Original Research Article

Study of structural and ferroelectric properties of the composite Ba$_5$RTi$_3$V$_7$O$_{30}$ (R=Pr, Tb)

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ABSTRACT	Polycrystalline Samples of Ba$_5$RTi$_3$V$_7$O$_{30}$ (R= Pr, Tb), members of tungsten bronze family were prepared by high temperature Solid State Reaction Technique. Preliminary X-ray analysis of the material has been done to ensure the single phase formation. Surface morphology was studied by Scanning electron microscope (SEM: JOEL-IT300). Dielectric characterization is done for frequency upto 1MHz at various temperatures by Impedance Analyser (HIOKI-IM3536).
KEYWORDS	Tungsten Bronze family, Solid State Reaction, Dielectric constant, Impedance Analyser.

INTRODUCTION

In current technical era Ferroelectric materials have a significant stance for their prevalent relevance in various fields as in electronics, electro-optic [1], computer and communication. Among varied structural groups or family, TB structural family covers the extensive number of ferroelectric materials, which has a general formula $[(A_1)_2(A_2)_4C_4][(B_1)_2(B_2)_8]O_{30}$. At sites A_1, A_2, Mono or divalent cations can be accommodated whereas at octahedral sites i.e. B_1 and B_2 with tri or pentavalent cations and C site (smallest interstice) generally remaining empty. Because of prospect of expansive class of cation substitution it is feasible to improve the properties of new material [2].

In the family of ferroelectrics of TB type, Niobates are noteworthy because of its various applications in various fields such as in the field of electro-optic, nonlinear optic, acoustic optic etc. Some examples of this type of ferroelectrics are PbNb$_2$O$_6$, (Pb-Ba)Nb$_2$O$_6$, (Ba-Sr)Nb$_2$O$_6$, BNN(barium-sodiumniobate). Among given examples BNN was more appealing for it shows diffused phase transition and shows better electro-optic coefficient, which, according to Jamieson [3] is related to orthorhombic symmetry in BNN [4]. Lots of research has been done on this particular area and hordes of new materials has been unearthed. One of such discovery is rare-earth doped niobate-titanate; Ba$_5$RTi$_3$Nb$_7$O$_{30}$ [5, 6] which shows diffuse phase transition with different T$_c$ with different rare earth element. Due to its

diffuse phase transition nature, it gives the scope to obtain different types of Ferroelectrics material by Rare earth element (R) substitution. It was also found that this niobate-titanate compound has a high calcination and sintering temperature. It has been reported that with vanadium (V) substitution in place of niobium the calcination and sintering temperatures considerably reduces [7].

Through literature survey it was found that the various study has been done on compound $Ba_5RTi_3V_7O_{30}$ with different rare-earths elements example with R= Ho, Gd, Y etc. [8,9] but still no study with Praseodymium and Terbium as R has been reported. So in our present study our objective is to study the effect of Pr and Tb in $Ba_5RTi_3V_7O_{30}$. So the quest for the better ferroelectrics materials continues.

EXPERIMENTAL PROCEDURE

For the synthesis of polycrystalline sample of $Ba_2TbTi_3V_7O_{30}$ (BTTV), high-temperature solid-state reaction technique was employed using high purity (≥99.9%) carbonates and oxides: $BaCO_3$, Tb_2O_3, Pr_2O_3, TiO_3 and V_2O_5 in proper stoichiometry ratio. Using agate mortar these ingredients were thoroughly dry mixed first in an environ atmosphere for 2 h, and then wet mixed with methanol for 1 h then is dried by a slow evaporation technique. The processed powder is then put into alumina crucible and fired for 750◦C (for 12 h) in muffle furnace. The process of grinding and calcinations is repeated till the compound is formed at an optimize calcined temperature of 800◦C for 12 h. The calcined powder is then further grounded to fine form so that the size will be in nanoscale. The powder is then cold die pressed using hydraulic press for about 7 tons of pressure to form a cylindrical pellet of about 13 mm diameter and 1–2 mm. Polyvinyl Butyral (PVB) is used as a binder to reduce the brittleness of the pellet. The pellet is then sintered at 800◦C for 12 h followed by cooling at 2◦C. The formation and quality of the compound is checked by an X-ray diffraction (XRD) technique. The X-ray diffraction pattern of the compound is recorded at room temperature using an X-ray powder diffractometer (Rigaku, Miniflex) with Cu-Kα radiation (λ = 1.5405 ˚A) in a wide range of Bragg's angles 2θ (20◦ ≤ θ ≤ 80◦) with scanning rate of 3◦/min. The surface morphology of the pellet was studied by a scanning electron microscope (SEM: JOEL-IT300).Finally the pallets are painted with silver paste to make it conducting on both sides then the electrical measurement is done.

RESULT AND DISCUSSION

Structural Characterisation
For structural characterisation of the calcined powder has been put into X-Ray Diffractometer (XRD) at room temperature. Fig1 and fig 2 shows a sharp and single diffraction peaks of XRD patterns for BTTV and BPTV at the expected regions confirms the formation of single phase compounds [10].
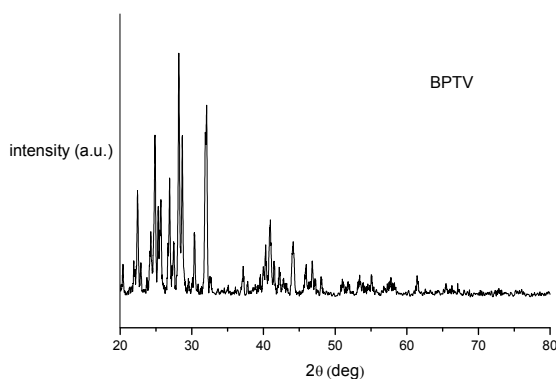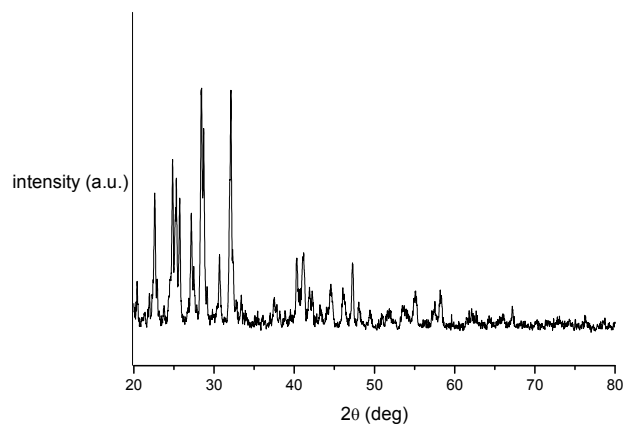
Figure 1: XRD for a) BPTV b) BTTV

Microstructural Analysis

The SEM micrographs of BTTV and BPTV shows that grain process is more or less complete in sintering process and no secondary re-crystallization has taken place as shown in Fig 2(a,b).It shows the presence of voids of irregular dimension indicates that the samples have certain degree of porosity and inhomogeneity. The grain size is evaluated from the micrographs using linear intercept method shows that BPTV has average grain size is around 0.75 µm and that of BTTV is about 0.89 µm. The micrograph of BPTV shows that its granule formed is of cuboid, agglomerate, elongated feature and that of BTTV is of oval, elongated, angular shape and more homogenous in nature. The shape and distribution of grains in the microstructure exhibit the polycrystalline nature of the samples. Porosity was found to decreases with increase in ionic radius of the doped rare earth element.
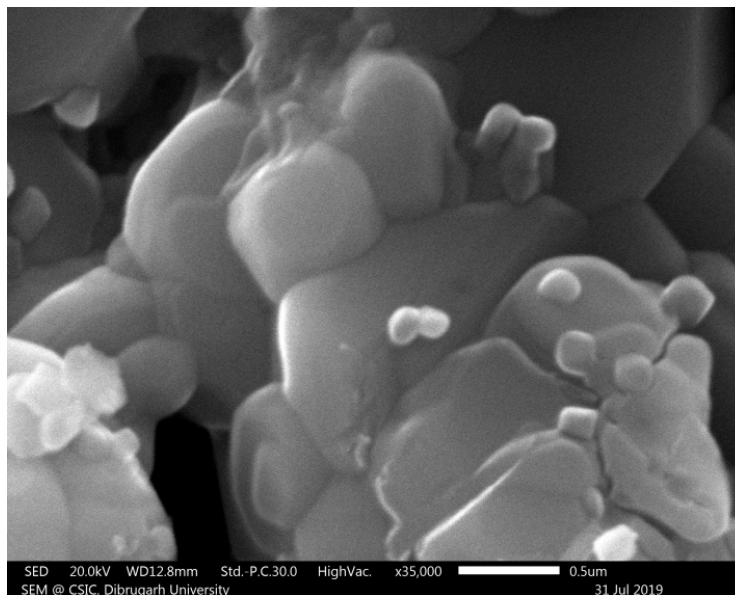
(a)
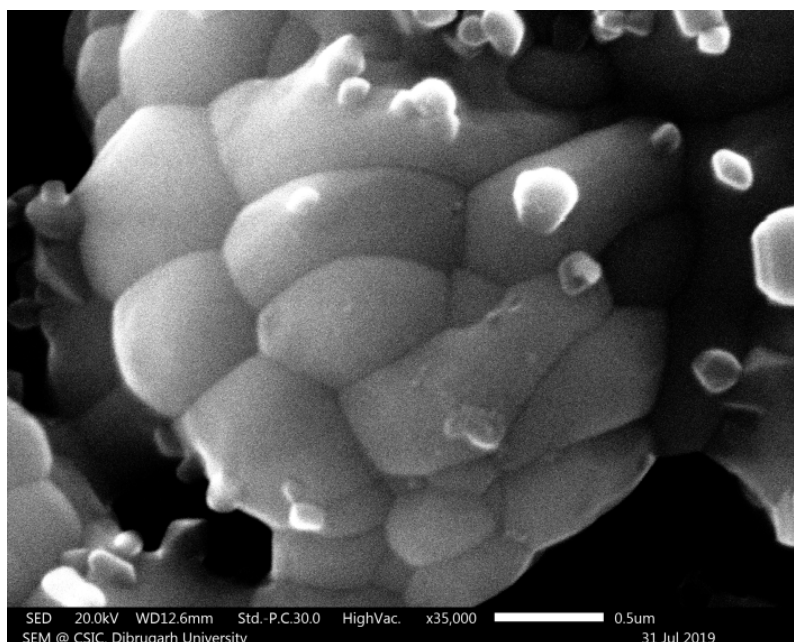
(b)

Figure 2: SEM micrographs of (a) BPTV, (b) BTTV

Dielectric properties

Variation of relative dielectric constant and tangent loss is measured for range of temperatures at the selected static or low frequency [11-13] of 1000Hz has been shown in fig 4. It shows that for BTTV the relative dielectrics decreases from ~246to ~22 for the increase infrequencies from 1kHz to 1MHz and also that tangent loss decreases from ~21.6 to 0.66, which is a general feature of polar dielectric materials. It can be seen that the value of dielectric constant (ε_r) first rises with temperature to reach the vertex which is its transition temperature (T_c) and then there is decrease of dielectric constant (ε_r) which further increases with increase in temperature.

From Table 1, it can be seen that the for BPTV dielectric constant (ε_{max}) is 377 and for BTTV dielectric constant (ε_{max}) is 1099, which means the dielectric constant of BTTV far exceed that of BPTV. Also, BTTV is much better dielectric than that of BPTV for the dielectric constant of BTTV at room temp is (ε_{RT} ~674) which is way more than maximum dielectric constant (ε_{max} ~ 377) which can be attained in BPTV. The Curie temperature (T_c) of BPTV is 343K and that of BTTV is 356K. The existence of dielectric anomaly is may be due to contribution from both the dipole orientation and long range migration of charge species. Further, above T_c, after certain duration there is rapid increase in the relative dielectric constant again. This may be due to the creation of space charge polarization at higher temperatures.

From fig. 3 it can be seen that the tangent loss (tan δ) for BPTV in comparison to BTTV is much higher in lower temperature but at higher temperature that tan δ for BPTV is lower in comparison to BTTV, which suggest there is lower tangent loss for BPTV in lower temperature and at higher temperature BTTV shows lower tangent loss. The general trend of increase of the value of tan δ of the compound at higher temperature is may be due to enhanced conductivity in the compound and the reduction in the ferroelectric domain wall's contribution at high temperature.
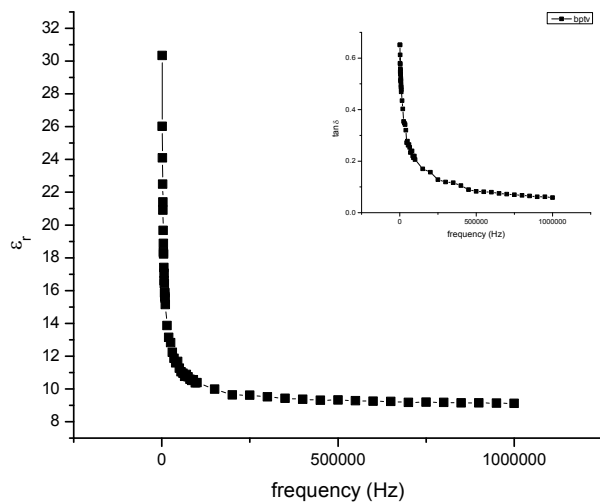
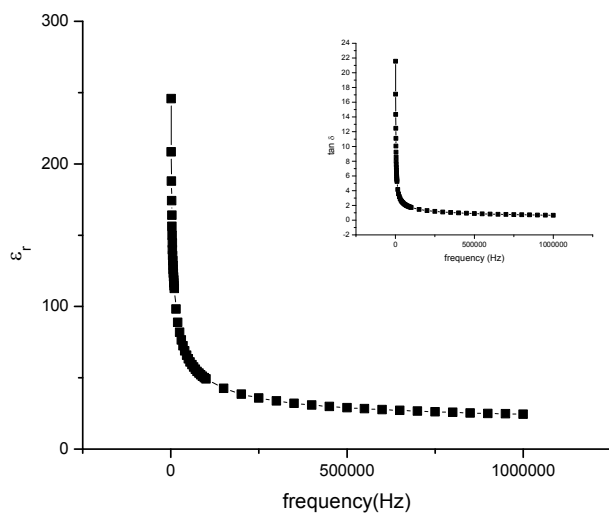**Figure 3:** Frequency variation of ε_r and tan δ of BPTV at room temp Ba$_5$PrTi$_3$V$_2$O$_{30}$

Figure 4: Frequency variation of ε_r and tan δ of BTTV at room temp Ba$_5$TbTi$_3$V$_2$O$_{30}$
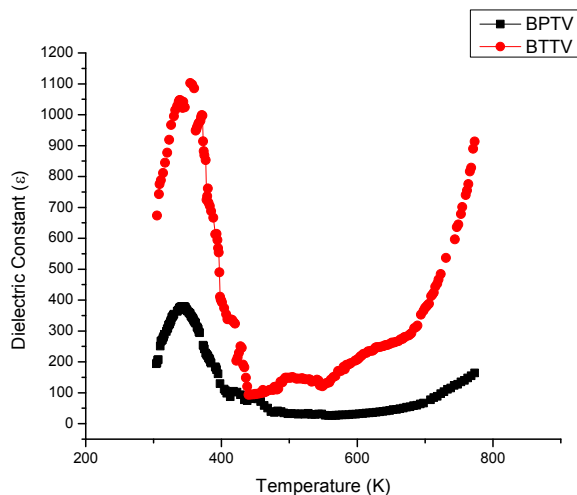
Figure 5: Variation of ε_r with temperature (K) at 1kHz frequencies.
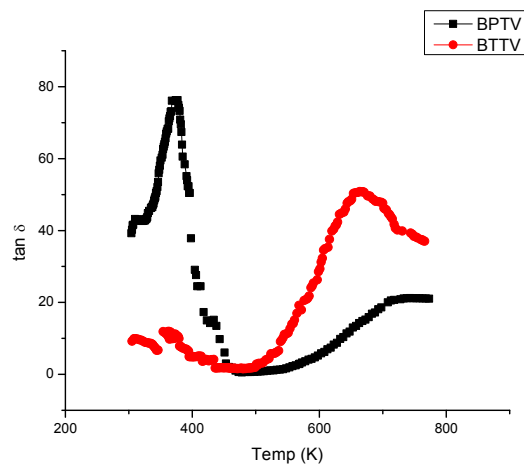
Figure 6: Variation of tangent loss with temperature (K) at 1000Hz frequency.

Table 1:

Compounds	T_c (K)	ε_{RT}	ε_{max}
BTTV	356	674	1099.838
BPTV	343	194	376.63

Conductivity study

Figure 7 shows the plot of ac conductivity ($\ln\sigma$) vs the inverse of absolute temperature ($10^3/T$) at selected frequency of 1kHz. The nature of observed curve supports the thermally activated transport properties of the materials obeying Arrhenius equation: $\sigma_{ac} = \sigma_o \exp(-E_a/K_BT)$, where the symbols have their usual meanings [14-16]. It is observed that the both the compound i.e. BPTV and BTTV shows similar kind of trend, ac conductivity of the material first increases with rise in temperature, and shows the negative coefficient of resistance behavior then it decreases at the similar region of transition temperature i.e for BPTV, $T_c \sim 343K$ and for BTTV, $T_c \sim 356K$. This change in conductivity may be due to change in phase i.e. from ferro to para and after certain temperature the conductivity further increases with rise in temperature. This behavior suggests that the conduction mechanism may be due to the hopping of charge carriers.
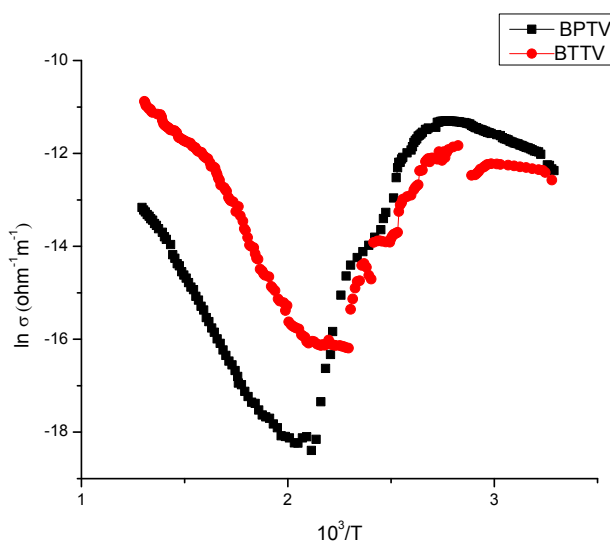

Figure 7: Variation of $\ln\sigma$ with $10^3/T$ at 1000 Hz

CONCLUSION

It was found that both BPTV and BTTV are ferroelectrics in nature. The transition temperature of BPTV is less than that of BTTV; also the maximum dielectric constant of BPTV is considerably lesser than that of BTTV. The explanation for the observed phenomenon may be due to difference in the Ionic radius of the rare earth element. The Ionic radius of Praseodyium (Pr) is 1.13A° and Ionic radius of Terbium (Tb) is 1.18A°. The smaller Ionic raduis of Pr might increase the mobility of ion which increases in conductivity thus decreases the dielectric constant. Also due to more mobility of charge carriers there is increase in the cross section collisions thus increase in the tangent loss. But at higher temperature the heavier charge carrier is more prominent hence the tangent loss is more for BTTV in comparision to BPTV. So, BTTV is a better ferroelectrics than BPTV.

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