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A comparative study of electrical properties of some rare earth based tungsten bronze ceramics

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ABSTRACT

The advent of nanoscience & technology have completely changed the orientation/direction of studies of eco-friendly (lead-free) materials bringing them at the forefront of scientific developments with considerably enhanced physical properties suitable for a wide variety of challenging applications. Barium based ferroelectric materials have gained much importance due to their vast applications as they possess high dielectric constant, non-linear spontaneous polarization, negative temperature coefficient of resistance behavior etc.. All these characteristics stimulated the researchers to replace toxic and hazardous lead based materials by barium based TB materials from industry. Our present research work deals with the synthesis of polycrystalline samples of $Ba_2Sr_3RTi_3V_7O_{30}$ (R = Gd, Sm) by a high temperature solid state reaction technique and a comparative study of the electrical 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 both the compounds. The electrical properties for both the samples are studied in a wide range of temperature (30–500^{o}C) and frequency (100Hz-1MHz). The dielectric properties suggest that both the compounds have undergone ferroelectric-paraelectric phase transition well above the room temperatures (i.e., 230 and 313^{0}C for R= Sm and Gd respectively at frequency 100 kHz).The bulk resistance of the materials exhibits negative temperature coefficient of resistance behavior as observed in semiconductors. Copyright © 2014 VBRI press.

Keywords: Ceramics; X-ray diffraction; electric properties.

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Introduction

Many ferroelectric compounds with tungsten bronze (TB) structure which exhibit dielectric behavior have been widely investigated and found application particularly in devices such as transducers, actuators, capacitors, and ferroelectric random access memory **[1, 2]**. Recently, owing to the rapid progress in microwave telecommunications, satellite broadcasting and other related technologies, a number of Ba based TB compounds with high dielectric constant have attracted much attention because of those being important in the miniaturization of microelectronic devices **[3, 4]**. The TB structure consists of a framework of distorted BO_6 octahedral sharing corners in such a way that three different types of interstices (A, B and C) are available for a wide variety of cations occupying in a general formula $(A_1)_2(A_2)_4(C)_4(B_1)_2(B_2)_8O_{30}$. It has been found that different ionic size substitutions at the above-mentioned sites can play an important role to tailor their physical properties. Detailed literature survey on synthesis and characterization of TB structured compounds reveals that a lot of work has been done on ferroelectric niobates and tantalates **[5-7]**. In our present work we have synthesized and studied the structural and electric properties of some rare earth doped vanadates and in this paper we have compared the above properties of $Ba_2Sr_3GdTi_3V_7O_{30}$ (BSGTV) and $Ba_2Sr_3SmTi_3V_7O_{30}$ (BSSTV) compounds.

Experimental details

Material preparation

Appropriate stoichiometric ratio of precursors; $BaCO_3$, $SrCO_3$, Gd_2O_3, Sm_2O_3 , TiO_2, V_2O_5(all from M/S Sarabhai M. Chemicals, India) of high purity (>99.9%) were weighed, and initially mixed mechanically in an agate mortar for 3h, first in air followed by wet (Methanol) atmosphere to get homogeneous mixture of the polycrystalline samples, $Ba_2Sr_3GdTi_3V_7O_{30}$ and $Ba_2Sr_3SmTi_3V_7O_{30}$. Subsequently, these were calcined in an alumina crucible at an optimized temperature and time (950^0C, 12h). The calcined powder so obtained were cold pressed into cylindrical pellets of diameter 10 mm and thickness 1-2 mm with polyvinyl alcohol (PVA) as binder, using a hydraulic press at a pressure of ~ 4×10^6N/m^2. The pellets were then sintered in an air atmosphere at an optimized temperature and time (950^0C, 12 h) and then polished to make their faces flat and parallel. The pellets were finally coated with high purity conducting silver paint, and then dried at 150^0C for 2h before carrying out electrical measurements.

Material Characterization

X-ray diffraction (XRD) data (pattern) of the material was obtained in a wide range of Bragg angle 2θ ($20^0\leq 2\theta \leq 80^0$) at a scanning speed of 3^0 min^{-1} by an X-ray diffractometer (Rigaku, Miniflex) with CuKα radiation (λ= 1.5405Å) at room temperature. Scanning electron micrograph of the material was recorded with a high-resolution scanning electron microscope (SEM: JOEL-JSM model: 5800F) to study the surface morphology of the sample (pellet). The impedance studies were carried out in the temperature range of 30^0 -500^0C and wide frequency range of 100Hz to 1MHz, using a computer-controlled impedance analyzer(PSM 1735, model: N 4L).

Results and discussion

Structural studies

The room temperature XRD pattern of the BSGTV and BSSTV compounds are compared in **Fig.1.**

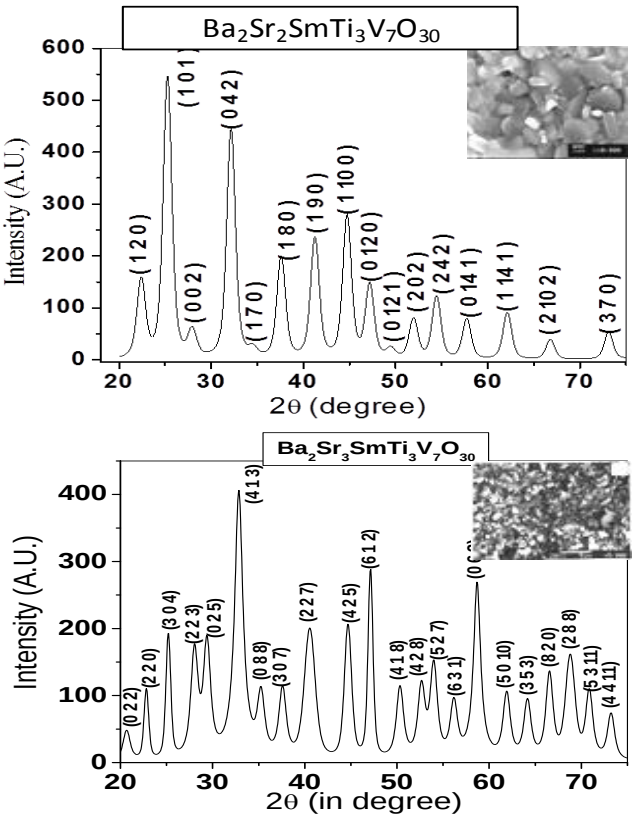

Fig. 1. Room temperature XRD pattern of the BSGTV and BSSTV compounds.

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All the diffractograms are largely similar with a small variation in the relative intensities and peak positions. The XRD peaks of both the samples are different from that of ingredients; suggest the formation of new single phase compounds. All the peaks are indexed in tetragonal or orthorhombic crystal system and in different cell configurations using software "POWD" **[8]**. With the observed (d_{obs}) and calculated (d_{cal}) inter-planar spacing of the XRD peaks, orthorhombic crystal system was selected, for which $\sum \Delta d = \sum (d_{obs} - d_{cal})$ was found to be minimum. The least-squares refined unit cell parameters of these compounds are: a =23.0868(26) Å, b = 4.2284(26) Å, c=6.3899(26) Å for BSGTV and a=10.6530(22) Å b=8.3610(22) Å, c = 22.0917(22) Å for BSSTV (estimated error in parenthesis). The coherently scattered crystallite size (D) of the compounds were determined using Scherrer's equation; **[9]** $D = 0.89\lambda / (\beta_{1/2}\cos\theta_{hkl})$, where $\lambda = 1.5405$ Å and $\beta_{1/2}$ = peak width of the reflection at half maxima. The contributions of strain, instrumental error and other unknown effects in the peak broadening have not been taken into account during the calculation of crystallite size. The average crystallite size of BSGTV and BSSTV are found to be 7.5 nm and 15nm respectively.

The SEM micrographs of both the compounds at room temperature are shown in **Fig. 1** (inset). The grain sizes evaluated from the micrographs are found to be 2.2 and 1.1 µm for BSGTV and BSSTV compounds respectively. The grains were found to be more or less homogenously and uniformly distributed over the entire surface of the sample. An expected grain size of all the samples obtained here are much larger as compared to the crystallite size calculated from Scherrer's equation. Thus, a single grain has several crystallites **[10]**. Similar microstructure was found in other materials of same family.

Dielectric study

Fig. 2 (a and **b)** shows the temperature dependence of relative dielectric constant (ε_r) and loss tangent (tanδ) at 50Hz-1MHz for BSGTV and BSSTV compounds.

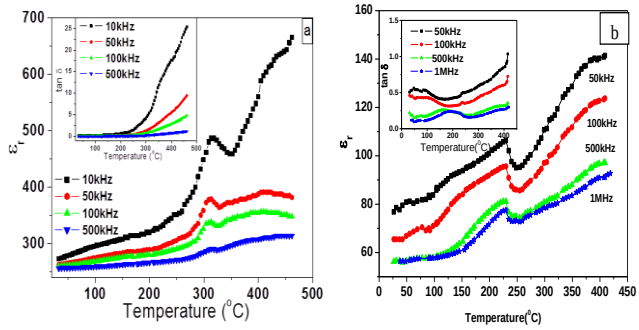

Fig. 2. Temperature dependence of relative dielectric constant (ε_r) and loss tangent (tanδ) at for BSGTV (a) and BSSTV (b) compounds.

The room temperature values of ε_r for BSGTV and BSSTV are 263 and 77 respectively at 50 kHz. The dielectric anomalies were observed at the temperature (transition temperature (T_c)) 313 and 230°C at (50 kHz-1MHz) for BSGTV and BSSTV respectively. These anomalies may be associated with ferroelectric-paraelectric phase transition. It has also been observed that ε_{max} is nearly independent of frequency, which suggests that these compounds have no relaxor behavior. The maximum value of dielectric constant at T_c (ε_{max}) for 50 and 100 kHz are 379 and 338 for BSGTV and the corresponding values for BSSTV are 106 and 96 respectively. Thus BSGTV compound has high dielectric constant as compared to BSSTV. These results agree well with the results of other compounds of the same family **[11, 12]**.

It that there are anomaly is observed in tan δ (**Fig. 2** (insert)) near the vicinity of T_c in BSSTV compound, but no anomaly is found for BSGTV compound. The tan δ values at room temperature are 0.05 for BSGTV and 0.5 for BSSTV at 50 kHz. The higher value of tan δ for BSSTV compound at high temperature may be due to the enhancement of conductivity and reduction in the ferroelectric domain wall contribution. It is also observed that both the parameters (ε_r and tan δ) decrease with frequency for both the compounds which is a general property of ferroelectric materials. The Gd doped compound shows high dielectric constant and low loss as compare to Sm doped compound.

Conductivity study

The Arrhenius plots of the electrical conductivity (dc) of both the compounds are as shown in the **Fig. 3**. It is observed that, the electrical conductivity of the compounds increases with rise in temperature, and hence the material shows negative temperature coefficient of resistance (NTCR) behavior. 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 1.36 and 0.34 eV for BSGTV and BSSTV respectively. The activation energy for BSGTV compound is more than that of BSSTV compound indicating BSGTV has higher dielectric constant than BSSTV compound. This is also confirmed from dielectric study.

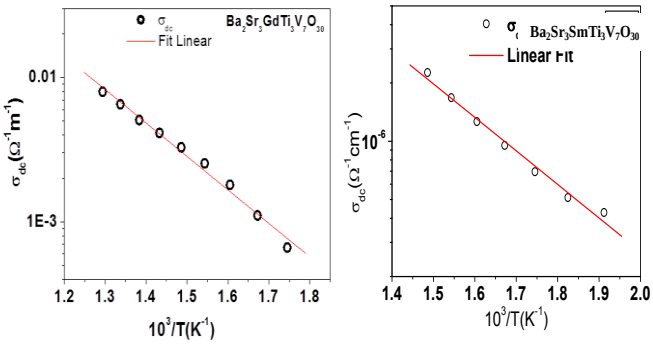

Fig. 3. Arrhenius plots of the electrical conductivity (dc) of BSGTV and BSSTV compounds.

Polarization study

The hysteresis loops of the poled samples are as shown in **Fig. 4**. The remnant polarization in the BSGTV material is found to be 0.028µC/cm^{2}at an applied electric field of 7.41 kV/cm where as for BSSTV it is 0.061 at an applied electric field of 6.4 kV/cm.

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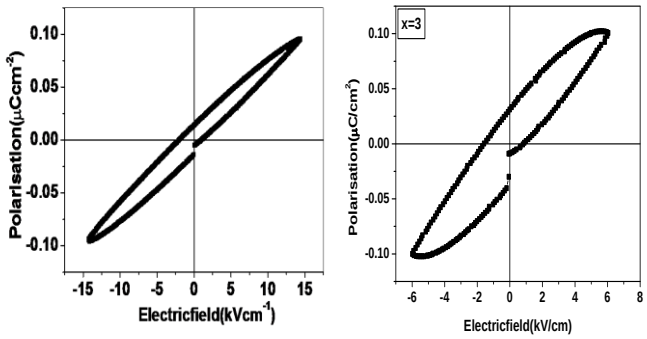

Fig. 4. Room temperature P~E loop of BSGTV and BSSTV compounds.

It is clear from the P~E loop that BSSTV compound is more lossy in compare to BSGTV compound, which is also observed in loss tangent graph. The appearance of hysteresis loop confirms the existence of ferroelectric–paraelectric phase transition in the material. A proper hysteresis loop could not be observed in both the compounds because of the lossy nature of the materials.

Conclusion

The BSGTV and BSSTV of tungsten–bronze family are prepared, and their structural, dielectric and electrical characteristics are investigated. Both the compounds are ferroelectrics and have an orthorhombic crystal structure at room temperature. The ferroelectrics phase transitions in the above-mentioned compounds are observed well above the room temperature. The BSGTV compound exhibit high dielectric constants, low dielectric losses. This material might have potential application in temperature-compensating capacitors. Comparatively, low room temperature dielectric constants observed in the BSSTV samples indicate that may have attractive benefits in electrooptic and infrared pyroelectric detector applications at lower temperature. Both the compounds also have negative temperature coefficient of resistivity (NTCR), which is most desirable for developing highly sensitive thermal detectors, sensors, etc.

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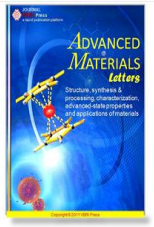

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