SEMICONDUCTIVITY BEHAVIOUR OF EGYPTIAN NATURAL SINTERED ORE
FOR THERMOTECHNOLOGICAL APPLICATIONS

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ABSTRACT

The polymetal (Zn, Pb, Fe, Cu, Mg, Cd, Ba, Ni, Ti, and SiO2) complex Umm-Gheig carbonate ore is subjected to sintering treatment at 573, 773, 973 and 1273 K, respectively, for four hours. Chemical, spectral, X-ray and differential thermal analyses are applied for the native ore as well as for the samples preheated and sintered. The I-V characteristics, bulk density (Db), percent shrinkage (% S), activation energy (Ea) and energy gap (Eg) are established for the sintered ore. The electrical conductivity (σ), thermal conductivity (K) and thermoelectric power coefficient (α) have been investigated as a function of applied temperature for the sintered ore materials. The electrical and thermal measurements show that the sintered ore has semiconductivity behaviour with temperature. The electrical conduction is mainly achieved by electrons or n-type. As the sintering temperature (Ts) increases the conduction of the ore is also increased owning to the recombination process taking place between the electrons and holes. Electrons hopping between Fe2+ and Fe3+ are the main charge carriers. The formation of Fe2O3 at high sintering temperature acts as an active mineralizer, thus inducing an increased degree of crystallinity and the more ordered crystal structure is produced.

Keywords: polymetal ore, sintering treatment, semiconductivity behaviour.

INTRODUCTION

The polymetal deposits of the Red Sea ore belt (a zone extending NW-SE for a distance of 130 km) represent a complex morphogenetic type of mineralization [1]. The chief minerals are hydrozincite, zinc blende, smithsonite and cerussite, while silica and carbonates constitute the bulk of the gangue. The investigated sample contains 30.7 % Zn, 7.99 % Pb, 5.05 % Fe and 6.58 % SiO2. The minerals present in the complex ore are often so closely intergrown that it is either difficult to obtain suitable high-grade concentrates at high recoveries [2] by physical methods, or the recovery of metals from the respective concentrates is poor. Madkour et al. [3-8] investigated experimentally the thermochemistry of the complex ores roasting, with giving some theoretical thermodynamic calculations, for the recovery of metal value. It is possible to control the calcine composition by controlling the temperature and air-solid ratio. It is very important for the understanding of properties and conduction mechanism of ZnO [9-11].

The solid state sintering is classical method for obtaining of materials with wide application possibilities, as microwave materials [12], ferrite materials [13] and others. In this sense, the aim of the present work is
to investigate the electrical and thermal properties of the natural polymetal complex ore on a series of sintering temperatures: 573, 773, 973 and 1273 K, respectively, as well as to directly examine the semiconductivity behaviour of the material, obtained by solid state sintering that may have thermotechnological applications.

**EXPERIMENTAL**

**Sampling**

Mineralized horizone ore (500 kg) was crushed to 100% minus 1.0 mm. The ore samples are finally mixed in an agate mortar to ensure homogeneous distribution. Discs of 1.1 cm in diameter and 0.15 cm thickness were pressed at about 500 kg cm⁻² in a steel die using hydraulic press. The pressed discs were then sintered at 573, 773, 973 and 1273 K, respectively, for four hours under atmospheric pressure. The discs were polished and coated on both flat surfaces with graphite paste for electrical measurements.

**Chemical analysis**

Analysis [14] of the ore sample was carried out at the Egyptian Geological Survey and Mining Authority.

**Thermal analysis**

Analysis for the native ore sample was carried out by means of a MOM derivatograph with α-Al₂O₃ as reference. The powdered ore sample was heated at the rate of 10°C/min up to 1000°C (constant sensitivities: DTA, 1/10, TG: 200 and DTG, 1/15). Differential thermal analysis (DTA) of the investigated sintered ore sample was carried out using a Schimadzu XD-3-thermal analyzer.

**X-ray analysis**

The X-ray powder diffraction pattern was obtained using CuKα radiation and nickel filter. A Phillips X-ray PW 1729 diffractometer has been used in the range 2θ = 12-80.

**Infrared spectra**

The infrared spectra (KBr discs) were recorded on a Perkin-Elmer 1430 Ratio Recording spectrophotometer and a Perkin-Elmer 683 spectrophotometer.

Fig. 1. Essential electric circuit.

Fig. 2. Cross-section of the apparatus used for thermal measurements.

**Electrical measurements**

The I-U characteristic measurements were obtained with a digital multimeter type KIETHLEY 130 A, as a voltmeter and as milliampermeter. The digital thermometer was used to measure the temperature with an accuracy of ±0.1°C. The essential electric circuit is shown in Fig. 1.

The apparatus used for the thermal measurements [15] is shown in Fig. 2. It consists of a sample holder held on three iron rods. The sample holder consists of a stainless steel bar which is fixed in the central axis of tubular stainless steel furnace working with a heater. The central steel bar, copper leads thermocouple wires and heater connections are insulated from the holder base plate by a ceramic disc. Various wires and thermocouples are connected to the outside by means of copper leads through teflon tubes. The sample S is slightly
pressed by means of a small load placed on its top just to maintain good contact between the sample surfaces and the two copper electrodes. A metal jacket cooled with water through a copper coil placed around it, rests on an annular vacuum rubber ring fixed to the base plate. The degree of vacuum was \(10^{-3}\) mm Hg, and the heat leak due to convection was practically negligible.

The thermal conductivity \(K\) was measured at different temperatures (30-240°C). This was achieved by controlling the furnace heater to maintain constant temperature at the lower surface of the sample and then the temperature gradient was measured.

**RESULTS AND DISCUSSION**

**Chemical composition and analysis**

The investigated Umm-Gheig native ore sample was found to contain 59.76 % \(\text{ZnCO}_3\), 6.02 % \(\text{PbCO}_3\), 4.86 % \(\text{PbSO}_4\), 5.05 % \(\text{Fe}\), 4.84 % \(\text{CaO}\), 6.58 % \(\text{SiO}_2\) and 2.58 % \(\text{MgO}\) as given in Table 1. Thus, the natural ore is considered as zinc concentrate. Its constituents of \(\text{FeO}\) and \(\text{Fe}_2\text{O}_3\) are relatively high.

Furthermore, the chemical analysis made on the sintered ore sample (after sintering at 1273 K for 4 h) indicates the increase of \(\text{Fe}_2\text{O}_4\) content at the expense of both originally present \(\text{FeO}\) and \(\text{Fe}_2\text{O}_3\) content.

**Thermal analysis**

Fig. 3a displays the differential thermal analysis (DTA), thermogravimetry (TG) and derivative thermogravimetry (DTG) of the native ore sample. The arrangement of minerals \([16,17]\) according to their abundance is as follows: hydrozincite \([\text{Zn}_2(\text{CO}_3)_3(\text{OH})_2]_1\); zinc blende (\(\text{ZnS}\)); smithsonite (\(\text{ZnCO}_3\)) and cerussite (\(\text{PbCO}_3\)).

The total loss on ignition in mass percent at 1100°C is 28.22 %. It can be seen that the native ore sample displays two endothermic peaks at 280°C and 370°C, respectively. This is assigned to loss of humidity content or physically combined water. Further temperature rise displays a whole intense broad exothermic hump covering the temperature range 400-550°C peaking at 500°C for the strongest one. This is due to collective phase changes \([16]\), corresponding to the following reactions:

\[
\text{Zn}_2(\text{CO}_3)_3(\text{OH})_2 + 3\text{H}_2\text{O} \rightarrow 2\text{Zn}(\text{OH})_2 + 3\text{CO}_2
\]

\[
\text{Zn}_2(\text{CO}_3)_3(\text{OH})_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Zn}(\text{OH})_2 + 3\text{CO}_2
\]
Fe₂O₃ $\rightarrow$ Fe₃O₄ (magnetite) $\rightarrow$ Fe₃O₄ (hematite) $\rightarrow$ Fe₅O₇ (magnetite)

X-ray analysis

X-ray diffraction studies ensured the chemical composition of the native Umm-Gheig natural ore and samples preheated and sintered at 573 - 1273 K, respectively, as shown in Fig. 4. The X-ray diffraction pattern of raw material sample (Fig. 4a) displays the essential characteristic peaks for ZnCO₃ ($\theta = 33.70$, 25.10, 51.25, 37.80, 46.40, 41.60 and 61.40). The essential characteristic peaks for PbCO₃ are: ($\theta = 25.80$, 36.40, 43.80, 29.00, 49.20, 36.40 and 47.30). The essential characteristic peaks for PbSO₄ are: ($\theta = 29.50$, 26.80, 44.50, 27.40 and 22.10). The essential characteristic peaks for $[\text{Zn}_2(\text{CO}_3)_3(\text{OH})_3]$ are: ($\theta = 36.40$, 33.70, 29.00, 25.10, 30.70 and 16.80). X-ray powder diffraction data shows that galena is mainly converted to cerussite. After sintering treatment at 573, 773, 973 and 1273 K for four hours respectively, the X-ray diffraction pattern of sintered ore samples (Fig. 4b-e) displays the characteristic deflection peaks for different metal oxides listed as follows: ZnO ($\theta = 36.10, 31.70$ and $33.80$), PbO ($\theta = 29.10, 31.60, 32.15, 48.70$ and $45.60$), PbO₂ ($\theta = 28.15, 49.55$ and $22.80$), Pb₃O₄ ($\theta = 29.50, 29.60$ and $27.40$), Pb₂O₃ ($\theta = 26.20, 31.60$ and $32.15$), FeO ($\theta = 41.95, 36.20$ and $61.00$), Fe₂O₃ ($\theta = 33.50, 35.60$ and $54.20$), Fe₃O₄ ($\theta = 35.60, 62.40$ and $29.60$).

The X-ray diffraction studies of sintered ore samples at higher sintering temperatures (Fig. 4) ensured a spinel phase formation ($x \text{Fe}_2\text{O}_4$) where, $x = \text{Zn}$ or Pb. The essential characteristic peaks for spinel ZnFe₂O₄ and PbFe₂O₄ are: ($\theta = 35.00, 29.60, 62.05, 56.60$) and ($\theta = 32.40, 46.00, 56.80, 74.40$ and $67.40$), respectively. Furthermore, there is no indication for the appearance of reflection peaks characteristics for the carbonate mineral or sulphate composition which originally present in the native ore before sintering processes at 573-1273 K. This is due to the thermal decomposition of the chief minerals present, into the corresponding metal oxides.

Infrared spectra

The IR frequencies of the native Umm-Gheig ore sample (a) and the sintered ore samples (b-e) along with their assignments are given in Fig. 5. The bands at 1677-1632 cm⁻¹ are assigned to the $\nu$ C=O groups. Metallic carbonyls absorb in the 1984 cm⁻¹ region [19]. Silicates give absorption bands in the 1168-915 cm⁻¹ region.
range. Appearance of new bands in the frequency region at 332 - 328 cm$^{-1}$ (Fig. 5b-d) is due to stretching vibration bands of metal oxide (M-O) bonds, where M = Zn, Pb or Fe. The existence of water molecules within the co-ordination sphere of the hydrated ore samples is supported by the presence of absorption bands in the region 3889-3422 cm$^{-1}$ and 1116-1073 cm$^{-1}$ in the spectra of the ore due to (OH) stretching, HOH deformation and H$_2$O rocking [20].

Effect of sintering temperature on the bulk density (Db) and shrinkage (% S)

The measured diameter of the sintered ore discs is decreased as the sintering temperature increases, therefore the percent shrinkage (% S) of the sintered ore samples is consequently increased with increasing the sintering temperature (Fig. 6). The bulk density $D_b$ is also measured for the different sintered ore discs and the data is plotted as a function of the sintering temperature $T_s$, as represented in Fig. 6. The results show that, the bulk density as well as the percentage shrinkage are increased gradually with increasing the studied sintering temperature from 573-1273 K. This behaviour may be due to the more intensive diffusion process [21] is occurring at high sintering temperature, leading to the reduction of the porosity. As a result of this contraction, the crystal structure becomes compactness and rigid at high sintering temperature. The observed small
values of $D_n$ and (\% S) at lower sintering temperatures can be attributed to the limited rearrangement of the crystal lattice structure through the movement of grain boundaries [22].

**Temperature dependence of electrical properties**

The $I$-$V$ characteristics have been measured on the sintered ore samples at the studied different sintering temperatures ranging from 573-1273 K, respectively, as shown in Fig. 7. It can be seen that the $I$ vs. $U$ plots are on the whole, straight lines at all different sintering temperatures. The plot is converted also to ln $I$ vs. ln $U$, as represented in Fig. 8. It is evident that at the applied dc voltages an ohmic relationship ($\alpha = 1$) is obtained for all sintered samples with the exception of the ore sample sintered at 773 K. The behaviour is called the current-ohmic range. But for the case of sintered sample at 773 K, the nonohmic relation, $I \equiv U^{\alpha}$, holds good. The parameter $\alpha$ which essentially defines the non-ohmic nature of the material is equals to 1.52 and 1.95 for the lower and upper branches lines, respectively. The non-ohmic region ($\alpha > 1$) in the $I$-$U$ curves, arises due to the space-charge effects and is termed as space-charge-limited current (SCLC) region. These observations show that the $I$-$U$ characteristics provide the best understanding of the conduction mechanism in the ore samples. The tested ore material may be considered to be composed of layers with different conductivities and thicknesses in series with each other. The well-conducting grains, having thickness $d_1$, conductivity $\sigma_1$ and permittivity $\varepsilon_1$ are separated by a thin layer of poorly conducting grain boundaries (GB) having thickness $d_2$, conductivity $\sigma_2$ and permittivity $\varepsilon_2$. It is reasonable to assume that $\sigma_1 >> \sigma_2$. If $U_1$ and $U_2$ are the dc voltage drops across the grain and the GB, respectively, then $U = U_1 + U_2$ is the externally applies dc voltage. The voltage drop will take place mainly across the grain boundary (i.e. $U_1$.

Table 2. The electrical resistivity ($\rho$) as a function of sintering temperature.

<table>
<thead>
<tr>
<th>Sintering temperature (K)</th>
<th>Resistivity ($\rho$, , $10^{-4}$ cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>573</td>
<td>73.84</td>
</tr>
<tr>
<td>773</td>
<td>21.10 (before $V_c$) and 8.43 (after $V_c$)</td>
</tr>
<tr>
<td>973</td>
<td>11.75</td>
</tr>
<tr>
<td>1273</td>
<td>11.09</td>
</tr>
</tbody>
</table>
If the current (i \(\Omega\)) through the grain is only ohmic and the current through the GB is ohmic (i \(\Omega_i\)) as well as space-charge limited (i \(\Omega_s\)), the total current \(I = i_{\Omega_0} + i_{\Omega_i} + i_{\Omega_s}\). The total current in the ore solid can be approximated as \(i_{\Omega_0} << i_{\Omega_i} \equiv I\). Thus, the I-U characteristic in the nonohmic region is given by \(i_{\Omega_i} \equiv U_2^\alpha\). The space-charge–limited current is determined mainly by the number of free charge carriers available in the grain-boundary layers. At the applied dc voltages on the ore samples, i.e. before the non-ohmic region (at 773 K sintered ore sample) the current is purely ohmic (\(\alpha = 1\)). In this region the total current through the ore solid is \(i_{\Omega_0} << i_{\Omega_i} \equiv I\), and hence an ohmic relation holds. According to this theory [23], the I-U curves are consisting of three parts:
- low-current ohmic range, for the sintered ore at 1273 K (\(\alpha = 0.93\));
- scf-current range or the non-ohmic range, for the sintered ore at 773 K (\(\alpha = 1.52, \alpha = 1.95\)), where (\(\alpha_1, \alpha_2\)), represent the values of \(\alpha\) at lower and upper, respectively;
- high-current ohmic range for the sintered ore at 573 K and (\(\alpha = 1\)).

The broken line of I-U characteristic for the tested sintered ore sample at 773 K shows that the critical voltage \(U_c\) at which the line is broken is 15 volts.

The dependence of the electrical resistivity of the sintered ore samples on the applied sintering temperature is given in Table 2. The obtained data indicates that the resistivity of the sintered ore samples decreases as the sintering temperature increases for the samples.

Electrical conductivity versus temperature characteristics (ln\(\sigma - 1/T\)) of all the investigated samples were measured and represented in Fig. 9. From the typical log \(\sigma\) vs. 1/T characteristics, as shown in Fig. 9, it is seen that the sintered ore samples had a good semiconductivity behaviour with increasing the applied temperature from 430-550 K according to a Boltzmann-distribution [24]:
\[
\sigma = \sigma_0 \exp(-E_a/kT)
\]

The parameter \(\sigma_0\), which is given by the intercept of the line at 1/T = 0 is called the pre-exponential factor or the frequency factor, \(kB\) is the Boltzmann constant and T is the absolute temperature. However, it is worth anticipating the interpretation of the activation energy \(E_a\) for the electric conduction in eV, which is motivated by writing the above equation as:
\[
\ln\sigma = \ln\sigma_0 - E_a/kT
\]

There we shall see that the activation energy \(E_a\) represents the minimum energy necessary for a molecule in the sample to possess in order to react. \(E_a\) is calculated from the slope of the straight line of this plot (Fig. 9). The values of activation energy \(E_a\) are plotted as a function of the sintering temperature. \(T_s\) as shown in Fig. 10. The experimental results in Figs. 9 and 10 indicate that the electrical conductivity increases and consequently the activation energies are decreased with increasing the sintering temperature. The obtained data of either electrical conductivity (Fig. 9) and/or activation energy (Fig. 10) are in a good agreement with those obtained from the previous studies of the resistivity values as given in Table 2. Also, the results obtained are in good agreement with other work [25] and can be explained on the basis that the propagation of lattice imperfection decreases and the more ordered crystal structure is produced.
Thus, all the investigated sintered ore samples have semiconductivity properties. Generally, in a semiconductor material the outer electrons or valence electrons are normally stable, i.e. bound to their atoms and not free to move. But when heat is applied or an impurity (a doping element) that serves to raise energy is incorporated, the application of a voltage will cause displacement of valence electrons in the material, i.e. turn then into charge carriers. So, an electric current in a sintered ore semiconductor may be induced and varied over a wide range only under the action of external influence, such as heat and doping. The higher the temperature, the greater the number of free electrons and the larger the conduction current in the semiconductor. Thus, electrical conduction [26] in all semiconductors is mainly by electrons or n-type. Since the electrons that participate in conduction are the semiconductor’s own electrons, its conduction is called intrinsic.

The atoms that lost their electrons turn into positive-charge ions bound and unable to move. The vacancy left by the electron in the outer ring of the atom is called a hole. An electron set free from the neighboring atom may fill the vacancy by moving to the hole and leaving instead a hole in its atom thereby turning it into a positively charged ion. The application of an electric current to a semiconductor will cause electrons to move from atom to atom in one direction and leave holes in the opposite direction. The hole is generally regarded as a positive particle equal in charge to the electron. The seeming movement of holes in the direction opposite to that of electrons is called hole current. The electric conduction in the semiconductor, conditioned by this current, hole or p-type conduction.

The movement of electrons in one direction and of holes in the opposite determines intrinsic electrical conduction in a semiconductor, because the charge carriers (electrons and holes) belong to the semiconductor’s own atoms. In this case, the conduction current I consists of the electron I_e and hole I_h current components, i.e. I = I_e + I_h.

With intrinsic conduction, concentration of electrons (N_e) and of holes (N_h) are equal. However, I_e > I_h because the mobility of electron is higher than that of hole. The mobility of a charge carrier is the ratio of the velocity of electron v_e or of hole v_h to the electric field strength E in the semiconductor. Then, the electron mobility μ_e = v_e/E and hole mobility μ_h = v_h/E.

Table 3. The effect of sintering temperature (Ts) on E_a and E_g values.

<table>
<thead>
<tr>
<th>Sintering temperature (K)</th>
<th>Activation energy E_a (eV)</th>
<th>Energy gap E_g (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>573</td>
<td>0.850</td>
<td>1.70</td>
</tr>
<tr>
<td>773</td>
<td>0.825</td>
<td>1.65</td>
</tr>
<tr>
<td>973</td>
<td>0.760</td>
<td>1.52</td>
</tr>
<tr>
<td>1273</td>
<td>0.580</td>
<td>1.16</td>
</tr>
</tbody>
</table>

In that way, mobility indicates the distance electron or hole covers per second in a field of strength E = 1V/cm. Considering the aforementioned, expressions for the electron and hole current components may be written as [26].

\[ I_e = N_e \epsilon v_e = N_e \epsilon \mu_e E \]

\[ I_h = N_h \epsilon v_h = N_h \epsilon \mu_h E \]

where \( \epsilon \) is the charge of electron or hole and E is the electric field strength.

The conduction current in a semiconductor is:

\[ I = I_e + I_h = N_e \epsilon v_e + N_h \epsilon v_h = N_e \epsilon \mu_e E + N_h \epsilon \mu_h E \]

With intrinsic conduction, concentration of electrons is equal to that of holes in semiconductor, i.e. \( N_e = N_h = N \)

and

\[ I = N \mu_e (\mu_e + \mu_h)E \]

In a pure (intrinsic) semiconductor impurities constitute not more than \( 10^{-11} % \).

The investigated natural Umm-Gheig sintered ore containing the iron atoms as impurities of a valency higher than the semiconductor’s material tend to give electrons thereby increasing the electron density. They play therole of donors. Thus, the atoms of iron impurities present originally in the native ore can modify its electrical properties. For example, to obtain a semiconductor that will exhibit n-type conduction. This leads to the formation of some Fe^{2+} ions from Fe^{3+} ions. The polarization of the ferrite is determined by local displacement [23] of electrons in the direction of an applied electric field, which is due to the electron exchange interaction: Fe^{2+} \rightarrow Fe^{3+} + e^-.

The energy gap E_g which is defined as the energy required for separating the highest-filled or valence band (VB) from the conduction band (CB) is equal twice [27] activation energy, i.e. \( E_g = 2E_a \).
The values of $E_i$ and $E_f$ for the investigated semiconductor sintered ore samples are calculated and given in Table 3.

**Temperature dependence of thermal conductivity ($K$)**

The coefficient of thermal conductivity of the sintered ore samples was estimated using the formula:

$$Q = I V / J = K A dT/dX$$

where $Q$ is the quantity of heat per unit time transferred through the sample of thickness $dX$, $J$ the Joule’s coefficient, $I$, $U$, $dT/dX$, $A$ are the current in amperes, voltage across the heater in volts, temperature gradient (degree/m) and sample area ($m^2$), respectively.

The heat transport through lattice vibrations (phonons) is mainly important for insulators and semiconductors. The thermal conductivity of the sintered ore sample crystals has contributions from two component [28], lattice vibration (phonons), and the carriers (electrons).

$$K = K_{\text{ph}} + K_e$$

If we consider the heat conduction by electron carriers due to the presence of Fe$^{2+}$ and Fe$^{3+}$ impurities, the temperature gradient will cause a carrier concentration gradient, this results in a diffusion current which transports heat energy. At temperatures lower than the Debye temperature, the inelastic scattering processes become important thus a strongly affecting the thermal conductivity. In this range there is a sharp drop in phonon concentration with rising temperature, leading to a sharp increase in $K$ which becomes proportional to $T^3$. But at temperatures higher than the Debye temperature, the scattering processes must be responsible for the thermal resistance and the elastic scattering is dominant since the phonon contribution to the thermal conductivity is relatively small compared with the electron contribution.

The measured thermal conductivity is approximately equal to the contribution from electrons. In this range $K$ is inversely proportional to the temperature ($K \approx T^{-1}$).

The temperature dependence of $K$ for the investigated sintered ore samples is shown in Fig. 11. A sharp rising of thermal conductivity with rising temperature can be observed up to the transition temperature. The concentration of phonons decreases with rising temperature leading to a consequent decrease in lattice vibrations. This decrease of lattice vibration gives diminishing to lattice scattering causing an increase in the mean free path which would result in an increase of $K$.

Thus, the thermal conductivity $K$ increases at low temperature due to the increase of modes of vibration of crystal lattice and the responsible for conduction is the phonons up to Debye temperature. Above the transition temperature or Debye temperature the concentration of phonons increases with rising temperature leading to lattice scattering causing a decrease in the mean free path which would result in a decrease of $K$. As shown in Fig. 11 the values of thermal conductivity $K$ increase as the sintering temperature of the tested sintered ore samples is also increased. As the sintering temperature increases the material becomes more dense and the pores are decreased. The pores act as scattering centers of phonons, so the decreasing of pores causes the observed increasing of the thermal conduction $K$. The maximum values of thermal conductivity of the tested ore samples sintered at 573, 773 and 973 K were as follows: 180, 210 and 390 K (W/m deg) $\times 10^{-3}$, respectively, as shown in Fig. 11. The results obtained from thermal conductivity $K$ measurements are in a good agreement with those obtained from the previous electrical conductivity $\sigma$ studies.

The thermoelectric power coefficient $\alpha$ was measured experimentally for the investigated sintered ore samples...
samples as a function of temperature. The $\alpha$ measured was of negative values, showed that the main charge carriers are electrons hopping between Fe$^{2+}$ and Fe$^{3+}$ ions which are present originally in the material as impurities (called dopants). Dopant or doping Fe element whose atoms tends to give electrons to the semiconductor thereby increasing the electron density and called donor. Iron impurities modify the electrical and thermal properties to obtain a semiconductor that will exhibit n-type conduction. It is clear that the electrons constituting the iron impurity conduction are the chief charge carrier in the investigated semiconductor sintered ore material. Finally, the conduction current in the investigated semiconductor sintered ore samples is the sum of electronic and hole currents, but electronic current is many times that of hole current.

Efficient solar conversion requires materials with band gaps [29] of 1.3±0.3 eV i.e. absorption of light in the spectral range of 250-1000 nm. Considerable attention has been given in the recent years to the application [30, 31] of semiconductor colloids, powders and films for conversion of solar energy into electricity and chemical energy. The concentration of current carriers and hence the semiconductivity increases with increasing temperature according to a Boltzmann distribution [24]. Thus, the obtained experimental energy gap values $E_g$ of the sintered ore samples under consideration as shown in Table 3 are suitable and optimum for using the tested natural sintered ore material as a highly absorbing semiconductor in the photoelectrochemical systems and thermo-technological applications as suggested in the following techniques:

(1) Nitrogen reduction to ammonia by photosensitized [32] electron transfer from dispersed ore oxides (Fe$_2$O$_3$, PbO$_2$, ZnO) doped TiO$_2$ semiconductor particles.

(2) Semiconductors in water treatment [33].

(3) Colloidal semiconductors in photovoltaic systems [27,34]. As known from the Schottky barrier theory, the low bias potential region might be controlled by recombination and trapping of electrons in the depletion region [35]. These processes occur most effectively in localized states energetically centered in the mid-gap position leading to a recombination current proportional to $\exp(qV/2kT)-1$[36,37].

(4) It is often necessary that semiconductor materials be exclusively of n- or p-type for many industrial applications, e.g. for semiconductor-based rectifiers to rectify alternating current into pulsating direct current. Thus a system of two semiconductors with different types of electric conduction resists reverse current flow. This property is highly valued for semiconductor rectifiers. Fusing together the two types forms a p-n junction that has the property of rectifying alternating current. If we apply an a.c. voltage to such a system of two semiconductors, the p-n junction will pass the current of only one half-cycle of voltage. In crystal diodes the p-n junction are used chiefly for rectifiers applications.

(5) Thermo-electric generation is essentially the same as the energy conversion and heat pumping (when a semiconductor material is used thermoelectrically as a heat pump) with p-type and n-type materials.

(6) Partial illumination of a semiconductor induces a photo emf between the illuminated and unilluminated areas of the material surface. This phenomenon is used for making sources of electric power, such as photovoltaic cells and solar batteries, semiconductor devices capable of solar-to-electric energy conversion.

**CONCLUSIONS**

The obtained results from the electron microscopic investigation for the either native ore and/or for the ore after sintering treatment confirmed by metal value data given in the ASTM. cards coincide well with those given by chemical analysis.

From the observations of I-U characteristics, ln $\sigma$ vs. 1/T and $K$ vs. T behaviours of the investigated natural sintered ore samples, we can summarize the following conclusions.

- The sintered ore material had a good semiconductivity behaviour with increasing temperature.
- The semiconductor sintered ore exhibits n-type conduction.
- Both values of $E_g$ and $E_a$ in eV decrease with increasing the applied sintering temperature from 573 to 1273 K. Consequently the electrical conductivity $\sigma$ increases in the same range of the studied sintering temperatures.
- The thermal phonon scattering and lattice vibration scattering are responsible of thermal conductivity $K$ for the behaviour of the material at changing temperatures.
• The measurements for electrical, thermal and semiconductivity behaviour of the investigated material, obtained by solid state sintering, suppose its thermotechnological industrial applications.

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