Oxygen vacancy related conduction behavior in BaZr$_{0.05}$Ti$_{0.95}$O$_3$ ceramic

G. Nag Bhargavi$^1$, Tanmaya Badapanda$^2$, Ayush Khare$^3$, M. Shahid Anwar$^4$ and Nameeta Brahme$^5$

$^1$Department of Physics, Govt. Pt. Shyamacharan Shukla College Dharsiwa Raipur-493221, India
$^2$Nanophotonics Laboratory, Department of Physics, C.V. Raman College of Engineering, Bhubaneswar-752054, India
$^3$Department of Physics, National Institute of Technology, Raipur-492010, India,
$^4$Colloids & Materials Chemistry, Institute of Minerals and Materials Technology, Bhubaneswar-751013, India
$^5$School of Studies in Physics and Astrophysics, Pt. Ravishankar Shukla University, Raipur-492010, India

Abstract. For this study, the microcrystalline powder of BaZr$_{0.05}$Ti$_{0.95}$O$_3$ (BZT) was prepared by the conventional solid state reaction method. The sample was calcined at 1200 °C for 4 hours and sintered at 1300 °C. The calcined powder was structurally characterized by X-ray diffraction (XRD), which showed that the specimen has a Perovskite structure having orthorhombic structure. On analyzing the scanning electron microscope (SEM) the calculated crystal size was observed to range between 20-30 μm. The dielectric study of BZT showed normal phase transition behavior. The conductivity studies as a function of temperature and frequency has been performed to study the role of oxygen vacancies. The results of the frequency dependence of the conductivity suggest that oxygen vacancy hopping processes, due to relaxations in oxygen vacancy-related dipoles, being mainly responsible for the conduction behavior in the studied system.

Keywords: Solid state reaction method, XRD, SEM, Dielectric study, Conductivity

1. Introduction

Barium titanate (BT) is a well known Perovskite structured material, which is known for its high dielectric constant, spontaneous polarization, ferroelectric properties and non linear optical properties. It is given in the open literature that the properties of BT can be enhanced by the substitution at Barium and/or Titanium sites by homovalent or aliovalent ions [1-6]. This lead (Pb) free compound has numerous applications in DRAMs, MLCCs, ultra sonic transducers, optical data storage at high density, sensors, actuators and optoelectronic devices [7-9]. Among the homovalent substituents Zr$^{4+}$ in place of Ti$^{4+}$ has been reported to improve the dielectric properties of BT [10-12]. This ceramic with general formula BaZr$_x$Ti$_{1-x}$O$_3$ shows promising piezoelectric and electrostrictive properties [13, 14]. Better thermal and chemical stability of Zr$^{4+}$ than Ti$^{4+}$ makes Zr$^{4+}$ a best choice as isovalent substituent for substitution at Ti sites [15]. Also, the ionic radius of Zr$^{4+}$ (0.087 nm) is larger than Ti$^{4+}$ (0.068 nm) which expand the unit cell and the possibility of electron hopping between Ti$^{4+}$ ions and Ti$^{3+}$ ions reduces to a large extent [15].

In case of all the oxide Perovskites the oxygen vacancies are the fundamental intrinsic defects that play a very critical impact on the electrical properties. The oxygen vacancies do not lost
their identity even after the process of sintering. In all the oxide ferroelectric materials the
dielectric relaxation is usually related to the vacancies produced at oxygen sites. It is
extensively accepted that the dielectric relaxation in oxide materials specifically at high
temperatures are usually related to oxygen vacancies, apart from this dielectric relaxation
appear in the low-frequency region is also attributed to oxygen-vacancies [16, 17]. So, it is
very interesting to study the conduction behavior of BZT system in terms of oxygen
vacancies.

The material performances are closely dependent on the methods of synthesis. In case of
ferroelectric ceramics the method of synthesis is prominent in determining the various
structural and electrical properties. There are various methods of synthesis like solid state
reaction method, ball milling, wet chemical synthesis, combustion technique, Sol-gel
technique etc. [18-20]. Among these some are chemical routes while some are physical (high
temperature diffusion) routes. In the present work, we have chosen the high temperature solid
state reaction methods. The chemical routes of processing require costly chemicals which are
very sensitive to the environment and physical conditions like light heat and moisture. On the
other hand the solid state reaction method uses carbonates and oxides which are easily
available and also cost effective.

So, in this study the main objective of the authors is to synthesize BaZr$_{0.05}$Ti$_{0.95}$O$_3$ ceramic
system by the conventional solid state reaction method and to study in detail the electrical
conduction behavior in terms of oxygen vacancies.

2. Experimental Procedure

The sample (BaZr$_{0.05}$Ti$_{0.95}$O$_3$) was synthesized by the traditional solid state reaction method.
The stoichiometric mixture of powders (BaCO$_3$, TiO$_2$, ZrO$_2$) was mixed and grinded in an
agate mortar with a little amount of distilled water. The mixture was fired at 1200 °C for
calcination for 4 hours in a high temperature furnace. The chemical reaction for the above
process is shown in eq. (1). The Perovskite phase structure of the sample was confirmed
under the X-ray diffraction analysis (X’pertPro Diffractometer). The analyzed 20 range was
10°-90° with a step rate of 0.02° and counting time of 0.5 minute for each step. The
microstructure of the sintered sample was observed by scanning electron microscope (Zeiss
EVO 18). The fired powder was formed as a thick disc (1mm) by cold pressing and sintering
was carried out at 1300 °C for 4 hours. The sintered disc was polished with silver paint to
make the surface conducting to carry out the electric studies (N4L-NumeriQ LCR meter,
Model PSM 1735).

\[
\text{BaCO}_3 + 0.05\text{ZrO}_2 + 0.95\text{TiO}_2 \rightarrow \text{BaZr}_{0.05}\text{Ti}_{0.95}\text{O}_3 + \text{CO}_2 \uparrow
\]  

(1)

3. Results and Discussion

3.1 Structural Characterization

Fig. 1 is presenting the XRD pattern of BaZr$_{0.05}$Ti$_{0.95}$O$_3$ system which is calcined at 1200 °C
for 4 hours. The X- ray diffraction pattern could be indexed as a pure Perovskite structure. No
impurity peak corresponding to any deleterious phase was found which confirms the single
phase nature of the compound. Moreover, the sharp intense and well defined diffraction
peaks indicate that the ceramic material has a long range degree of crystallinity. The obtained
phase was indexed using the orthorhombic space group \textit{Amm2} which is in close agreement with the earlier reports [15, 21].

![XRD pattern of BaZr$_{0.05}$Ti$_{0.95}$O$_3$ ceramic](image)

**Fig. 1** XRD pattern of BaZr$_{0.05}$Ti$_{0.95}$O$_3$ ceramic

### 3.2 Microstructural studies

Fig. 2(a) shows the morphological image of BaZr$_{0.05}$Ti$_{0.95}$O$_3$ ceramic pellet sintered at 1300 °C taken from SEM. The SEM investigation has shown that the microstructures of the specimen exhibit a good growth of grains. The image showed that the grains are in irregular polygon shape. Also the grains developed with irregular morphology have multiple grain boundaries. This characteristic is mainly attributed to the matter transportation mechanism at high temperatures during the solid state reaction. Also, the average crystallite size is estimated by line intercept method which is observed to be 20-30 µm. The compositional characterization of BaZr$_{0.05}$Ti$_{0.95}$O$_3$ ceramic sintered at 1300 °C was also done using Energy dispersive X-ray spectroscopy (EDX) which is shown in fig. 2(b). The measurements were taken at different locations and then averaged. Table 1 shows the calculated and EDX derived composition of BaZr$_{0.05}$Ti$_{0.95}$O$_3$ ceramic. There exist small variation in both the data which possibly due the deficiency of oxygen during sintering at high temperature. Moreover, in solid state reaction method it is always difficult to get the microscopic uniformity.
Fig. 2(a) SEM image of BaZr$_{0.05}$Ti$_{0.95}$O$_3$ ceramic sintered at 1300 °C

Fig. 2(b) EDX spectrum showing the elemental composition of BaZr$_{0.05}$Ti$_{0.95}$O$_3$ ceramic

| Element | Wt.% calculated | Wt.% from EDX |
|---------|-----------------|---------------|
| Ba      | 57.59           | 57.65         |
| Zr      | 1.48            | 1.59          |
| Ti      | 18.52           | 18.12         |
| O       | 22.41           | 22.64         |

3.3 The Ferroelectric – Paraelectric phase transition

Fig. 3 depicts the change in inverse of permittivity (1/ε’) as a function of temperature performed at 100 kHz. It is known that for normal ferroelectrics the ferro- to – paraelectric
phase transition is known to be first order when $T_0 < T_c$ and of second order when $T_c = T_0$, here $T_c$ is the Curie-Weiss temperature which is defined by the following relation:

$$\frac{1}{\varepsilon_r} = \frac{T - T_c}{C}$$  \hspace{1cm} (2)

Curie - Weiss law is no longer valid in the case where relaxation and diffuseness are present. For all the relaxor ferroelectrics (having diffuse phase transition) a deviation from Curie – Weiss law is observed which is a typical behavior of relaxors. The parameter $\Delta T_m = T_{CW} - T_m$, where $T_{CW}$ denotes that temperature from which the dielectric permittivity starts to deviate from the Curie - Weiss law while $T_m$ is the temperature of dielectric maximum. In the present study for BaZr$_{0.05}$Ti$_{0.95}$O$_3$ the phase transition was observed to be first order i.e. no deviation from ideal Curie Weiss law is observed. Also, the phase transition temperature was measured to be 400 K.

![Graph](image_url)

**Fig. 3** Change in $1/\varepsilon'$ with respect to temperature measured at 1 kHz

### 3.4 AC Conductivity in ferroelectric phase

Fig. 4 shows the variation of AC conductivity of BaZr$_{0.05}$Ti$_{0.95}$O$_3$ with reciprocal of temperature ($10^3/T$) measured at 1 KHz. The observed variation in AC conductivity with temperature could be divided into two distinct regions in the scale namely the lower temperature region and the higher temperature region. Being activated by the various temperatures the oxygen vacancies behaves as trapping centres for the mobile charge carriers. Also an increase in the conductivity considerably in the high temperature region is seen probably this is due to the hopping of the charge carriers among the available oxygen vacancies. Another important fact we observed from the graph is the changing slopes that appear in different regions of temperature scale, which is an indication of involvement of multiple activation processes having different activation energies. The AC conductivity first
increases with temperature up to 125 °C and then decreases with increasing in temperature, which also represents the transition temperature.

![Graph](image)

**Fig. 4 AC conductivity of BZT ceramic plotted against 1000/T measured at 1 kHz**

In all the dielectric materials there exist several polarization mechanisms; these mechanisms have some relationships with the relaxation behaviour like space charge polarization, interfacial polarization, dipolar polarization etc. The dielectric relaxation due to space charge polarization, interfacial polarization, domain wall motion, long range structural disorder and defect relaxation etc. usually occurs at low frequency region while the dipolar relaxation occurs at higher frequency region. It is given in the open literature that the dielectric relaxation in all the dielectric materials in the temperature above room temperature is usually related to the available oxygen vacancies and hopping motion of singly and doubly ionized oxygen vacancies leads to the relaxation process. Thus, it can be considered that in the low frequency spectral region the relaxation belongs to space charge that is related to the oxygen vacancies and the defect sites. While sintering at high temperatures produces Barium vacancies which results in oxygen vacancies due to the constraints of charge neutrality. At high temperatures the ionization of oxygen vacancies takes place that create conducting electrons in the Perovskite structure as a result single ionized and double ionized oxygen vacancies are left where \( V'_o \) and \( V''_o \) are respectively the single ionised and double ionised states. Thus, as described by the Kroger-Vink notation:

\[
V_o \leftrightarrow V'_o + e' \tag{3}
\]

\[
V'_o \leftrightarrow V''_o + e' \tag{4}
\]

\[
Ba^{3+}_Ba + O^{2-}_O \rightarrow V'_{Ba} + V''_o + BaO \uparrow \tag{5}
\]

Further to understand the transport mechanism in the samples the electrical conductivity behavior was investigated. The transport mechanism is basically due to the presence of space charge in the material. The origin of conductivity mechanism is related to the level and mobility of oxygen vacancies which is a common phenomenon in perovskites. As it is known the AC conductivity of the samples is directly related to the dielectric properties of the sample. To evaluate the bulk conductivity (\( \sigma_{ac} \)) of the samples the formula used is \( \sigma_{ac} = \tau/Z' A \) where \( \tau \) is the thickness, \( A \) is the surface area of the samples and \( Z' \) is the real part of the
impedance. Fig. 5(a) indicates the ac conductivity of the BaZr_{0.05}Ti_{0.95}O_3 samples at various frequencies (from RT to T_c). Initially, with increasing frequency, $\sigma$ is almost independent of frequency followed by dispersion at higher frequencies. By extrapolating the graph towards lower frequency side the value of $\sigma_{dc}$ can be determined which is credited to the long range translational motion of charge carriers. It is also observed that with increasing temperature conductivity increases for all frequencies. Conduction in perovskites is basically due to the hopping mechanism of different species of ions present in the material. The excess electrons interact with the lattice and distort the surroundings as a result a potential well is created which raise the conduction. As the temperature increases the number of excess electrons increases and get sufficient energy to cross the well, thus with increasing temperature conductivity increases. The change in AC conductivity in the lower frequency region is mainly due to the polarization effect at electrode and electrolyte interface. At much lower frequencies the charge accumulates at the electrode and electrolyte interface and reduces the conductivity almost equal to the DC conductivity. At higher frequencies the characteristic of conductivity spectra can be explained as according to the Jonscher’s power law. According to which $\sigma_{ac} = \sigma_{dc} + A\omega^n$ ($0 < n < 1$) where, $A$ is the pre-exponential factor and ‘$n$’ is the exponent of power law which gives the idea of interaction between mobile ions and lattice. ‘$A$’ gives the idea of strength of polarizability in the samples.

The variation of AC conductivity with respect to inverse of temperature by means of Arrhenius law is shown in fig. 5(b). The slope of this graph determines the value of activation energy involved in the conduction process. Conduction induced by oxygen vacancies becomes dominant with increasing temperature because the mobility of oxygen ions becomes higher in high temperature region. It has been reported in the literature that the when the activation energy lies in the range of 0.3-0.4eV, the oxygen vacancies lies in the single ionized state while for the doubly ionized oxygen vacancies the value lies between 0.6-1.2eV. The experimental value of activation energy associated with the DC conductivity for the studied sample is 1.1eV. The results are in good agreement with the values reported for the doubly ionized oxygen vacancies.

Fig. 5(a) AC conductivity as a function of frequency at various temperatures
4 Conclusions

Thus, we conclude that polycrystalline sample of $\text{BaZr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ ceramic has been synthesized by the high temperature solid state reaction method. The X-ray diffraction studies revealed the presence of orthorhombic phase. The dielectric measurements of $\text{BaZr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ ceramic with respect to temperature at 1 kHz has been analyzed, no deviation from Curie – Weiss law has been seen indicating the normal ferroelectric phase transition in the sample. The studies show that the conduction was caused by the presence of oxygen vacancies. Also, the dielectric relaxation at high temperature was related to the presence of oxygen vacancies.

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