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Comparison of impedance Properties of $BaSr_4RTi_3V_7O_{30}$ (R = Dy, Sm)

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Abstract : Ferroelectric materials play an important role in the field of materials research as they exhibit non-linear spontaneous polarization, high dielectric constant, negative temperature coefficient of resistance behavior which lead to their applications in many devices like ferroelectric random access memory and display, microwave dielectric resonators etc.. In the present research work, polycrystalline samples of $BaSr_4RTi_3V_7O_{30}$ (R = Dy, Sm) are synthesized by a high temperature solid state reaction technique. The effect of temperature on impedance parameters is studied using an impedance analyzer in a wide frequency range (10^2–10^6 Hz) at different temperatures. The real and imaginary part of complex impedance traces semicircle(s) in the complex planes for both the compounds. The bulk resistance of the material decreases with rise in temperature. This exhibits a typical negative temperature coefficient of resistance (NTCR) behavior of the material. The temperature dependent modulus plots reveal the presence of both bulk and grain boundary effects at higher temperature.

Keywords: Ceramics; electric properties. Impedance properties

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1. Introduction

Tungsten bronze (TB) structured ferroelectric compounds have gained a great deal of attention, mainly due to their device applications. Some applications of ferroelectric ceramic materials utilize polarization switching in their operations, including ferroelectric memory devices, electro optical devices, capacitors and actuators [1]. 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 material of a general formula, $[(A_1)_2(A_2)_4C_4][(B_1)_2(B_2)_8]O_{30}$[2]. The nine-coordinated C-site has the smallest space to occupy among all the three different types of tunnels created by the framework of the octahedra. The structural flexibility and the chemical versatility of this TB family make it more usable for many applications such as electro-optic, actuators, elasto-optic, electro-optic memory, optical devices [3-8] etc. In this view, we have synthesized and studied the impedance properties of some rare earth doped vanadates and in this paper we have compared the above properties of $BaSr_4RTi_3V_7O_{30}$ (R = Dy, Sm)

2. Experimental details

The polycrystalline ceramic samples of $BaSr_4RTi_3V_7O_{30}$ (R = Dy, Sm)), i.e. $BaSr_4DyTi_3V_7O_{30}$ (BSDTV), $BaSr_4SmTi_3V_7O_{30}$ (BSSTV) were prepared by a high-temperature solid-state reaction technique using high purity (>99.9%) precursors; $BaCO_3$, $SrCO_3$, Sm_2O_3, Dy_2O_3, TiO_2 (all from M/S Sarabhai M. Chemicals, India), V_2O_5 (M/s. Koch Light Ltd., England) in a suitable stoichiometry. The stoichiometric mixtures of raw materials (powders) are thoroughly mixed and grinded for 3 h in air atmosphere, and in wet methanol to obtain fine homogenous powders. The mixed powders were then calcined in an alumina crucible at an optimized temperature and time (950^0C, 12h). Cylindrical pellets of dimensions 1–2 mm in thickness and10 mm in diameter were made from the calcined powders at a pressure of 4×10^6 N/m^2 using a hydraulic press. Requisite amount of PVA (polyvinyl alcohol) binder (which is burnt out during high temperature sintering) was added to the powders and grinded well to provide free flow of granules and to reduce the brittleness in final stage of pellet. The pellets are then sintered in an air atmosphere at an optimized temperature and time (950^0C, 12 h) and then polished to make their faces flat and parallel. The pellets are finally coated with high purity conducting silver paint, and then dried at 150^0C for 2h before carrying out electrical measurements. X-ray diffraction (XRD) data (pattern) of the materials were obtained in a wide range of Bragg angle 2θ ($20^0 \leq 2\theta \leq 80^0$) at a scanning speed of 3^0 min^{-1} by an X-ray diffractometer (Rigaku, Miniflex) with CuK_α radiation (λ= 1.5405Å) at room temperature. The XRD pattern in the material is observed to be of different nature from that of the ingredient oxides confirmed the formation of a single-phase new compound. The impedance studies were carried out in the temperature range of 30^0 -500^0C and wide frequency range of 100Hz to 1MHz, using a computer-controlled impedance analyzer (PSM 1735, model: N 4L).

3. Results and discussion

3.1. Impedance Properties

Complex impedance spectroscopy (CIS) [9] is a 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 materials. Fig. 1 shows the temperature dependence Nyquist plot of BSDTV and BSSTV compounds measured at some selected temperatures (200–500^{0}C) and frequencies. In $BaSr_4DyTi_3V_7O_{30}$ compound a linear response is clearly marked. This trend indicates the insulating behavior or high resistance in the sample [9]. But with the increase in temperature, the curve bends towards real (Z′) axis forming semicircular arcs. Unlike $BaSr_4DyTi_3V_7O_{30,}$ in $BaSr_4SmTi_3V_7O_{30}$ compound, single semicircular arcs are observed in the complex plane with a single relaxation process at higher temperature, which confirms that the impedance contribution is mainly due to the grains. The center of the semicircular arc shifts towards the origin on increasing temperature which indicates that the conductivity of the samples increases with increase in temperature. This electrical behavior was modeled in terms of an equivalent circuit comprising of a parallel *RC* circuits (inset).

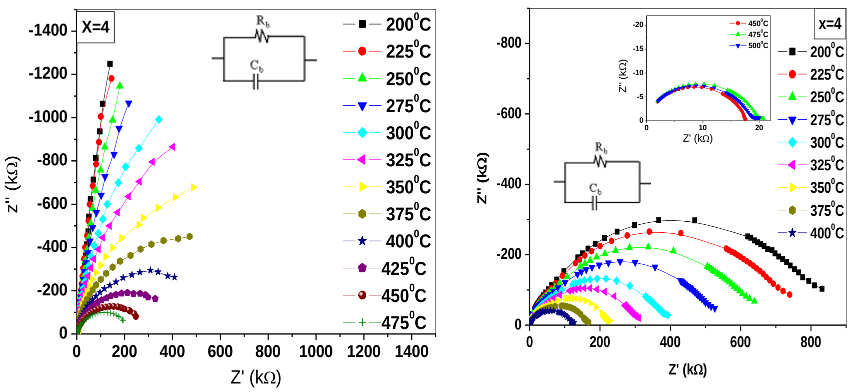

Fig 1. Comparison of Nyquist plot (Z$^{''}$ vs Z′ graph) of $BaSr_4DyTi_3V_7O_{30}$ (left) and $BaSr_4SmTi_3V_7O_{30}$ (right) compounds at some selected temperature

The loss spectra of $BaSr_4RTi_3V_7O_{30}$ (R = Dy, Sm) at different temperatures are shown in Fig. 2. In $BaSr_4DyTi_3V_7O_{30}$ compound Z″ peaks are not observed at lower temperature. This suggests decrease in capacitive effect on increasing the net impedance of the materials; thereby the barrier property in the material is enhanced. But the peaks are observed to appear at a particular frequency at higher temperatures and peak height decreases with a shift in the peak frequency towards the higher frequency side with rise in temperature. This type of impedance spectrum may arise due to presence of space charge in the materials. Unlike in $BaSr_4DyTi_3V_7O_{30}$ compound in $BaSr_4SmTi_3V_7O_{30}$ peaks tend to appear at all temperatures. For both the compounds, the merger of all the curves at high frequency, which indicates the depletion of space charges at those frequencies [10]. The higher the frequency, the lesser the time is for the space charges to relax and the faster the recombination. Since the space charge polarization is reduced on increasing frequency, all the curves appear to merge at higher frequencies.

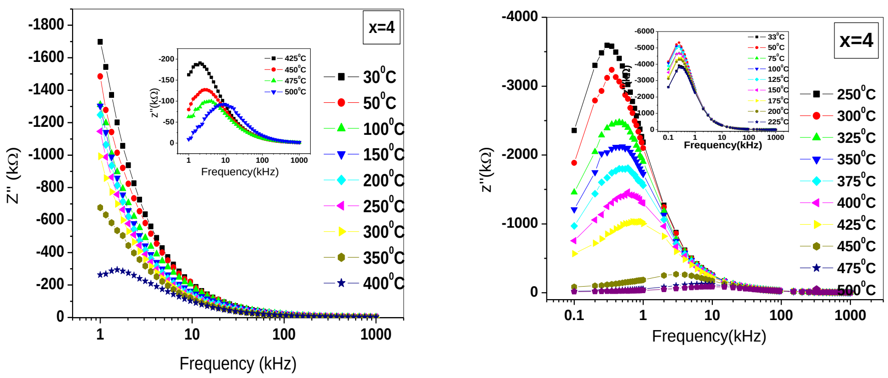

Fig.2. Comparison of Variation of imaginary part (Z'') of complex impedance of $BaSr_4DyTi_3V_7O_{30}$ (left) and $BaSr_4SmTi_3V_7O_{30}$ (right) compounds at some selected temperature

3.2 Modulus study

The complex electric modulus spectra (M' vs M$''$) of the $Ba_{5-x}Sr_xDyTi_3V_7O_{30}$ (x = 2, 3) are shown in Fig.3. For $BaSr_4SmTi_3V_7O_{30}$ compound two semicircles are clearly observed even at lower temperatures, but for $BaSr_4DyTi_3V_7O_{30}$ compound these are observed at higher temperature which may be interpreted as the two capacitances effect; the low frequency semicircle is considered due to the grain boundary and the higher frequency semicircle shows the bulk effect. For both the compounds the grain boundary effect is more than that of bulk effect at higher temperatures. The plots become temperature independent, (merged to a single arc) of the modulus curve indicates the temperature independent capacitance. It may be associated with non ferroelectric regions [11]. Since the different in relaxation time are less than ~2 (Figs. 5.3.26 -27), so they are not resolved [12].

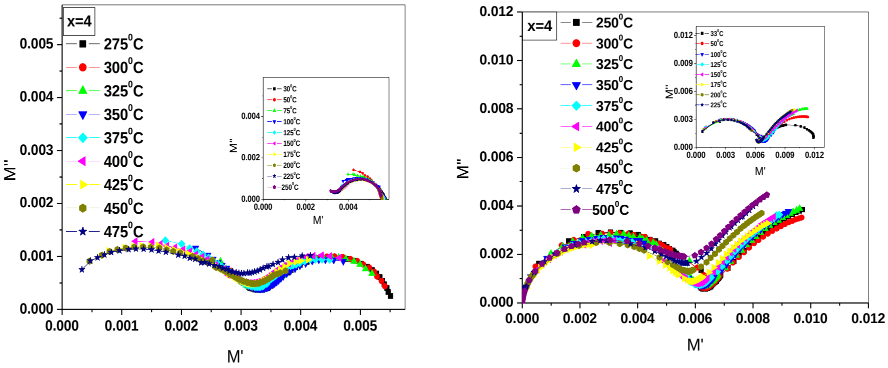

Fig 3. Comparison of Complex modulus spectra (M″ vs M′) of $BaSr_4DyTi_3V_7O_{30}$ (left) and $BaSr_4SmTi_3V_7O_{30}$ (right) compounds at some selected temperature

4. Conclusion

The BSDTV and BSSTV of tungsten–bronze family are prepared, and immittance properties are investigated. For both the compounds the single semicircular arcs are observed in the complex impedance plane with a single relaxation process at higher temperature due to the grains. In $BaSr_4DyTi_3V_7O_{30}$ compound peaks are observed at higher temperatures, whereas in $BaSr_4SmTi_3V_7O_{30}$ peaks tend to appear at all temperatures. For $BaSr_4SmTi_3V_7O_{30}$ compound two semicircles are clearly observed even at lower temperatures, but for $BaSr_4DyTi_3V_7O_{30}$ compound these are observed at higher temperature which may be interpreted as the two capacitances effect (due to grain and grain boundary).

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