Pb_2X_2W_2Ti_4Nb_4O_{30}$. This sharp increase in tan δ at higher temperature due to some inherent defects in the sample scattering of thermally activated charge carriers and due to creation of oxygen vacancies during high temperature sintering.

Thus ,all rare substituted polycrystalline tungsten bronze ceramics are considered as functional materials ,which exhibits dielectricity and ferroelectricity. These extraordinary properties are indispensable for high temperature applications such as sensors, multilayer capacitors, spintronics and new type of multistate memories devices.

In all the above TB ceramics the degree of disorder or diffusivity (γ) and relaxation described by Curie –Weiss law. It can be expressed by following equation:

$$\frac{1}{\epsilon} - \frac{1}{\epsilon max} = \frac{(T - Tmax)^\gamma}{C}$$

where γ is a measurement of diffusivity which indicate whether the phase transitions is or is not completely diffused. £max is its maximum dielectric constant, and C is a constant. γ is an exponent that can vary from 1 for normal ferroelectric behavior to 2 for an ideal relaxor ferroelectrics. The diffuse nature of the phase transition can be explained in term of oxygen vacancies. All TB structured ceramics lose oxygen during sintering at high temperature, the Kroger and Vink representation can be used to understand that appeareance:

$$O_o \longrightarrow O_2 + V_o^{**} + 2e^-$$
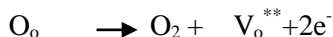
Where V_o^{**} denotes the oxygen vacancies, which induce disorder in the system and result in diffuse type ferroelectric –paraelectric phase transition.

Ferroelectric Study

The P-E hysteresis loop of all Tungsten Bronze ferroelectric ceramics recorded at room temperature. Hysteresis loop is one of the important criteria for the confirmation of existence of ferroelectric property in a compound and suitable for high temperature applications.

In $Ba_5SmTi_3Nb_7O_{30}$ & BRTN ($Ba_4RETiNb_9O_{30}$) R=La, Pr, Nd, Sm, Eu, Gd) Polarization electrical field (PE) hysteresis loop at room temperature show ferroelectricity. Also in $KCaNb_5O_{15}$(KCN) , $NaCa_2V_5O_{15}$ (NCV) variation of polarization as function of electric field at room temperature show remanent polarization are very small (2Pr=0.048μ/cm²) at an applied electric field of 18.87 Kv/cm and (2Pr=0.08μ/cm²) at an applied electric field of 18.87 Kv/cm .Smaller remanent polarization mean existence of ferroelectric properties. But in some sample the

P-E hysteresis loop are observed to be saturated indicating that sample show ferroelectricity or ferroelectric properties. The variation in remanent polarization can be understood on the basis of grain size. There are two major effects of grain boundary on polarization. The smaller grain size result in large no. of grain boundaries and it is well known that grain boundaries are low permittivity region ,hence poor ferroelectricity. Also there is polarization discontinuity (2Pr) decreases. The coercive field decreases with increase in rare earth content. This is possibly due to the fact that energy barrier for switching ferroelectric domain gets reduced as the grain size increases. Polarization reversal of a ferroelectric domain is much easier inside a larger grain compared to that in smaller grain.

The remanent polarization (2Pr) is found to increase on Ca substitution, i.e., for x = 1. The increase in remanent polarization is pronounced due to structural distortion arising by the partial substitution of smaller

cationCa at Ba-site .But for higher concentration of calcium, 2Pr decreases and finally the loop becomes a straight line for x = 5 confirmed that the compound is no longer ferroelectric on completely replacing barium by calcium, which is in conformity with dielectric observations. The temperature variation of P–E hysteresis loop for x = 0 (i.e., $Ba_5SmTi_3Nb_7O_{30}$ specimen show that the remanent polarization (2Pr) value decreases with increasing temperature and finally it becomes zero at the transition temperature (Tc), i.e.170 °C.

Conclusions

Polycrystalline tungsten bronze ferroelectric ceramics with different A and B site substitution studied in detail with their dielectric and ferroelectric properties. Dielectric properties show that dielectric constant as function of frequency at various temperature decrease with increasing frequency due to presence of oxygen vacancies change in valency (Nb^{5+} ,Nb^{4+}) and in all polycrystalline complex tungsten bronze dielectric anamoly related to ferroelectric-paraelectric phase transition and give confirmation of hysteresis loop at different temperature but below transition temperature (T_c), tungsten bronze ceramics have small remanent polarization show the existence of ferroelectric properties. . Now it is necessary to pay more attention to established more complex theories to model simulate or predict better performance of tungsten bronze material, so specific materials designed for high temperature device applications.

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