Structural and Electrical Conduction Studies of Zirconia-Graphite Composites

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Abstract: The present study aims to develop zirconia-carbon (graphite) composites through mould die technique and to study conduction mechanism of the composites. SEM shows the porous surface morphology of zirconia-graphite composite materials. The electrical resistivity of the sample was measured using a four probe method. The results of the resistivity as a function of temperature and Arrhenius plots (inverse temperature vs. log resistivity) to find the activation energy are shown in figure. A close examination of the plots reveals that at higher temperatures the slope tends to be less steeper compared to the low temperature ones but we had followed a least square fit with respect to a single line and then the activation energy was determined. The activation energies ranging from 0.8eV to 0.814eV are characteristic of ionic conductivity along with conductivities due to oxygen vacancies in the bulk.

Index Terms - Zirconia-Carbon Composites, Activation Energy, Resistivity, Mould Die Technique

I. INTRODUCTION

Zirconia is an inert ceramic in its pure form which possesses extraordinary properties when doped with certain stabilizing oxides such as yttria, magnesia and calcia. Pure zirconia is monoclinic at room temperature. This phase is stable up to 1170°C. Above this temperature it transforms into tetragonal and then into cubic phase at 2370°C. Graphite is an allotrope of carbon with a density of 2.21 g/cm³. Graphite is generally greyish-black, opaque and has a lustrous black sheen. Alumina-zirconia composites are one of the relatively good and promising candidates for biomaterials application, due to biocompatibility and their mechanical properties that combine high flexural strength with high toughness [1]. Wen-Cheng *et al*. [2] studied ZrO_2/mullite composites with homogeneously dispersed ZrO_2 grains from colloidal or sol-gel processes of the precursors. W. Pyda [3] studied the reaction between carbon and titanium originated from zirconia-titania solid solution to produce TiC inclusions in situ in zirconia powders and dense materials. Anne *et al*. [4] prepared Yttria-stabilised zirconia (YTZP) based composites with carbide (WC) content up to 50 vol. % from nanopowders by means of conventional hot pressing. Liang *et al*. [5-6] prepared zirconia-mullite nanocomposite ceramics by in-situ controlled crystallization of Si-Al-Zr-O amorphous bulk, which were first treated at 900-1000°C for nucleation, then treated at higher temperature for crystallization to obtain ultra-fine zirconiamullite composite ceramics. Tahir Ahmad and Othman Mamat [7] studied the development of zirconia-Silica sand nanoparticles composites through powder processing route. From above cited literature, no researcher still had used Carbon and Zirconia for composites, therefore in the present work; an attempt has been made to study conduction mechanism of Zirconia-Carbon (Graphite) Composites. "

II. EXPERIMENTAL

Initially porous zirconia monoliths were developed by using different content of zirconia oxide powder with polyvinyl alcohol (PVA) and sintering the green compact. The PVA acts as binder for zirconia powder at green stage. The composites were developed by compression match mould die technique. The mixture was poured in the cavity of die mould and die mould was kept on the hot plate of hydraulic press. The mixture was molded at 275°C above the melting point of PVA and suddenly freezed (quenched) to allow dentric growth of PVA within the matrix, thus a resultant composite called green composite was formed. The green composites were heated initially at 1000°C, in air atmosphere to burn out PVA and generate the porosity as much as possible. Later on, the composite template was heated at 1200°C and 1400°C in air atmosphere without any isostatic pressure. A Lindberg Model 51314 box furnace was used to perform sintering. Green disks were placed on a bed of TZ-3YB powder in a covered alumina crucible (McDanel Refractory Company), which was then placed in the center of the furnace. A heating ramp rate of 5°C per minute and a maximum cooling rate of 10°C per minute were used for all samples during sintering. The peak temperatures for samples in Set LPLT, HPLT and LPHT were 1275, 1275 and 1315°C respectively. Five samples in each set were held at the peak temperature for 0.1, 0.5, 1, 5, 10 hours respectively. The sixth sample in the set LPLT was held at the peak temperature for 50 hours. After sintering, samples were heated at a rate of 5°C per minute to a target temperature, then were held at the peak temperature for a desired time, finally were cooled down at a rate of 10°C per minute to room temperature. Both types of porous zirconia composites were impregnated by coal tar pitch melt as carbon source which having carbon yield of 50 % on carbonization at 1000°C. The composites were impregnated and carbonized at 1000°C in an inert atmosphere. After all grinding

and polishing, samples were put in an Isotemp Vacuum Oven 282A to undergo a 10 minutes baking process at 100ºC. Although a number of samples were made by varying ZrO_2 and PVA such that the volume percentage of the resulting sintered zirconia monolith was around 50%. In this work we have chosen six samples viz. S1, S2, S3, S4, S5 and S6 for characterization. S1, S2, and S3 are ZrO_2 samples sintered at 1200ºC possessing 50, 55 and 60% of the ceramic, while S4, S5 and S6 are ZrO_2 samples sintered at 1400ºC possessing 50, 55 and 60% of the ceramic respectively. The electrical conductivity was measured by the conventional four probe method at a constant current supply (100mA).

III. Results and Discussion:

Figure 1(a) Shows the SEM micrograph of monolith sample S1 showing the interconnectivity of pores. (b) SEM micrograph of monolith sample S2 showing the interconnectivity of pores. (c) SEM micrograph of monolith sample S6, showing the interconnectivity of pores, the magnification is higher than the previous micrographs and (d) SEM micrograph of monolith sample of 50% ZrO_2 (S4) HTT 1400ºC, reinforced with carbon nano tubes, to observe infiltration of nano tubes.The Scanning electron micrograph of the composite samples was recorded to exactly determine the connectivity of the sample. It is very important to verify the connectivity because we have assumed the material to possess a 3-3 connectivity and the SEMs shall give a direct insight into the material. The SEMs of porous ZrO_2 ceramic monolith in its pristine forms were first recorded, and then the subsequent composites were viewed in the light of the pristine templates. Table 1: shows the porosity of the zirconia-graphite composite sample is decreases with increase in temperature as well as zirconia content.

The electrical resistivity of the sample was measured using a four probe method. The results of the resistivity as function of temperature and consequent plots (inverse temperature vs. log resistivity) to find the activation energy are given in figure. The activation energies are calculated from the respective graphs. The conduction mechanism was determined by analyzing the activation energies. The conductivities in the composites are activated by different charge carriers. Electrons (holes), ions, space charge, etc, each with its characteristic activation energies. The Arrhenius plot [ln *(conductivity or resistivity) vs (inverse temperature)*] gives a sum total of all the activation energies at high temperatures. At low temperatures the higher activation energies are suppressed and therefore the slopes of the plot at low temperatures are the most important in segregating the different effects due to different species of charge carriers. In the present study average activation energy (bulk activation energy) has been calculated without going into finer details about the various conduction mechanisms. A close examination of the plots reveals that at higher temperatures the slope tends to be less steeper compared to the low temperature ones but we had followed a least square fit with respect to a single line and then the activation energy was determined.

IV. Conclusions:

The SEMs of porous ZrO_2 ceramic monolith in its pristine forms were first recorded, and then the subsequent composites were viewed in the light of the pristine templates. The electrical resistivity as a function of temperature shows the resistivity decreases with temperature showing a semiconductor type behavior, also the Arrhenius plot as shows ionic conductivity. The activation energies are typical of charge carriers with mobilities resembling ions and oxygen vacancies. The activation energies calculated from the Arrhenius plots (log ρ vs T^{-1}) are mentioned in figure, where E_a the activation energies ranging from 0.8eV to 0.814eV, are characteristic of ionic conductivity along with conductivities due to oxygen vacancies in the bulk.
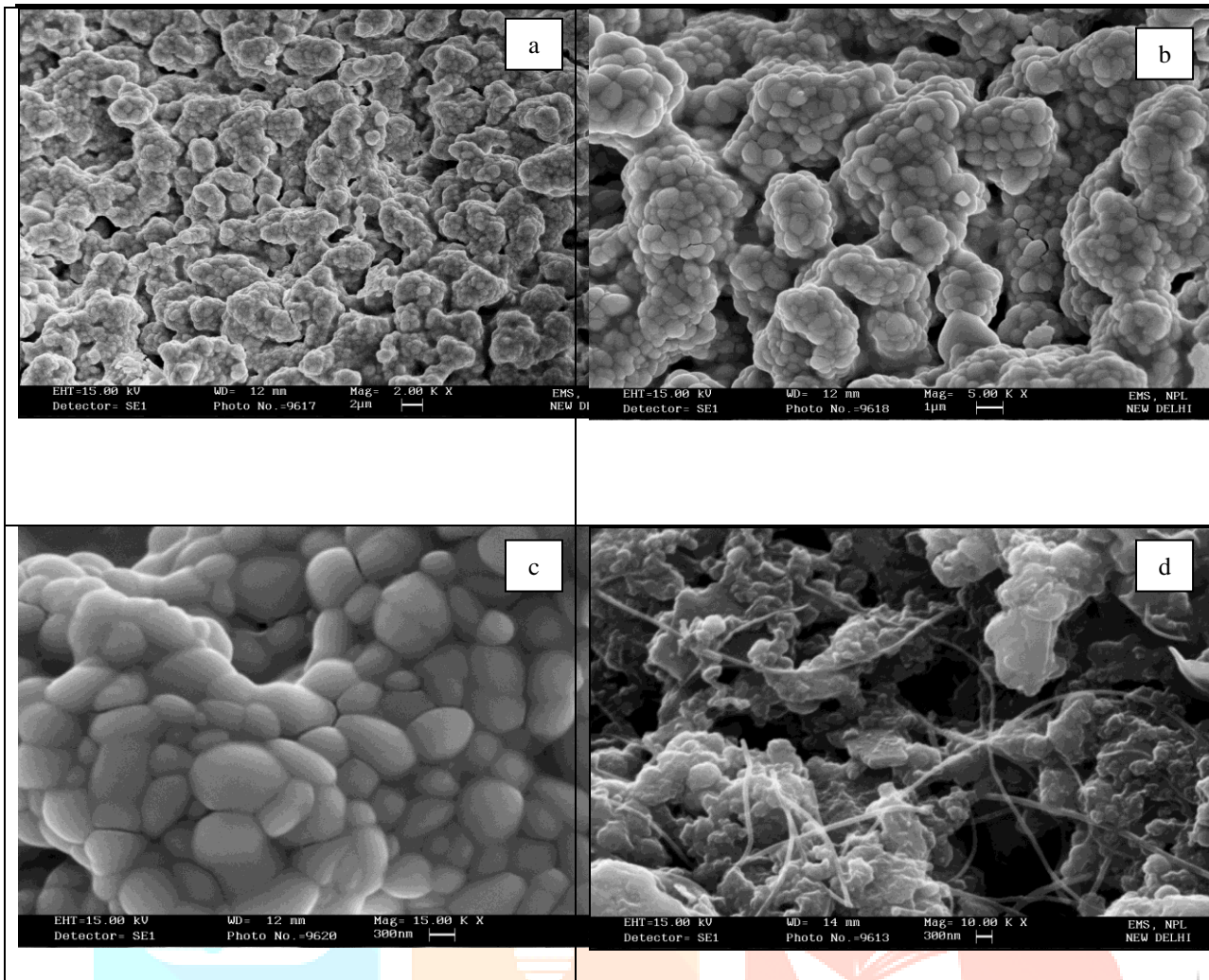
V. Acknowledgements

Figure 1(a) SEM micrograph of monolith sample S1 showing the interconnectivity of pores (b) SEM micrograph of monolith sample S2 showing the interconnectivity of pores (c) SEM micrograph of monolith sample S6, showing the interconnectivity of pores, the magnification is higher than the previous micrographs (d) SEM micrograph of monolith sample of 50% ZrO_2 (S4) HTT 1400ºC , reinforced with carbon nano tubes, to observe infiltration of nano tubes.
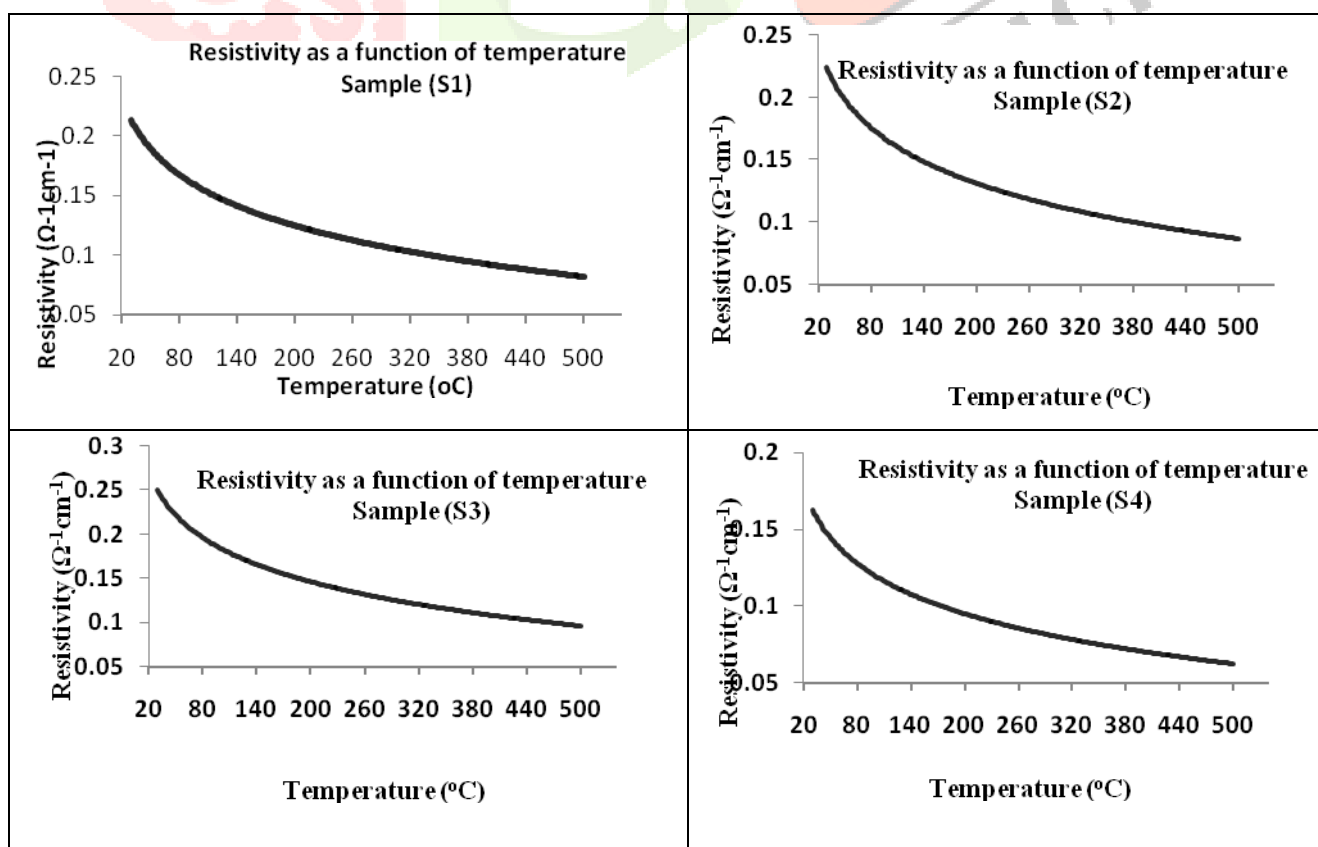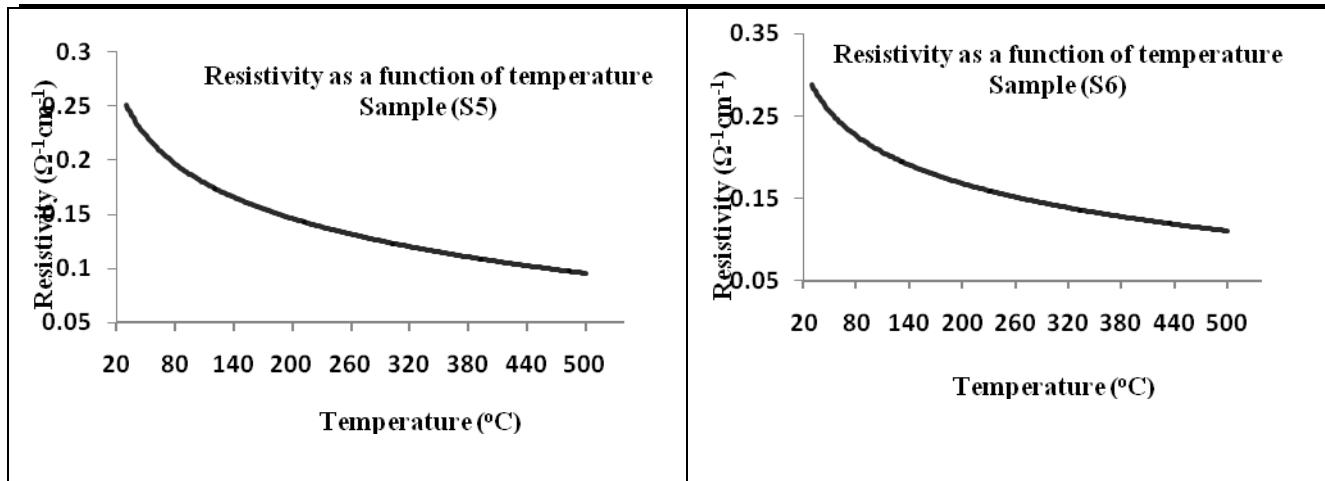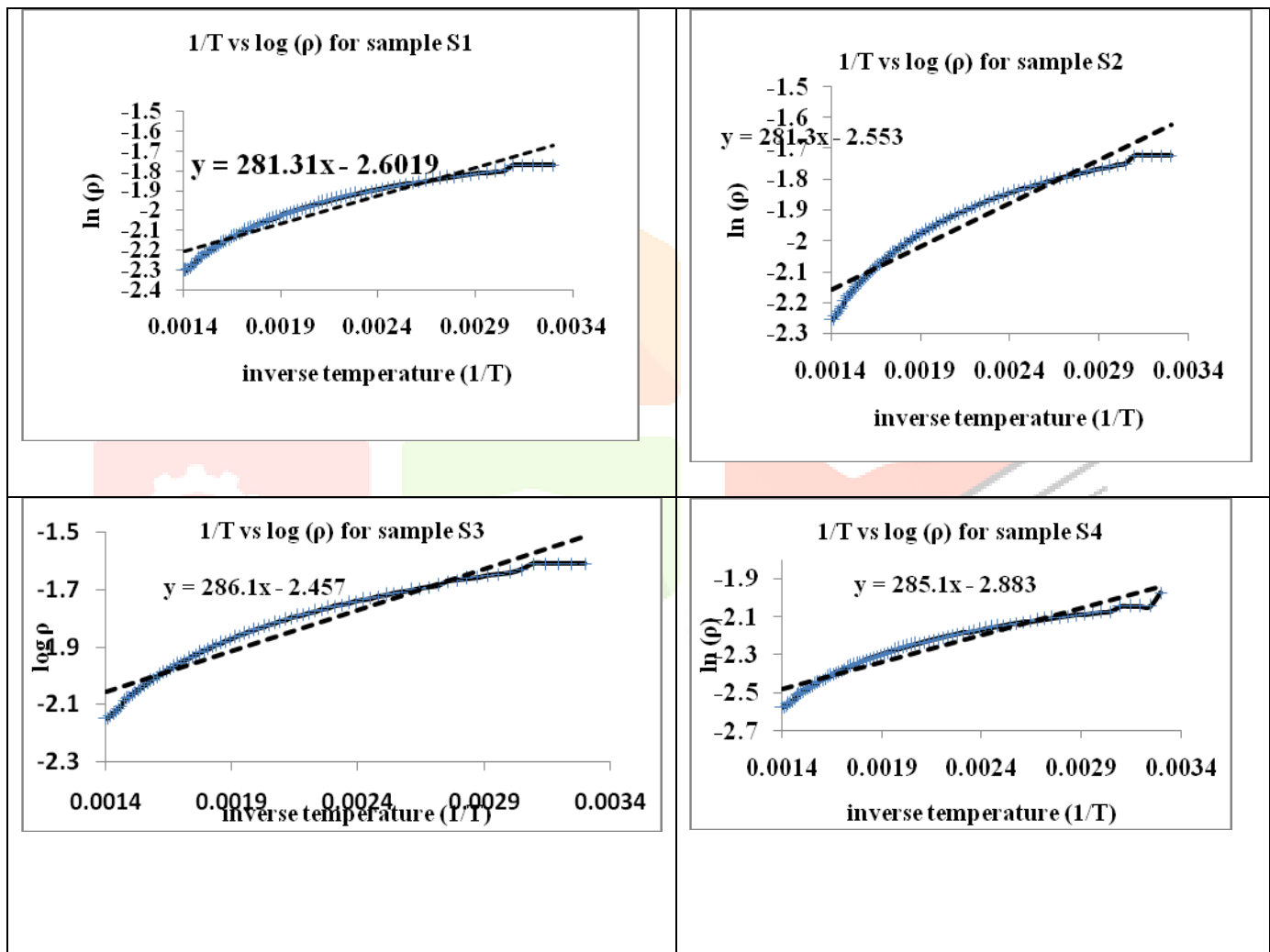
Figure 2: Resistivity of the zirconia –graphite composite of sample S1, S2, S3, S4, S5, and S6 as a function of temperature
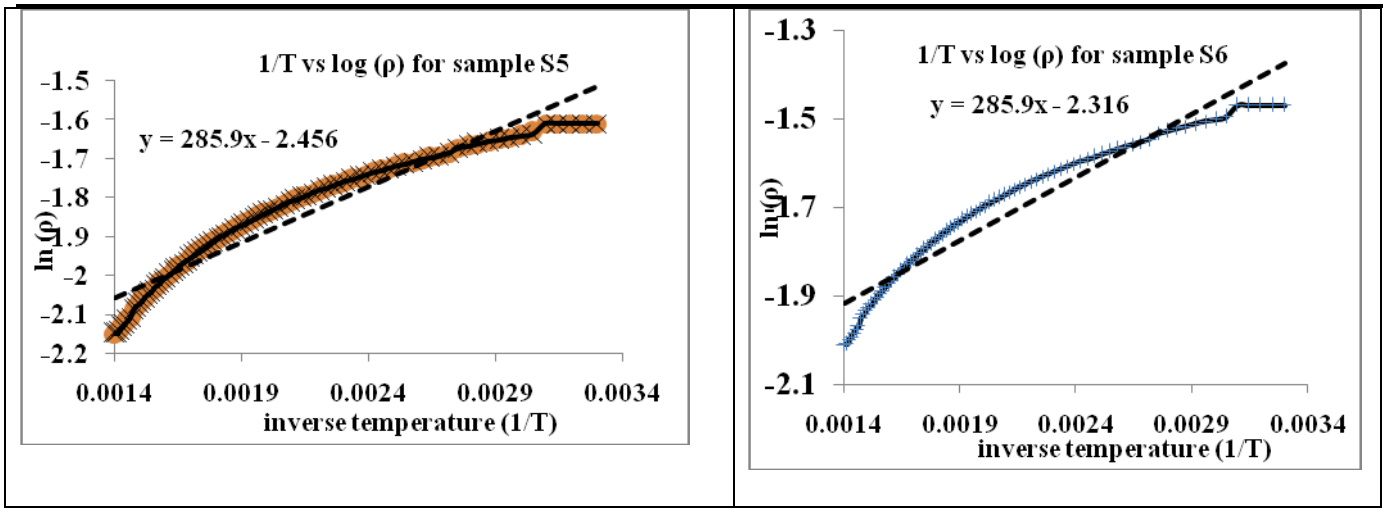
Figure 3: Arrehenius plot of the zirconia-graphite composite sample S1, S2, S3, S4, S5 and S6 along with the linearly regressed fit to the resistivity data, to calculate the activation energy (band gap) of the sample.
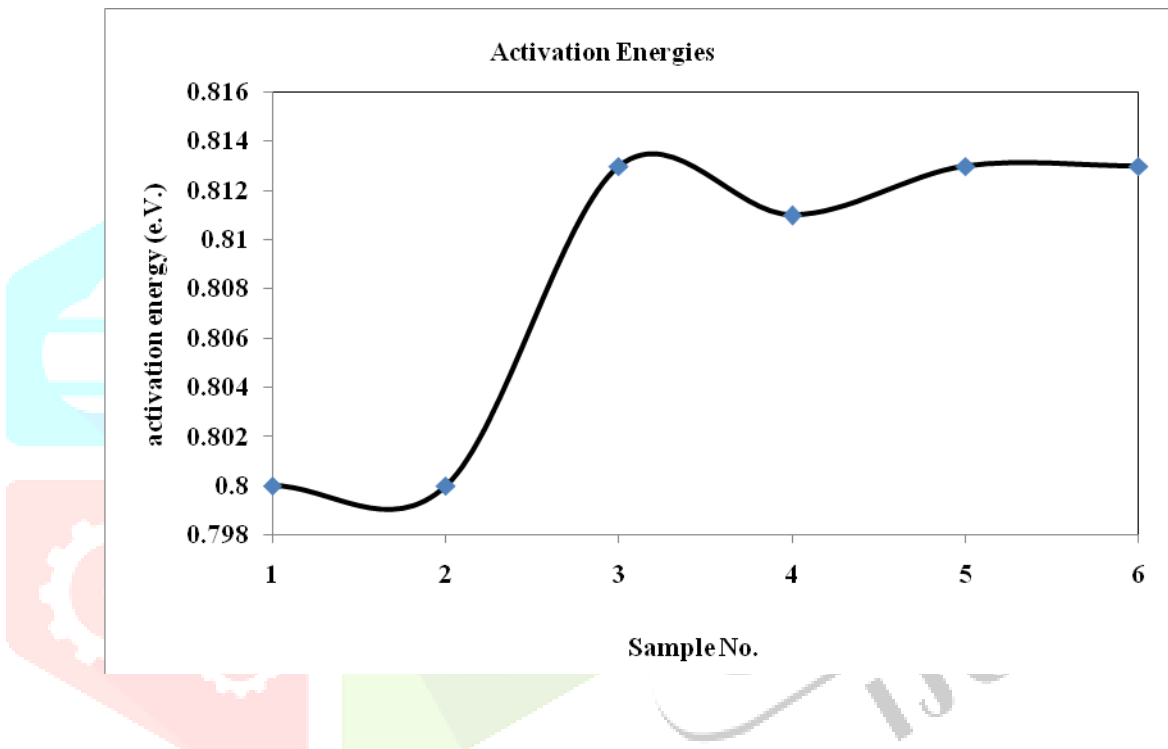

Figure 4: The activation energies of the different samples from S1 to S6 as calculated from the above graphs.

Table 1: Porosities of the zirconia–graphite composites samples.

S. No.	Sample	ZrO$_2$ %	Temperature (°C)	Porosity
1	S1	50	1200	50
2	S2	55	1200	45.4
3	S3	60	1200	41.8
4	S4	50	1400	49.1
5	S5	55	1400	45.5
6	S6	60	1400	38.8

References:

1. M. C. C. de S. e B. de Moraes and C. Elias, "Mechanical Properties of Alumina-Zirconia Composites for Ceramic Abutments," *Journal of Materials Research, Vol. 7*, No. 4, 2004, pp. 643-649.
2. J. W.C. Wei, H. C. Kao and M. H. Lo, "Phase Transformation and Grain Coarsening of Zirconia/Mullite Composites," *Journal of the European Ceramic Society, Vol.* 16, No. 2, 1996, pp. 239-247.
3. W. Pyda, "Microstructure and Properties of Zirconia- Based Nanocomposites Derived from a Powder Containing TiC Crystallised in Situ and Carbon*," Ceramics International, Vol. 30*, No. 3, 2004, pp. 333-342.
4. G. Anne, S. Put, K. Vanmeensel and D. T. Jiang, "Hardness, Tough and Strong ZrO2-WC Composites from Nanosized Powders*," Journal of the European. Ceramic Society*, Vol. 25, No. 1, 2005, pp. 55-63.
5. S.Q. Liang, J. Zhong, X.-P. Tan and Y. Tang, "Mechanical Properties and Structure of Zirconia-Mullite Ceramics Prepared by In-situ Controlled Crystallization of Si-Al-Zr-O Amorphous Bulk," *Transaction of Nonferrous Metals Society of China*, Vol. 18, No. 4, 2008, pp. 799-803.
6. S.Q. Liang, J. Zhong, X.-P. Tan and Y. Tang, "Preparation of Mullite-Zirconia Composites with Ultra Fine Grains Ceramics by In-situ Controlled Crystallization from Si-Al-Zr-O Amorphous Bulk*," Nanoscience,* Vol. 11, No. 1, 2006, pp. 32-37.
7. Tahir Ahmad, Othman Mamat, "The Development and Characterization of Zirconia-Silica Sand Nanoparticles Composites", *World Journal of Nano Science and Engineering*, 2011, 1, 7-14.
8. K. Pandey, M. M Dwivedi, M Tripathi., M. Singh & S.L. Agrawal, *Ionics,* 14 (2008) 515-523.
9. K Pandey., M.M. Dwivedi, M. Singh & S. L Agrawal., *Phase transitions* (2011)1-14.
10. K Pandey, M.M. Dwivedi, M. Singh & S. L Agrawal., *Journal of Polymer Research* 17 (2010) 127- 134.
11. S.L. Agrawal, M.Singh, M. M. Dwivedi & K. Pandey, *J. Fibers and Polymer*, Vol. 12, 7 (2011) 864-874.
12. K.Pandey, M.Singh, N.Asthana, M. M. Dwivedi & S.L.Agrawal, *International J. of Material Sciences*, Vol-1, 1(2011) 9-17.