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Effect of Zr substitution on the conductivity of $Ba_5GdTi_3V_7O_{30}$ ceramics

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Abstract : $Ba_5GdTi_2ZrV_7O_{30}$,-a polycrystalline tungsten bronze structure compound was developed by Solid State reaction route at high temperature (950^0C). XRD analysis confirmed orthorhombic structure of the compound. SEM study revealed non-uniform shape grains distributed homogeneously on the surface of the samples. No dielectric anomaly is observed within experimental temperature range. The variation of the ac conductivity with inverse temperature (303 K – 773K) exhibits semiconductor type negative temperature coefficient of resistance (NTCR) behavior. The separate values of activation energy in different temperature regions, recommend the mixed-type conduction process (i.e., ionic–polaronic and space charge generated from the oxygen ion vacancies) in the material.

Keywords*:* TB Structure; Solid-state reaction; XRD analysis.

1. Introduction

The different structural forms (perovskite, tungsten bronze etc.) of dielectric and ferroelectric materials have always been at the prime focus of scientific and industrial research. Eco-friendly lead free $BaTiO_3$, $LiNbO_3$, potassium lanthanum niobate, barium sodium niobate etc., both in single crystal and polycrystalline forms have found extensive attention in the field of materials research. The emergence of nanoscience & technology have enhanced the focus on this class of eco-friendly materials taking them to the cutting edge of scientific advancements

with significant enhancement in their properties appropriate for a diverse range of demanding applications.

The tungsten-bronze (TB) structured materials are prime members of family of dielectric materials, which exhibit exciting ferroelectric, pyroelectric, piezoelectric, and nonlinear optical properties for applications in various electric devices, such as transducers, actuators, capacitors, and ferroelectric random-access memory [1-3]. Recent development in research shows that a number of Ba based TB compounds possessing high dielectric constant have drawn much attentions for their importance in the miniaturization of microelectronic devices [4].The present work describes the synthesis and characterization of the physical properties of a single-phase polycrystalline compound belonging to TB Structure with formula $Ba_5GdTi_2ZrV_7O_{30}$. In this paper, we have carried out a systematic study on conductivity of the polycrystalline ceramic $Ba_5GdTi_2ZrV_7O_{30}$, prepared through a standard solid-state reaction process.

2. Experimental details

2.1. Material preparation

The polycrystalline sample $Ba_5GdTi_2ZrV_7O_{30}$ (BGTZV) was prepared using high purity (>99.9%) precursors; Ba_2CO_3, Gd_2O_3, TiO_2, ZrO_2, V_2O_5 by Mixed Oxide Process. These precursors were taken in appropriate amount to satisfy stoichiometry of $Ba_5GdTi_2ZrV_7O_{30}$,with formula;

$$5BaCO_3+1/2Gd_2O_3+(3-x)TiO_2 +xZrCO_3+7/2V_2O_5 = Ba_5GdTi_{3-x}\ Zr_xV_7O_{30}$$

The mixing of the ingredients was done mechanically in an agate mortar for 3h in air atmosphere followed by wet atmosphere (methanol) to get homogeneous mixture. Subsequently, it is calcined in an alumina crucible starting from 650 ^{o}C in steps of 50^{o}C and formation of compound was checked by XRD analysis. The formation of compound was obtained at an optimized temperature and time (950^{0}C, 12h), which was confirmed from XRD analysis. Cylindrical pellets of diameter about 10 mm and thickness 1-2 mm are made from the calcined powder so obtained was cold pressed into cylindrical pellets of diameter 10 mm and thickness 1-2 mm using a hydraulic press at a pressure of ~ $4x10^6N/m^2$ with polyvinyl alcohol (PVA) as binder which burnt out during high temperature sintering. The pellets were then sintered in 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

conductive silver paint, and then dried at 150^0C for 2h before carrying out electrical measurements to make them moisture free.

2.2. Material characterization

The room temperature X-ray diffraction (XRD) data (pattern) of the material iss obtained in a wide range of Bragg ̀s angle 2θ ($20^0 \leq 2\theta \leq 75^0$) at a scanning speed of 3^0 min^{-1} by an X-ray diffractometer (Rigaku, Miniflex) with CuKα radiation (λ= 1.5405Å). Scanning electron micrograph of the material is recorded with a high-resolution scanning electron microscope (SEM: JOEL-JSM model: 5800F) to study the surface morphology of the sample. The dielectric and impedance studies are carried out in the temperature range of 33^0 -500^0C and wide frequency range of 100Hz to 1MHz, using a computer-controlled impedance analyzer (Hioki LCR meter).

3. Results and discussion

3.1. Structural and microstructural analysis.

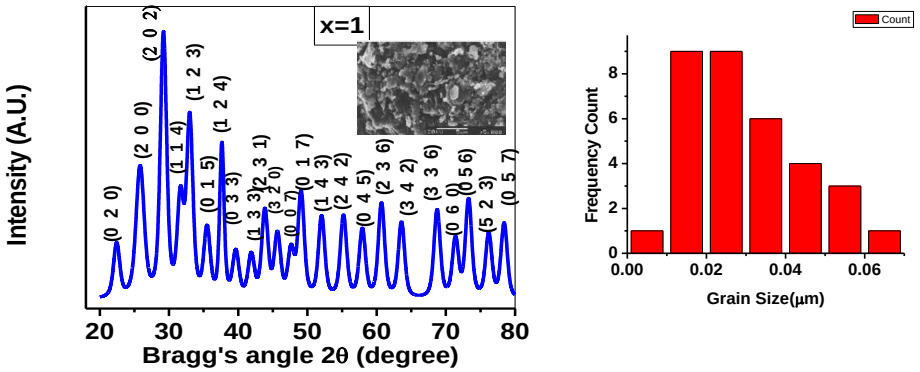

Fig.1. Room temperature XRD patterns(left), SEM micrographs (inset) and histogram (right) of $Ba_5GdTi_2ZrV_7O_{30}$.

The XRD pattern of the BGTZV is shown in Figure 1.The XRD pattern observed in the material are different in nature from that of the ingredient oxides confirming the formation of a single-phase new compound. All the reflection peaks are indexed and the lattice parameters are determined in various crystal systems and with cell configurations using computer software "POWDMULT" [5].On the basis of the best agreement between observed (obs) and calculated (cal) inter-planer distance *d* (i.e., Σ (d_{obs} −d_{cal}) = minimum), a suitable unit cell (orthorhombic system) with lattice parameters: a=6.87729(38) Å, b=7.9184(38) Å, c= 13.3490(38) Å (estimated standard deviations in parentheses) were chosen.

The crystallite size of the sample was estimated from the broadening of the peaks ($\beta_{1/2}$) using Scherrer's equation [6]; $P= K\lambda/\beta_{1/2} \cos\theta_{h\ k\ l}$, where K = constant= 0.89, λ = 1.5405 Å and $\beta_{1/2}$ = peak width of the reflection at half height. The average crystallite size of the compound was found to be 9 nm.

Figure 1 (inset) shows scanning electron micrograph of BGTZV compound describing the surface property and microstructure. The SEM study exhibits the polycrystalline texture of the compound. Nearly homogeneously distributed grains are observed throughout the surface. These are of non-uniform shape like triangular, spherical etc. Microstructure of this compound is comparable with that of other materials of this family [7].

3.2. ac conductivity

The ac conductivity (σ_{ac}) of the material is calculated by using the formula:

$$\sigma_{ac}= \epsilon_o\epsilon_r\omega \tan\delta$$

Where ϵ_o is the permittivity of free space, ε_r is the relative permittivity, ω is the angular frequency and tan δ is the dielectric loss.

3.2.1Variation of ac conductivity with inverse absolute temperature at some selected frequencies

Fig.2. shows the variation of σ_{ac} with inverse absolute temperature (10^3/T) at different frequencies for BGTZV compound. The solid line in the figure shows the linear fit. The activation energy measured from the slope of the curve at different temperatures has been compared in Table.1.

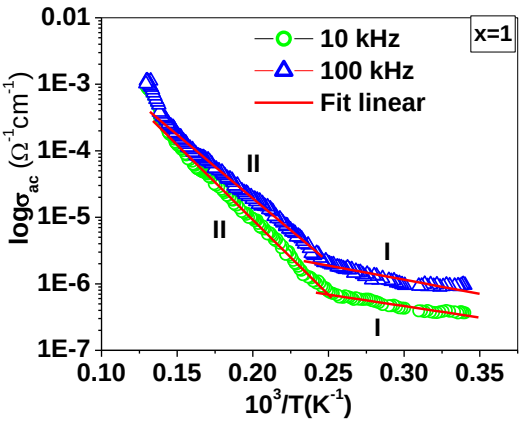

Fig.2. Variation of σ_{ac} with 1000/T of $Ba_5GdTi_2\ ZrV_7O_{30}$at two selected frequencies

The graph is divided into two distinct regions: one in the high and the other in the low temperature region. The two regions are characterized by different slopes giving different values of activation energy. At some higher temperature, all the curves merge into a single curve irrespective of frequency. Further, it is noticed that there is an increase in ac conductivity with increase in temperature showing negative temperature coefficient of resistance behavior of the samples as seen in case of semiconductors. At low frequencies conductivity is due to the hopping of charge carriers over a large distance but at low temperature hopping of charge carrier is limited only to the nearest neighbor defect sites [8]. No anomaly is observed in any graph. The higher conductivity at higher temperature may be attributed to the associated interlayer ionic conduction with suppressed electronic hopping conduction [9]. The conduction mechanism for the low temperature region is possibly due to short range charge jumping, which has smaller energy barriers. The mechanism for the high temperature region is long range charge conduction which has to overcome relatively high energy barriers.

Table 1: Variation of σ_{ac} with 1000/T of $Ba_5GdTi_2ZrV_7O_{30}$ compound

Compounds	f (kHz)	E_a (eV)	
		I	II
$Ba_5GdTi_2ZrV_7O_{30}$	10	0.8389	3.7954
	100	0.6832	4.4759

3.2.2. Variation of ac conductivity with frequency at different temperatures

The behavior of ac conductivity can be explained using Jonscher universal power law [10]:

$$\sigma_{ac}(\omega) = \sigma_{dc} + \sigma_1(\omega)$$

$$\sigma_{ac}(\omega) = \sigma_{dc} + A\omega^n$$

Where σ_{dc} is the dc conductivity term that depends on temperature and composition of materials. Coefficient A is the thermally activated and material dependent quantities. The exponent n is also dependent on the composition of the materials and temperature. $\sigma_1(\omega)$ is frequency dependent term It is related to the interaction of charges like ionic, electronic, oxygen vacancies etc.

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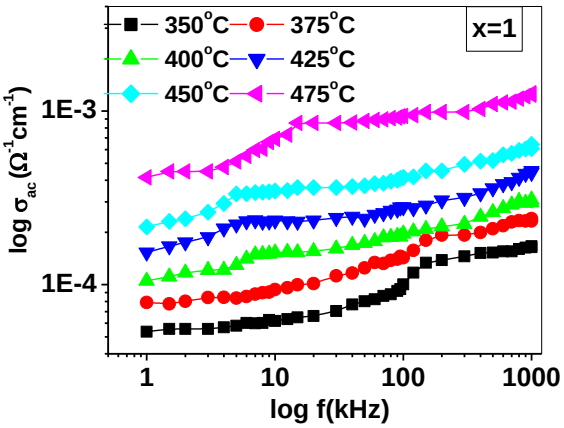

Fig.3. Variation of σ_{ac} with frequency $Ba_5GdTi_2ZrV_7O_{30}$ compounds at different temperatures

Fig.3. shows the frequency dependent conductivity (σ_{ac}) of BGTZV compound at various temperatures. The plot exhibits both low and high frequency dispersion phenomena. In the lower frequency region, the increasing trend of σ_{ac} with increase of frequency may be attributed to the disordering of cations [8] between neighboring sites and the presence of space charge in the material that vanishes at higher temperature and frequency[8].

5. Conclusion:

X-Ray diffraction study of the $Ba_5GdTi_2ZrV_7O_{30}$ compound confirmed its orthorhombic structure. The SEM study exhibited nearly homogeneously distributed non-uniform shape grains throughout the surface of the samples. In σ_{ac} vs inverse temperature plots an increase in ac conductivity with increase in temperature shows negative temperature coefficient of resistance behavior of the samples as seen in case of semiconductors. In σ_{ac} vs. frequency graph, both low and high frequency dispersion phenomena are observed.

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