

## AC CONDUCTIVITY AND DIELECTRIC RELAXATION STUDIES OF SANDSTONE- A CORRELATION WITH ITS THERMOLUMINESCENCE

Tanmoy Roy Choudhury\*, Amitabha Basu<sup>a</sup>

*Department of Applied Physics, Indian School of Mines University,  
Dhanbad-826004 Jharkhand, India*

*<sup>a</sup>Department of Applied Physics, Indian School of Mines University, Dhanbad-826004, Jharkhand India*

Raw sample collected from Rajapur open cast project (Jharia coal fields) was examined and characterized by impedance spectroscopy technique, thermoluminescence analyzer and XRD. Ac conductivity, dielectric relaxation and the TL response for the sample were recorded. The relaxational behaviour has been examined using the ac conductivity results and modulus formalism and it is found to be thermally activated. Nyquist plots were drawn to know the bulk and interface contributions. The activation energies calculated from the  $\sigma_{ac}$  values and the TL glow curve are in good agreement, thereby indicating a possible correlation between the two processes. It is found that  $\sigma_{ac}(v)$  can be described by the relation  $Av^s$ , ( $s < 1$ ) where  $s$  is found to decrease with increase of temperature. This is in agreement with the Overlapping Large Polaron Tunneling Model (OLPT) [1-3].

(Received March 15, 2008; accepted March 21, 2008)

*Keywords:* Dielectric Relaxation, Sandstone, Thermoluminescence

### 1. Introduction

The basic principle in studying rocks and rock masses by electrical methods is to get a better insight into the conduction mechanism and the relaxational processes that take place inside the specimen. This paper attempts to study the same in sandstone using impedance spectroscopy and the TL response of the sample. The variation of the dielectric properties ( $\epsilon_r$ ,  $\epsilon_{r(img)}$ ,  $Z'$ ,  $Z''$  and  $\sigma_{ac}$ ) with frequency and temperature were studied. The Modulus spectrum showed a typical relaxational peak at 207 °C (480 K) which was also confirmed by the Nyquist plots. The relation  $\sigma_{ac} = Av^s$  is observed for the frequency dependence of the ac conductivity [4] where  $s$  is found to decrease with increase of temperature. This suggests that the conduction is due to charge carriers hopping between localized states [5-8]. The TL glow curve also indicates that the luminescence may be due to the coupling between the  $(AlO_4)^{\ominus}$  and  $(AlO_4/M^{\oplus})$  centers [9]. The activation energies from the dielectric and the TL studies are in good agreement, which indicates that, the events, diffusion and thermoluminescence, are different manifestations of the same ionic movement.

### 2. Experimental work

Samples of sandstone were collected from *Rajapur open cast* coal field of Jharia coal belt. They were cut to cubes of side 0.5cm for dielectric measurements.

XRD and dielectric properties measurements were done in the Department of physics and meteorology at IIT KGP. Minerals were identified using JCPDS software (Table 1).

---

\*Corresponding author: tny\_80@rediffmail.com

Dielectric properties for the samples were measured by HIOKI LCR 3532-50 meter. The sample surface was first made smooth with sandpaper, which was then coated with silver paint. The continuity was checked and was put in the oven whose temperature could be varied using a variac and was directly read by a *thermo voltmeter*. The variation of dielectric properties like Impedance, Capacitance, Dielectric loss and phase with frequency (100 Hz to 1 MHz) and temperature (303 K to 625 K) were noted. These data were used to calculate the real and imaginary part of dielectric constant, real and imaginary part of impedance and the ac conductivity. The formulae used are as follows:

$$Z' = Z \cdot \cos(3.141 \times \text{phase}/180)$$

$$Z'' = Z \cdot \sin(3.141 \times \text{phase}/180)$$

$$\epsilon_r = -Z'' / (\omega C_0 \times Z^2)$$

$$\epsilon_{r(\text{img})} = Z' / (\omega C_0 \times Z^2)$$

The thermoluminescence glow curve for the sample was recorded by a thermoluminescence analyzer in the Department of Applied Physics, ISMU Dhanbad after irradiating the sample for 10 min with X-ray. The activation energy was calculated by glow curve shape method (Chens method).

Table 1. Mineral composition of the sandstone sample

Sample	Mineral Name	Chemical Formula
Sandstone	Quartz	SiO <sub>2</sub>
	Illite	(KH <sub>3</sub> O)Al <sub>2</sub> Si <sub>3</sub> AlO <sub>10</sub> (OH) <sub>2</sub>
	Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>
	Zeolite P1	Na <sub>6</sub> Al <sub>6</sub> Si <sub>10</sub> O <sub>32</sub> .12H <sub>2</sub> O

## 2.1 Glossary of symbols

$\epsilon$  ----- Complex Dielectric constant

$\epsilon_r$  ----- Real part of Dielectric constant

$\epsilon_{r(\text{img})}$  ----- Imaginary part of dielectric constant

$Z$  ----- Complex impedance

$Z'$  ----- Real part of impedance

$Z''$  ----- Imaginary part of impedance

$\omega$  ----- Angular frequency

$C_0$  -----  $0.3753 \times 10^{-12}$

$D$  ----- Dielectric loss

$\sigma_{ac}$  ----- ac conductivity

$M''$  ----- Imaginary part of the Electric Modulus

$E_a$  ----- Activation energy for Ac conductivity

### 3. Results

#### 3.1 Dielectric Studies

The real and imaginary parts of the dielectric constant decrease exponentially with frequency (Fig.1 and Fig. 2). There are two peaks observed at around 400 K and 495 K for temperature variation of  $\epsilon_r, \epsilon_{r(img)}$  and  $\sigma_{ac}$  ( Fig. 3, Fig. 4 and Fig. 5). The frequency variation of  $\sigma_{ac}$  is shown in Fig. 6 which shows a power law dependence of  $\sigma_{ac}$  on  $\nu$  i.e.:  $\sigma_{ac} = A\nu^s$  where  $s$  is the frequency exponent (<1) strongly dependent on temperature. The temperature variation of  $s$  is shown in Fig 7, which indicates  $s$  decreases down to a minimum value and then increases. The activation energy is calculated from the relation  $\nu = \nu_0 e^{-E_a/kT_m}$  [10] with the help of the graph between frequency and the temperature for maximum conductivity, which follows the Arrhenius relation (Fig. 8). Here  $E_a$  is the activation energy for ac conductivity and  $T_m$  is the temperature corresponding to the conductivity peak at a particular frequency. The activation energy is calculated to be 1.235 eV for diffusion (Table 2).

Table 2. Comparison of activation energies calculated by two different methods.

$E_a$ calculated by $\sigma_{ac}$	$E_a$ calculated by TL glow curve
1.235 eV	1.20 eV

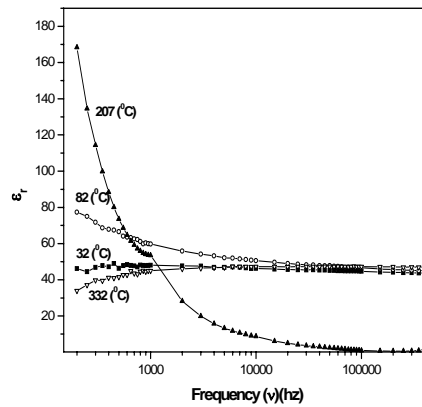


Fig. 1. Variation of  $\epsilon_r$  with frequency.

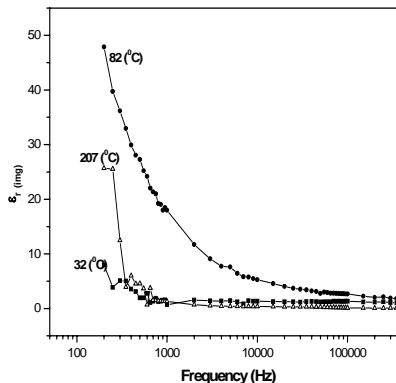


Fig.2 . Variation of  $\epsilon_{r(img)}$  with frequency.

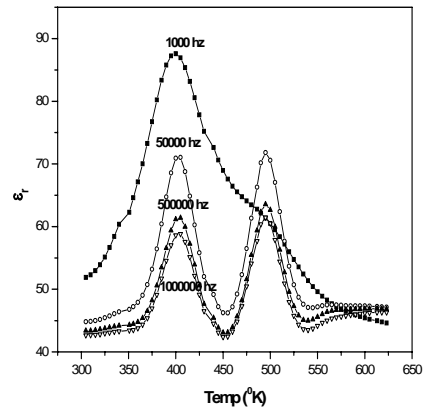


Fig 3. Variation of  $\epsilon_r$  with temperature.

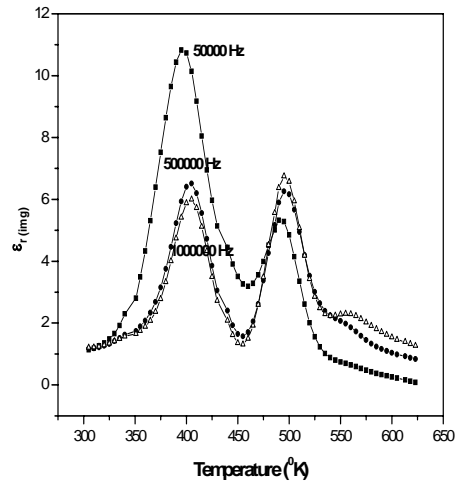


Fig. 4. Variation of  $\epsilon_{r(imag)}$  with temperature.

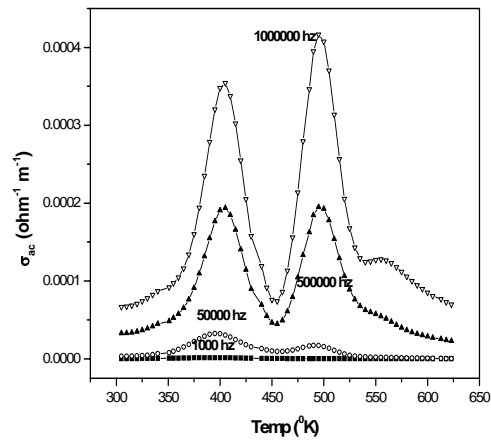


Fig 5. Variation of  $\sigma_{ac}$  with temperature.

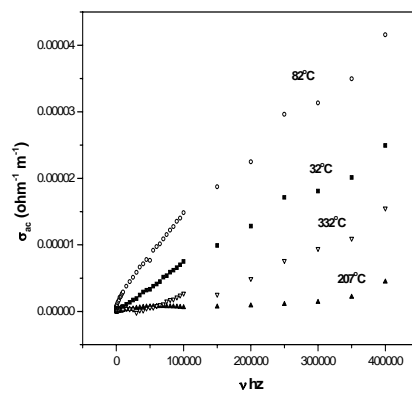


Fig. 6. Variation of  $\sigma_{ac}$  with frequency.

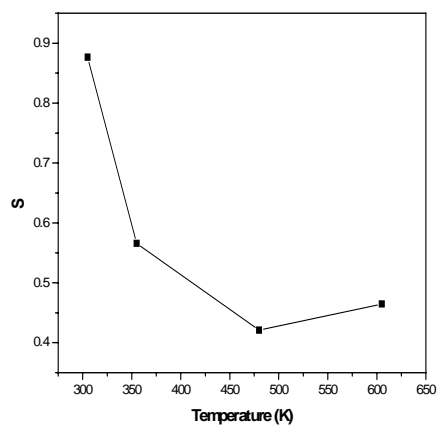


Fig. 7. Variation of frequency exponent  $s$  with temperature.

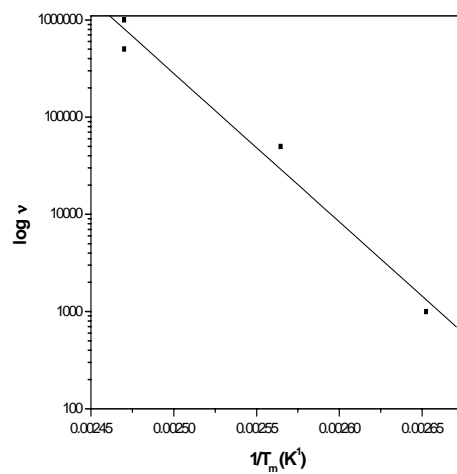


Fig. 8. Variation of  $\log v$  with inverse of peak temperature ( $T_m$ ).

Electric Modulus:

The imaginary part of the electric modulus  $M''$  is calculated using the formula [11]

$$M'' = \epsilon_{r(\text{img})} / (\epsilon_{r(\text{img})}^2 + \epsilon_r^2)$$

The variation of  $M''$  with  $\log \nu$  is shown in Fig 9, which shows a typical relaxation peak at 207°C (480K).

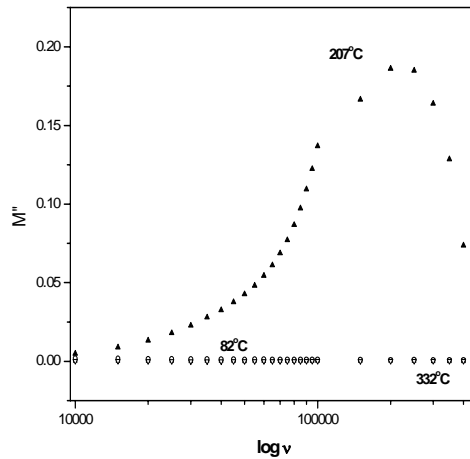


Fig 9. Plot of  $M''$  v/s  $\log \nu$ .

Nyquist Plots:

Plots between  $-Z''$  and  $Z'$  were drawn at different temperatures which showed arcs of semicircle (Fig 10), the radius of which is decreasing with increase of temperature.

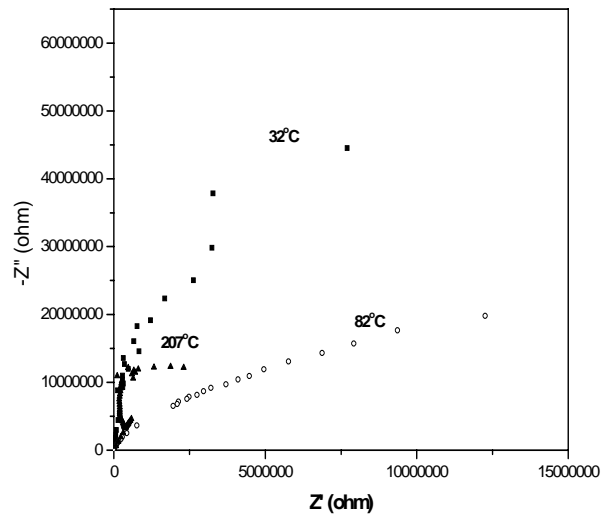


Fig 10. Nyquist plot between  $-Z''$  and  $Z'$  at different temperatures.

### TL glow curve:

Fig 11 shows the TL glow curve of the sample. The peak temperature is 242 °C(515 K) and the activation energy is found to be 1.2 eV (Table 2) using Chens method.

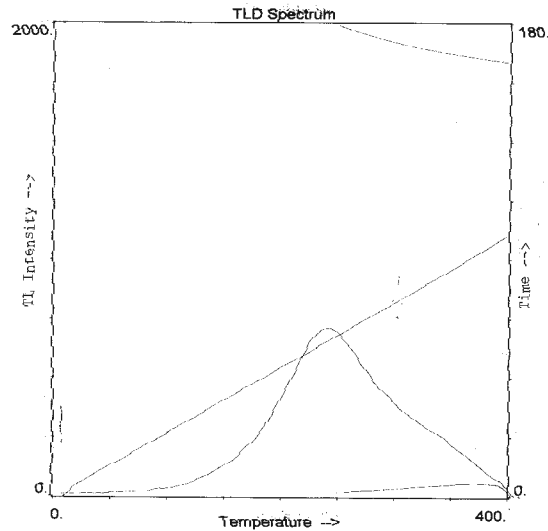


Fig 11. Variation of TL intensity with temperature.

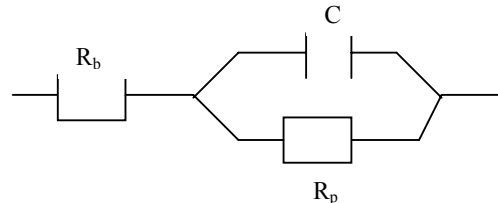


Fig. 12. Equivalent circuit model (Randles cell)

### XRD studies:

The mineral composition of the sandstone is given in Table 1. It primarily contains Quartz and traces of Illite, Dolomite and Zeolite.

## **4. Discussion**

The exponential decrease of the dielectric constant is attributed to the fact that the different type of polarization ceases to contribute as the frequency increases. The observed peak at around 400 K for  $\epsilon_{r(img)}$ ,  $\epsilon_r$  and  $\sigma_{ac}$  may be due to the residual moisture present in the pores of the sample, since water has a very high dielectric constant and increases the conductivity as well. As soon as the temperature reaches 100 °C the water starts to evaporate and the values of  $\epsilon_{r(img)}$ ,  $\epsilon_r$  and  $\sigma_{ac}$  decrease. The variation of  $\epsilon_{r(img)}$  with temperature was explained by Stevels [12] who divided relaxational phenomena into conduction losses and dipole losses. At low temperatures the

conduction losses have a minimum value. As the temperature increases  $\sigma_{ac}$  increases and so the conduction losses also increase. The second peak at 495 K is because of hopping of Na<sup>+</sup> ions between coupled localized defect sites. This type of conduction mechanism is explained by Overlapping Large Polaron Tunneling model (OLPT) [13] which is confirmed by the fact that the frequency exponent  $s$  decreases with increasing temperature to a minimum value and then increases with increasing temperature as shown in the Fig 7. The Nyquist plots at different temperatures show arcs of semicircle. At 207°C(480K) the radius of the arc is drastically reduced which shows the contribution is primarily due to bulk and its interfacial effects are diminished to a large extent. Further the decrease in radius with increasing temperature suggests pronounced increase of dc conduction [14]. The arcs can be interpreted by equivalent circuit model which in this case is a Randles Cell [15] that is a double layer capacitance in parallel with a polarisation resistance ( $R_p$ ) and the combination being in series with the bulk resistance ( $R_b$ ) (Fig. 12).

The electric modulus plots show a peak only at 207°C (480K) which indicates that the relaxational losses present are due to the bulk and the interfacial effects are absent, which comply well with the Nyquist plots and the ac conductivity results.

The TL glow curve shows a single peak at 242°C (515K), which may, possibly, be due to ionic motion [16]. In Alkali alumino silicates the Al<sup>3+</sup> ions commonly substitute the Si<sup>4+</sup>. For local charge compensation an alkali ion (Na<sup>+</sup>) or a hole is generally trapped making AlO<sub>4</sub>/Na<sup>+</sup> and (AlO<sub>4</sub>)<sup>o</sup> centers. These centers are coupled during thermal self-diffusion process through bulk and interfaces. The production-annihilation of (AlO<sub>4</sub>)<sup>o</sup> centers can be analyzed in terms of ionic self diffusion through localized states. The activation energy calculated for TL (1.2 eV) is in good agreement with that of  $\sigma_{ac}$  which suggests the possibility of hopping of Na<sup>+</sup> ions between defect sites associated with the (AlO<sub>4</sub>)<sup>o</sup> centers.

## 5. Conclusion

The Nyquist plots and the electric modulus spectrum show that there is a strong bulk contribution at 207 °C (480 K) towards the relaxation process. The ac conductivity results indicate that the conduction mechanism is due to hopping of Na<sup>+</sup> ions between defect sites (OLPT) identified as (AlO<sub>4</sub>)<sup>o</sup> centers in quartz, which is also confirmed by the TL response of the sample.

## References

- [1] M. Pollak, Philos Mag **23**, 519 (1971).
- [2] M. Pollak, T. H. Gaballe, Phys Rev B **22**, 1742 (1961).
- [3] M. Pollak, G. E. Pike, Phys Rev Lett **28**, 1449 (1972).
- [4] Jeppe C.Dyre., J. Appl. Phys. **64**, 2456(1988).
- [5] M. Pollak, Phil. Mag. **22**, 519 (1971).
- [6] X. Ledecq, J. Physique **40**, 27(1979)
- [7] K. Shimakawa, Phil.Mag. **46**, 123(1978)
- [8] S. Tolansky, Multiple- Beam interferometry of surfaces and films(Oxford University Press, London 1948) p.147
- [9] J. Garcia-Guinea, P. D. Townsend, L. Sanchez-Munoz, J. M. Rojo, Phys Chem Minerals **26**, 658 (1999).
- [10] J. Ortiz-Lopez, R. Gomez-Agullar, Revista Mexicana De Fisica **49**(6), 529(2003).
- [11] N. Zouari, H. Khemakhem, T. Mhiri, A. Daoud, J. of Phys and Chem. of Solids **60**, 1779 (1999).
- [12] J. M. Stevels, The electrical properties of glasses p.350 (1975).
- [13] A. M. Farid, A. E. Bekheet, Vacuum **59**, 932 (2000).
- [14] Fathy Salman, Turk J Phys **28**, 41 (2004).
- [15] GAMRY Instruments, Electrochemical Impedance Spectroscopy Theory: A Primer.
- [16] Y. Kirsh, Phys. Stat. Sol(a) **129**(15), 15(1993).