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Study of a.c. and d.c. Conductivities of Lead Free $Sr_5LaTi_3V_7O_{30}$ cCramic

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Abstract : Ceramics are very widely used as base materials for composite film and high frequency resistors for their good insulating behavior. So it needs a careful study of the ac and dc conductivity of these materials. $Sr_5LaTi_3V_7O_{30}$ is a lead free Tungsten Bronze ceramic prepared by high temperature solid state reaction route. The preliminary structural analysis of the compound confirms the formation of single-phase orthorhombic structures at room temperature. Surface morphology of the compound is studied by scanning electron microscopy. The sample showed no structural differences, non-uniformly distributed grains, no ferro-paraelectric transition temperature within observed experimental temperature range. Ferroelectrics exhibit different conduction mechanism. In this paper focuss is made on the study of a.c. and dc electrical conductivity The frequency dependent a.c. conductivity obeys the Jonscher's power law. The nature of variation of dc conductivity with temperature suggests Arrhenius type of electrical conductivity.

Keywords: Ceramics, X-ray diffraction, SEM, Electrical conductivity.

1. Introduction

Materials of tungsten-bronze (TB) structure belong to an important family of dielectric materials, which display interesting 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].The study of the nature of electrical conductivity is an important aspect of the physics of ferroelectrics. In dielectrics, electrical conduction is due to the ordered motion of weakly bound charge particles under the influence of an external electric field. Depending on the type of charge carriers that predominate the conduction process like electrons/holes or cations/anions, the solids may be classified primarily as an electronic or ionic conductor. In case of ionic crystals the process of electrical conduction is due to the motion of weakly bound ions under the influence of the electric field. In real crystal, at high temperature, the electrical conductivity is mainly intrinsic but at low temperature it is extrinsic. The variation of electrical conductivity (σ) with temperature can be described by an Arrhenius equation [4]: $\sigma_{ac} = \sigma_0 \exp(-E_a/k_BT)$,where E_a activation energy for intrinsic conduction process of the materials. The value of activation energy corresponds to the energy required for the polaron to jump over the grain boundaries. The a.c. electrical conductivity (σ_{ac}) of the materials under study is calculated from the conductivity relation, $\sigma_{ac} = \omega\varepsilon\varepsilon_0\tan\delta$, where ε_0 is the vacuum dielectric constant, ε is the dielectric constant of the material, ω is the angular frequency and $\tan\delta$ is the dielectric loss of the materials.

2. Experimental details

2.1 *Material preparation and characterization*

The polycrystalline sample $Sr_5LaTi_3V_7O_3$ (SLTV) was prepared using the high-purity (>99.9%) precursors; $SrCO_3$, La_2O_3, TiO_2, V_2O_5 by a mixed-oxide method. The stoichiometric mixtures of the high purity(99.9 %) powders of $SrCO_3$,TiO_2,La_2O_3 (All from M/s Sarabhai M. Chemicals Pvt. Ltd., India), and V_2O_5 (M/s. Koch Light Ltd, England) were weighed and thoroughly grinded in an agate mortar to obtain homogeneous mixtures and calcined at an optimum temperature (950^0C for 12 hrs). The calcined powders were grinded and dried, followed by mixing with organic binder polyvinyl alcohol (PVA) to prepare cylindrical pellets of 10 mm diameter and 1-2 mm thickness at a pressure of 4×10^6 N/m^2. The pellets were sintered in air at 1000^0C for 12 hrs to yield dense ceramics. The formation and quality of the compound was checked by an X-ray diffraction (XRD) technique. The X-ray diffraction pattern of the compounds was recorded at room temperature using an X-ray powder diffractometer (Rigaku, Miniflex) with CuKα radiation (λ=1.5405 Å) in a wide range of Bragg's angles 2θ ($20^0 > 2\theta > 75^0$) with a scanning rate of 3^0/ minute. To study the surface morphology of the sintered pellets, both the surfaces were made flat and parallel. Microstructures of sintered pellets were recorded by JEOL –JSM: 5800F model scanning electron microscope (SEM). The average grain size was determined by a linear intercept method. The electrical properties of the sintered pellets were studied with the data recorded by an impedance analyzer (PSM 1735, model: N 4L) over a wide frequency range (10^2–10^6 Hz) at different temperatures (31–500^{0}C).

3. Results and discussion

A. *Structural analysis*

Fig.1a. shows the XRD pattern of the calcined powder of $Sr_5LaTi_3V_7O_{30}$. All the peaks of XRD pattern were in different unit 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= 9.7423(39)Å, b=6.7237(39) Å, c= 9.4213(39)Å (estimated standard deviations in parentheses) were finally selected. The coherently scattered crystallite size of the sample was estimated from the broadening ($\beta_{1/2}$) of few peaks using Scherrer's equation [6]; P= $K\lambda/\beta_{1/2}\cos\theta_{hkl}$, 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 14 nm.

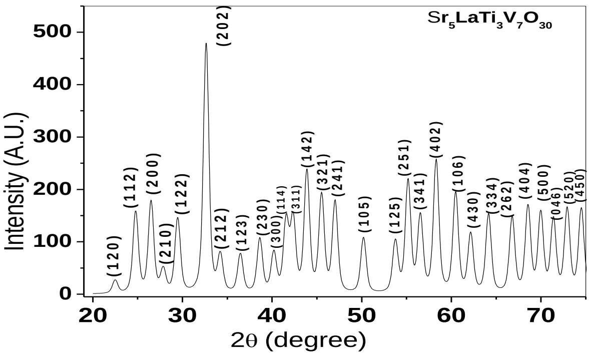

Fig.1a : Room temperature XRD pattern of $Sr_5LaTi_3V_7O_{30}$

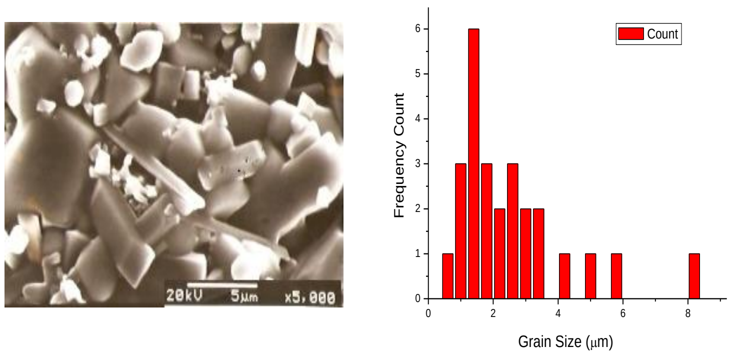

Fig. 1b: SEM and histogram (right) of $Sr_5LaTi_3V_7O_{30}$

B. *Micro structural analysis*

Fig.1b. shows the room temperature scanning electron micrograph of the sample describing their surface property and microstructure. From micrographs the granules are observed to be spherical and columnar. Some plates like irregular shaped grains are also observed. The porosity seems to be decreased with the growth of grains. The average grain size of the pellet sample was found to be ~ 2.5 µm obtained from the histogram.

C. *Conductivity analysis*

i) ac electrical conductivity: The a.c. electrical conductivity is discussed as follows-.

a) Variation of ac conductivity with inverse absolute temperature at some selected frequencies:

The plot of σ_{ac} with inverse of absolute temperature(10^3/T) at some selected frequencies are as shown in Fig. 2a. The graphs are divided independently of frequency, in different regions, characterized by different slopes. The change in ac conductivity for both the frequencies is very small at low temperature (up to~200^{o}C) and is more at higher temperature. The compound follows Arrhenius behavior and shows the negative temperature coefficient of resistance (NTCR) behavior. It is clear that the ac conductivity (σ_{ac}) in the $Sr_5LaTi_3V_7O_{30}$ compound is governed by the polaron hoping mechanism and the conductivity is influenced by both frequency and temperature.

b) Variation of ac conductivity with frequency at different temperatures:

As per Jonscher the origin of the frequency dependence of conductivity lies in the relaxation phenomena arising due to mobile charge carriers. Fig.2.b. shows the frequency dependence of σ_{ac} for $Sr_5LaTi_3V_7O_{30}$ at various temperatures fitted with Jonscher's power response. The plot indicates the increase in σ_{ac} with an increase in frequency. In low frequency-high temperature region, the conductivity response flattens due to transition from long range hoping to short range ion motion and conductivity relaxation phenomenon occurs [7]. The increase in conductivity with increase in temperature and frequency shows the existence of negative temperature coefficient of resistance (NTCR) behaviour.

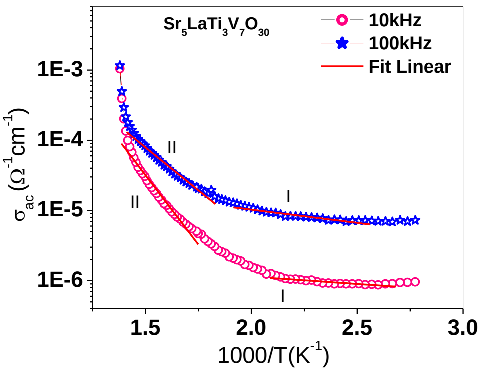

Fig.2a: Variation of σ_{ac} with inverse of absolute temperature(10^3/T)

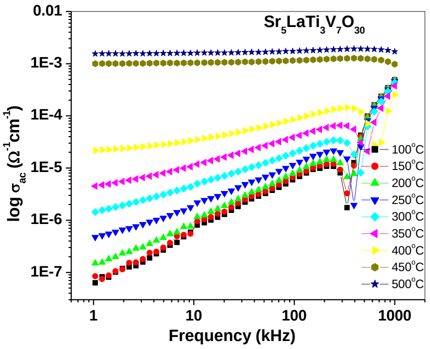

Fig.2b: Variation of σ_{ac} with frequency

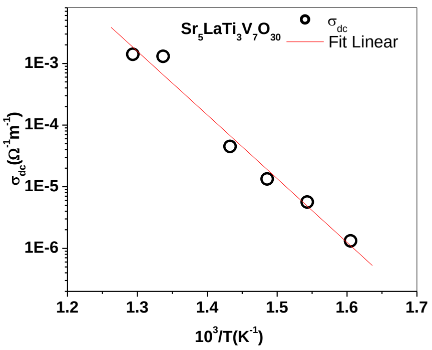

Fig.3: Variation of σ_{dc} with inverse absolute temperature (10^3/T)

c) *dc Electrical Conductivity*

The value of bulk conductivity of a compound can be evaluated from the impedance data using a relation; $\sigma_{dc}=t/R_bA$, where R_b is the bulk resistance, t is the thickness and A is the area of the electrode deposited on the sample. The low frequency intercept of the semicircle on the real axis (Z') in the complex impedance plot gives the value of bulk resistance (R_b). The dc conductivity also follows the Arrhenius law and the activation energy E_a is calculated from the slope of the linear portion of the plots. The variation of σ_{dc} with 10^3/T for $Sr_5LaTi_3V_7O_{30}$ compound is as shown in Fig.3. From the plots it is observed that there is an increase in dc conductivity with the increase in temperature for the observed sample. Due to the addition of thermal energy, the electrons clouds could be set free from O^{-2} ions. The activation energy (due to bulk effect) of these materials in the high temperature region is 2.05eV

4. Conclusion:

Polycrystalline sample of $Sr_5LaTi_3V_7O_{30}$ is prepared by high temperature solid state reaction route. From the XRD pattern, formation of single-phase orthorhombic crystal structure is observed at room temperature. The frequency dependent a.c. conductivity obeys the Jonscher's power law. The nature of variation of dc conductivity with temperature suggests Arrhenius type of electrical conductivity. The different activation energy of the compound observed in different regions indicates the presence of different conduction mechanisms.

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