

Dielectric and electrical properties of $0.5(\text{BiGd}_{0.05}\text{Fe}_{0.95}\text{O}_3)-0.5(\text{PbZrO}_3)$ composite

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The $0.5(\text{BiGd}_{0.05}\text{Fe}_{0.95}\text{O}_3)-0.5(\text{PbZrO}_3)$ composite was synthesized by means of a high temperature solid-state reaction technique using high purity ingredients. Preliminary X-ray structural analysis confirms the formation of the composite. The dielectric constant and loss tangent have been studied. The impedance parameters have been measured using an impedance analyzer in a wide range of frequency ($10^2 - 10^6$ Hz) at different temperatures. The Nyquist plot suggests the contribution of bulk effect only and the bulk resistance decreases with a rise in temperature. Electrical impedance confirms the presence of grain effect and hopping mechanism in the electrical transport of the material. The dc conductivity increases with a rise of temperature. The frequency variation of ac conductivity shows that the compound obeys Jonscher's universal power law and from Jonscher's power law fit confirms the Small Polaron (SP) tunneling effect. Temperature dependence of dc and ac conductivity indicates that electrical conduction in the material is a thermally activated process.

Keywords: XRD; dielectric constant; impedance; electrical conductivity

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1. Introduction

The activation energy in the case of conductivity is an important parameter in material science. The activation energy is frequency dependent but at higher temperature it may be frequency independent [1]. The sensitivity of a thermistor for temp-sensing is described by the activation energy of the electrical conduction [2]. Recently, electrical conductivity is one of the most frequently studied properties in a composite. BiFeO_3 (BFO) is an extensively studied simple perovskite that exhibits multiferroic (ferroelectric and antiferromagnetic) characteristics at room temperature [3]. BFO has a rhombohedral crystal structure in the bulk form [4] and its magnetic Neel temperature and ferroelectric Curie temperature are 400°C and 820°C , respectively [5, 6]. Conductivity plays an important role in BFO [7–10]. Due to high conductivity in BiFeO_3 it is possible to develop a MERAM (Magnetoelectric Random Access Memory) [11], which can be easily integrated into functional microelectronic devices [12]. Lead zirconate, PbZrO_3 (PZO), a pe-

rovskite type compound, is the first material which shows antiferroelectricity [13]. Due to its antiferroelectric behavior, PZO is technologically important for applications involving actuators and high energy storage devices [14–19]. The conductivity of $\text{Pb}(\text{Zr or Ti})\text{O}_3$ has been studied intensively for last few years [20, 21]. A new ferroelectric phase has been found in $\text{BiFeO}_3\text{--PbZrO}_3$ (BFO-PZO) system, which appears to have the same crystal structure as PbZrO_3 and whose value of T_c is about 400°C at 20 MHz [22]. Moreover, the magnetic property was also observed in a double perovskite structure $\text{BiFeO}_3\text{--PbZrO}_3$ [23]. Realizing the behavior of rare earth substitution, recently we have reported on the electrical conduction mechanism of Gd doped $\text{BiFeO}_3\text{--PbZrO}_3$ composite [24] and in this work, we report the dielectric and electric properties of $0.5\text{BiGd}_{0.05}\text{Fe}_{0.95}\text{O}_3\text{--}0.5\text{PbTiO}_3$ composites.

2. Experimental details

Gd doped BFO-PZO with a formula $0.5(\text{BiGd}_{0.05}\text{Fe}_{0.95}\text{O}_3)-0.5(\text{PbZrO}_3)$ was prepared by solid state reaction technique. It was

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prepared from high purity ingredients, i.e. Bi_2O_3 , Gd_2O_3 , Fe_2O_3 , PbO and ZrO_2 in a suitable stoichiometry. The oxides were thoroughly mixed, first in air atmosphere for 2 h, and then in alcohol for 1 h. The mixed powders were calcined at an optimized temperature of 750 °C for 5 h. The calcined powder was cold pressed into cylindrical pellets of 10 mm diameter and 1 – 2 mm of thickness at a pressure of $3.5 \times 10^6 \text{ N/m}^2$ using a hydraulic press. PVA (polyvinyl alcohol) was used as a binder to reduce the brittleness of the pellet, which was burnt out during the sintering. Then the pellets were sintered at 800 °C for 6 h in an air atmosphere. The formation and quality of the compound was studied by an X-ray diffraction (XRD) technique at room temperature with a powder diffractometer (Rigaku Miniflex, Japan) using $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$) in a wide range of Bragg's angles 2θ ($20^\circ \leq 2\theta \leq 80^\circ$) with a scanning rate of $3^\circ/\text{min}$. To study the electrical properties of the composites, the sintered pellets were electroded with air-drying conducting silver paste. After electroding, the pellets were dried at 150 °C for 4 h to remove moisture, if any, and then cooled to room temperature before taking any measurement. The dielectric constant (ϵ_r), dielectric loss ($\tan\delta$) and impedance as a function of temperature and frequency were measured using a computer-controlled LCR meter (HIOKI Model 3532) in the frequency range of $10^2 - 10^6 \text{ Hz}$ from 25 – 450 °C.

3. Result and discussion

3.1. Structural study

Fig. 1 shows the X-ray diffraction pattern of $0.5(\text{BiGd}_{0.05}\text{Fe}_{0.95}\text{O}_3)-0.5(\text{PbZrO}_3)$. The diffraction peaks of the composite were indexed in different crystal systems and unit cell configurations. An orthorhombic unit cell was selected on the basis of good agreement between observed and calculated interplanar spacing d (i.e., $\sum \Delta d = d_{\text{obs}} - d_{\text{cal}} = \text{minimum}$). The lattice parameters of the selected unit cell were refined using a standard computer program package "POWD" [25]. These refined lattice parameters are: $a = 9.1240 \text{ \AA}$, $b = 10.0470 \text{ \AA}$,

$c = 12.7288 \text{ \AA}$ and $V = 1166.834 \text{ \AA}^3$. These unit cell parameters are consistent, and are in good agreement with those reported for an orthorhombic structure [24]. The crystallite size (P) of Gd doped BFO-PZO was roughly estimated from the broadening of a few XRD peaks (in a wide 2θ range) using the Scherrer's equation [26],

$$P = k\lambda / (\beta_{\frac{1}{2}} \cos \theta_{hkl}) \quad (1)$$

where $k = \text{constant} = 0.89$, $\lambda = 1.5405 \text{ \AA}$ and $\beta_{\frac{1}{2}} =$ peak width of the reflection at half intensity. The average value of P was found to be 33 nm. The effect of strain, instruments, and other defects on indexing has been ignored in the calculations.

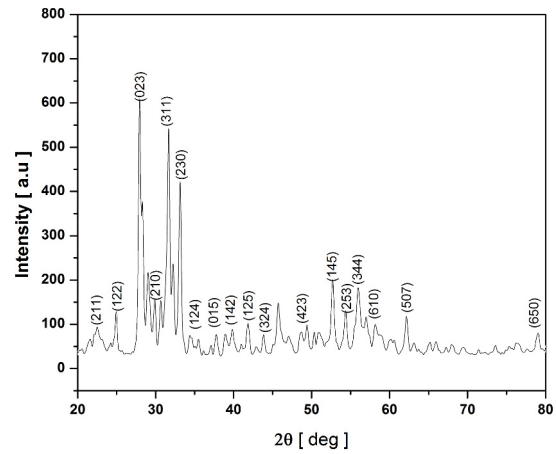


Fig. 1. XRD pattern of $0.5(\text{BiGd}_{0.05}\text{Fe}_{0.95}\text{O}_3)-0.5(\text{PbZrO}_3)$.

3.2. Dielectric study

Fig. 2 shows the variation of ϵ_r and $\tan\delta$ (inset) of $0.5(\text{BiGd}_{0.05}\text{Fe}_{0.95}\text{O}_3)-0.5(\text{PbZrO}_3)$ with temperature at different frequencies (10 kHz – 1 MHz). It is observed that both ϵ_r and $\tan\delta$ decrease on increasing frequency, which is a general feature of polar dielectric materials [27]. At low frequency, dielectric constant of a polar material is due to contribution of polarizability i.e., electronic, ionic, dipolar and interfacial. As the frequency increases, some of the polarizations cease, and hence the dielectric constant decreases. The values of dielectric constant and loss tangent increase on increasing temperature. In the high-temperature region, higher

value of dielectric constant may be due to space charge polarization, which comes from mobility of ions and imperfections in the material. These combined effects produce a sharp increase in the dielectric constant on increasing temperature. The variation of loss tangent follows the same behavior as that of dielectric constant.

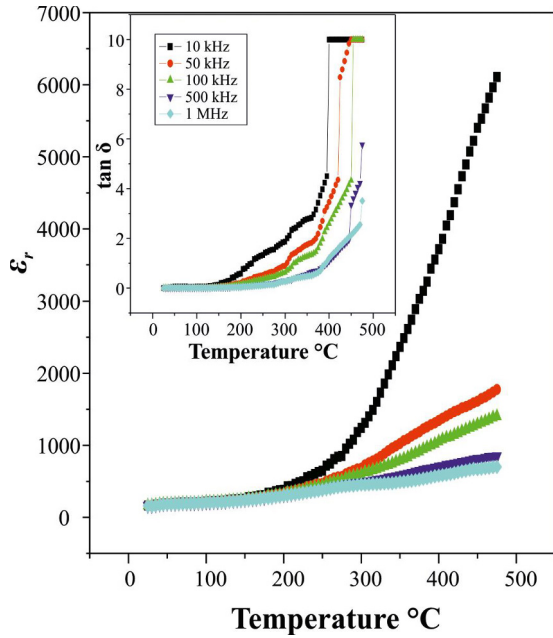


Fig. 2. Temperature dependence of dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) (inset).

3.3. Impedance study

Impedance spectroscopy is stated explicitly or in detail from electrical measurement that can be readily automated and whose results may often be correlated with many complex materials. Electrical ac data of a material may be represented in any of the four basic formalisms which are correlated to each other [28]. Complex impedance:

$$Z^* = Z' - jZ'' = R - j/\omega C \quad (2)$$

Complex admittance:

$$Y^* = Y' + jY'' = 1/R + \phi\omega X, \quad (3)$$

Complex modulus:

$$M^* = 1/\epsilon^* = M' + jM'' = j\omega C_0 Z \quad (4)$$

Complex permittivity:

$$\epsilon^* = \epsilon' - j\epsilon'' \quad (5)$$

loss tangent:

$$\tan \delta = \epsilon''/\epsilon' = M''/M' = -Z'/Z'' = Y'/Y'' \quad (6)$$

Fig. 3 shows the variation in real part of impedance (Z') with the frequency at different temperatures (200 – 275 °C). It is observed that Z' decreases with an increase in frequency at different temperatures and at higher frequency the values of Z' merge. This is due to the release of space charge as a result of a reduction in the barrier properties of the material with the rise in temperature and may be a factor responsible for the enhancement of the ac conductivity of the material with temperature at higher frequencies [29]. The Z' value decreases with a rise in temperature, and the compound exhibits a negative temperature coefficient of resistance – (NTCR)-type behavior like that of semiconductors [30].

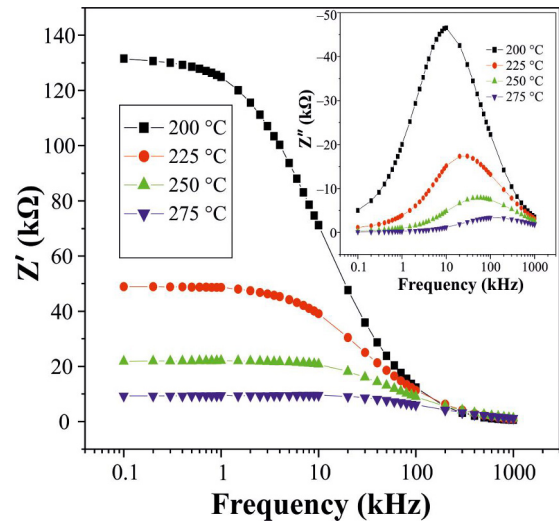


Fig. 3. Variation of Z' and Z'' (inset) with frequency.

Fig. 3 (inset) shows the variation in imaginary part of impedance with the frequency at different temperatures. The material gets relaxed in certain frequency range and the peaks become asymmetric as the temperature increases. It means that the peaks are shifted towards the higher frequency as

the temperature increases. The asymmetric broadening of the peaks in the frequency plots of Z'' suggests that there is a spread of relaxation times i.e., the existence of a temperature dependent electrical relaxation phenomenon in the material [31].

Fig. 4 shows the variations in real and imaginary parts of impedance (Nyquist plot) of the composite at different temperatures (200 – 275 °C) over a wide range of frequency ($10^2 - 10^6$ Hz) along with appropriate equivalent circuit (inset). This plot shows one semicircle which indicates the presence of bulk effect and slight indication of grain boundary effect in the composite. From the figure, it is clear that the semicircular arc shifts towards the origin indicating the increase in the conductivity as the temperature increases, and its conduction mechanism is similar to that in semiconductor materials. The semicircular pattern in the impedance spectrum is representative of the electrical process taking place in the material. This Nyquist plot contains one semicircle, and the equivalent circuit is excellently fitted with R(CR)(QR), where R, C and Q are resistance, capacitance and constant phase element (CPE). Admittance of the CPE can be written as:

$$\gamma_{CPE} = \gamma_o(j\omega)^n \quad (7)$$

where γ_o is a constant pre-factor and n the exponent. It is clearly demonstrated that the simple R(CR)(QR) circuit could represent the impedance data ($\chi^2 \sim 10^{-3}$) and the parameters of each fitting are summarized in Table 1.

3.4. Conductivity study

The electrical conductivity study was performed to incorporate the effect of conduction mechanism and different types of charge carriers in the materials. The value of ac conductivity (σ_{ac}) of the material was evaluated by using an empirical formula:

$$\sigma_{ac} = \epsilon_0 \epsilon_r \omega \tan \delta \quad (8)$$

where the symbols have their usual meaning.

Fig. 5 shows the frequency dependence of ac conductivity at various temperatures. It is observed that at low frequency the charge accumulation at

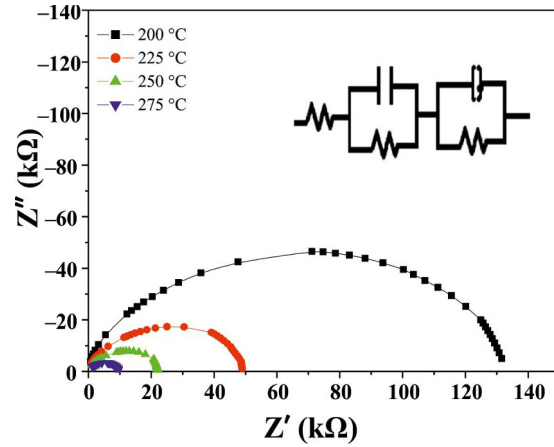


Fig. 4. Variation of imaginary impedance (Z'') with real impedance (Z') for various temperatures.

Table 1. Summarizing of fitting parameters corresponding to equivalent circuits of Fig. 4.

Parameters	R(CR)(QR)-Circuit
Resistance (R_1)	$1 \times 10^{-7} (\Omega)$
Capacitance (C)	$1.061 \times 10^{-10} (F)$
Resistance (R_2)	$2.013 \times 10^4 (\Omega)$
CPE, (γ_0)	$1.053 \times 10^{-9} (S-s^{0.5}/cm^2)$
Resistance (R_3)	$1.131 \times 10^5 (\Omega)$
Frequency power (n)	0.8303
Chi-Square (χ^2)	0.02311

the electrode-interface takes place which reduces the conductivity. The high frequency region of the ac conductivity is frequency independent due to the random diffusion of the ionic charge carriers [32] and the values correspond to dc conductivity. The appearance of the dc plateau is an evidence of the formation of conducting path in the material. This can be described by a relation:

$$\sigma_{ac} = \sigma_o + A\omega^n \quad (9)$$

which is Jonscher's power law [33] where A is the temperature dependent pre-exponential factor and n is the fractional exponent ranging between 0 and 1 for the electrolyte. The values of A, n and σ_{dc} are given in the Table 2. They were calculated by non-linear fit of the above equation with experimental data. The value of n lies in the range of 0.52 – 0.97

(200 – 300 °C). Fig. 6 shows the variation of the A and n with temperature. It is observed that the value of n increases rather monotonically with temperature (200 – 300 °C), which may be a result of the enhanced contribution of electrode polarization with temperature [34]. This type of behavior may be associated with the small polaron (SP) tunneling models [35]. Basically, n is a temperature dependent factor in correlated barrier hopping (CBH) models, overlapping large polarons (OVL) models and small polarons (SP) tunneling models, whereas it is temperature independent in the quantum mechanical tunneling (QMT) model [36].

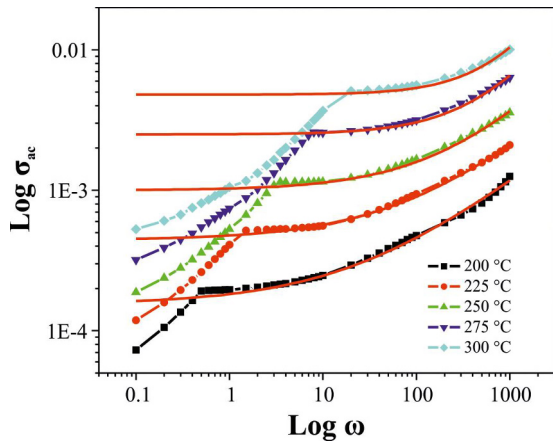


Fig. 5. Ac conductivity as a function of frequency for various temperatures.

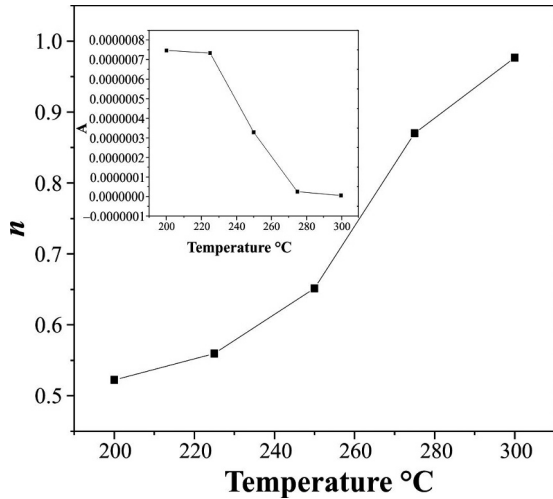


Fig. 6. Variation of A and n with temperature.

Fig. 7 shows the variation of ac conductivity (σ_{ac}) with inverse of temperature at different frequencies (10 kHz, 50 kHz, 100 kHz, 500 kHz and 1 MHz). This indicates that hopping dominates the conduction process since the activation energy is low at temperatures between 145 – 450 °C and the conductivity increases with frequency. But in low temperature region (25 – 110 °C) the activation energy decreases as the frequency increases (see Table 3). Due to the high activation energy the conductivity decreases as temperature increases. The activation energy shown in Table 3 has been calculated from the slope of linear portion of $\ln\sigma_{ac}$ vs. $10^3/T$ graph (Fig. 7). The trend in variation indicates a substantial enhancement in the ac conductivity with a rise in temperature in the high-frequency region. At higher temperatures, the conductivities at different frequencies appear to be approaching each other. These results agree well with the low frequency dispersion and high-frequency plateau obtained at higher temperatures.

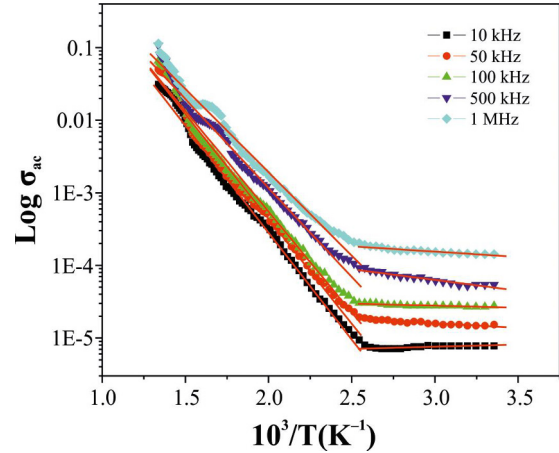


Fig. 7. Variation of ac conductivity with inverse temperature at different frequencies.

Fig. 8 shows the variation of $\ln\sigma_{dc}$ (bulk) with inverse of absolute temperature ($10^3/T$). The bulk conductivity of the material was evaluated from the complex impedance plots of the sample at the above temperatures. The variation of $\ln\sigma_{dc}$ with inverse temperature is linear and the nature of variation follows the Arrhenius law;

$$\sigma = \sigma_o \exp(-E_a/k_B T) \quad (10)$$

Table 2. Fitting parameters obtained from the Jonscher power law at different temperatures. Comparisons between dc conductivity obtained from the fitted parameters and from Nyquist plots (parenthesis).

T (°C)	σ_{dc} ($\Omega^{-1}\text{m}^{-1}$)	A	n	Goodness of fit (R^2)
200	0.00015 (0.3527E-3)	7.4646E-7	0.52254	0.990
225	0.00044 (0.6784E-3)	7.3382E-7	0.55945	0.971
250	0.001 (1.9266E-3)	3.2824E-7	0.65143	0.901
275	0.0025 (4.14876E-3)	2.4538E-8	0.87011	0.831
300	0.0048 (8.19118E-3)	5.398E-9	0.97651	0.798

Table 3. Ac activation energy with temperature at different frequency ranges.

Frequency (kHz)	Temperature (25 – 110 °C)	Temperature (135 – 445 °C)
10	0.5846 (eV)	0.01189 (eV)
50	0.5734 (eV)	0.024576 (eV)
100	0.5511 (eV)	0.0108 (eV)
500	0.4864 (eV)	0.05833 (eV)
1000	0.4555 (eV)	0.02916 (eV)

where σ_o is a pre-exponential term, E_a is activation energy and k_B is Boltzmann constant. The activation energy was estimated to be 0.724 eV in the temperature range of 200 – 300 °C. Fig. 8 (inset) shows the relation between relaxation time (τ) and ($10^3/T$). The τ was calculated from Z'' vs. frequency plot by using the relation $\omega_{max}\tau = 1$. The variation of $\ln\tau$ as a function of inverse of absolute temperature appears to be linear which follows the relation:

$$\tau = \tau_o \exp(-E_a/k_B T) \quad (11)$$

where τ_o is the pre-exponential factor and the activation energy calculated from this relation is found to be 0.66 eV which is very close to the E_a found from dc conductivity vs. inverse of temperature plot. The activation energy was found to be less as compared to the activation energy of the composite 0.67BiFeO₃–0.33PbTiO₃ with various concentrations [30].

4. Conclusion

The composite of 0.5(BiGd_{0.05}Fe_{0.95}O₃)–0.5(PbZrO₃) has been prepared by a high temperature solid state reaction technique. X-ray analysis

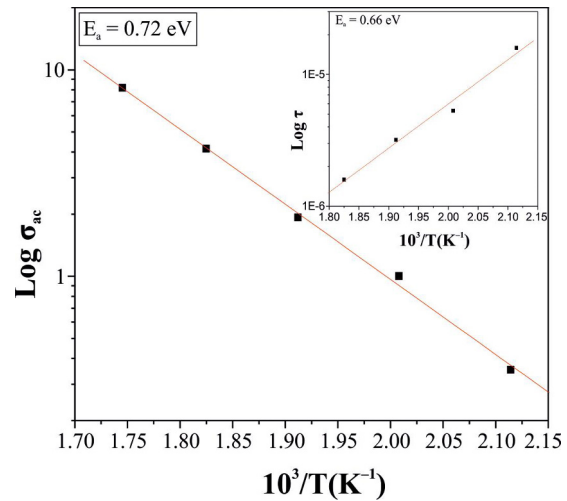


Fig. 8. Variation of dc conductivity and relaxation time (inset) with inverse of temperature.

exhibits the orthorhombic crystal structure of the composite at room temperature. Impedance studies reveal the contribution of grain (bulk) effect only and a slight indication of grain boundary effect. The bulk resistance of the material decreases with a rise in temperature and exhibits a NTCR behavior. In the frequency dependence of ac conductivity,

the variation of n with temperature confirms the Small Polaron (SP) tunneling effect. The variation of ac and dc conductivity of the material as a function of temperature exhibits Arrhenius type of electrical conductivity. The activation energy calculated from dc conductivity of the composite is found to be 0.72 eV in the high temperature region and the activation energy calculated from the relaxation time is found to be 0.66 eV. The ac conductivity is found to obey the universal power law and thermally activated conduction process.

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References

- [1] SHIHUB S.I., GOULD. R.D., *Thin Solid Films*, 354 (1995), 187.
- [2] WEN S. et al., *Sensor. Actuator.*, 78 (1999), 180.
- [3] RANJITH R. et al., *Appl. Phys. Lett.*, 96 (2010), 022902.
- [4] KUBEL F., SCHMID H., *Acta Crystallogr. B*, 46 (1990), 698.
- [5] KISELEV S.V., OZEROV R.P., ZHDANOV G.S., *Soviet Physics-Doklady*, 7 (1963), 742.
- [6] SPALDIN N.A., CHEONG S-W., RAMESH R., *Phys. Today*, 63 (2010), 38.
- [7] VENGALISA B. et al., *Acta Phys. Pol. A*, 113 (2008) 1095.
- [8] GREIČIUS S., BANYS J., SZAFRANIAK-WIZA I., *PAC*, 3 (2009), 85.
- [9] CATALAN G., *Ferroelectrics*, 433 (2012), 65.
- [10] MAKSYMOWYCH P. et al., *Nano Lett.*, 11 (2011), 1906.
- [11] BIBES M., BARTHÉLÉMY A., *Nat. Mater.*, 7 (2008), 425.
- [12] CATALAN G., SCOTT J.F., *Adv. Mater.*, 21 (2009), 2463.
- [13] TAGANTSEV A.K. et al., *Nat. Commun.*, 4 (2013), 1.
- [14] SENGUPTA S.S., ROBERTS D., LI J.F., KIM M.C., PAYNE D.A., *J. Appl. Phys.*, 78 (1995), 1171.
- [15] XU B., MOSES P., PAI N.G., CROSS L.E., *Appl. Phys. Lett.*, 72 (1998) 593.
- [16] YAMAKAWA K., MCKINSTRY S.T., DOUGHERTY J.P., KRUPANIDHI S.B., *Appl. Phys. Lett.*, 67 (1995), 2014.
- [17] SEVENO R.H., GUNDEL W., SEIFERT S., *Appl. Phys. Lett.*, 79 (2001), 4204.
- [18] JANG J.H., YOON K.H., SHIN H., *Appl. Phys. Lett.*, 73 (1998), 1823.
- [19] XU B., YE Y., CROSS L.E., *J. Appl. Phys.*, 87 (2000), 2507.
- [20] KETSUWAN P. et al., *Ferroelectrics*, 382 (2009), 49.
- [21] PARUI. J., KRUPANIDHI. S.B., *J. Appl. Phys.*, 100 (2006), 044102.
- [22] GERSON R., CHOU P.C., W.J. JAMES, *J. Appl. Phys.*, 38 (1967), 55.
- [23] RAO B., UMA MAHESHWAR, SRINIVASAN G., BABU V. SURESH, SEEHRA M.S., *J. Appl. Phys.*, 69 (1991) 5463.
- [24] SATPATHY S.K., MOHANTY N.K., BEHERA A.K., BEHERA BANARJI, NAYAK P., *Front. Mater. Sci.*, 7 (2013) 295.
- [25] WU E., *J. Appl. Crystallogr.*, 22 (1989), 506.
- [26] PATTERSON A., *Phys. Rev.*, 56 (1939), 978.
- [27] IZCI ERTUGRUL , IZCI ALIME, *Turk. J. Chem.*, 31 (2007), 523.
- [28] HODGE I.M., INGRAM M.D., WEST A.R., *J. Electroanal. Chem.*, 74 (1976), 125.
- [29] JAMES A.R., SRINIVAS K., *Mater. Res. Bull.*, 34 (1999), 1301.
- [30] SUMAN C.K., PRASAD K., CHOUDHARY R.N.P., *J. Mater. Sci.*, 41 (2006), 369.
- [31] SUMAN C.K., PRASAD K., CHOUDHARY R.N.P., *Adv. Appl. Ceram.*, 104 (2005), 294.
- [32] KARMAKAR A., GHOSH A., *J. Appl. Phys.*, 110 (2011), 034101.
- [33] JONSCHER A.K., *Nature*, 267 (1977), 673.
- [34] MAHAMOUD HAIBADO, LOUATI B., HLEL F., GUIDARA K., *Bull. Mater. Sci.*, 34 (2011), 1069.
- [35] ATA-ALLAH S.S., SAYEDAHMED F.M., KAISER M., HASHHASH A.M., *J. Mater. Sci.*, 40 (2005), 2923.
- [36] ELLIOTT S.R., *Adv. Phys.*, 36 (1987), 135.

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