

Effect of Strontium Substitution on Impedance Properties of $\text{Ba}_5\text{GdTi}_3\text{V}_7\text{O}_{30}$ Ceramics

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How to cite this paper: Mohanty, B.B., Sahoo, P.S., Giri, B.K., Panda, J.N. and Choudhary, R.N.P. (2018) Effect of Strontium Substitution on Impedance Properties of $\text{Ba}_5\text{GdTi}_3\text{V}_7\text{O}_{30}$ Ceramics. *Journal of Modern Physics*, 9, 620-627.

<https://doi.org/10.4236/jmp.2018.94043>

Received: January 29, 2018

Accepted: March 18, 2018

Published: March 21, 2018

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Abstract

A series of compounds $\text{Ba}_{5-x}\text{Sr}_x\text{GdTi}_3\text{V}_7\text{O}_{30}$ ($x = 0 - 5$), belonging to tungsten bronze family were prepared by a high-temperature solid-state reaction route. Using X-Ray diffraction technique and Scanning Electron Micrograph, the formation and surface morphology of the compounds were studied. The X-Ray diffraction study informs the formation of single-phase orthorhombic structures. The substitution of Sr ion with increasing concentration in the compounds as per formula resulted in a variation of the electrical properties. Study of electrical properties using impedance analyzer exhibits: 1) the presence of negative temperature coefficients of resistance (NTCR) behavior; 2) presence of temperature dependent electrical relaxation phenomena; 3) evidences of single electrical relaxation attributed to the presence of bulk contribution to the electrical properties for pure $\text{Ba}_5\text{GdTi}_3\text{V}_7\text{O}_{30}$ compound; 4) an enhancement in the barrier to the mobility of charge carriers on Sr-substitution. The effects of Sr on changes in the electrical conductivity as a function of temperature at different frequency are described based on impedance spectrum analysis.

Keywords

Ferroelectrics, Complex Impedance Spectroscopy, Electrical Conduction, Modulus Spectroscopy

1. Introduction

The discovery of ferroelectricity in BaTiO_3 [1], fascinated the young researchers

and scientists into the field of materials research. As a result, a large number of oxides of different structures such as perovskite, tungsten bronze, layer structure etc., have been studied for their applications in devices like transducers, actuators, multi-layer capacitors, ferroelectric random access memory and display, microwave dielectric resonators etc. [2]-[7]. This activated the researchers to develop and design thermally stable new electronic materials possessing high dielectric constant and low dielectric loss. In this context, some ferroelectric oxides of tungsten bronze (TB) structural family have been widely investigated because their favorable dielectric properties show wide applications in devices. The TB structure consists of a complex array of distorted BO_6 octahedral sharing corners in such a way that three different types of interstices (A, B and C) are available for cation substitutions in a general formula $(\text{A}_1)_2(\text{A}_2)_4(\text{C})_4(\text{B}_1)_2(\text{B}_2)_8\text{O}_{30}$. Mono or divalent cations can be accommodated at A_1 and A_2 sites, tri or pentavalent cations at octahedral sites B_1 and B_2 [8], with C site (smallest interstice) generally empty; hence the general formula for tungsten bronze structure is $\text{A}_6\text{B}_{10}\text{O}_{30}$. It is an observed fact that the substitution of varieties of cations at the A and B sites (with different size and charge distribution) causes a significant variation in the physical properties of the materials [9]. Further, since the structural and/or micro-structural changes in a system drastically modify their physical properties, a detailed study of electrical (impedance) properties of Sr-substituted $\text{Ba}_5\text{GdTi}_3\text{V}_7\text{O}_{30}$ (BSGTV) assumes greater significance in order to have a complete picture of properties of these ceramics. This aspect has motivated us for the present work comprising of a detailed analysis of the effect of dopant concentration on electrical properties of Sr-modified BGTV.

2. Experimental

The series of ceramic compound $\text{Ba}_{5-x}\text{Sr}_x\text{GdTi}_3\text{V}_7\text{O}_{30}$ (BSGTV) ($x = 0 - 5$) have been synthesized with Sr substitution by mixed oxide process. High purity (AR grade) oxides and carbonates, BaCO_3 , SrCO_3 , Gd_2O_3 , TiO_2 , V_2O_5 (M/S Sarabhai M. Chemicals, India) in a suitable stoichiometry were weighed, thoroughly mixed and then grounded in dry (air) and wet (methanol) medium for 2 h each in an agate mortar. Calcination of the grounded mixtures was done at an optimized temperature and time (950°C for 24 hs). Pellets were prepared from the calcined powder with addition of a small amount of polyvinyl alcohol by applying a uniaxial pressure of $5 \times 10^6 \text{ N/m}^2$. The pellets were subsequently sintered at an optimized temperature $10,000^\circ\text{C}$ for 12 hs. in an air atmosphere using high purity alumina crucibles. The formation and quality of the compounds were checked using X-ray diffraction (XRD) technique. The X-ray diffraction patterns of the compounds were recorded at room temperature using an X-ray powder diffractometer (Rigaku, Miniflex) with CuK_α radiation (1.5405 \AA) in a wide range of Bragg's angles 2θ ($20^\circ \leq 2\theta \leq 80^\circ$) with a scanning rate of 30/min. The XRD peaks of all the samples are observed to be different from that of the ingredients, suggesting the formation of new single phase compounds. All the peaks were indexed taking their 2θ values using a computer program package,

“POWDMULT” [10] 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.*, $\Sigma(d_{\text{obs}} - d_{\text{cal}}) = \text{minimum}$), an orthorhombic unit cell was selected. The Structural properties of compounds are reported earlier [11]. Surface morphology of the sintered pellets was studied at room temperature using scanning electron microscope (SEM) (JEOL-JSM-5800). The samples were preheated to 1500°C for 4 hs to remove the moisture, if any. Measurements of impedance, electrical modulus and conductivity as a function of temperature (30°C - 500°C) at different frequency (1 kHz - 1 MHz) were carried out using computer interfaced impedance analyzer PSM 1735, model: N4L. Silver electrodes were deposited on the polished surfaces of pellets to perform the above studies.

3. Results and Discussion

3.1. Impedance Analysis

Impedance properties arise due to intragrain, intergrain and electrode effects. Generally space charges are created due to the disparity in defect concentration and the inhomogeneity of the applied field, which does not allow the speedy recombination of the charges [12]. As a result, the space charges existing in the samples may well be trapped in the grain boundary and grain-electrode interfaces. The motion of charges could occur in a variety of ways, namely charge displacement (long-range or short-range), dipole re-orientation, space charge formation etc.

Complex impedance spectroscopy (CIS) is a very important experimental technique [13] used to characterize the electrical properties (*i.e.*, transport properties) of the polycrystalline BSGTV samples in a wide range of frequencies (10^3 - 10^6 Hz) at different temperatures (30°C - 500°C).

Figure 1 ($x = 0$ to $x = 5$) shows complex impedance spectra (Nyquist plots) for different Sr concentration of BSGTV at some selected temperatures.

Presence of single semicircular arcs at all studied temperatures for $\text{Ba}_5\text{GdTi}_3\text{V}_7\text{O}_{30}$ compound suggests the electrical response is completely dominated by the bulk properties of the material. But with Sr ion substitution at Ba site second semicircular arc tends to appear in BSGTV compounds indicating the electrical response in the materials are due to grain and grain boundary effect. The merging of the semicircular arcs indicates that the two resistances are not comparable [14].

For all the compounds (from $x = 0$ to $x = 5$) at all studied temperatures with rise in temperature, shifting in intercept of the semicircular arcs on real (x) axis towards the origin, informs the decrease in resistance of the samples (frequency independent impedance) with rise in temperature and it confirms the NTCR behaviour of the materials like semiconductors.

3.2. Modulus Analysis

Complex modulus analysis is an alternative method for the study of electrical

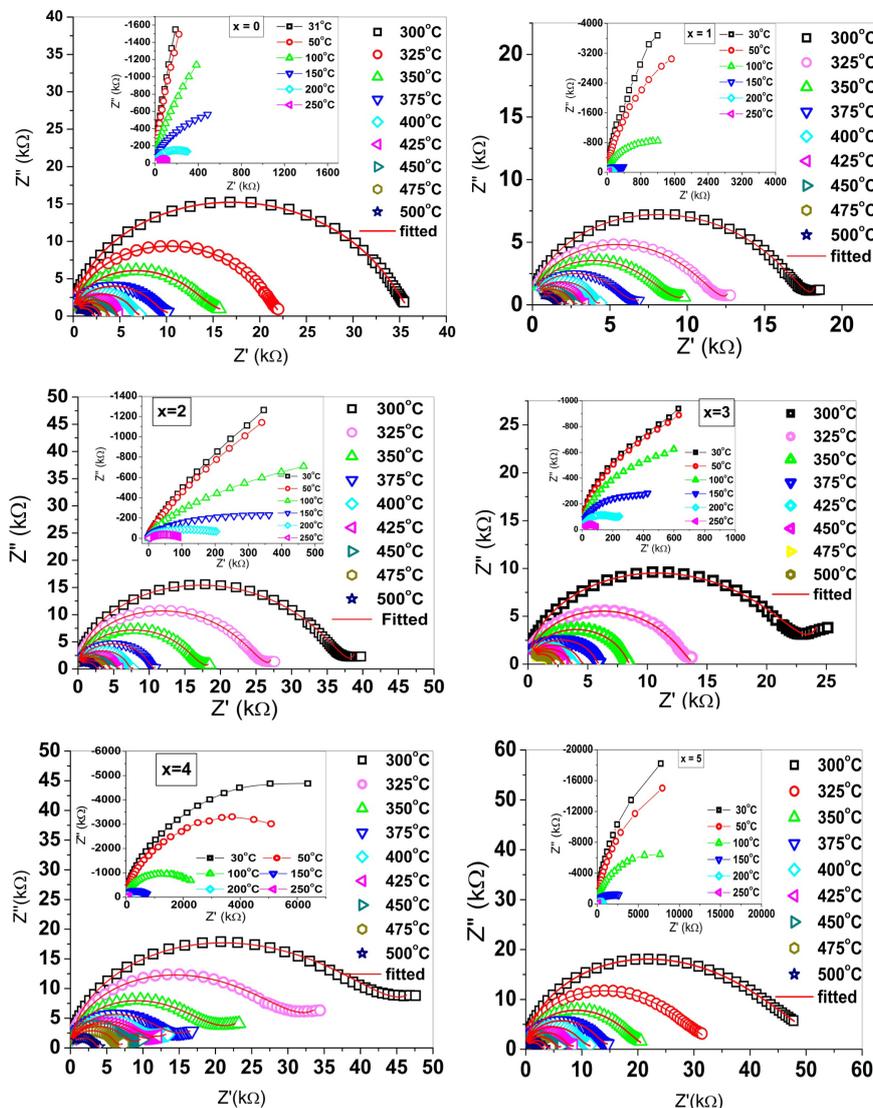


Figure 1. Z' vs Z'' plots of $Ba_{5-x}Sr_xGdTi_3V_7O_{30}$ ($x = 0 - 5$) Compounds at different temperatures.

behaviour of the samples based on polarization analysis. The desirable feature of following complex electric modulus formalism is that it can demarcate against electrode polarization and grain boundary conduction process. This is particularly useful for separating components with similar resistance but different capacitance.

The modulus spectra are thrashed by the smallest capacitance (C) [15] and impedance spectra by the largest R values obtained from the parallel RC elements in the complex impedance spectrum. According to Moynihan, Boesch, and Laberge [16] sometimes when it becomes difficult for the analysis of the dielectric dispersion data in absence of a well-defined dielectric loss $\epsilon(\omega)$ peak, one can get information about the relaxation mechanism from the dielectric modulus representation.

Figure 2 represents the Complex modulus spectrum of $Ba_{5-x}Sr_xGdTi_3V_7O_{30}$

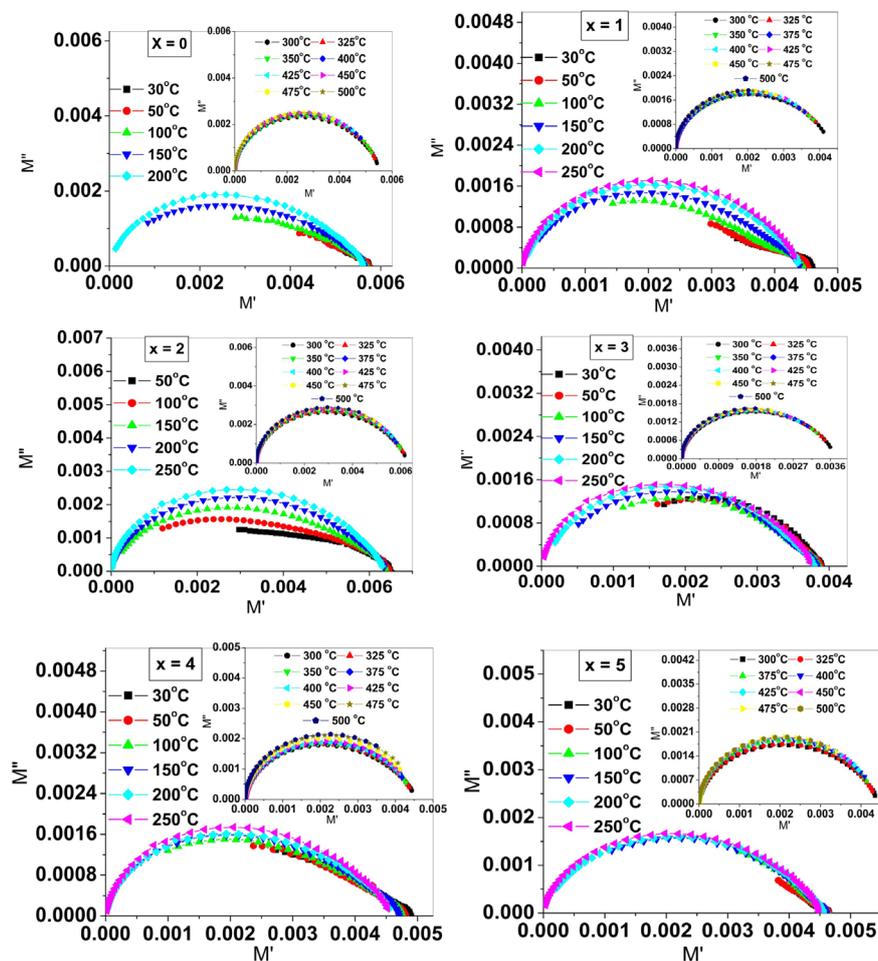


Figure 2. M'' versus M' plots of $Ba_{5-x}Sr_xGdTi_3V_7O_{30}$ ($x = 0 - 5$) Compounds at different temperatures.

($x = 0 - 5$) at different temperatures. The M'' vs M' plots start from low frequency sides at low temperatures, due to dominating grain boundary response and also high capacitive nature of all the samples at such temperatures. Marked changes in the shape of the spectra are observed with rise in temperature suggesting a probable change in the capacitance of the materials.

Broadening observed in the semicircular arcs in Nyquist plot of $Ba_5GdTi_3V_7O_{30}$ at low temperature, showing an involvement of both bulk and grain boundary towards electrical capacitance in the ceramic samples on increasing Sr-concentration the capacitance of the material decreases, thereby implies an increase in impedance which was also observed in impedance graphs. The decentralization of the curves in these spectra for all the compounds indicates the spread of relaxation with different mean time constant and non-Debye type of relaxation in these materials.

3.3. Comparison of Relaxation Process in Impedance and Modulus Loss Spectra

Figure 3 demonstrates a simultaneous representation of frequency variation of

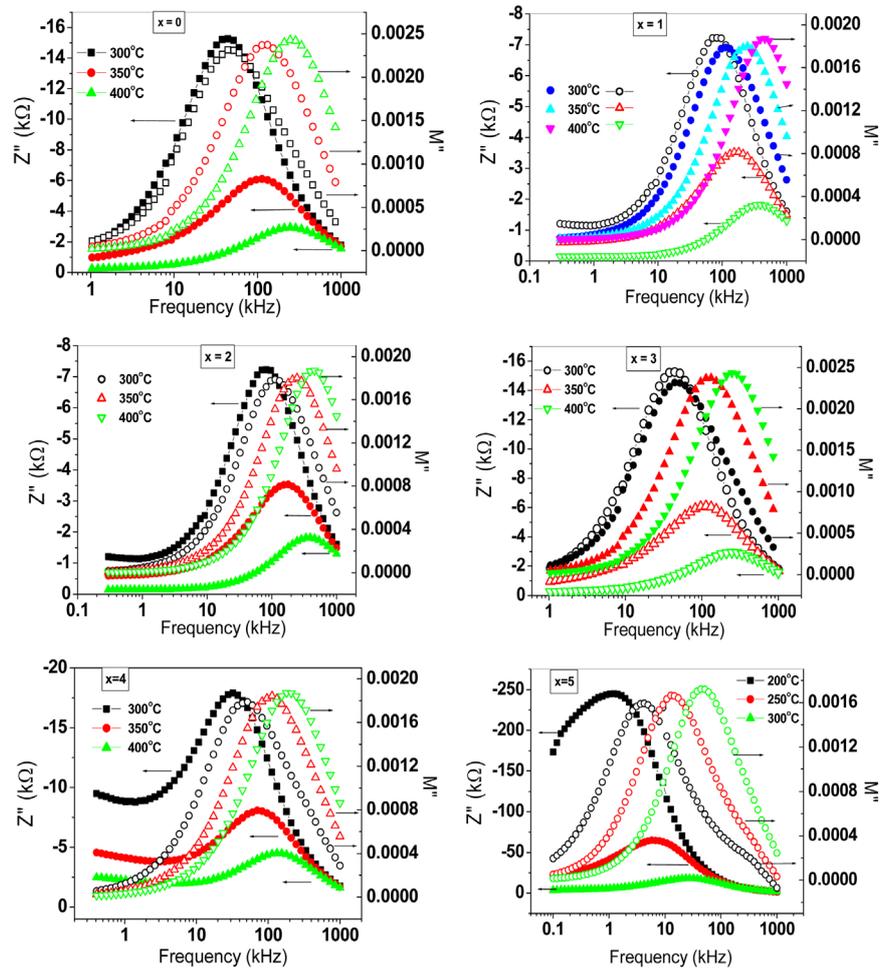


Figure 3. Frequency response of Z'' and M'' of $Ba_{5-x}Sr_xGdTi_3V_7O_{30}$ ($x = 0 - 5$) Compounds at three different temperatures.

Z'' and M'' for both the groups of compounds at different temperatures.

The two data *i.e.*, Z'' vs. frequency and M'' vs frequency, instead of collapsing to a single curve shows two peaks at two different frequencies which is due to two relaxation processes; first one (solid symbols) in Z'' vs. frequency corresponding to grain boundary relaxation caused by non-localized conduction and second one (hollow symbols) in M'' vs frequency corresponding to bulk relaxation caused by localized conduction in polycrystalline sample. In addition to the above physical mechanisms there exists a finite probability of ion diffusion from grain boundary to grain, suggesting a polarization relaxation resulting in stretching of conductivity response [17]. However, with increasing Sr concentration, this peak gradually diminishes. This is possibly due to increase in ionic conductivity in ceramic samples. This can also be ascribed to accumulation in mobility due to increase in defects with rise in Sr concentration.

4. Conclusion

An analysis of the electrical properties of Sr-modified $Ba_5GdTi_3V_7O_{30}$ is reported

in this paper using an AC impedance technique. Conventional Mixed Oxide process was used to synthesize the compound which was confirmed by X-ray diffraction studies. Appearance of two merged semicircular arcs at high temperatures ($\geq 300^\circ\text{C}$) for Sr modified BGTV compounds observed in the complex planes, interprets that the electrical response of the compounds is due to the grain and grain boundary effect, whereas, the presence of temperature dependent single semicircular arcs for pure BGTV compound shows that the electrical response is due to grain only. It has been observed that Sr substitution at the Ba-site has enhanced the barrier properties of the material, which results in a corresponding decrease in the electrical conduction. This may be due to the weakening in the capacitive (reactive) effects resulting in an enhancement of the bulk resistance on Sr substitution. Modulus analysis indicated the presence of non-Debye type conductivity relaxation in the materials.

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