

Electrical Properties and Infrared Studies of Heated Mica Sheets

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Dielectric constant (ϵ'), dielectric loss (ϵ'') and ($\tan \delta$) have been measured for heated Mica sheets at different temperatures (200-900°C) for 2 hours in the frequency range (0.1-100KHz). It has been found that the dielectric constant and dielectric loss are nearly stable till 600°C but showing an increase at 800 and 900°C. The dielectric loss and $\tan \delta$ show maximum 800 and 900°C. The activation energy values of dielectric relaxation have been calculated for mica sheets for the latter temperatures. It was observed that the activation energy values go on increasing with increasing heating temperature from 800°C to 900°C. The resistivity of mica sheets was studied also as a function of temperature in the range (30-70°C) for the samples heated at 800°C and 900°C over frequency range [0.1-100 KHz]. It was found that the resistivity increases with temperature and decreases with frequency. The resistivity at 900°C is higher than 800°C overall the range used. Infrared spectra were studied to link the influence of the structure of heated mica with their thermal behavior.

Introduction:

Mica is a generic name given to a family of hydrous potassium aluminum silicates having similar physical properties. Some of the familiar known mica are muscovite, phlogopite, biotite, lepidolite and vermiculite (although the last is not commercially classified as a mica). Only the first two have commercial demand in rubber and plastics application. The major markets for dry and wet ground mica are for joint cement, roofing, well drilling mud, and paints. The plastic and rubber industries consume less than 10 % of the total U.S. mica produced [1-3].

The muscovite structure is dioctahedral, with one out of three octahedral positions being open. The phlogopite structure is tri-octahedral with all octahedral positions being filled. In other words, the replacement of the two Al^{+3} ions is neutralized by three ions of Mg^{+2} and/or Fe^{+2} . Isomorphous substitution within the silica-alumina frame work, as well as with bridging cation, can be readily accomplished. Much isomorphous substitution work with synthetic fluorophlogopites has been published [4&5].

The abundance, the relatively low cost of mica and the inherently good electrical properties of this mineral are factors, which have maintained interest in the use of mica in various applications. A mica-alumina combination is selected for the insulating system at temperatures higher than 500°C. The aging condition was to apply 1.5 k.v.as voltage in nitrogen atmosphere at 550°C [6].

A mica–alumina–silicon combination was selected for insulation system at higher temperatures. Using this insulation system, an aging pretest was performed in order to give information about its stability. Several well established tests have been implemented to better understand the electrical and thermal aging mechanisms of mica-based stator insulating system. The measurement of dielectric properties, weight loss and observable deterioration pattern of an insulation sample at several isotherms is used to establish a reliable operating temperature limit. An emergency temperature limit is determined by short-term exposure to high temperatures and detection of insulation delimitation by acoustic spectrum analysis of specimen resonant frequencies. Test results are compared between mature system and proposed system. This procedure is used to establish operating limitations for rewind equipment as well as estimate the remaining service life of existing machines [7].

Infrared absorption spectra can provide information on the structure of the oxide glasses [8]. The vibrational spectra can be used to identify glasses or specific groups, which are present in it [9&10]. DTA, TG and DTG investigated

several isomorphous groups of different types of mica. The combination of thermal and IR- spectra of hydroxyl analyses permits to link the Order-Disorder data with thermal properties of mica [11].

The aim of this work is to study the effect of heat treatment till 900°C on the dielectric properties and electrical resistivity of natural Mica. Infrared absorption spectra of natural mica sheets were studied also to link the influence of the structure of mica with their thermal behavior.

Experimental:

Natural mica sheets, from Waddy El-Alaky, East Desert, Egypt, were prepared for measurements as discs of 12mm diameter and 1mm thickness. The prepared samples were thermally heat-treated at different temperatures (200-900°C) for 2 hours. An AG-4311 B RCL-meter (Ando-Japan) was used to measure the Dielectric properties (dielectric constant ϵ' , dielectric loss ϵ'' and $\tan\delta$). The resistivity measurements of the treated samples were measured in the frequency range (0.1-100 KHz). Infrared spectra were carried out using Jasco Fourier Transformation Infrared (FT/IR) 300E Spectrophotometer. The samples were measured as Potassium Bromide (KBr) discs covering the range (100-4000 cm^{-1}).

Spectrographic Elemental Analysis of Mica:

Natural mica sheet were exposed to semiquantative spectrographic analysis. Mica content in percent are listed in Table (1). Forty mg of the mica was mixed with an equal amount of spec pure graphite in a clean agate mortar. The samples were burn according to the following specifications:

Spectrograph: Zeiss Jena medium quartz prism spectrograph type, Q-24.

Slit width: 14 μ .

Lens diaphragm: 3.2 mm.

Electrode: RWI spec pure graphite electrode.

Excitation: 220 V, D.C. anode excitation.

Current: 9 amperes.

Plate: ORWO yellow extrahard 9 x 24 cm.

Exposure time: 0/90 sec. Followed by arck for another 60 sec.

Processing: 5 min. in freshly prepared ORWDI developer and 10 min. in hypo fixer.

Carl Zeiss spectrum projector by examined the spectrum

Comparison with spectrum was spec standards.

Table (1): Semiquantitative spectrographic analysis of mica sample.

Elements Present	Approximate Quantity
Al, Fe & Si	Major 10 %
Mg, Mn, & Na	Minor 1-10 %
Ca, Ga, K, & Ti	Trace 0.1-1 %
Ba, Cu, V, & Zn	Faint trace 0.01-0.1 %
Be, Ni, Pb, & Sn	Very faint trace 0.001- 0.01 %

Results and Discussion:

I- Dielectric Properties:

I-1 Effect of Thermal Heating:

Mica sheets under investigation were subjected to thermal heating for 2 hours at 200,400,600,800 and 900°C. The dielectric properties as dielectric constant ϵ' , dielectric loss ϵ'' and $\tan\delta$ after each stage of heating were measured in the frequency range (0.1-100 KHz). The results obtained are shown in Fig. (1). It can be noticed that the dielectric constant ϵ' increases with rising temperature. This can be attributed to the increase in the mobility and ease of rotation of molecule resulting from the decrease in the dipole-dipole interactions. Also, it can be noticed gradual decrease in dielectric constant as the frequency of the applied field increased. The dielectric dispersion occurs specially at high frequencies. This decrease of ϵ'' with increasing frequency can be explained by the lag of the molecules behind the alterations of the applied electric field. The tendency of change after the heating process was clarified to be caused by a decrease of organic component in the insulation which remained due to incomplete burning. Effects on the dielectric properties can be concluded as follows:

- 1- The dielectric constant ϵ' for mica sheet are unaffected by thermal heating till 600°C in this range frequency. But, the dielectric constant at 800 and 900°C increased to reach $\epsilon'_{800} = 40 > \epsilon'_{900} = 22$ at $f=100\text{Hz}$.
- 2- The dielectric loss ϵ'' increases, gradually from 200 to 800°C and then decrease in 900°C.
- 3- $\tan \delta$ of mica samples is very low and stable after heating temperatures from 200-600°C and overall the frequency range used. At 800°C and 900°C $\tan\delta$ increases showing maximum values ($\tan\delta = 0.4$ and 0.8) for samples heated at 900°C and 800°C respectively.

Previous notices indicate that, the dielectric properties for heated sample below 600°C showed some stability or resistance to thermal heating process. While, the stability of the samples heated at 800°C and 900°C fall down showing increase in the dielectric properties. Thus, these samples were chosen to study briefly. The stability occurred to the sample till 600°C may be arises from the scattering of the conducting electron by lattice defects due to

vacancies interstitial in the structure. As the thermal heating increased to 800°C, the concentration of the induced defect is expected to cease or fall. Vacancies and interstitial recombine or vacancies migration to the surface. Eventually, migration becomes very slow or cease. Then further heating to 900°C will lead to corresponding reduction of the concentration of defects and vacancies.

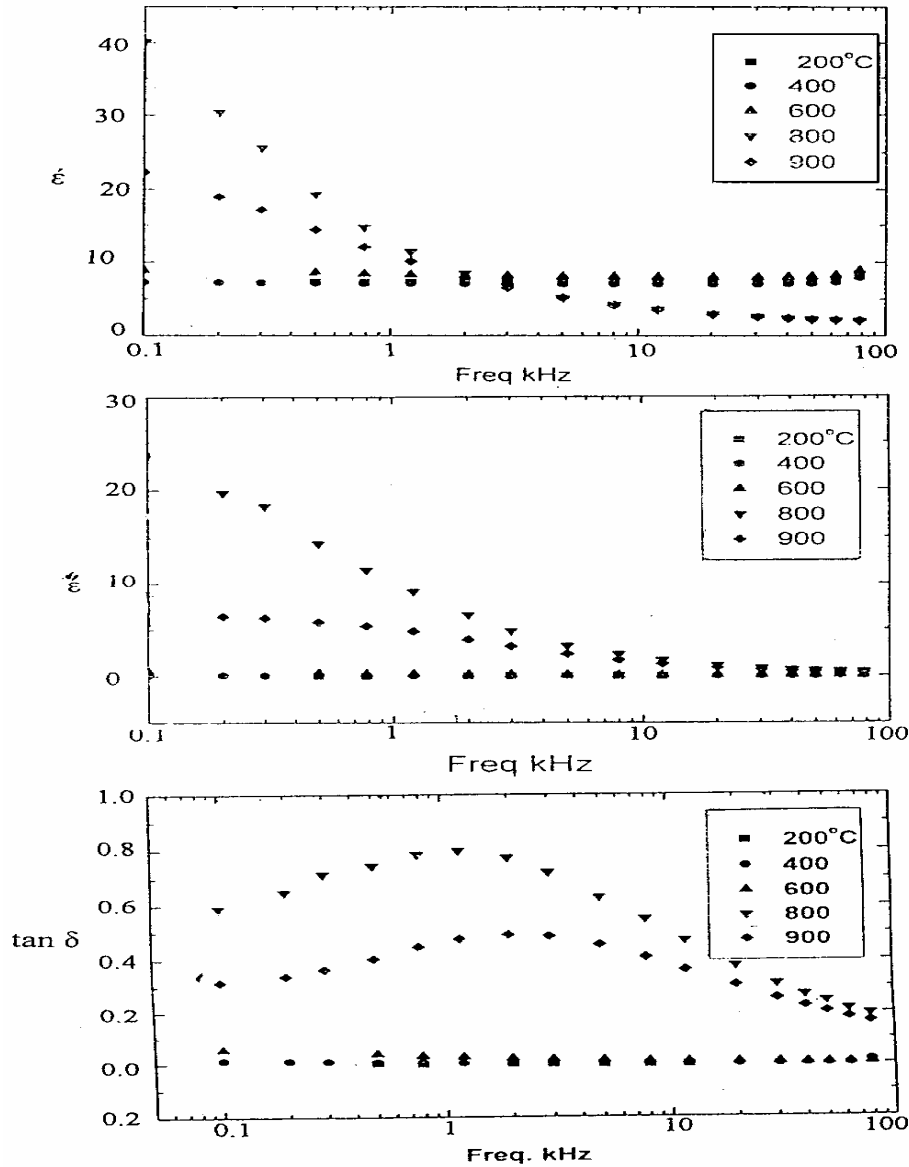


Fig. (1): Variation of the dielectric const. ϵ' , dielectric loss ϵ'' and $\tan \delta$ with frequency for mica sheets different heating temperatures.

1.2 – Effect of Temperature:

Mica samples heated at 800°C and 900°C were chosen to study the dependence of the dielectric properties on temperature and frequencies. The dielectric properties ϵ' , ϵ'' , and $\tan\delta$ of chosen samples at different temperatures and frequencies are shown in Fig. (2&3). It can be noticed that the dielectric constant ϵ' decreases by increasing each of frequency and temperature. The decrease in ϵ' at higher temperature may be due to the thermal agitation, which will not allow the dipoles to be oriented. Moreover, this lowering is observed clearly at lower frequencies where the effect of space charge polarization can be felt [12]. At higher frequency, the real part of dielectric constant changes little with frequency, and the imaginary part is small. The dependence of the dielectric loss ϵ'' on temperature for selected samples at fixed frequencies showed a loss peak at lower frequencies, and ϵ' decreases with increasing frequency in the rang of the loss. The increase in loss at lower frequencies probably results from the DC resistivity of the sample.

$\tan\delta$ – frequency plot showed loss maximum. Samples heated at 800°C has higher values of $\tan \delta$ than that heated at 900°C. Its position shifts to lower frequency as increasing temperature. Maximum loss of $\tan \delta$ uprising due to dc conductance and increase interference by the conductivity loss at higher temperature.

Generally, there are four primary mechanisms for glass loss spectrum in order of increasing frequency, (1) d.c. conduction ions, (2) ionic relaxation loss refers to ions migrating limited distances and not to rotation of dipoles, (3) Deformation loss, due to structural ionic dipoles (such as Si-O) and (4) Vibrational loss of the ions themselves[13]. Relaxation process is regarded as the jumping of a molecule from one equilibrium position to another over a potential energy barrier. The dipole molecule needs a certain amount of energy (activation energy) to overcome the potential energy barrier separating these two mean equilibrium positions.

To calculate the apparent activation energy for these samples, the logarithm of the frequency corresponding to f maximum was plotted against the reciprocal of the absolute temperature the apparent activation energy was calculated using the equation:

$$\tau = A \exp[-(\Delta H / RT)]$$

where $\tau = 1/2\pi f_m$ is the relaxation time at the frequency of maximum loss, R is the gas constant and T is the absolute temperature. Relaxation is pictured as the jumping of molecule from one equilibrium position to another. It is assumed that the process of molecular rotation requires an activation energy sufficient to overcome the energy barriers separating the two main equilibrium positions. The relaxation times, the activation enthalpies and the entropy changes of the dielectric relaxation are given in the Table (2). It can be noticed that, increasing heating temperature from 800°C to 900°C the rotation of dipoles is less easy this certainly enhance the activation energies.

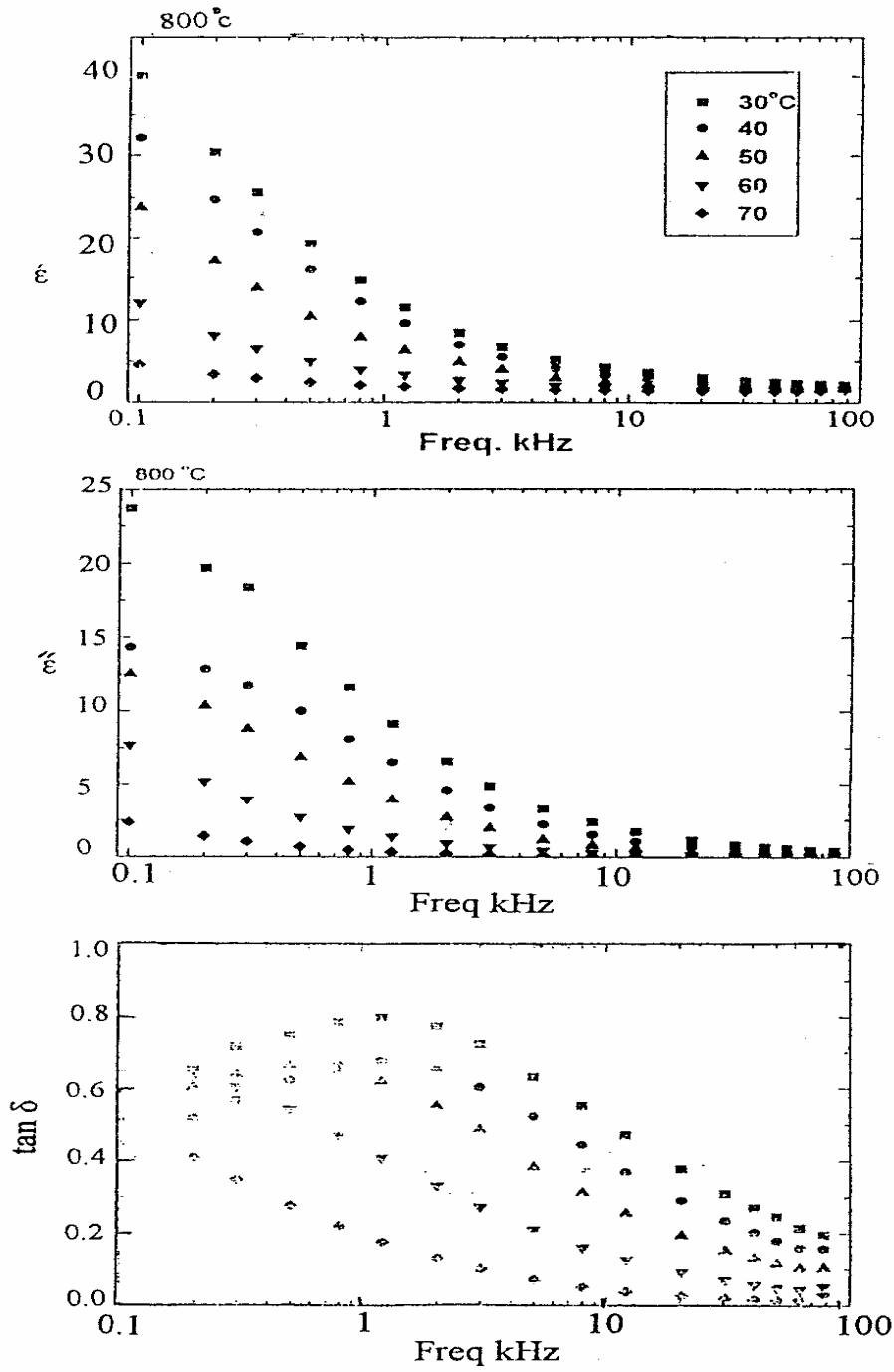


Fig. (2): Variation of dielectric constant ϵ' , dielectric loss ϵ'' and $\tan \delta$ for mica sheet heated at 800°C at different temperature.

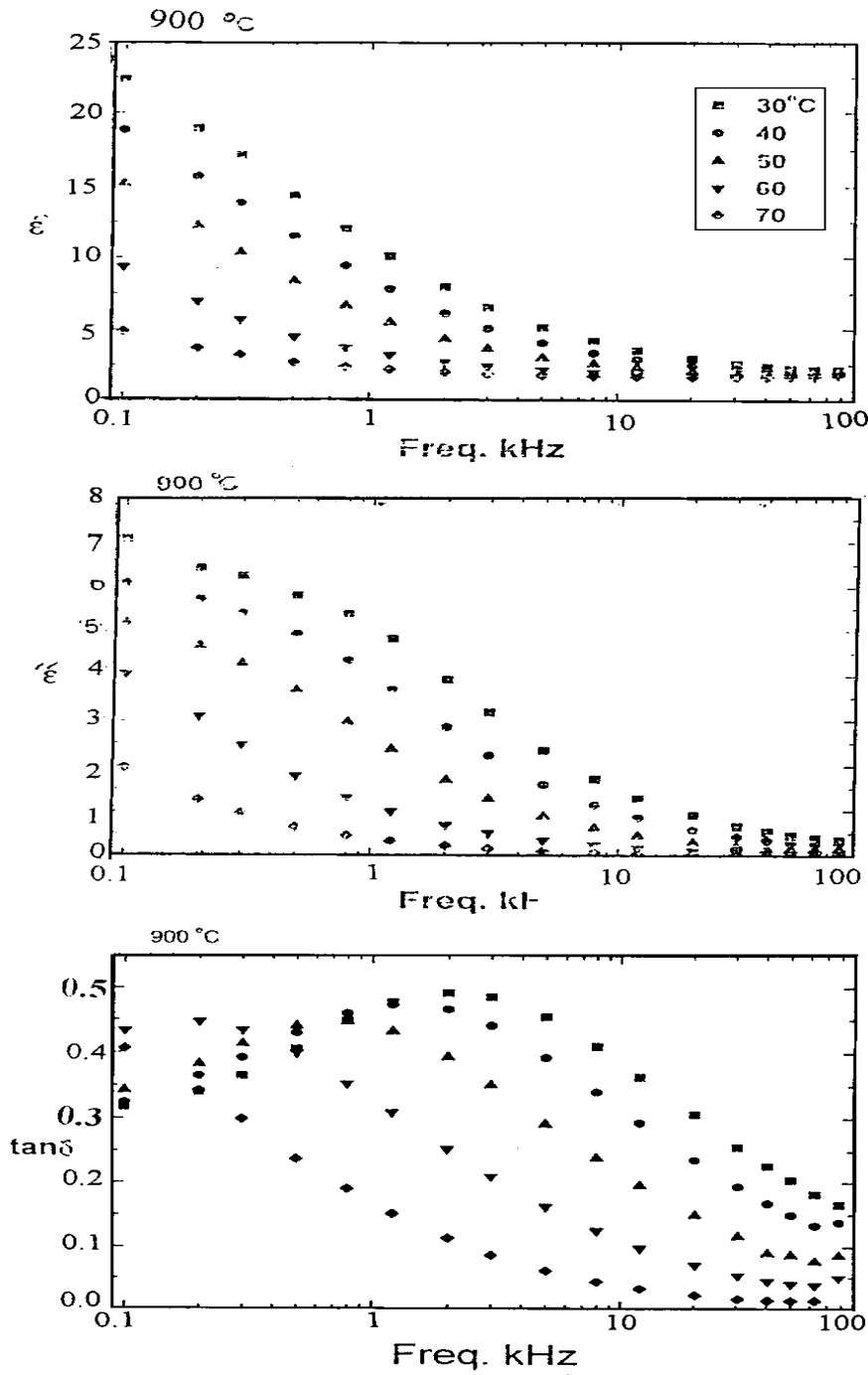


Fig. (3): Variation of dielectric const. ϵ' , dielectric loss ϵ'' and $\tan \delta$ for mica sheet heated at 900°C.

Table (2): The apparent relaxation times τ , the activation enthalpies ΔH , and ΔS Entropy of dielectric relaxation for mica samples heated at 800°C and 900°C.

Sample Type.	Mica 800°C			Mica 900°C		
	$\tau \times 10^{-3}$ (S)	ΔH (Kcal/mole)	ΔS (Kcal/mole)	$\tau \times 10^{-3}$ (S)	ΔH (Kcal/mole)	ΔS (Kcal/mole)
40	1.22488	13.72676	13.713	0.758265	18.28629	18.276
50	1.3266			1.592356		
60	3.1847			7.961783		
70	7.9617			15.92356		

II- Electrical Resistivity of Mica:

The resistivity-temperature relationship for mica sheets heated at 800°C and 900°C in the frequency range (0.1-100 KHz) is shown in Fig. (4). It can be noticed that the resistivity increases with increasing temperature from 30°C to 70°C. Also, the sample heated at 900°C has higher values of resistivity than that heated 800°C. The difference in resistivity between the two samples decreases as the frequency increase. This figure showed also that the resistivity decreases gradually with increasing frequency from 0.2–78 KHz.

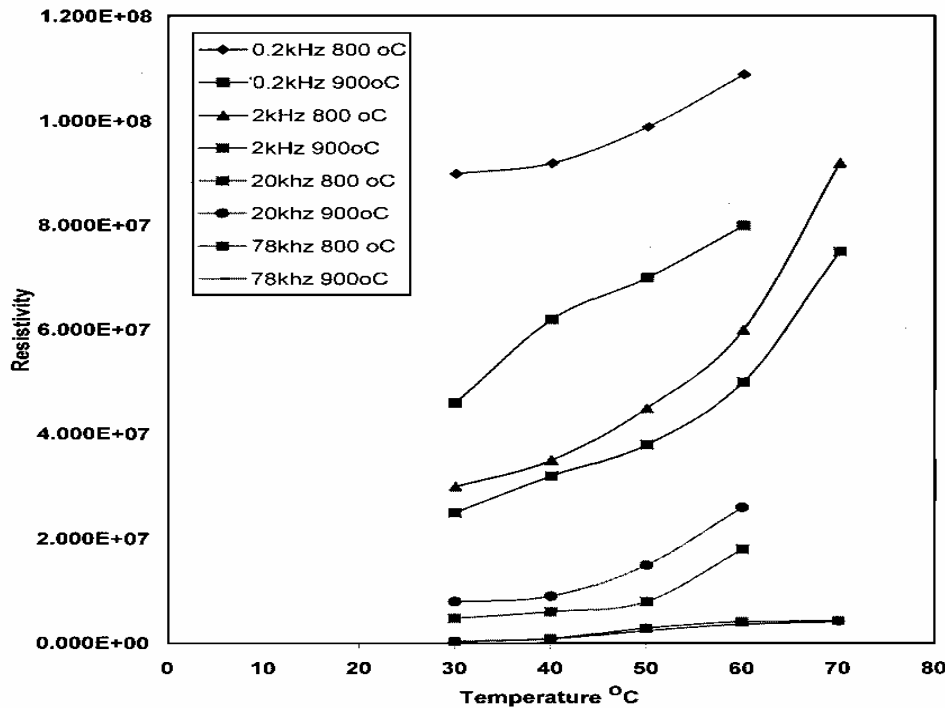


Fig. (4): Variation of resistivity of mica sheet heated at 800 °C and 900 °C with temperature at different frequencies.

The above result can be interpreted as the resistivity of a metal arises from the scattering of the conduction electron by static lattice defects such as vacancies and the thermal scatters which are created by the thermal motion of atoms or electrons. Mica heated at 900°C has fewer defects than mica at 800°C as a result of recombination of vacancies and or migration to the surface.

AC-conductivity (σ_{ac}) values are calculated from dielectric measurements using the following expression [14].

$$\sigma_{ac} = f \epsilon \tan \delta \cdot 1.8 \times 10^{10}$$

A representative plot of $\log \sigma_{ac}$ versus frequency $\log f$ (at 300° K) and for Mica heated 800 and Mica 900°C are given in Fig. (5). The nearly linear dependence of AC-conductivity with frequency accounts for the electronic conduction via a hopping process [15]. Also, the relation:

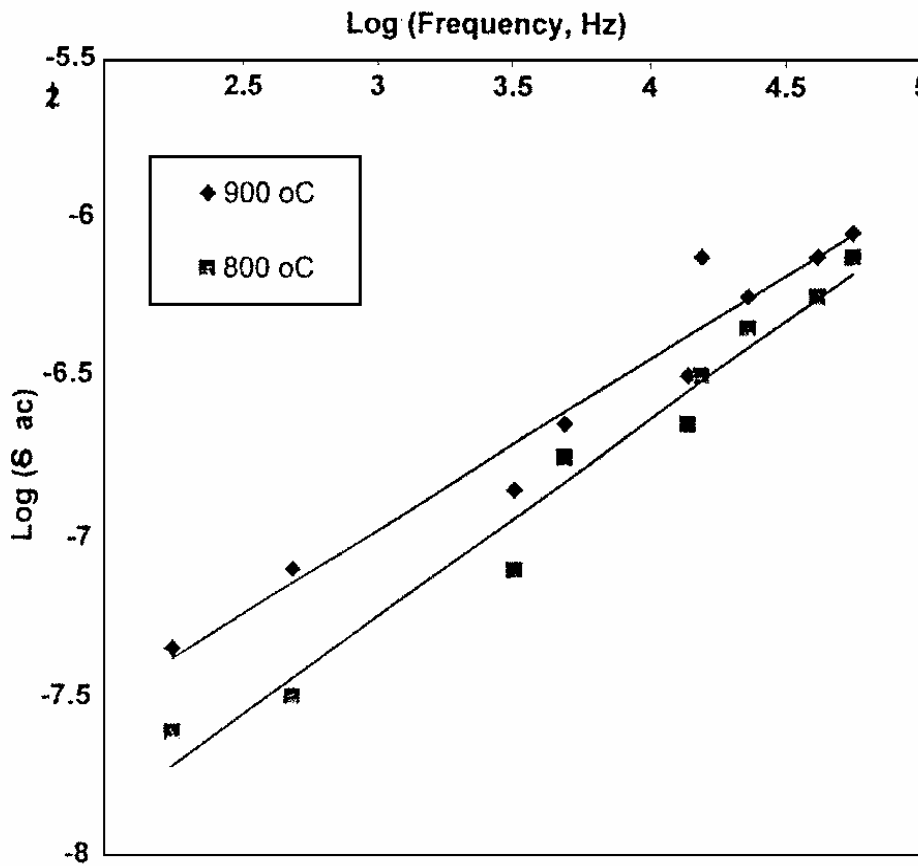


Fig. (5): Variation of $\log \sigma_{ac}$ versus frequency $\log f$.
 $\sigma_{ac} \propto f^n$

where n lies between $0.5 > n > 1$ characterize the electronic conduction via hopping process. In the present study n equal 0.6 and 0.8 for mica heated at 800°C and 900°C respectively.

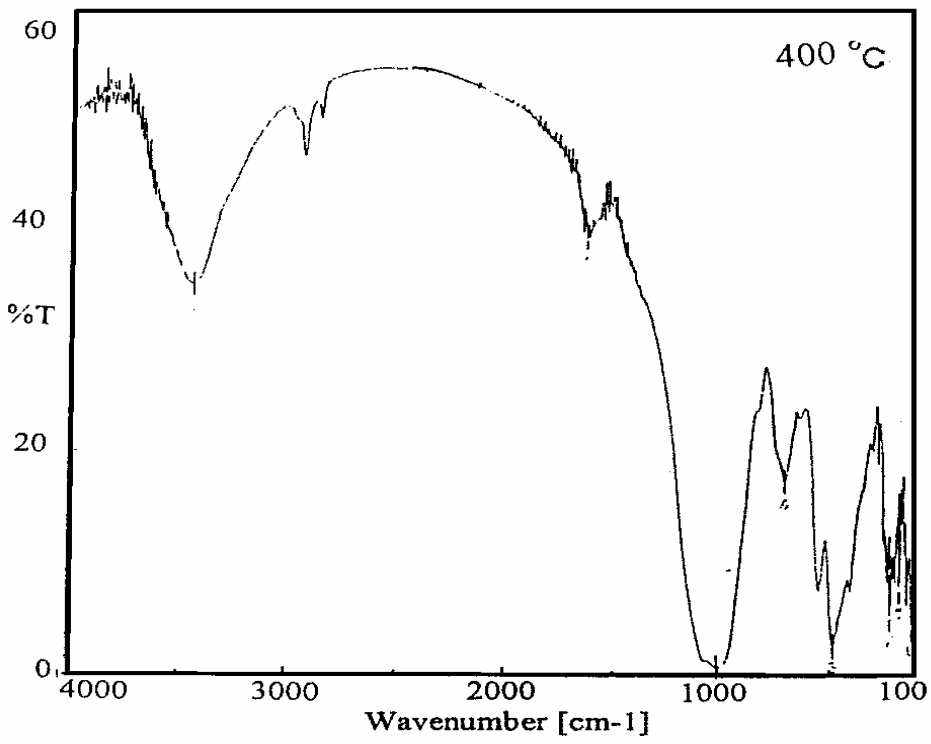
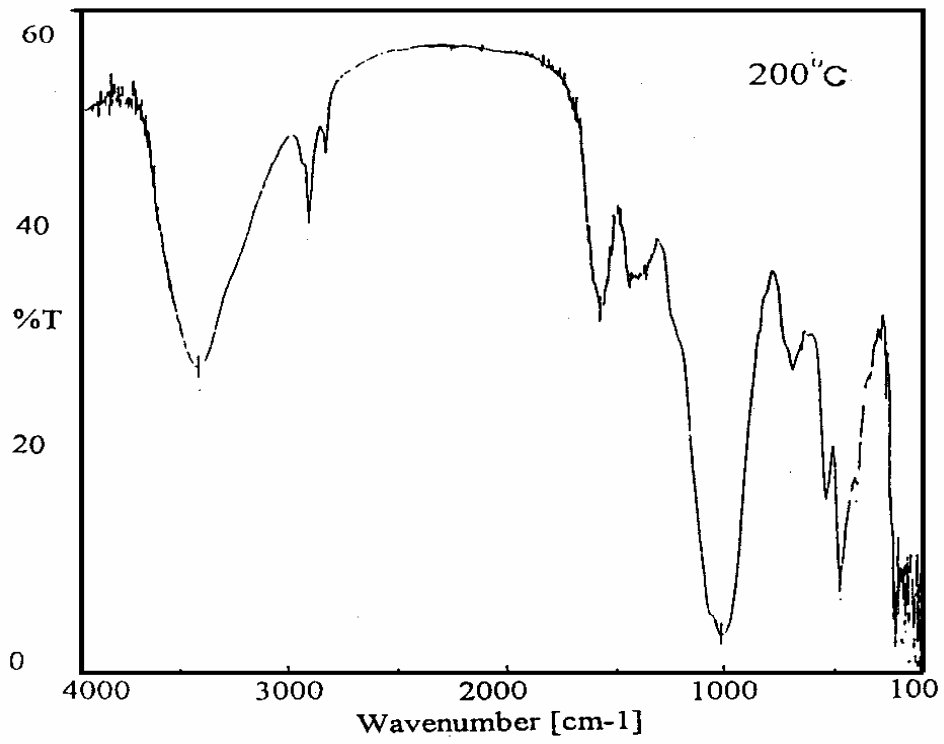
III-IR Spectra

The infrared spectra of heated mica sheet at 400, 600 800 and 900°C are shown in Fig. (6). Comparing the spectra at different heating temperature is nearly the same except the following:

- 1- Decrease in the intensity of OH-bending band at 1537 cm^{-1} and OH -st at 3430 cm^{-1} is illustrated as a result of heating and disappearance of the last band at 800 and 900°C.
- 2- Also, the IR bands of Si-O-Si and M-O-Si bending at 400 and 700 cm^{-1} are slightly sharpened and decrease in transmission percent.
- 3- No pronounced shift to higher or lower frequency of the characteristic strong bands of SiO_4 at 455, 775 and 1050 cm^{-1} was observed.
- 4- The band at nearly 2923-cm^{-1} characterizes C-H aliphatic compound decreases in intensity with increasing temperature.

Table (3): Effect of heat treatments for 2 hr on the infrared absorption bands of Mica sheets.

Frequency in cm^{-1}					Assignment (Approximate Description)
Heat treatment (Temperature °C)					
200	400	600	800	900	
405	400	400	400	401	Si-O-Si band.
500	499	490	490	480	Si-O-Si band.
510	510	510	510	551	Si-O-M
700	700	700	711	709	B-O-Si band.or B-O-B band
1014	1008	1008	1008	1008	Si-O stretching
1400					M-O stretching
1600	1600	1637	1637		H-O-H Bending
2923	2995	2998	2998	2998	C-H aliphatic
				3400	
3480	3460	3460	3432	3448	O-H stretching



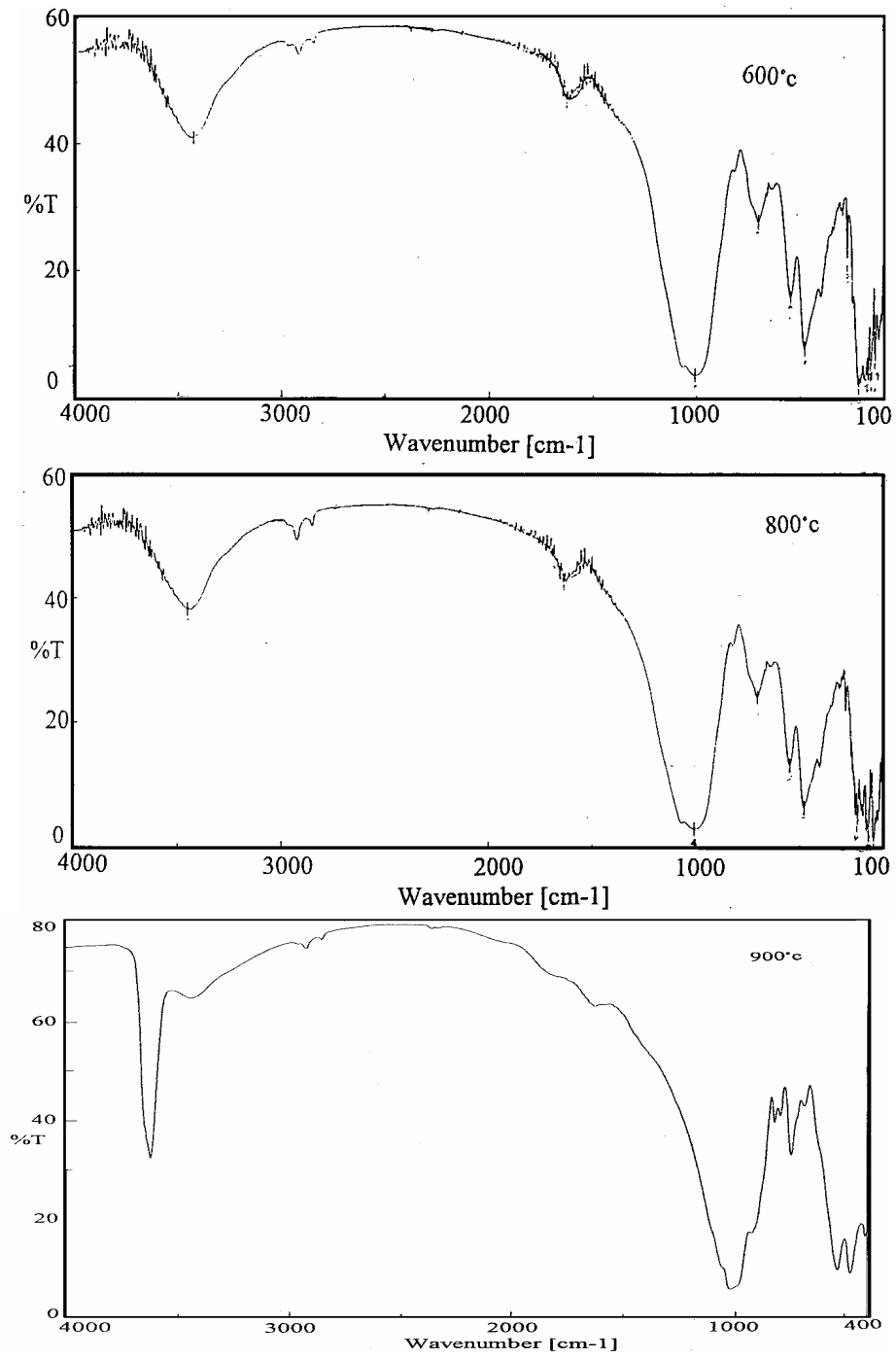


Fig. (6): IR spectra of mica sheet at different thermal heating temperatures.

Effect of heat treatment for 2 hours in the temperature range 200-900°C on the infrared absorption spectra of mica sheet are shown in Table (3). The characteristic bands of SiO_4 tetrahedral units were between 400-485 cm^{-1} (Si-O-Si) bending [16], 675-775 cm^{-1} (M-O-Si) stretching [17] and 1040-1050 cm^{-1} (Si-O) stretching [18]. There is no frequency shift in the positions of these bands in temperature range 200-600°C, but the shift occurred at 800 and 900°C due to destruction. The absorbency of these bands, were increased to 800°C then decrease at 900°C as shown in Fig. (7). The absorbency of the infrared bands at 1637 cm^{-1} (H-OH) bending due to the water absorbed decreased mainly after 800 to 900°C, but the band at 1650 cm^{-1} diminished. The band at 3480 cm^{-1} of (O-H) stretching vibration band decrease at 900°C and sharpened.

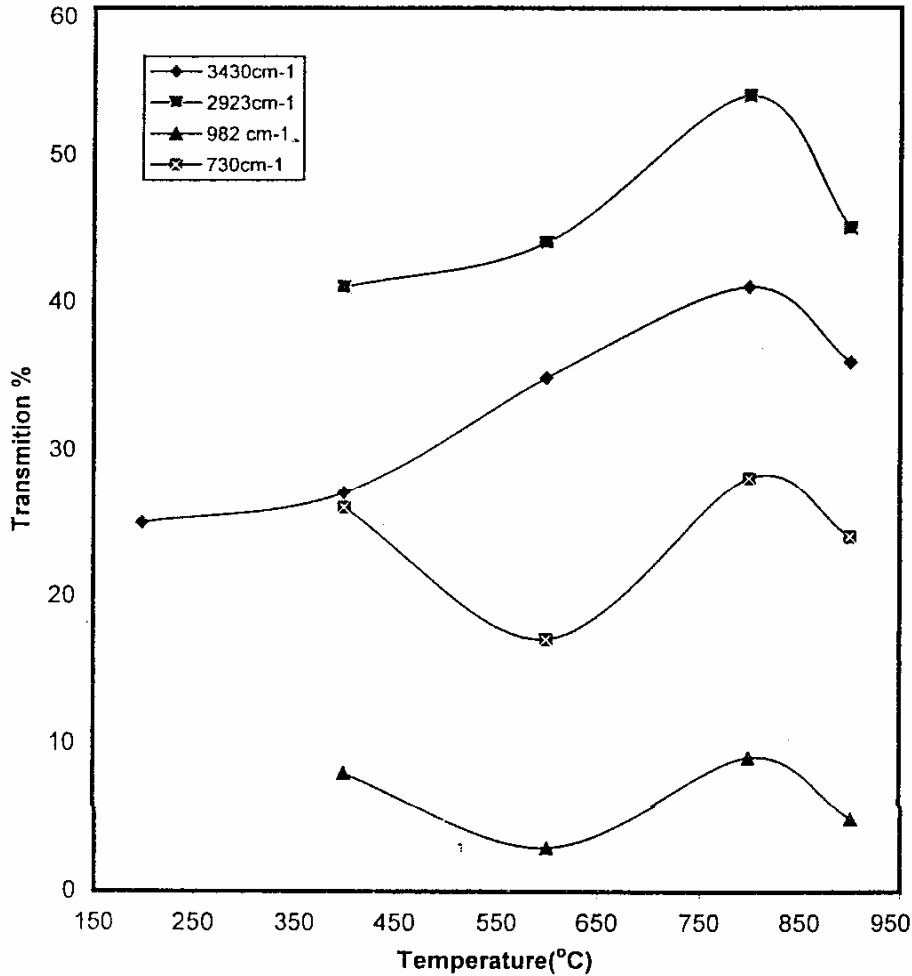


Fig. (7): Effect of thermal heating on the intensity of transimision of mica sheet.

Mica is a naturally laminated composite of flakes or platelets. The properties of mica vary greatly from one source to another, however many of the variations are not critical in resin composites. Silicate materials as mica have alternating structure of the oxygen and silicon atoms in covalent bonding forming tetrahedral units. Lower oxygen atoms have all the shared electron pairs available to hold adjacent sheets of the structure together. There are two major commercial categories of natural mica, Muscovite [$Al_2(OH)_2AlSi_3O_{10}$] and Phlogopite similar in composition [$K_2Al_4(Al_2Si_6O_{20})(OH)_4$]. This natural mica is related to mixture of the two types the molecular structure in layer system, each layer consists of a pseudo-octahedral gibbsite plane chemically bonded by bridging oxygen and hydroxyl groups to two tetrahedral silica planes. This two dimensional layer is negatively charged and is held to adjacent layers by positive potassium ions. The potassium ions are in 12-fold coordination interaction with 6-atom from each layer. This ionic interaction is weak because of impurities replacing many potassium ions in natural mica.

Several processes have been occurred on heating layer silicates such as mica as dehydroxylation, mica lattice destruction, destruction of the network, partial melting of material formation of a new phase etc. There is also a correlation between mica composition and product of its thermal destruction [11]. An amorphous phase was present in the final product of all the mica. There is a possibility of isomorphic substitution in octahedral position by several cations, mainly Mg, Fe^{2+} , Al^{3+} , Fe^{3+} , Li and F, O^{2-} in hydroxyl position. One of the three octahedral positions of mica may also be vacant, therefore there is a complicated system of solid solution although not necessarily a continuous one. According to Vedder and Willkins[19] after static heating at 500-600°C the units with vacancies disappear. It seems that the sequence of unit cell dehydroxylation is as follows; (1) units of Fe^{3+} only; (2) units of the Fe^{3+} and Fe^{2+} combinations; (3) units of the Fe^{2+} only; (4) units of the Mg, Fe^{3+} and Fe^{2+} combinations; (5) units of the MgMg and Fe^{2+} and Fe^{3+} combinations; (6) units of the Mg only. The influence of the fine structure of mica will interpret their thermal behavior in IR and Dielectric properties due to phase change occurred after 800°C.

Conclusion:

IR spectra showed no frequency shift in the position of the bands in the temperature range 200-600°C, but small shift occur in the temperature range 800-900°C. The absorbency the bands increased till 800°C, then decreased at 900°C, indicating phase transition at 900°C. The absorbencies of the infrared bands at ($1600-1637\text{Cm}^{-1}$ H-OH bending) due to absorbed water decreased mainly till 800°C and diminished at 900°C. These results confirmed with the stability of the dielectric properties till 600°C while there is change in the electrical behavior after heating at 800 and 900°C.

The linear dependence of AC-conductivity with frequency accounts for the electronic conduction via hopping process.

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