Orissa Journal of Physics
ISSN 0974-8202

Vol. 21, No.1
February 2014
pp. 49-55

# A comparative study of electrical properties of $Ba_4SrRTi_3V_7O_{30}$ (R = Gd, La) TB ceramics

P S SAHOO[A] , B B MOHANTY[A,*] and R N P CHOUDHARY[B,C]

[a] Department of Physics, Betnoti College Betnoti, Mayurbhanj, Orissa, India
[b] Department of Physics & Meteorology, IIT, Kharagpur 721302, India
[c] Department of Physics, I T E R, Bhubaneswar Odisha, India
E-mail address: banabihar4u@gmail.com

*Received: 7.12.2013 ; Revised: 25.12.2013 ; Accepted: 18.1.2014*

**Abstract :** The discovery of ferroelectricity in $BaTiO_{30}$ opened plethora of research activities in ferroelectric materials having similar structure as well as unveiling ferroelectricity in other crystal structures. Barium based tungsten bronze (TB) oxides having high dielectric constant and low loss, can be effectively used as transducers, actuators, capacitors and also in memory devices. All these characteristics stimulated the researchers to replace toxic and hazardous lead based materials by barium based TB materials from scientific and industrial studies. In the present research work, polycrystalline samples of $Ba_4SrRTi_3V_7O_{30}$ (R = Gd, La) were synthesized by a high temperature solid state reaction technique and a comparative study of the dielectric properties of the samples.. Preliminary structural (XRD) analyses of these compounds show the formation of single-phase orthorhombic structures at room temperature having average crystallite size of the order of some nanometer for all the compounds. The scanning electron micrographs (SEM) provided information on the quality of the samples and show more or less homogeneous distribution of grains over the entire surface of the samples. The dielectric properties suggest that the Gd modified compound undergoes ferroelectric-paraelectric phase transition at two temperatures well above the room temperatures (i.e., $371^0$C) whereas no such phase transition is observed in La modified compound in our experimental range.

**Keywords:** Ceramics; X-ray diffraction; Ferroelectricity; Dielectric properties; Electrical conductivity.

## 1. Introduction

Materials of tungsten-bronze (TB) structure belong to an important family of dielectric materials, which display interesting ferroelectric, pyroelectric, piezoelectric, and nonlinear optical properties. The TB structure consists of a skeleton framework of $BO_6$ octahedra, sharing corners to form three different types of tunnels parallel to the c-axis in the unit cell of material of a general formula, $[(A_1)_2(A_2)_4C_4][(B_1)_2(B_2)_8]O_{30}$[1]. The nine-coordinated C-site has the smallest space to occupy among all the three different types of tunnels created by the framework of the octahedra. Hence, varieties of cation substitution at different interstitial sites ($A_1$, $A_2$, C, $B_1$ and $B_2$) are possible [2-5]. The structural flexibility and the chemical versatility of TB family make it more usable for many devices application such as electro-optic, actuators, elasto-optic, electro-optic memory, optical devices [6-11] etc. A lot of works on the niobate and vanadate compounds of TB structural family have been reported in the past [12-15]. Looking to the above, we have synthesized and studied the structural and electric properties of some rare earth doped vanadates and in this paper we have compared the dielectric and conductivity properties of $Ba_4SrRTi_3V_7O_{30}$(R=Gd, La).

## 2. Experimental

### 2.1 *Sample preparation*

Appropriate stoichiometric ratio of precursors; $BaCO_3$, $SrCO_3$, $Gd_2O_3$, $La_2O_3$, $TiO_2$, $V_2O_5$ of high purity (>99.9%) were weighed, and initially mixed mechanically in dry and wet (Methanol) atmosphere by an agate mortar for 3 h to obtain homogeneous mixture of the polycrystalline samples, $Ba_4SrRTi_3V_7O_{30}$ (R = Gd, La) i.e., $Ba_4SrGdTi_3V_7O_{30}$ (BSGTV), $Ba_4SrLaTi_3V_7O_{30}$ (BSLTV). Subsequently, it was calcined in an alumina crucible at an optimized temperature and time ($950^0$C, 12h). Compact disks of 10 mm diameter and 1–2 mm thickness were prepared from calcined powders at a pressure of $4\times10^6$ N/m$^2$ with polyvinyl alcohol (PVA) as binder, using a hydraulic press. The pellets were then sintered in an air atmosphere at an optimized temperature and time ($950^0$C, 12 h) and then polished with fine emery paper to make their faces flat and parallel. The pellets were finally coated with high purity conducting silver paint, and then dried at $150^0$C for 2h before carrying out electrical measurements.

2.2. *Characterization*

The formation of the compounds were confirmed from the X-ray diffraction (XRD) of the calcined powder using an X-ray powder diffractometer (Rigaku, Miniflex) at room temperature with $CuK_\alpha$ radiation ($\lambda$=1.5405 Å) in a wide range of Bragg's angles $2\theta$ ($20^0 \leq 2\theta \leq 70^0$) having a scanning rate of three degree per minute. The dieelectric properties and ac conductivity for both the compounds have been measured as a function of frequency (100 Hz–1 MHz) at different temperatures (33–500 $^0$C) with a computer-controlled impedance analyzer (PSM 1735, model: N4L). For the measurements, Ag paste was painted on either side of the disk and fired at 150 $^0$C for 1 hr.

## 3. Results and Discussion

3.1 *Structural studies*

Fig.1 compares the XRD pattern of the BSGTV and BSLTV compounds at room temperature. All the reflection peaks are found to be sharp, which are different from that of ingredients and confirms the formation of new single-phase compound. All the peaks were indexed taking their $2\theta$ values using a computer program package, "POWDMULT"[16] in different crystal system and cell configuration. On the basis of the best agreement (based on least – squares refinement) between observed (obs) and calculated (cal) interplaner distance d (i.e., $\Sigma$ ($d_{obs} - d_{cal}$) = minimum), an orthorhombic unit cell was selected. The least-squares refined unit cell parameters of these compounds are: a=34.5929(17), Å b=3.5927(17) Å, c = 7.8619(17)Å for BSGTV and a= 7.5513 Å(12), b= 8.1027 Å, c=18.6666 Å(12) for BSLTV(estimated error in parenthesis). The coherently scattered crystallite size (D) of the compound was determined using Scherrer's equation; $D = 0.89\lambda / (\beta_{1/2}\cos\theta_{hkl})$, where $\lambda$ = 1.5405 Å and $\beta_{1/2}$ = peak width of the reflection at half maxima [17] . The contributions of strain, instrumental error and other unknown effects in the peak broadening have not been taken into account during the crystallite size calculation. The average crystallite size of BSGTV and BSLTV are found to be 13nm and 14 nm respectively. The SEM micrograph of the compound with different magnifications at room temperature is shown in Fig.1 (inset). The avarage grain size evaluated from the histogram was 1.6 and 1.3μm BSGTV and BSLTV respectively. It was found that the grains were homogenously and uniformly distributed over the entire surface of both the samples. For BSLTV ceramics the grains are spherical and irregular in shape, where as elongated and

rectangular shaped grains are observed in BSGTV compounds. A similar type of microstructure was found in other materials of same family [18, 19].

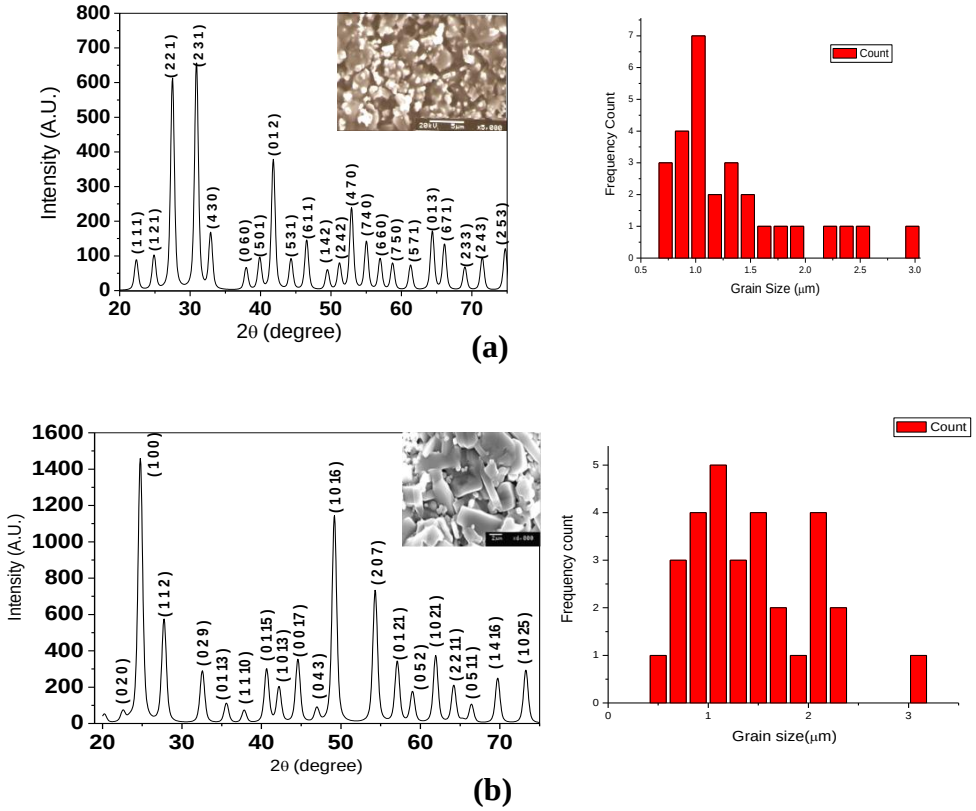


**Fig. 1:** Room temperature XRD pattern, SEM (inset) and histogram of $Ba_4SrGdTi_3V_7O_{30}$ (right) and $Ba_4SrLaTi_3V_7O_{30}$ (left) ceramics

3.2. *Dielectric study*

Fig.2(a) and (b) shows the temperature variation of relative dielectric constant and loss tangent for both the compounds at some selected temperature. Two frequency independent dielectric anomalies (at 255$^o$C and 371$^o$C) are observed in case of BSGTV compound in which the upper transition at 371 $^o$C is a ferroelectric to paraelectric transition, while the lower transition at 255 $^o$C is a ferroelastic to ferroelectric transition, but in case of BSLTV no dielectric anomaly is observed in the experimental temperature range. Such types of two phase transitions are found only in the orthorhombic tungsten bronze ferroelectrics [16, 17]. The farther increase in $\varepsilon_r$ value with temperature may be

due to space charge polarization, that comes from the mobility of ions and imperfections in the materials. These combined effects produce a sharp increase in the relative dielectric constant at higher temperatures [18, 19]. The maximum value of dielectric constant ($\varepsilon_{max}$) at $T_c$ for 50 and 100 kHz are374and 315 for BSGTV but in case of BSLTV compound there is no transition and hence no $\varepsilon_{max}$ within the experimental temperature range. It is also observed that the tanδ values of La modified compound (0.008) is less compared to that of Gd modified compound (0.06).

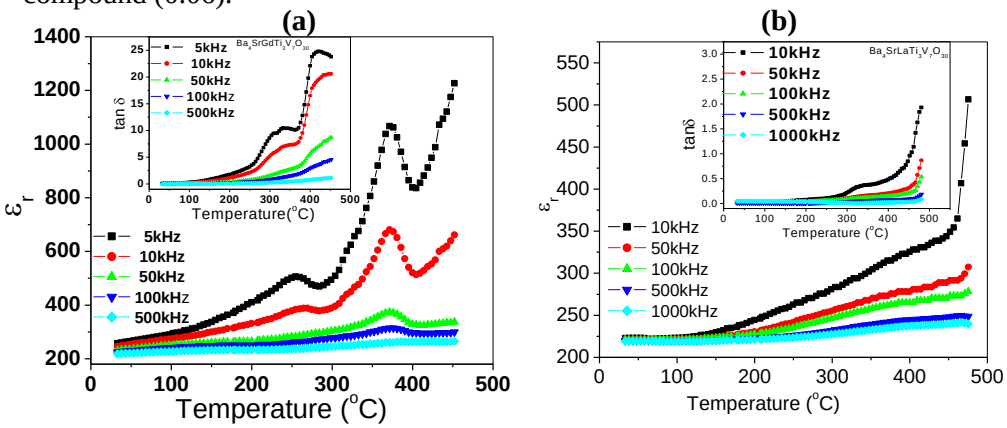


**Fig. 2:** Temperature variation of $\varepsilon_r$ and tanδ (insert) of $Ba_4SrGdTi_3V_7O_{30}$ and $Ba_4SrLaTi_3V_7O_{30}$ ceramics

3.3 *Conductivity study*

The Arrhenius plots of the electrical conductivity (dc) of both the compounds are as shown in the Fig.3 (a) and (b).

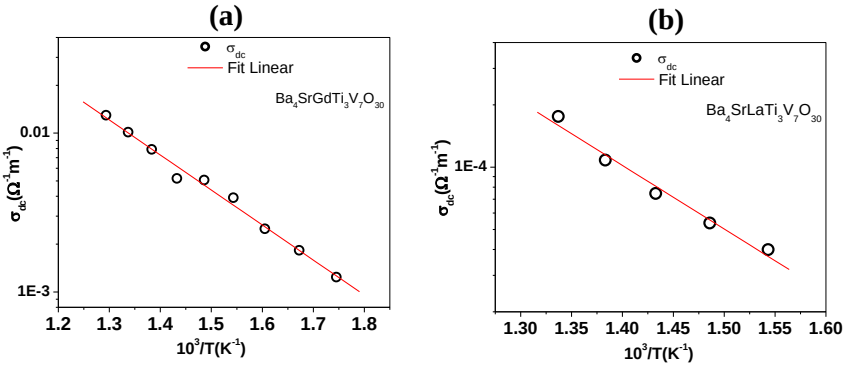


**Fig. 3:** Variation of $\sigma_{dc}$ with inverse temperature of $Ba_4SrGdTi_3V_7O_{30}$ and $Ba_4SrLaTi_3V_7O_{30}$ ceramics

It is cleared that, there is an increase in electrical conductivity with rise in temperature, confirming the negative temperature coefficient of resistance (NTCR) behavior of both the compounds. The activation energy for the conduction process are derived from the slope of the plots, which follows the Arrhenius relation $\sigma_{ac}= \omega\varepsilon_r\varepsilon_o\tan\delta = \sigma_{dc}\exp(-E_a/kT)$. The (dc) activation energies of the materials were estimated to be 0.44 and 0.6**1**eV for BSGTV and BSLTV respectively.

## 4. Conclusion

The BSGTV and BSLTV of tungsten–bronze family were prepared, and their structural and dielectric electrical characteristics were investigated. The ferroelectrics phase transitions in the BSGTV compound is observed well above the room temperature, where as no such phase transition is observed in BSLTV compound. As these ceramics exhibit high dielectric constants, low dielectric losses at higher temperature, so might have potential application in temperature-compensating capacitors. Comparatively, low room temperature dielectric constants observed in the ceramic samples indicate that may have attractive benefits in electrooptic and infrared pyroelectric detector applications at lower temperature. The negative temperature coefficient of resistivity (NTCR) property observed in both the compound can be used in developing highly sensitive thermal detectors, sensors, etc.

## References

[1] R R Neurgaonkar, M H Kalisher, T C Lim, E J Staples and K L Keester, *Materials Research Bulletin* **15( 9)**, 1235 (1980)

[2] W Sakamoto, Yu-saku Horie, Yogo Toshinobu, Shin-ichi, *Japanese Journal of Applied Physics*, **40**, 5599 (2001)

[3] Ganguly Prasun, A K Jha, *Journal of Alloys and Compounds* **484(1-2)**, 40 (2009)

[4] M R Ranga Raju, R N P Choudhary and S Ram, *Physica status solidi* (b) **239(2)**, 480 (2003)

[5] P V Bijumon, V Kohli , Om Parkash, M R Varma, M T Sebastian, *Materials Science and Engineering: B,* **113(1)**, 13 (2004)

[6] L X Zhang, WChen, and X Ren *Journal of Applied Physics Letter*, **85**, 5658 (2004)

**[7]** W L She, K K Lee, W K Lee *Journal of Physical Review Letter*, 2000, 85, 2498 (2000)

[8] M E Lines and A M Glass (Clarendon Press, Oxford, 1977)

[9] B Jaffe, W R Cook and H Jaffe, *Piezoelectric Ceramics* (Academic Press, London, 1971)

[10] K Uchino, *Piezoelectric Actuators and Ultrasonic Motors* (Kluwer Academics, Boston, 1997)

[11] B Muktha, A Simon, J Darriet and T N Guru *Row Chemistry of Materials*, **18(6)**, 5240 (2006)

[12] M R Ranga Raju and R N P Choudhary, *J. Materials Letters* 57, 2980 (2003)

[13] Hui Zhang, Z Q Liu, C L Diao, R Z Yuan and Fang Liang, *J. Materials Letters* **59 (21)**, 2634 (2005)

[14] X H Zheng, X H Zhou, *J. Mat. Sc.: Mat. Elect*, **17(12)**, 987 (2006)

**[15]** L Fang, H Zhang, J FYang, X K Hong and F C Meng, *J. Mat.Sc.: Mat. Elect*. **15(6)**, 355 (2004)

[16] E Wu, POWD, *An Interactive Powder Diffraction Data Interpretation and Index Program*, Ver.2.1 (School of Physical Science, Flinders University South Bedford Park, Australia)

[17] H P Klug and L E Alexander, *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, (Willey-Interscience, New York, 1974).

[18] S Allen and E Thomas, *The Structure of Materials*, ( John Wiley &Sons, Inc., New York, 1999)

[19] B Behera, P Nayak and R N P Choudhary, *Mater. Lett*. **59,** 3489 (2007)

[20] R-Jun Xie, Y Akimune, K Matsuo, T Sugiyama, N Hirosaki and T Sekiya, *Appl. Phys. Lett*. 80, 835 (2002)

[21] L Fang, H Zhang, B Wu, R Yuan, *Prog. Cryst. Gro. Charac. Mat*. 161 (2000)

[22] M Dammak, H Khemakhem, N Zouari, AW Kolsi and T Mhiri, *Solid State Ionics* **127** (2000) 125.

[23] Y Y Yao, C H Song, P Bao, D Su, X M Lu, J S Zhu and Y N Wang, *J. Applied Physics* **95(6)**, 3126 (2004)