Impedance spectroscopy and morphology of SrBi_4Ti_4O_15 ceramics prepared by soft chemical method

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Abstract

In this work, we have synthesized polycrystalline SrBi_4Ti_4O_15 (SBiT) ceramics by soft chemical method. These ceramics were structurally characterized by analysis of X-ray diffraction (XRD) patterns, indicating that SBit ceramics present an orthorhombic structure. Scanning electron micrograph shows that the grains exhibit a plate like morphology. Dielectric relaxations of the SBit ceramics were investigated in the temperature range 100–700 °C. Using the Cole–Cole model, an analysis of the dielectric loss with frequency was performed, assuming a distribution of relaxation time. The presence of the peaks in temperature dependent dielectric loss indicates that the hopping of charge carriers is responsible for the relaxation. Impedance studies show a non-Debye type relaxation, and relaxation frequency shift to higher side with increase in temperature. A significant shift in impedance loss peaks towards higher frequency side indicates conduction in material and favoring the long range motion of mobile charge carriers. The Nyquist plot shows overlapping semicircles, for grain and grain boundary of SBit ceramics. The frequency dependent ac conductivity at different temperatures indicates that the conduction process is thermally activated process and the spectra follow the universal power law. The hopping frequency shifts towards higher frequency side with increase of temperature, below which the conductivity is frequency independent. The variation of dc conductivity confirms that the SBit ceramics exhibits negative temperature coefficient of resistance behavior in high temperature.

Keywords:
Ceramics
Chemical synthesis
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1. Introduction

The bismuth layer-structured ferroelectrics (BLSFs) have a crystal structure containing interleaved bismuth oxide (Bi_2O_2)^2+ layers and pseudo-perovskite blocks which contains BO_6 octahedral and generally formulated as (Bi_2O_2)^2+ (A_m1 B_{m-1} O_{2m+1}). In these notations A represents a mono-, bi- or trivalent ion, B denotes a tetra-, penta- or hexavalent ion, and m is the number of BO_6 octahedral in each pseudo-perovskite block (m = 1–5) [1]. The physical properties of this ceramic are strongly affected by the structure and morphology [2]. Sr-based layered perovskite is currently one of the most promising candidates for a new generation of nonvolatilizable ferroelectric random access memories (NvFRAM) devices [3]. Among several BLSF materials, SrBi_4Ti_4O_15 (SBiT) is extensively studied by many researchers from possible applications in piezoelectric device [4]. Recently, much attention has been paid to SBit due to its high Curie temperature, barrier type property, large and stable 2Pf after up to 10^11 cycles, and anisotropic physical properties [4–6]. Because of its properties and performances, SBit, prepared by various methods, was investigated by several other researchers [7,8].

Complex impedance spectroscopy (CIS) is a flexible tool for simultaneous electrical and dielectric characterization of materials. This powerful technique has been widely used to characterize the dielectric behavior of single crystal, polycrystalline, and amorphous ceramic materials [9]. The experimental data contains three variables, real and imaginary component of the electrical response and frequencies together with four inter related electrical response formalisms: impedance (Z*), admittance (Y*), relative permittivity (ε*), and electric modulus (M*). Consequently, data can be presented in many formats; in practice, it is often found that different formats may highlight different electrical characteristics of a sample. It is the most commonly used experimental technique to
analyze the dynamics of the ionic movement in solids. Contribution of various microscopic elements such as grain, grain boundary and interfaces to total dielectric response in polycrystalline solids can be identified by a reference to an equivalent circuit, which contains a series of array of parallel RC elements. The purpose of this work are: (a) synthesis of SBiT ceramic at relatively lower temperature to avoid the volatility of Bi\(^{13}\), (b) apply the variable-frequency technique of impedance spectroscopy to SBiT ceramic over a wide temperature range, even across the transition temperature, and (c) characterize the grain and grain boundary resistance using CIS, from which one can calculate their capacitance and can model the equivalent circuit.

2. Experimental

The basic materials used in the synthesis of SrBi\(_4\)Ti\(_4\)O\(_{15}\) (SBiT) ceramic were Sr\((\text{NO}_3\)\)_\(_2\), Bi\((\text{NO}_3\)\)_\(_3\), TiO\(_2\) (d\(_{10}\) = 0.27 Å, d\(_{50}\) = 0.35 Å, and d\(_{90}\) = 0.48 Å) and oxalic acid. All the chemicals were more than 99.5% pure. An aqueous solution of 0.2 M strontium nitrate and bismuth nitrate using deionized water was prepared. An appropriate amount of TiO\(_2\) was added to a 0.2-M oxalic acid solution and was ultrasonicated for 10 min to break TiO\(_2\) agglomeration and kept on stirrer for continuous stirring to ensure suspension. The solution containing alkaline earth metal nitrate and bismuth nitrate were added drop wise into the suspension of TiO\(_2\) in oxalic acid solution under stirring. Finally the pH of the solution was maintained at 7 by adding ammonia solution. All of the above experiments were carried out at room temperature. This process precipitated alkaline earth metal oxalate on the surface of fine TiO\(_2\) particles by nucleation. Similar types of ceramic synthesis have been reported by other methods\[15\]. The average lengths to thickness ratio (aspect ratio) of the grain are found to be more than 15.

Silver electrodes were applied on the opposite disk faces by sputter (Cressington dc sputter, Cressington, Inc., USA). Dielectric measurements were carried out over the frequency range 10 Hz to 10 MHz using an impedance analyzer (HP 4192A, USA). Real dielectric data was collected at an interval of 25\(^\circ\)C and 1 kHz, 100 kHz and 1 MHz were measured in traditional fixed frequency format (figure not shown). The result showed a normal ferroelectric to paraelectric transition around 525\(^\circ\)C. This ferroelectric transition temperature for SBiT has been reported since 1960\[16\] where author observed the extrapolated Curie Weiss temperature, T\(_0\), was at least 20\(^\circ\)C lower than the Curie temperature. Difference between the value of T\(_0\) and T\(_c\) have been noticed many times in ceramics which are attributed to the presence of different grain size, porosity, and grain boundary impedances\[17,18\] in the samples, but it is probably true to say that the influence of these effects are not clearly defined. In order to carry out a more thorough analysis of permittivity and their temperature dependence, it is necessary to separate the contributions of the various grain and impurity phases.

3. Results and discussion

Fig. 1 shows the room temperature powder XRD pattern of SBiT ceramic recorded by using Cu K\(_\alpha\) radiation. The preparation of Bi layered ceramics is always troubled by the coexisting of a pyrochlore phase, which is observed due to the thermal decomposition reaction caused by the vaporization of bismuth species [13]. In this work, there is no such evidence of the existence of any impurity phase or its quantity is too small to be detected. All peaks were indexed in the orthorhombic symmetry. The lattice parameters were found to be a = 5.4507, b = 5.4376 and c = 40.9841 Å for SBiT layered ceramic. The observed lattice parameters were in excellent agreement with that reported elsewhere [14].

Fig. 2 shows the SEM micrograph of SBiT ceramic prepared by soft chemical method. Fig. 2 shows that the grains of SBiT ceramics exhibit a plate like morphology. It was also found from the SEM micrograph that the grains of different sizes are homogeneously distributed. Similar grain morphology was observed in SBiT prepared by other methods[15]. The average lengths to thickness ratio (aspect ratio) of the grain are found to be more than 15.

As a first step in data analysis, relative permittivity values \(\epsilon'\) at 10 kHz, 100 kHz and 1 MHz were measured in traditional fixed frequency format (figure not shown). The result showed a normal ferroelectric to paraelectric transition around 525\(^\circ\)C. This ferroelectric transition temperature for SBiT has been reported since 1960[16] where author observed the extrapolated Curie Weiss temperature, T\(_0\), was at least 20\(^\circ\)C lower than the Curie temperature. Difference between the value of T\(_0\) and T\(_c\) have been noticed many times in ceramics which are attributed to the presence of different grain size, porosity, and grain boundary impedances[17,18] in the samples, but it is probably true to say that the influence of these effects are not clearly defined. In order to carry out a more thorough analysis of permittivity and their temperature dependence, it is necessary to separate the contributions of the various grain and impurity phases.

Fig. 3. Frequency dependent real part of the complex permittivity of SBiT at different temperatures.
grain boundary components. The importance of making this separation is shown in Fig. 3, in which the permittivity data, at several temperatures is plotted as a function of frequency.

The plot showed three different behaviors in whole frequency range. In the low frequency range the permittivity increases with increase in temperature. This may be caused due to grain boundary effect and presence of all type of polarization in the materials. The observed high value of permittivity, both at low frequency and high temperature probably due to some kind of surface layer formed by the diffusion of the electrode materials. In the high frequency range (3–10 MHz) the permittivity showed a dispersion. That dispersion shifts toward lower frequency side with increase in temperature up to 525 °C and again move towards higher frequency side with increase in temperature in the paraelectric phase. Similar behavior was observed in paraelectric BaTiO3 [19] ceramic. Around this dispersion frequency dielectric loss spectrum also gives a peak and that peak frequency follows similar behavior as that of permittivity. The frequency dependence dielectric loss spectrum shown in Fig. 4 implies that the hopping of charge carriers plays an important role in their transport processes because a loss peak is an essential feature of the charge carrier hopping transport [20].

For a more detailed analysis we have adopted impedance spectroscopic technique. Electrical ac data may be presented in any of the four interrelated formalisms:

Relative permittivity
\[
\varepsilon' = \varepsilon' - j\varepsilon'', \quad (1)
\]
Impedance
\[
(Z^*) = Z' - jZ'' = \frac{1}{j\omega C_0 \varepsilon''}, \quad (2)
\]
Electric modulus
\[
(M^*) = M' + jM'' = \frac{1}{\varepsilon''}, \quad (3)
\]
Admittance
\[
(Y^*) = Y' + jY'' = j\omega C_0 \varepsilon''^*, \quad (4)
\]
and
\[
\tan \delta = \varepsilon'' / \varepsilon' = M'' / M' = Z'' / Z' = Y'' / Y', \quad (5)
\]

where \(\omega = 2\pi f\) is the angular frequency, \(C_0 = \varepsilon_0 A d^{-1}\) is the geometrical capacitance, \(j = \sqrt{-1}\), \(\varepsilon_0\) is the permittivity of free space, \(8.854 \times 10^{-14} \text{ F cm}^{-1}\), \(d\) and \(A\) are the thickness and area of the pellet. It is assumed that the impedance data can be represented ideally by an equivalent circuit consisting of two parallel RC elements in series. This circuit is used very widely with materials whose properties are some combination of bulk and grain boundary impedances connected in series. The impedance for this circuit can be describe as

\[
Z^* = [R_b^{-1} + j\omega C_b]^{-1} + [R_{gb}^{-1} + j\omega C_{gb}]^{-1}, \quad (6)
\]

where the subscripts \(b\) and \(gb\) refer to bulk and grain boundary. In cases 
where \(C_b < C_{gb}\) and \(R_b < R_{gb}\) the real part of \(\varepsilon''^*\), can be calculated from Eqs (1) and (6) as

\[
\varepsilon' = \frac{\varepsilon_{gb}^{-1} + (\omega R_b C_b)^{-2}(\varepsilon_b^{-1} + \varepsilon_{gb}^{-1})}{\varepsilon_{gb}^{-2} + (\omega R_b C_b)^{-2}(\varepsilon_b^{-1} + \varepsilon_{gb}^{-1})^{-2}}. \quad (7)
\]

The frequency dependence of \(\varepsilon'\) for this circuit has the following characteristics:

(a) A low frequency plateau (\(\varepsilon'\) when \(\omega \rightarrow 0\)) is given by (Fig. 3)
\[
\varepsilon' = \varepsilon_{gb}. \quad (8)
\]
(b) A dispersion centered on a frequency, \(f_m\), which also corresponds to a maximum in \(\varepsilon''\) and for which (Fig. 4)
\[
f_m = \frac{2\pi \varepsilon_{gb}(\varepsilon_b^{-1} + \varepsilon_{gb}^{-1})}{(2\pi R_b(C_b + C_{gb}))^{-1}}. \quad (9)
\]
(c) A high frequency plateau (when \(\omega \rightarrow \infty\)) is given by (Fig. 3)
\[
\varepsilon' = (\varepsilon_b^{-1} + \varepsilon_{gb}^{-1})^{-1} = \varepsilon_H. \quad (10)
\]

The high frequency and low frequency region in Fig. 3 are labeled accordingly. It is worth mentioning here that low frequency region should also show a plateau like behavior but in the present case failed to detect within the limit of the impedance analyzer. It could be noticed from Fig. 4 that high frequency plateau and the dispersion move to higher frequency side with increase of temperature. This behavior is because \(C_b\) decreases with increase of temperature above \(T_c\) and resistance (both \(R_b\) and \(R_{gb}\)) is expected to be thermally activated and decrease with temperature with Arrhenius dependence of the form

\[
R = \beta \exp(E_a/k_b T). \quad (11)
\]

Hence, the dispersion centered on a frequency, \(f_m\), increases at the same time as the value of \(\varepsilon_b\) decreases with increase in temperature.

Fig. 5 shows the variation of the real part of impedance (\(Z'\)) with frequency at various temperatures. It is observed that the magnitude of \(Z'\) decreases with increase in both frequency as well as temperature, indicating an increase in ac conductivity with rise in temperature and frequency. The \(Z'\) values for all temperatures merge at high frequency. This is due to the release of space charge as a result of reduction in barrier properties of the material with rise in temperature [21,22] and may be a responsible factor for the enhancement of ac conductivity of the material with temperature at high frequencies. Further, at low frequency \(Z'\) values decrease with
increase in temperature show negative temperature coefficient of resistance (NTCR) type behavior similar to that of semiconductors. It can also be noticed from Fig. 5 that the real part of impedance ($Z'$) gives a dip prior to merge at high frequency and that decreases with increase in temperature in the paraelectric phase. This dip may be associated with the charge carrier hopping and supports Fig. 4.

Fig. 6 shows the variation of the imaginary part of impedance ($Z''$) with frequency at different temperatures. The curves show that the $Z''$ values reach a maximum peak ($Z''_{\text{max}}$) for the temperature $\geq 400^\circ$C and the position of $Z''_{\text{max}}$ shifts to higher frequency with increase of temperature (inset of Fig. 6). This shift in frequency maximum indicates active conduction through the grain boundary [21]. The magnitude of $Z''_{\text{max}}$ also decreases with increase in temperature. The merger of $Z''$ values in the high frequency domain may be possibly an indication of the accumulation of space charges in the material at low frequency and at higher temperature (see Fig. 3) [22].

Fig. 7 shows the variation of relaxation time with inverse of absolute temperature ($10^3 T^{-1}$). In a relaxation system, the relaxation time ($\tau$) can be calculated from $Z''$ versus $\log f$ plot using the relation

$$\tau = 1/\omega = 1/2\pi f_{\text{max}},$$

where $f_{\text{max}}$ is the relaxation frequency. It is observed that the value of $\tau$ decreases with increase of temperature, which is a typical semiconductor behavior. The activation energy ($E_a$) of this compound was calculated from Arrhenius relation:

$$\tau = \tau_0 \exp\left(-E_a/k_B T\right),$$

where $\tau_0$ is the pre exponential factor, $k_B$ is the Boltzmann constant and $T$ is the absolute temperature. The value of activation energy calculated from the slope of log $\tau$ versus $10^3 T^{-1}$ (see Fig. 7) was found to be 1.4 eV.

Fig. 8 shows the impedance data taken over a wide frequencies range over at several temperatures as a Nyquist diagram (complex impedance spectrum). It is observed that with increase of temperature the slope of the lines decreases and their curve shift towards real ($Z'$) axis and at temperature $450^\circ$C and onwards two semicircles could be traced with different values of resistance for grain ($R_g$) and grain boundary ($R_{gb}$). Hence grain and grain boundary effects could be separated at these temperatures. These values of $R_g$ and $R_{gb}$ are obtained from the intercepts of the traced semicircles with $Z'$ axis. It can be clearly noticed that the values of $R_g$ and $R_{gb}$ decreases with rise in temperature, which obviously indicates the NTCR character of SBT and supports Fig. 5. The capacitances ($C_g$ and $C_{gb}$) due to these effects can be calculated using the relation $2\pi f_{\text{max}} RC = 1$, where $f_{\text{max}}$ is the frequency corresponding to the maximum of semicircle.

Resistance data for both $R_g$ and $R_{gb}$ along with their relaxation frequencies are summarized in the form of a Arrhenius plot in Fig. 9(a) and (b). At all temperatures, $R_g \ll R_{gb}$ and $R_g$ and $R_{gb}$ give a linear Arrhenius plot (see Fig. 9(a)) with activation energy 1.0 eV and 1.46 eV respectively. The grain and grain boundary relaxation frequencies are recorded from the maxima of the semicircles and used for calculation of activation energy of grains and grain boundaries. The activation energy for grain boundaries is found to be higher than that of grains indicating higher resistive behavior than that of the grains. The activation energy calculated using the grain boundary resistance data (1.43 eV, see Fig. 9(a)) and their relaxation frequency (1.45 eV, Fig. 9(b)) are almost equal. Comparing the grain boundaries activation energy with the activation energy calculated from the frequency dependence imaginary part of the resistance (Fig. 7) one can conclude that the grain boundaries resistances are the dominating character for the overall electrical behavior of the material. These observed low values of activation energy in SBT ceramic compared to other perovskites, may be due to the presence of charges carriers inside the grains and some extrinsic charge carrier created due to the use of silver electrode at elevated temperatures [19].

The ac electrical conductivity was obtained in accordance with the literature [20], relation $\sigma_{ac} = d/A Z'$, where $d$ is the thickness and $A$ is the surface area of the specimen. The log–log plot of electrical conductivity versus frequency at different measuring tempera-
Fig. 9. Arrhenius plot for (a) grain and grain boundary resistance, and (b) their relaxation frequency derived from complex impedance plots.

ture is shown in Fig. 10. The plot shows conductivity increases with increase of temperature. Frequency independent behavior of the conductivity in the low frequency region is observed but that become sensitive at high frequency region. In the low frequency region where conductivity increases is due to hopping of charge carrier in finite clusters. Frequency independent ac conductivity has been observed in the high temperature, indicates the long range movement of mobile charge carriers. The three order jump of conductivity in the studied temperature range indicates the enhancement of mobile charge carrier through the grain boundary which well supports the conclusion drawn from complex impedance spectra. The high frequency variation of $\sigma_{ac}$ found to obey universal Jonscher’s power law behavior, $\sigma_{ac} = Ko^s$ [23], with $0 \leq s \leq 1$, where $\omega$ is angular frequency of ac field, in the frequency sensitive region. Nature of the plot shows a decreasing trend of $s$ with increase of temperature. The model based on classical hopping of electrons over barrier predicts a decrease in the value of the index $s$ with increase in temperature.

In perovskite ferroelectric materials oxygen vacancies are considered to be one of the mobile charge carriers and mostly in titanates, the ionization of oxygen vacancies create conduction electrons, a process which is defined by Kroger-Ving notation [24]. The excess electron and oxygen vacancies are formed in the reduction reaction,

$$O_2^x \rightarrow \frac{1}{2}O_2 + V_{O}^{**} + 2e^- \quad (14)$$

and they may bond to $Ti^{4+}$ in the form $Ti^{4+} + e^- \rightarrow Ti^{3+}$. The formation of oxygen vacancies, can be due to the three different charge states: neutral ($V_{O}^0$) state, which it is able to capture two electrons and it is neutral in the lattice, singly ionized ($V_{O}^-$) state and doubly ionized ($V_{O}^{**}$) state, which it is not trap any electron and it is twofold positively, can be thermally activated, thus enhancing the conduction process. Double charge oxygen vacancies ($V_{O}^{**}$) are considered to be most mobile charge in perovskite and play important role in conduction. In addition to this the chemical inhomogeneity, may be due to the difference in the ionic environment of $Sr^{2+}$ and $Bi^{3+}$ [25,26]. Furthermore the sharing in the A site of perovskite and $[Bi_2O_2]^+$ slabs may also contributes to the conduction mechanism, piezoelectric response and photoluminescent properties [27–30].

The dc conductivity of the sample was evaluated from the impedance spectrum using the relation

$$\sigma_{dc} = \frac{d}{RA}, \quad (15)$$

where $R$ is the resistance of the component (resistance of grain or grain boundary), $d$ the thickness of the pellet and $A$ is the electrode area. An Arrhenius plot of $\sigma_{dc}$ against inverse of absolute temperature is shown in Fig. 11. It follows a typical semiconductor behavior with NTCR characteristics. At all temperature the conductivity of the grain is higher than that of grain boundaries confirming the high resistive behavior of the grain boundaries.
4. Conclusions

Polycrystalline SrBi$_4$Ti$_4$O$_{15}$ (SBiT) ceramics were prepared successfully by a soft chemical method. XRD patterns analysis showed that all the SBiT ceramics crystallize in a perovskite-type orthorhombic structure. The plate like grains morphologies were observed with aspect ratio more than 15. Impedance analysis indicated the presence of grain and grain boundary effect in SBiT. The sample showed dielectric relaxation which is found to be non-Debye type and the relaxation frequency shifted to higher frequency side with increase in temperature. At all temperatures, $R_b \ll R_{gb}$ and $R_b$ and $R_{gb}$ give a linear Arrhenius plot with activation energy 1.0 eV and 1.43 eV respectively. The Nyquist plot and conductivity studies showed the NTCR character for SBiT. The frequency dependent ac conductivity at different temperatures indicated that the conduction process is thermally activated process and the spectra follow the universal power law. Long range mobility of charge carrier are playing effective role in conduction process at elevated temperature. The activation energies from the impedance loss and Nyquist plot suggest oxygen vacancies/ions or defects are responsible for long range motion of charge carriers.

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