

Impedance Spectroscopy of Zr Modified Ba₅SmZr₃V₇O₃₀ Ceramic

B. K. Giri¹, B. B. Mohanty², P. S. Sahoo^{3*}, R. N. P. Choudhary⁴

¹Department of Physics, Barbil College, Barbil, Orissa, India
²Department of Physics, Betnoti College, Betnoti, Mayurbhanj, Orissa, India
³Department of Physics, North Orissa University, Baripada, Odisha, India
⁴Department of Physics, ITER, Bhubaneswar, Odisha, India
Email: *s_rilly@yahoo.com

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Abstract

 $Ba_5SmZr_3V_7O_{30}$ is a new tungsten bronze structured ceramic compound prepared by substituting Zr at Ti site in $Ba_5GdTi_3V_7O_{30}$ following high-temperature solid-state reaction route. The X-ray diffraction analysis of the compound confirms the formation of single-phase orthorhombic structures at room temperature. Surface morphology of the compound was studied by scanning electron microscopy. Using a Hioki LCR meter, the effects of temperature ($32^{\circ}C - 500^{\circ}C$) and frequency ($10^2 - 10^6$ Hz) on structural and electrical properties were studied. Detailed analysis of impedance parameters furnishes a better conception of the electrical properties and type of relaxation processes in the material. The plateau region of the Z'~ frequency plot also indicates the presence of relaxation process in the material. The bulk resistance is observed to be decreased with rise in temperature showing a typical negative temperature coefficient of resistance (NTCR) behavior.

Subject Areas

Functional Materials

Keywords

Ceramics, Tungsten Bronze Structure, Solid-State Reaction, X-Ray Diffraction

1. Introduction

Compounds of Tungsten bronze (TB) structure family have drawn special attention due to their technological applications [1] [2] [3] [4] including ferroelectric memory devices, electro optical devices, and actuators [5]. The TB structure consists of a skeletal framework of BO_6 octahedra, sharing corners to form three different types of tunnels parallel to the c-axis in the unit cell of a general formula, $[(A_1)_2(A_2)_4C_4][(B_1)_2(B_2)_8]O_{30}$ [6]. The emergence of nanoscience & technology has entirely changed the direction of studies on eco-friendly (lead-free) materials and puts them at the forefront of scientific evolution with considerably enhanced physical properties suitable for a wide variety of challenging applications. Looking to the above, we have synthesized $Ba_5SmZr_3V_7O_{30}$ and studied the structural and electric properties for device applications.

2. Experimental Details

A suitable stoichiometric ratio of precursors; $BaCO_3$, Sm_2O_3 , TiO_3 , V_2O_5 , ZrO_2 of high purity (>99.9%) were weighed, and mixed mechanically in an agate mortar first in air and then in wet methanol condition for 3 h each to get a homogenous mixture of the compound. After proper mixing the compound was calcined using an alumina crucible at an optimized temperature and time (950°C, 12 h). Cylindrical pellets of diameter 10 mm and thickness 1 - 2 mm were made out of the calcined powder using a hydraulic press at a pressure of $\sim 4 \text{ N/m}^2$. The pellets were then sintered in an air atmosphere at an optimized temperature and time (950°C, 12 h) and then the faces were polished flat with fine emery paper. The pellets were finally coated with high purity conductive silver paint, and were dried at 150°C for 2 h before carrying out electrical measurements. X-ray diffraction (XRD) data (pattern) of the material was obtained in a wide range of Bragg angle $2\theta (20^\circ \le 2\theta \le 80^\circ)$ at a scanning speed of 3°min^{-1} by an X-ray diffractometer (Rigaku, Miniflex) with CuKa radiation ($\lambda = 1.5405$ Å) 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 32°C - 500°C and frequency range of 1 kHz to 1 MHz, using a computer-controlled Hioki LCR meter.

3. Results and Discussion

3.1. Structural Analysis

The XRD pattern of the Ba₅SmZr₃V₇O₃₀ (BSZV) sample is shown in **Figure 1**. Presence of sharp and single reflection peaks which are different from those of the ingredients confirms the formation of new single-phase compound. All the peaks were indexed taking their 2 θ values using a computer program package, "POWDMULT" [7] 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.*, Σ (d_{obs} – d_{cal}) = minimum), an orthorhombic unit cell was selected with lattice parameters: a = 24.3193 (29) Å, b = 3.9569 (29), c = 10.7005 (29) Å (estimated standard deviation in parenthesis) which are consistence with the reported ones [8]. The coherently scattered crystallite size (D) of the compound was determined using



Figure 1. Room temperature XRD pattern (left), SEM (inset) and histogram (right) of Ba₅SmZr₃V₇O₃₀ ceramics.

Scherrer's equation; $P = 0.89\lambda/(\beta_{1/2}\cos\theta_{hkl})$, where $\lambda = 1.5405^{\circ}$ Å and $\beta_{1/2} =$ peak width of the reflection at half maxima [9]. 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 was found to be ~15 nm. The SEM micrograph of the compound at room temperature is shown in **Figure 1** (inset). The avarage grain size evaluated from the histogram was 1.8 µm by Gaussian fitting.

3.2. Impedance Study

Complex impedance spectroscopy (CIS) [10] is an important experimental technique to differentiate grain (intragrain) and grain boundaries (intergrain) contributions in transport properties of the material.

The temperature dependent Nyquist Plots (fitted complex impedance spectrum) of BSZV measured at some selected temperatures ($350^{\circ}C - 500^{\circ}C$) are shown in **Figure 2**. Single semicircular arcs are noticed at lower temperature (inset) with a single relaxation process confirms that the impedance contribution is mainly due to grains. But two merged semicircular arcs are observed at high temperatures ($\geq 350^{\circ}C$), explaining the electrical response is mainly due to the grain and grain boundary effect and are not comparable. The merging of the semicircular arcs is a clear indication of the above two resistances are not comparable [11]. There is a decrease in the area of the semicircles on increasing temperature, suggests the variation of relaxation process of the sample with the temperature in the studied frequency range [11]. The semicircles have their centers located below the real axis, indicating the presence of relaxation species, and hence non-Debye type of relaxation process occurs in the materials.

Figure 2 (middle) shows the frequency variation of Z' at some selected temperatures (350°C - 500°C). The figure shows dispersion at low frequency region followed by a plateau region, and finally all the curves coalesce above 500 kHz irrespective of temperature. There is a decrease in Z' values with frequency may



Figure 2. Nyquist plot (left), Z'~ frequency (middle) and Z' frequency (right) graph of Ba₅SmZr₃V₇O₃₀.

be caused by a slow dynamics relaxation process in the material due to space charges. The appearance of plateau region is related to frequency independent (dc conductivity) electrical property of the material. The merger of the plots at higher frequency may be referred to the release of space charge as a result of reduction in the barrier properties of material with the rise in temperature thereby enhancing the AC conductivity of material with temperature at higher frequencies [10]. The negative temperature coefficient of resistance (NTCR) type behavior in the material is confirmed from the decreasing value of Z' with rise in both temperature and frequency which is an important property of semiconductors.

Figure 2 (right) shows the loss spectrum (logf $\sim Z^{\prime\prime}$). Low frequency dispersion is marked for compounds which is due to release of space charges (generally ions). Like Z', the value of Z'' decreases on increasing frequency at all the temperatures. The broadening of peaks on increasing temperature confirms the existence of temperature dependent relaxation phenomena in the material [11]. This may be due to defect/vacancies at high temperatures. Further, the magnitude of Z'' decreases with the shift of peaks towards higher frequency side. Merging of the curves in the high-frequency region, may be due to the accumulation of space charge of the material.

4. Conclusion

The polycrystalline sample of BSZV was prepared by a high-temperature solid-state-reaction route. X-ray analysis confirms the orthorhombic crystal structure at room temperature. The surface morphology of the compound is studied through SEM. From the impedance study, relaxation process is non-Debye type and the loss spectra suggest the existence of hoping mechanism of electrical conduction in the materials. The relaxation frequencies shifted to higher frequency side with increase in temperature. The high temperature complex impedance plots reveal the main contribution of grain and grain boundary in it.

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References

- Zhang, L.X., Chen, W. and Ren, X. (2004) Large Recoverable Electrostrain in Mn-Doped (Ba,Sr) TiO₃ Ceramics. *Applied Physics Letters*, 85, 5658-5660. https://doi.org/10.1063/1.1829394
- She, W.L., Lee, K.K. and Lee, W.K. (2000) All Optical Quasi Steady-State Photorefractive Spatial Solitons. *Applied Physics Letters*, 85, 2498-2501. https://doi.org/10.1103/PhysRevLett.85.2498
- [3] Lines, M.E. and Glass, A.M. (1977) Principles and Applications of Ferroelectrics and Related Materials. Clarendon Press, Oxford.
- [4] Jaffe, B., Cook, W.R. and Jaffe, H. (1971) Piezoelectric Ceramics. Academic Press, London.
- [5] Uchino, K. (1997) Piezoelectric Actuators and Ultrasonic Motors. Kluwer Academics, Boston.
- [6] Neurgaonkar, R.R., Kalisher, M.H., Lim, T.C., Staples, E.J. and Keester, K.L. (1980) Czochralski Single Crystal Growth of Sr_{.61}Ba₃₉Nb₂O₆ for Surface Acoustic Wave Applications. *Materials Research Bulletin*, **15**, 1235-1240. https://doi.org/10.1016/0025-5408(80)90025-2
- [7] Wu, E. (1989) POWD, An Interactive Powder Diffraction Data Interpretation and Index Program. Ver. 2.1, School of Physical Science, Flinders University South Bedford Park, Australia.
- [8] Geiss, E.A., Scott, B.A., Burns, G., O'Kane, D.F. and Segmuller, A. ((1989) Alkali Strontium-Barium-Lead Niobate Systems with a Tungsten Bronze Structure: Crystallographic Properties and Curie Points. *Journal of American Ceramic Society*, 52, 276. <u>https://doi.org/10.1111/j.1151-2916.1969.tb09183.x</u>
- [9] James, A.R., Priya, S., Uchino, K., Srinivas, K., Kiran, V.V. and Japanese, J. (2002) Part 1: Regular. Papers Short Notes & Review Papers, Investigation of Intrinsic Defect Structure in 0.91 Pb (Zn_{1/3}Nb_{2/3})O₃-0.09PbTiO₃ Single Crystal through AC Conductivity. *Appl. Phys.*, **41**, 5272-5276.
- [10] Klug, H.P. and Alexander, L.E. (1974) X-Ray Diffraction Procedures for Polycrystalline and Amorphous Materials. Willey-Interscience, New York.
- [11] Jonscher, A. K. (1977) The Universal Dielectric Response. *Nature*, 267, 673-679. <u>https://doi.org/10.1038/267673a0</u>