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Structural and electrical properties of $Ba_3Sr_2GdTi_3V_7O_{30}$

B. B. Mohanty[a], P. S. Sahoo[a]*, M. P. K. Sahoo[b] and R. N. P. Choudhary[c]

[a]*Department of Physics, Betnoti College Betnoti, Mayurbhanj, Orissa, India*
[b]*Department of physics, RGU-IIIT, Nuazvada, Krishna, Andhra Pradesh, India*
[c]*Department of Physics, ITER, Bhubaneswar Odisha, India*

*Corresponding author. Tel: (+91) 8895070947; E-mail: ps_rilly@yahoo.com

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ABSTRACT

The polycrystalline $Ba_3Sr_2GdTi_3V_7O_{30}$ material of tungsten bronze structural family was prepared by a high-temperature solid-state reaction technique. Preliminary X-ray diffraction analysis exhibits the formation of single-phase compound with orthorhombic crystal system. Surface micrograph recorded by scanning electron microscopic (SEM) technique has well defined but non-uniformly distributed grains throughout the surface of the pellet sample. Detailed studies of dielectric properties as a function of temperature (306-773 K) and frequencies (10^2-10^6Hz) suggest that the compound has frequency independent diffused dielectric anomaly at a temperature ~620 K which may be related to ferroelectric phase transition which is confirmed from polarization study. The frequency and temperature dependence of impedance property of the material were analyzed using a complex impedance spectroscopy. The Nyquist plots confirmed the presence of grain and grain boundary effect in the material. Copyright © 2012 VBRI press.

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Bana Bihari Mohanty, obtained his M.Sc. degree in Physics in 1992, from Ravenshaw (Auto) College, Utkal University, VaniVihar, India. He is currently working as Lecturer in Physics at Betnoti College, Betnoti, Odisha. Presently he is doing his Ph.D. under the guidance of Dr. P.S.Sahoo at N.O.U., Takatpur, Odisha. In his short (two and half years) research career, he has four numbers of publications in different International Journals. In 2011, he had presented his papers in the International Conferences, ICMAT-2011, held at Suntec City, Singapore, CONIAPS-XIV, at SVNIT, Surat and ICAMP, at IIT, Kharagpur. He has organized two National Seminars as Organising secretary. Presently Mr. Mohanty is Principal Investigator of U.G.C. sponsored Minor Research Project and is working on non-lead based energy harvesting ferroelectric materials.

Priyadarshini Sanghamitra Sahoo, obtained her M.Sc. in Physics from Ravenshaw College in 1988 and M. Phil. in 1990 from Utkal University, Vani Vihar, India. She is awarded her Ph.D. under the guidance of Prof. R.N.P.Choudhary in 2009 from North Orissa University, Takhatpur, Odisha. She is currently working as Lecturer in Physics at Betnoti College, Betnoti, Odisha. In span of 6 years of her research career, she has fourteen numbers of research publications in different highly reputed international/national journals. Recently in 2011, she had presented her papers in the International Conferences, ICMAT-2011, held at Suntec City, Singapore, CONIAPS-XIV, at SVNIT, Surat and ICAMP, at IIT, Kharagpur. She has organized two National Seminars as convener. Dr. Sahoo has completed one U.G.C. sponsored Minor Research Project and presently, she is Principal Investigator of U.G.C. sponsored Major Research Project and is engaged in synthesis and characterization of Lead free ferroelectric-piezoelectric systems for sensor applications. Dr. Sahoo is presently guiding one Ph.D. student in the field of "Ferroelectrics and Multiferroics".

R. N. P. Choudhary (Ex-Professor of Indian Institute of Tecnology, Kharagpur) is currently working as a Professor in the Institute of Technical Education and Research (SOA University) Bhubaneswar(India).In last three decades of his research career he has made outstanding contributions in the field of ferroelectrics. He has published more than five hundreds research papers in highly reputed international/national journals and guided more than four dozens of Ph D students. Other than his research work at different levels he has provided academic services to a large number of organisations in India and abroad. He has served/serving a member of Editorial board of half a dozen of international journals. Professor Choudhary is currently guiding many PhD students in the field of multiferroics".

Introduction

Since the discovery of non-linearity in dielectric constant and polarization (i.e., ferroelectricity) in some oxides of perovskite and tungsten bronze (TB) structures [**1-2**], a large number of oxides of these family have been investigated for devices such as transducers, actuators, capacitors, and nonvolatile ferroelectric random access memory [**3–4**]. Recently, owing to the rapid progress in microwave telecommunications, satellite broadcasting and other related technologies, a number of Ba based TB compounds (lead free) with dielectric constant nearly 100 have attracted much attention of researchers because of those being important in miniaturization of microelectronic devices. It has been found that different ionic size substitutions at the A, B and C sites of TB compounds of a general formula $(A_1)_2(A_2)_4(C)_4(B_1)_2(B_2)_8O_{30}$ can play an important role in tailoring their physical properties for devices. Detailed literature survey on synthesis and characterization of TB structured compounds shows that most of the work has been done on ferroelectric niobates and tantalates [**5-7**]. As the vanadium (V) containing compounds have many interesting features and properties, an attempt has been made to study the role of V on structural, dielectric, polarization and electrical properties some TB structured vandates. In this paper we report the structural, dielectric and electrical properties of $Ba_3Sr_2GdTi_3V_7O_{30}$.

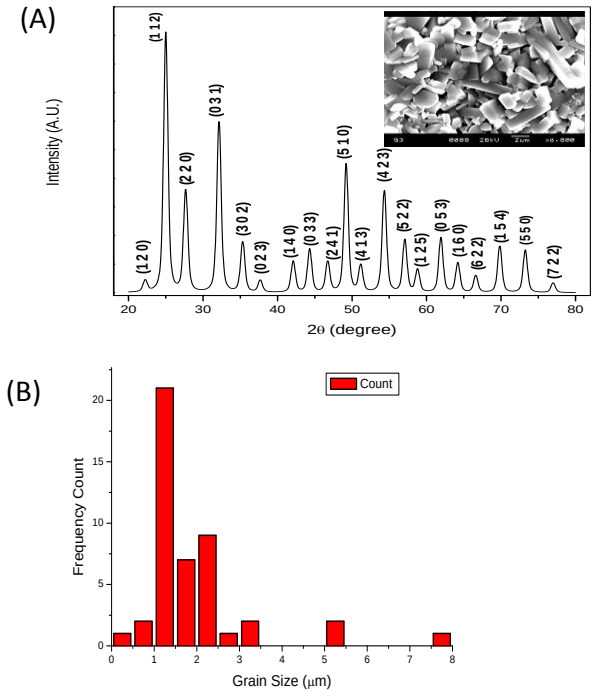

Fig. 1. (A) Room temperature XRD and SEM micrograph (inset) of $Ba_3Sr_2GdTi_3V_7O_{30}$ and (B) histograms showing the grain size distribution.

Experimental

The polycrystalline samples of $Ba_3Sr_2GdTi_3V_7O_{30}$ [BSGTV] was prepared using a high-temperature solid-state reaction techniques. The stoichiometric mixtures of the high purity (>99.9 %) powders of $BaCO_3$, $SrCO_3$, TiO_2, Gd_2O_3 (all from M/s Sarabhai M. Chemicals Pvt. Ltd., India), and V_2O_5 (M/s. Koch Light Ltd., England) were weighed and thoroughly mixed and grinded in an agate mortar to obtain homogeneous mixtures, and calcined in optimized conditions (900^0C for 12 h in air). The calcined powders were re-grinded into very fine powders (with polyvinyl alcohol which was burnt out during sintering) and palletized into disks of 10 mm diameter and about 1-2 mm thickness using iso-static press at a pressure of 5×10^6 N/m^2. The pellets were sintered in air at 950^0C for 12 h. The formation and quality of the compounds were checked by an X-ray diffraction (XRD) technique using an X-ray powder diffractometer (Rigaku, Miniflex) with CuK_α radiation (λ=1.5405 Å) in a wide range of Bragg's angles 2θ ($20^0 \leq 2\theta \leq 80^0$) with a scanning rate of 3^0/ minute at room temperature. Microstructures of sintered pellets were recorded by JEOL –JSM: 5800 model scanning electron microscope (SEM). The electrical properties of the sintered pellets were studied with the data recorded by an impedance analyzer (PSM 1735, model: N 4L) over a wide frequency range (10^2–10^6 Hz) at different temperatures (306-773 K). The hysteresis loops (P-E Loop) of the poled samples were obtained at room temperature using precision material analyzer (M/S. Radiant Technologies Inc., NM and USA) integrated with 4 kV voltage amplifiers.

Results and discussion

Structural analysis

The room temperature XRD pattern (**Fig. 1**) of the calcined powder, which is different from those of the ingredients (JCPDS file nos. 22-1141, 02-0364 and 75-0457), shows the formation of a single phase new compound. The peaks of the pattern were indexed in different cell configurations using software "POWD" [**8**]. An orthorhombic system with a particular unit cell was selected on the basis of the best agreement between observed (obs) and calculated (cal) inter-planer spacing d (i.e., $\Sigma \Delta d = d_{obs} - d_{cal}$ = minimum). The selected unit cell parameters, refined using the least-squares method, are: a = 9.4661(7) Å, b =8.8100 (7) Å, c = 8.5346 (7) Å and volume V =711.75 Å^3 (the number in parenthesis is estimated standard deviation of unit cell parameters).

The unit cell parameters are consistent, and are in good agreement with those reported earlier [**9, 10**] for TB structural family. The crystallite size (P) of $Ba_3Sr_2GdTi_3V_7O_{30}$ (BSGTV) was roughly estimated from the broadening of a few XRD peaks (in wide 2θ range) using the Scherrer's equation [**11**]: $P = K\lambda / (\beta_{1/2} \cos \theta_{hkl})$ (where K = constant = 0.89, λ = 1.5405 Å and $\beta_{1/2}$ = peak width of the reflection at half intensity). The average value of P was found to be ~14 nm. The effects of strain, instrument and other defects on broadening were ignored in the calculation because of collection of XRD pattern on powder. The room temperature SEM micrograph of the compound is shown in **Fig. 1** (inset). It was found that the grains are in-homogeneously but uniformly distributed over the entire sample surface. The mean grain size

evaluated from the histogram was found to be in the range of 1.88 µm. A similar type of microstructure was found in many materials of this family [**12, 13**].

Dielectric study

The temperature dependence of relative dielectric constant (ε_r) for BSGTV is shown in **Fig. 2.** The relative dielectric constant first increases and then decreases with rise in temperature showing a dielectric anomaly. The dielectric anomaly was observed at 620 K (T_c) (where ε_{max} = 345 and 203 at 5 and 50 kHz respectively). However, no such anomaly was observed in temperature dependent loss tangent (tanδ) graph (**Fig. 2**).

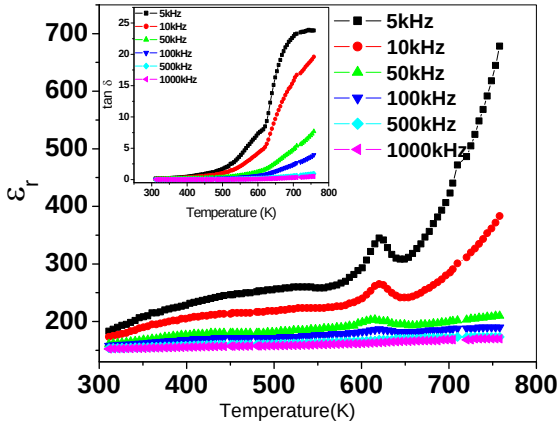

Fig. 2. Variation of ε_r and dielectric loss (tan δ) at 1kHz(inset) -50 kHz of $Ba_3Sr_2GdTi_3V_7O_{30}$.

The dielectric anomaly was assumed to be related to ferroelectric–paraelectric phase transition. A similar type of anomaly was found in other materials of this family [**10, 12**].

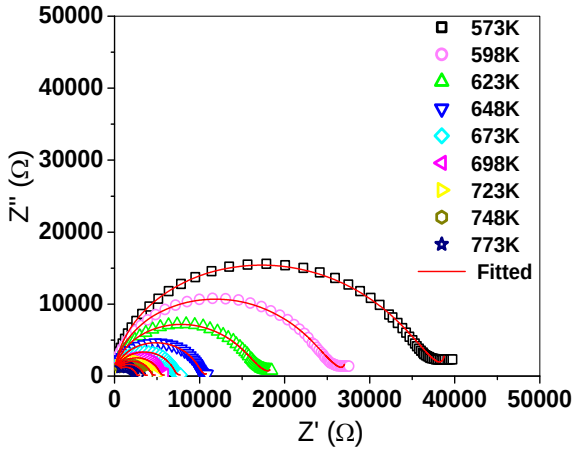

Fig. 3. Nyquist plot of $Ba_3Sr_2GdTi_3V_7O_3$ at different temperatures.

Impedance study

Fig. 3 shows temperature dependence Nyquist Plots of BSGTV measured at some selected temperatures (573–773 K). The spectra is characterized by the appearance of a two merged semicircular arcs whose pattern of evolution changes with rise in temperature indicating the contribution of both grain and grain boundary within the material sample [**12**] which is modeled (fitted) in terms of an equivalent circuit comprising of a series combination of two parallel RC circuits (inset). In addition, the shifting of point of intercept of the arcs on the real axis has towards the origin suggests a decrease in the resistive behavior of the sample assisted by the grain boundary conduction with rise in temperature [**13**].

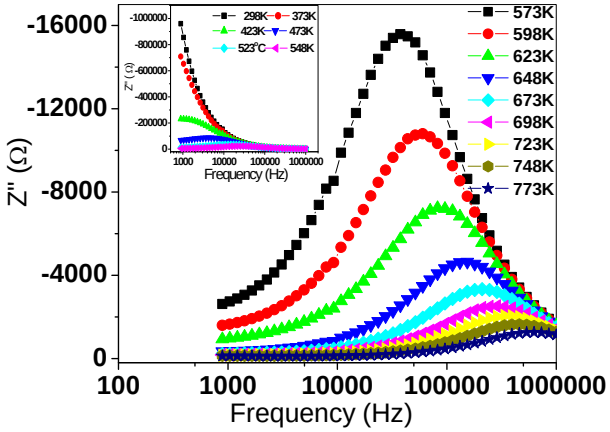

Fig. 4. Variation of Z″ with frequency of $Ba_3Sr_2GdTi_3V_7O_{30}$ at different temperatures.

Fig. 4 shows the loss spectrum (Z″-f graph). The non-existence of Z″ peak in the temperature region below 548 K is due to the absence of current dissipation in the material. Subsequently, the appearance of peak (>573 K) suggests the existence of relaxation properties of the material. The broadening of peaks on increasing temperature confirms the existence of temperature dependent relaxation phenomena in the material. This may be due to the immobile species/electrons at low temperatures and defect/vacancies at high temperatures. The magnitude of Z″ decreases with the shifts of peaks towards higher frequency side. Finally, all the curves merge in one at the high-frequency, which may be due to the accumulation of space charges of the material.

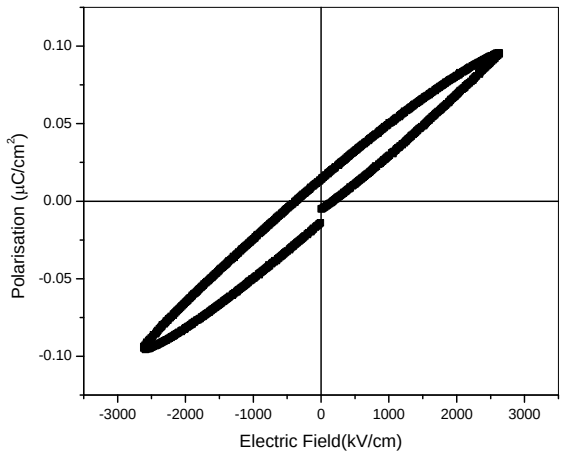

Fig. 5. Room temperature P-E loop of $Ba_3Sr_2GdTi_3V_7O_{30}$.

Polarization study

The ferroelectric hysteresis loop of poled samples was recorded at room temperature with the application of electric fields of about 4kV/cm (**Fig. 5**) which confirms the ferroelectric nature. The remanent polarization ($2P_r$) is found to be 0.028 μC/cm^2. Similar type of hysteresis loop was observed in other materials of same family [**13, 14**].

Conclusion

The polycrystalline compound BSGTV, formed by high-temperature solid-state reaction technique, is characterized to be single phase with orthorhombic structure at room temperature and undergoes dielectric anomaly at around 620 K. The comparatively low room temperature dielectric constant (149 at 50 kHz at room temperature) indicates that these materials may have attractive benefits in electro-optic and infrared pyro-electric detector applications when grown in bulk single crystal or thin-film form. The electrical conduction in this compound is due to bulk and grain boundary effect. The bulk resistance decreases with rise in temperature indicating a typical NTCR behavior of the compound.

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