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Impedance Spectroscopy of $Ba_4SrGdTi_3V_7O_{30}$ ceramic

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Abstract : $Ba_4SrGdTi_3V_7O_{30}$ ceramic belonging to tungsten bronze family was synthesized by a high-temperature solid-state reaction method. Preliminary structural analysis of the compound shows the formation of single-phase orthorhombic structures at room temperature. Surface morphology of the compound was studied by scanning electron microscopy. Detailed studies of impedance parameters provide a better understanding of the electrical properties and type of relaxation processes in the material. The effect of temperature on impedance parameters was studied using an impedance analyzer in a wide frequency range (10^2–10^6 Hz) at different temperatures. The temperature dependent plots of real and imaginary part of complex impedance traces semicircle(s) in the complex plane which reveal the presence of both bulk and grain boundary effects. The bulk resistance of the material decreases with rise in temperature exhibiting a typical negative temperature coefficient of resistance (NTCR) behavior of the material. The nature of variation of dc conductivity suggests Arrhenius type of electrical conductivity.

Keywords: Ceramics; X ray diffraction, TB structure, Solid-state reaction, electrical conductivity.

1. Introduction

Tungsten bronze (TB) structure ceramics constitute a family of materials which have got special attention due to their technological applications [1–4] including ferroelectric memory devices, electro optical devices, and actuators [5]. The TB structure consists of a skeleton 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 advent of

nanoscience & technology have completely changed the direction of studies on 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. In view of this, we have synthesized and studied the structural and electric properties of rare earth doped $Ba_4SrGdTi_3V_7O_{30}$ vanadate.

2. Experimental

2.1 *Sample preparation*

Gadolinium modified $Ba_4SrGdTi_3V_7O_{30}$ (BSGTV) ceramic was synthesized by Mixed Oxide Process. High purity (AR grade) oxides and carbonates, $BaCO_3$, $SrCO_3$, Gd_2O_3, TiO_2, V_2O_5 (all from M/S Sarabhai M. Chemicals, India) were weighed in a suitable stoichiometry and grinded homogeneously using an agate mortar in air atmosphere for 3 h and then in methanol medium for 3 h. Subsequently, the grinded mixture was calcined at an optimized temperature and time (950^0C for 24 h). Compact disks of 10 mm diameter and 1–2 mm thickness were prepared from calcined powders at a pressure of 4×10^6 N/m^2 using a hydraulic press. Requisite amount of PVA (polyvinyl alcohol) binder was added to the powders and grinded well to provide free flow of granules and reduce the brittleness in final stage of pellet. The binder was burnt out during high temperature sintering. The pellets were sintered at 950^0C for 12 h in an air atmosphere using high purity alumina crucibles. The formation and quality of the compounds were checked by an X-ray diffraction (XRD) technique. Microstructures of sintered pellets were recorded by JEOL –JSM: 5800 model scanning electron microscope (SEM). Measurements of electrical properties and conductivity as a function of temperature (30–500^0C) at different frequency (100Hz – 1MHz) were carried out using computer interfaced impedance analyzer PSM 1735, model: N4L.

3. Results and Discussion

3.1 *Structural Study*

The room temperature XRD pattern of the sample is shown in Fig. 1. All peaks of the pattern were indexed by using 'POWD MULT' computer software package [7] which did not provide any evidence for secondary phase(s) present. Thus BSGTV exhibits single phase orthorhombic TB structure. The best agreement between the observed (obs) and calculated (cal) inter planer spacing (d) (Σ (d_{obs} - d_{cal}) = minimum) of the compound was found in this system at room

temperature. The least-squares refined unit cell parameters of the ceramics refined by the least-square method are: a=34.5929(17), Å b=3.5927(17) Å, c = 7.8619(17)Å for BSGTV (with standard deviation in parenthesis). Using the refined lattice parameters, interplaner spacing d of each reflection of the compound was calculated and compared with its observed value. The crystallite/particle size of the sample was estimated from the broadening of the XRD peaks ($\beta_{1/2}$), using Scherrer's equation [8]; $P = K\lambda / \beta_{1/2}Cos\theta_{hkl}$, where K = constant = 0.89 and λ = 1.5405 Å. The average crystallite size of the compound was found to be 13 nm. The broadening of reflections due to mechanical strain and other effects has been ignored. The cell parameters are consistent and comparable to some of the compounds of this family [9]. The SEM micrograph of the compound with different magnifications at room temperature is shown in Fig.1 (inset). The avarage grain size evaluated from the histogram was 1.6 μm.

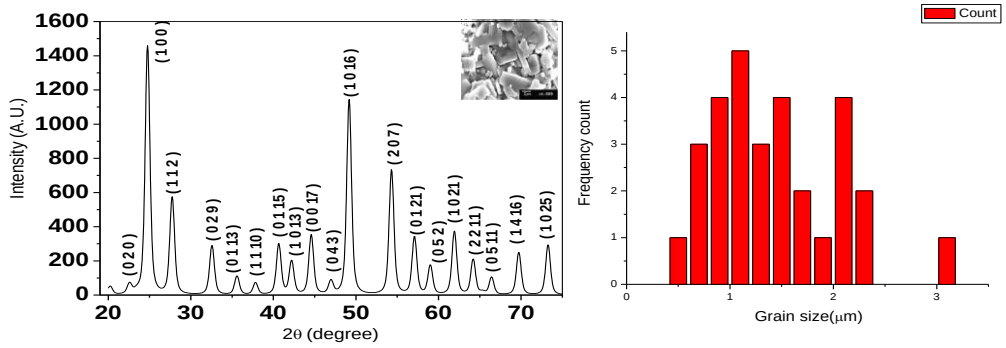

Fig. 1: Room temperature XRD pattern, SEM (inset) and histogram of $Ba_4SrGdTi_3V_7O_{30}$ ceramics

3.2 *Impedance Study*

Complex impedance spectroscopy (CIS) [10] is a powerful experimental technique to characterize the electrical behavior of a system in which a number of strongly coupled processes exist. It helps to separate grain (intragrain) and grain boundaries (intergrain) contributions in transport properties of the material..

The temperature dependent Nyquist Plots (Fig 2) (fitted complex impedance spectrum) of BSGTV measured at some selected temperatures (300–500^{0}C) are shown in Fig.1. Presence of single semicircular arcs at lower temperature 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

(≥300^{o}C), which can be interpreted as the electrical response is mainly due to the grain and grain boundary effect. The merging of the semicircular arcs indicates that the above two resistances are not comparable [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.

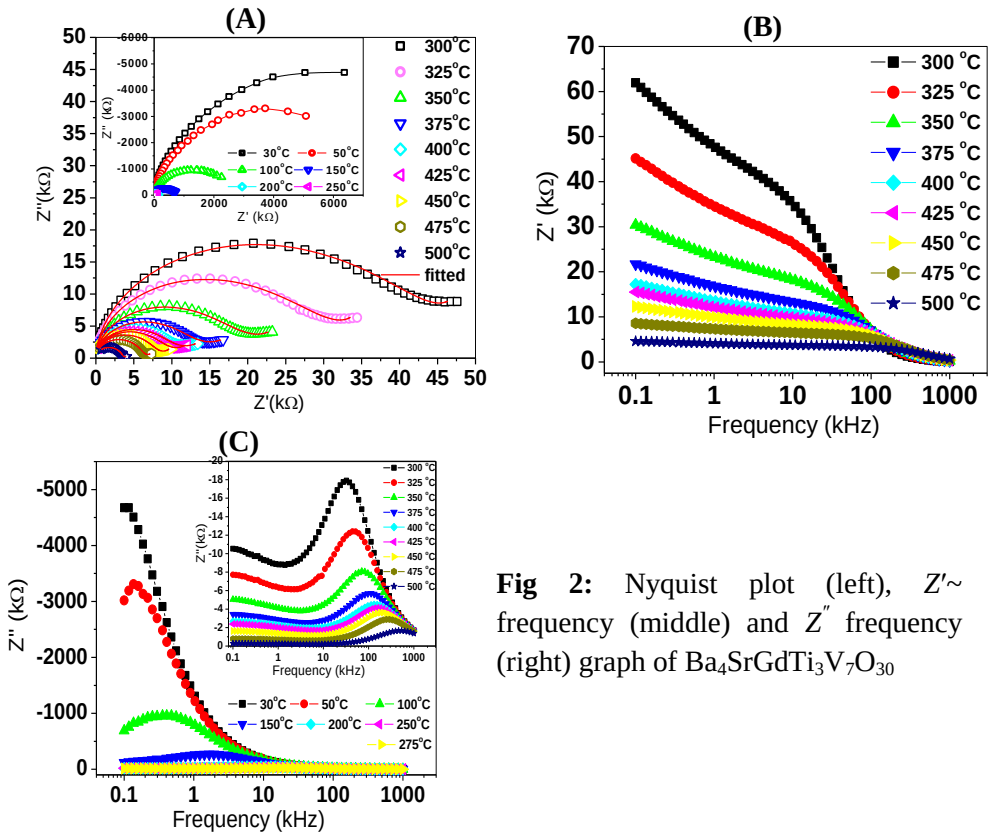

Fig 2: Nyquist plot (left), Z'~ frequency (middle) and Z'' frequency (right) graph of $Ba_4SrGdTi_3V_7O_{30}$

Fig. 2 (B) shows the variation of Z' as a function of frequency (0.1–1000 kHz) at some selected temperatures (300–500^{0}C). The plots show a low frequency dispersion followed by a plateau region, and finally all the curves merge/coalesce above 100 kHz irrespective of temperature. Initially there is a decrease in Z' values with frequency; this may be due to a slow dynamics relaxation process in the material probably due to space charges. At high temperatures, low frequency the appearance of plateau region may be related to frequency invariant (dc conductivity) electrical property of the material.

The merger of the pattern at higher frequency may be attributed to the release of space charge as a result of reduction in the barrier properties of material with the rise in temperature and may be a responsible factor for the enhancement of AC conductivity of material with temperature at higher frequencies [12]. It is observed that the value of Z' decreases with rise in both temperature and frequency indicating the existence of negative temperature coefficient of resistance (NTCR) type behavior in the material as is observed in semiconductors.

Fig. 2(C) shows the frequency–temperature dependence of Z'' (loss spectrum). Like Z', the value of Z'' decreases on increasing frequency at all the temperatures up to 125 ^{o}C. The non-existence of Z'' peak in this temperature region is due to the absence of current dissipation in the material. Subsequently, the appearance of peak in the loss spectrum (>175 ^{o}C) 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 [13]. This may be due to the immobile species/electrons at low temperatures and defect/vacancies at high temperatures. Further, the magnitude of Z'' decreases with the shift of peaks towards higher frequency side. Finally, all the curves merge in the high-frequency region, which may be due to the accumulation of space charge of the material.

4. Conclusion

The polycrystalline sample of BSGTV was prepared by a high-temperature solid-state-reaction route. Preliminary 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 the material showed relaxation effects which are non-Debye type and the loss spectra suggests 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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