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Ceramics International 36 (2010) 917–921

CERAMICS INTERNATIONAL

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# Electrical resistivity of porcelain bodies with natural zeolite addition

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Received 20 February 2009; received in revised form 3 September 2009; accepted 20 October 2009
Available online 20 November 2009

## Abstract

In this study, the effect of natural zeolite addition on the electrical properties of porcelain bodies was investigated. Clinoptilolite, which is a type of natural zeolite, was added partially or fully in replacement of quartz in selected electro-porcelain compositions. Samples were fired in an electric furnace with a heating rate of 10 °C/min at 1200 and 1250 °C with a period of 60 min. The electrical resistance measurements of samples were performed at 50, 200, 400 and 600 °C. It was shown that the resistivity of samples increased at 50 °C temperature after zeolite addition, while it was decreasing after zeolite addition at higher temperatures. At the same time, it was recognized that the resistivity of samples depends on sintering temperature. The activation energy of electrical resistivity of samples was found to be in the range of 0.79–0.87 eV.

*Keywords:* C. Electrical properties; D. Porcelain; D. Silicate; E. Insulators; Zeolites

## 1. Introduction

Ceramic materials are very good insulators due to their resistance to passage of electricity and are widely used in the microelectronic devices, ceramic heaters, heating elements, semiconducting material as well as in power transmission lines [1–3]. Porcelain is one of the important types of ceramic materials and basically an insulator which has electrical resistivity value about $10^{12}$–$10^{14}$ ohm cm at room temperature. But, it drops with the rise in temperature [1,3]. The body of standard porcelain is made up of a mix of kaolin, feldspar and quartz and contains an aggregate of mullite and quartz crystals embedded in a glassy matrix [4–7].

Zeolites are crystalline aluminosilicates with a three-dimensional framework structure based on repeated units of silicon-oxygen ($SiO_4$) and aluminium-oxygen ($AlO_4$) tetrahedra. They contain exchangeable alkaline and alkaline earth metal cations such as $Na^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$ that maintain charge neutrality and have channels, interconnected voids and water molecules [8–10].

The price of conventional raw materials used in porcelain production is higher than that of zeolite. Also feldspar and silica are both harder raw materials than zeolite and their crushing and millings are costly compare to zeolite. Natural zeolites are abundant raw materials in many countries [11,12]. Therefore it may be advantageous to replace silica containing raw materials such as silica and feldspar with zeolite as described in details elsewhere [11].

The aim of this study is to investigate the effect of zeolite addition on electrical resistivity of porcelain bodies. The electrical resistivity of samples, which were produced with varying amount of zeolite addition at various sintering temperature, was measured at 50, 200, 400 and 600 °C and then activation energy was also calculated.

## 2. Experimental procedure

### 2.1. Preparation of samples

Four different mixtures were prepared for experimental studies. (i) **Z0**, the reference electro-porcelain composition (45 wt.% kaolin, 30 wt.% potash-feldspar, 25 wt.% quartz), (ii) **Z5** (45 wt.% kaolin, 30 wt.% potash-feldspar, 20 wt.% quartz and 5 wt.% clinoptilolite i.e. natural zeolite), (iii) **Z15** (45 wt.% kaolin, 30 wt.% potash-feldspar, 10 wt.% quartz and 15 wt.% clinoptilolite) and (iv) **Z25** (45 wt.% kaolin, 30 wt.% potash-feldspar, instead of quartz 25 wt. zeolite). Zeolites used in the present study were obtained from Turkey. The chemical

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doi:10.1016/j.ceramint.2009.10.029

compositions of raw materials are given in Table 1. Each composition was prepared by dry ball milling and mixed for 4 h and then sieved to pass through −75 μm. Then, water was added as a binder and disc samples (∅ = 25 mm, with 5 mm thick) were shaped by uniaxial dry pressing at pressing pressure of 1.5 ton. After shaping, samples were dried at 110 °C for 24 h in an oven. Dried samples were fired in an electric furnace with a heating rate of 10 °C/min at 1200 and 1250 °C for 60 min. Then, the fired samples were cooled down to room temperature in the furnace.

### 2.2. Characterization of sintered samples

#### 2.2.1. Phase identification of samples

Phase identification was carried out on sintered samples after grinding and sieving to pass through −75 μm. Then, the phases were determined by X-ray diffractometer (JEOL MDI/JADE6) operating with Cu Kα (λ = 1.54056 Å) radiation. The microstructural characterization of sintered samples was performed using a JEOL JSM 5600 scanning electron microscopy (SEM) with EDS attachment.

#### 2.2.2. Measurement of electrical resistivity

The electrical resistivity measurements were made by a “two probes method” which involves a disk-shaped sintered sample possessing one electrode on each planar face. The two probes method is one of the standard and commonly used method for the measurement of resistivity of very high resistivity samples – near insulators. However, there is a limit in this technique, and measurements affected by contact and wire resistivity.

The sintered samples were grounded and polished. A silver wire was given a spiral shape to connect both parallel surfaces of the samples which was adhered with silver paste. Then, these samples were dried up to 30 min. The silver wires on both surfaces of the samples were passed through quartz pipe and come out of the furnace. The samples were suspended at the centre of electrically heated furnace.

An electrometer and DC power supply were used for electrical measurement for the experimental studies. Different voltages between 25 and 200 V at 25 V intervals were supplied to the samples from a source at 50, 200, 400 and 600 °C and the currents across voltages were measured by the electrometer. The plots of V versus I were drawn and the resistance ($R$) of samples from the slopes of these plots was calculated by using the following equation:

$$R = \frac{V}{I} \tag{1}$$

The resistivity ($\rho$) of the samples was calculated by the relationship as follows:

$$\rho = R\frac{A}{\ell} \tag{2}$$

Table 1
Chemical composition of raw materials.

| | Raw materials (wt.%) | | | |
|---|---|---|---|---|
| | Quartz | Potash-feldspar | Kaolin | Zeolite |
| $SiO_2$ | 99.72 | 65.61 | 54.50 | 79.28 |
| $Al_2O_3$ | 0.08 | 19.65 | 42.01 | 11.22 |
| $Na_2O$ | 0.01 | 3.02 | 0.11 | 0.15 |
| $K_2O$ | 0.06 | 11.09 | 2.10 | 4.22 |
| $Fe_2O_3$ | 0.05 | 0.12 | 0.85 | 1.20 |
| CaO | 0.05 | 0.37 | 0.07 | 2.52 |
| MgO | 0.01 | 0.12 | 0.34 | 1.22 |
| $TiO_2$ | 0.02 | 0.02 | 0.02 | 0.08 |
| SrO | – | – | – | 0.06 |
| $Rb_2O$ | – | – | – | 0.03 |
| ZnO | – | – | – | 0.02 |

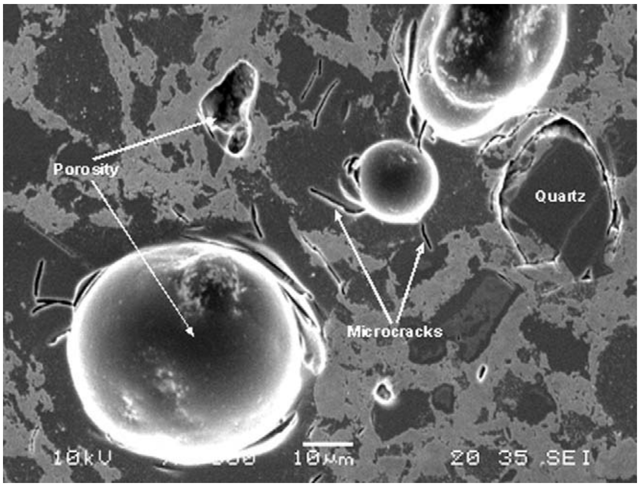

Fig. 1. SEM micrograph of Z25 composition sintered at 1250 °C for 60 min.

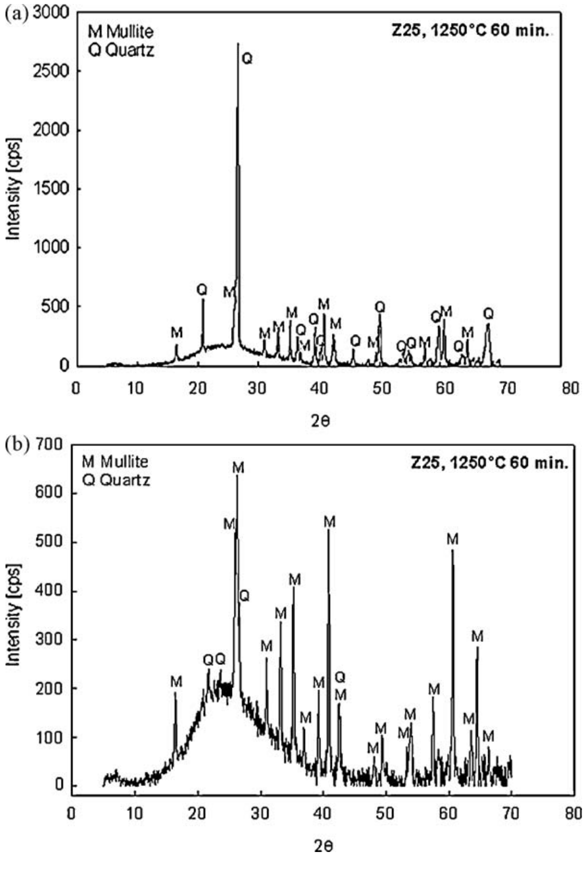

Fig. 2. XRD patterns of Z0 (a) and Z25 (b) samples sintered at 1250 °C for 60 min.

where, $R$, $A$, $\ell$ are resistance, area and thickness of the samples, respectively [1,3].

### 2.3. Determination of activation energy

The electrical resistivity of the samples can be calculated using the activation energy equation which is as follows:

$$\rho = e^{\Delta E/kT} \tag{3}$$

where, $\rho$ is resistivity of samples at any temperature and $\Delta E$, $k$ and $T$ are activation energy, Boltzman constant ($8.62 \times 10^{-5}$ eV) and absolute temperature, respectively [3,13,14].

A plot of $\ln \rho$ versus $1/T$ was drawn for each samples between 50, 200, 400 and 600 °C. The activation energy of electrical resistivity of the samples was calculated in eV unit from the slope of the plots.

## 3. Results and discussion

Microstructural observations and XRD analysis after sintering at various temperatures revealed various features and phases including micro-cracks, porosity and unreacted or residual quartz grains, mullite, glassy phase respectively (Fig. 1).

The XRD patterns of two compositions (0 and 25 wt.% zeolite addition) sintered at 1250 °C with a sintering time of 60 min are shown in Fig. 2. As depicted in Fig. 2, the intensity of quartz peaks decreases with increasing zeolite addition, while the intensity of mullite peaks rises with increasing zeolite addition. In addition to this, the glassy phase increases gradually with increasing zeolite addition as shown in XRD peaks in Fig. 2(a) and (b). It was also observed that rising glassy phase in conjunction with increasing zeolite addition caused lower sintering temperature and decrease in sintering time in the porcelain when compared with porcelain with no zeolite addition. This result suggests that increasing zeolite addition facilitates liquid phase sintering mechanism.

The electrical insulators are materials with very low electrical conductivity. Their conductivity values are between $10^{-10}$ and $10^{-20}$ ohm m$^{-1}$ [14]. The porcelain is insulator materials because the electrical resistivity values of porcelain are also in this range which is $10^{12}$–$10^{14}$ ohm cm [1,3].

The electrical resistivity of the sintered samples at 1200 and 1250 °C measured at 50, 200, 400 and 600 °C. The electrical resistivity results obtained from experimental studies are presented in Figs. 3 and 4. As shown in Figs. 3 and 4, the electrical resistivity of the samples except for Z5 increased with addition zeolite at low temperature (50 °C). All of the sample's

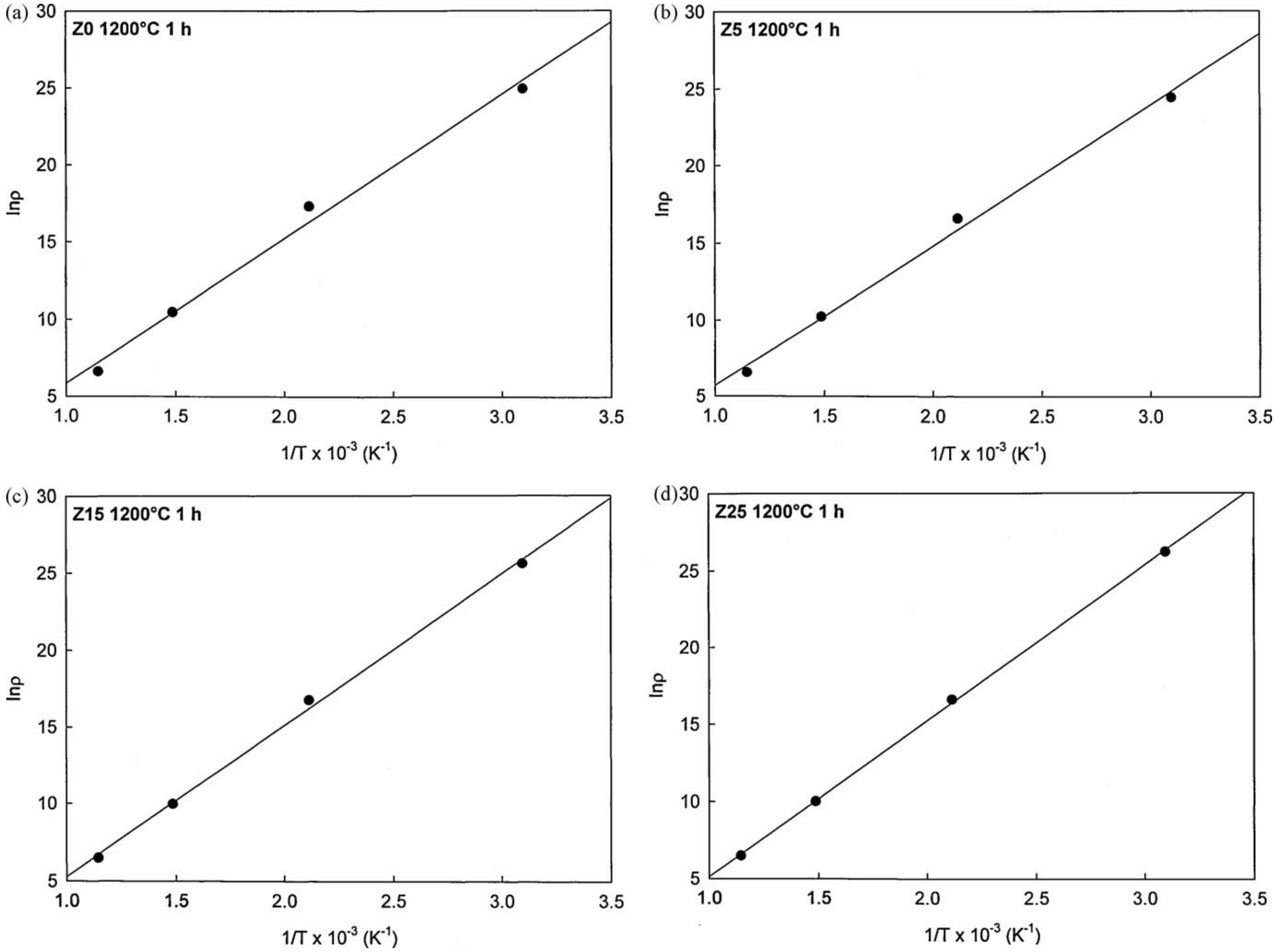

Fig. 3. ln $\rho$ versus $1/T$ graphics for (a) Z0, (b) Z5, (c) Z15 and (d) Z25 compositions sintered at 1200 °C.

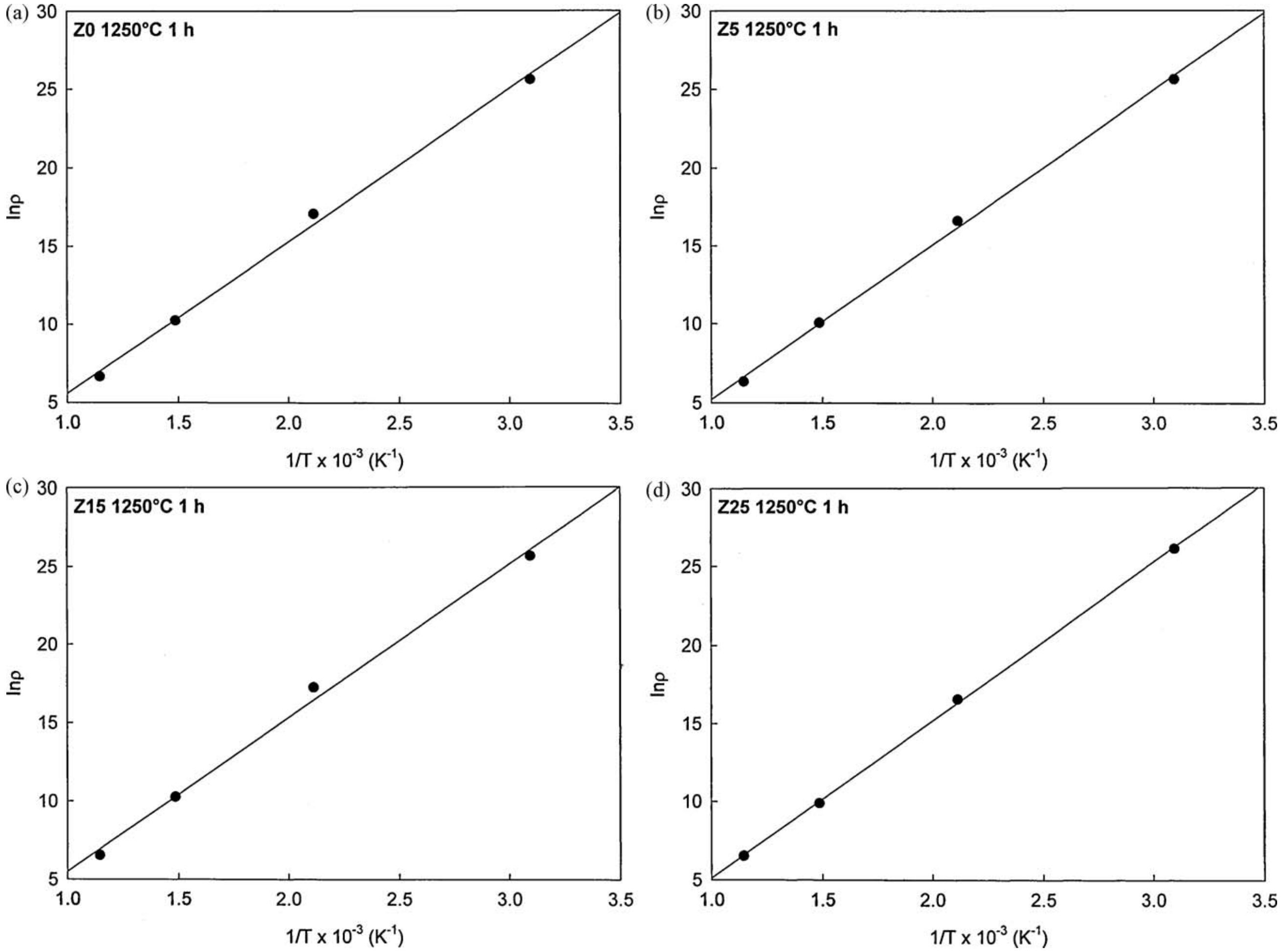

Fig. 4. ln $\rho$ versus 1/$T$ graphics for (a) Z0, (b) Z5, (c) Z15 and (d) Z25 compositions sintered at 1250 °C.

electrical resistivity decreased with increasing temperature. Electrical conductivity increase in rising temperature is possibly due to the ionic mobility [15].

In ceramic materials, ions can be carriers to provide electrical conduction. The degree of conductivity is largely dependent on the energy barrier that must be overcome for the ion to move from one lattice position to the next. At low temperature, conductivity is low. However, if the temperature is high enough to overcome the barrier for lattice diffusion, the conductivity increases. The existence of lattice defects such as vacancies and interstitials in the structure aids conduction [1].

Furthermore, each phase in the porcelain body has its specific influence on the resistivity [2,3,7]. The electrical resistivity of mullite is high at room temperature and is approximately $10^{13}$ ohm cm which is well within the resistivity of insulators. Its electrical resistivity drops noticeably with the rise in temperature. Mullite behaves like semiconductor at high temperature. The band gap energy (Eg) of mullite is 1.43 eV and this value is in the semiconductor interval [13].

Quartz has high electrical resistivity at room temperature and its conductivity decreases with increasing temperature [3].

In this study, the glassy phase is derived from the potash-feldspar and zeolite component in the porcelain composition. According to Chaudhuri et al. [3,13], the ions in the feldspathic glass of porcelain are held together by moderately strong bonds and the movement of the alkali ions ($K^+$, $Na^+$) in the applied electric field became restricted. Consequently, the electrical resistivity of glass in porcelain was high [3]. But, Islam et al. [2] stated that where dielectric performance such as high dielectric strength is required glassy phase and mobile ion content must be minimized. The glassy phase will have a harmful effect if the amount is quite high. When there is a low amount of glassy phase content it is quite advantageous to the ceramic insulator as it only fills up the pores. But when the amount gets higher it only just increases the volume and decreases the density and that is why decreases the dielectric strength. Increased glassy phase and decreasing the quartz content tends to decrease the bending and dielectric strength of the porcelain ceramic insulator. At 1350 °C, there will be a considerable amount of glassy phase. When there is a large amount of glassy phase present in the structure the mobile ions such as $Na^+$, $K^+$ and $Li^+$ finds an easy path to move and hence increases the conductivity.

If there is a large amount of undissolved quartz then it creates an obstacle in the way of conductive path that is glassy phase in which mobile ion can easily move. If it were possible to retain the undissolved quartz with higher amount of mullite then the strength would be greatly increased. Another reason for low dielectric and bending strength is the presence of

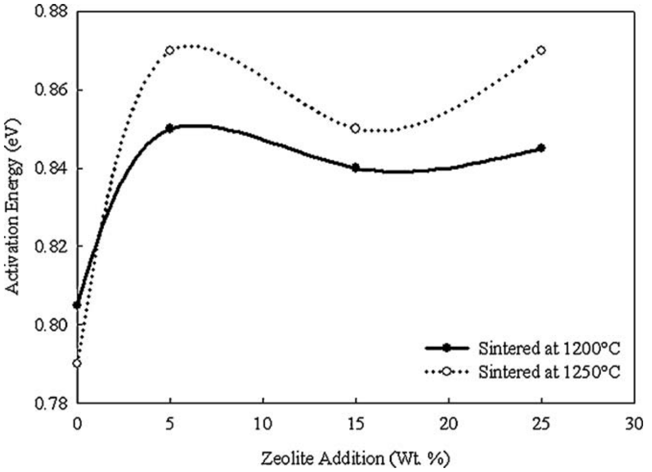

Fig. 5. Variation of activation energy as a function of zeolite addition in samples sintered at 1200 and 1250 °C.

micro-cracks in the ceramic insulator. The cracks are observed mainly near the quartz particles as observed in Fig. 1 and those regions where the crystalline phase or mullite phase is less or absent. The cracks are peripheral around the quartz grains. At the crack tip some expansion cracks are also to be observed. So this type of micro-cracks surely deteriorates the dielectric and mechanical properties of ceramic insulator [2].

The difference between valence band and conduction band gives the magnitude of the band gap energy. In insulator materials, the filled valence band is separated from the empty conduction band by a relatively large band gap (>2 eV). The electron band structure found in the semiconductors which is the same as for insulators except that the band gap is relatively narrow (<2 eV) [14].

A plot of ln $\rho$ versus $1/T$ was drawn for each samples between 50, 200, 400 and 600 °C. The activation energy of electrical resistivity of the samples was calculated in eV unit from the slope of the plot. A plot of ln $\rho$ versus $1/T$ for each samples sintered at 1200 and 1250 °C is shown in Figs. 3 and 4. The variation of activation energy as a function of zeolite addition in sintered samples at 1200 and 1250 °C is given in Fig. 5 where the activation energy values were obtained from the slope of the plots of Figs. 3 and 4. The activation energy values of Z0, Z5, Z15 and Z25 samples sintered at and 1200 and 1250 °C are in the range of 0.79–0.87 eV, respectively.

## 4. Conclusions

The present study was designed to determine the effect of electrical resistivity of porcelain bodies with natural zeolite addition. The following conclusions can be drawn from the present study as follows:

(1) The electrical resistivity of sintered samples at 1250 °C is higher than that of sintered samples at 1200 °C.
(2) The electrical resistivity of sintered Z0, Z5, Z15 and Z25 at 1250 °C is $1.32 \times 10^{11}$, $1.34 \times 10^{11}$, $1.37 \times 10^{11}$, $2.18 \times 10^{11}$ ohm m, respectively which revealed that the electrical resistivity of samples increased slightly with increasing zeolite addition.
(3) The electrical resistivity of samples decreased with increasing temperature, i.e., from $10^{11}$ ohm m at low temperature to $10^{2}$ ohm m at 600 °C.
(4) The activation energy of porcelain samples changed from 0.79 to 0.87 eV. Although porcelains are considered as insulators, their activation energy values are in the range of semiconductors. The porcelains behave like semiconductors above room temperature. Our results were in very good agreement with that statement.

These findings suggest that in general zeolite added porcelain bodies are good insulators with slightly higher resistivity values when compared with conventional porcelains at room temperature. But their resistivity drops and they behave like a semiconductors with increasing temperature. Consequently the results of this investigation show that natural zeolite addition into porcelain could improve the electrical resistivity of conventional porcelain.

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