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Wiedemann-Franz Law in Lithium-borosilicate glasses

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Abstract:- Wiedemann-Franz law is applied for the lithium-borosilicate glasses. The product LT is proportional to the ratio of thermal conductivity to electrical conductivity. Graphically it exactly passing through origin, hence it gives y=x and $R^2=1$. It is observed that Lorenz number is decreasing with increasing temperatures due to increase of electrical conductivity and decrease in thermal conductivity. Functional dependence of σ and K on reciprocal of temperature has also helps in getting the values of activation energies for all the compositions under study. Activation energy shows opposite nature. Maximum values of electrical conductivity is 9.0469 e^{-3}S/Cm where as, maximum thermal conductivity is 8.8168 e^{-4}Cal/sec cm ^oC. The maximum value of Lorenz number is 2.294 e^{-1} watt-ohm/(deg)^2 at 250^{o}C.

Keywords:- Thermal conductivity, phonon interaction, atomic vibrations, DSC, Lorentz number.

I. INTRODUCTION

Thermal Conductivity is a measure of the ability of a material to transfer heat. When heat is applied to a portion of a material, it moves through the material. This movement of heat through a material is called the thermal current. Depending on the composition of the atoms of that material, the heat may move very slowly, or it may move very quickly. This dependence is quantified by the coefficient of thermal conductivity. A high coefficient means heat moves very quickly; a low coefficient means heat moves very slowly. The molecules of the solids are rigidly held in their mean position thus conduction is the only mode of transfer of heat in solids. There are two types of conductions (a) thermal conduction and (b) electrical conduction. It is understood as a thermal process in which the heat energy is transferred by the phonon interaction. Atomic vibrations represent phonon. On heating crystal expands and due to expansion the amplitude of atomic vibrations increase and these vibrating lattice waves collide with other molecules and transfer energy to them and so they vibrate more vigorously causes thermal conduction. In general the total thermal conductivity can be written as the sum of the contribution from the electrons and the phonon as below
$K_{total} = K_{electron} + K_{phonon}$

In metal electron contribution is predominate and in insulator phonon carry most of the heat. It is the scattering process that prevents easy heat conduction by the electrons and phonons. The electrons and phonons are scattered by collisions among themselves and also by collisions with impurities and imperfections/disorder. As the present work deals with glasses, a highly disordered system it is thought imperative to make an attempt to arrive at thermal conduction at the microscopic level. A very exhaustive DSC data giving the parameters like time, temperature, heat flow, heat capacity, reversible heat flow, and non-reversible has helped a lot in calculating thermal conductivity. The instrument has the facility to hold the sample in the pellet form and so area and the thickness was known during the DSC scan.

II. EXPERIMENTAL

In the present work fifteen glasses have been synthesized using high purity from Aldrich grade chemicals (Li_2CO_3), (B_2O_3) and (SiO_2) Mixtures of these materials in appropriate proportions were thoroughly ground under acetone in an agate mortar to achieve a homogenous powder. The glasses have been synthesized by the familiar melt quenching method. All the samples were annealed below their transition temperature.

The amorphous state of the glasses was checked by the X-ray diffraction method. The Differential Scanning Calorimetric (DSC) thermograms of all samples showed the glass transition temperature T_g. The accuracy in the measurement of T_g is ±1^{o}K. X-ray diffraction and DSC Characterizations were carried out from IUCA, Indore.

Electrical conductivity measurements were carried out from MSRL lab RTM, University, Nagpur. A impedance analyzer (Hewlett Packard HP 4192), has a built in capability to measure real and imaginary parts of impedance gain phase analyzer from 10 Hz to 13MHz in the temperature range of 523-673 ^{o}K. A programmable signal level allows applying voltage less than decomposition potential of solid electrolyte. The Keithley 7001 main frame system preinstalled with 6001 referred. Switchboard facilitates selection of 10 samples as per operator's choice. Both these instruments have built in remote operation capability via IEEE-488 interface bus. The furnace with power pack is used for heating and cooling procedures. Home–made GUI (graphic user interface) computer software was used to acquire the data and subsequent analysis. A home built cell assembly (6-terminal capacitor configuration and spring loaded silver electrodes) was used for all measurements. A sample temperature was measured by using a Pt-Rh thermocouple positioned very close to the sample. Annealed circular glass pieces were, spirited by spiriting unit on both sides, to serve as electrodes for electrical measurements.

Glass samples belonging to the systems I and II were prepared by fixing N, (N=ratio of the mixed former B_2O_3+SiO_2 to the modifier Li_2O) at a value 1.35 and varying Y, (Y=ratio of former B_2O_3 to the mixed former B_2O_3+SiO_2), while, in the third system III maintaining Y=0.5, N was varied. Table-1 Shows, compositional details of glasses belonging to systems, SI, SII and SIII.

Table 2.1 Composition in mol% of SI, SII & SIII, glass systems; with N and Y.

At N = 1.35	Composition in Mol %	Y	At N= 1.35	Composition in Mol %	Y	At Y = 0.5	Composition in Mol %	N
System	**Li_2O:B_2O_3: SiO_2**		**System**	**Li_2O:B_2O_3:SiO_2**		**System**	**Li_2O:B_2O_3:SiO_2**	
S I.1	**42.5:57.5:0**	**1**	**S II.1**	**42.5:0:57.5**	**0**	**S III.1**	**40:30:30**	**1.5**
S I.2	**42.5:52.5:5**	**0.91**	**S II.2**	**42.5:5:52.5**	**0.09**	**S III.2**	**42.5:28.75:28.75**	**1.35**
S I.3	**42.5:47.5:10**	**0.83**	**S II.3**	**42.5:10:47.5**	**0.17**	**S III.3**	**45:27.5:27.5**	**1.22**
S I.4	**42.5:37.5:20**	**0.65**	**S II.4**	**42.5:20:37.5**	**0.35**	**S III.4**	**50:25:25**	**1**
S I.5	**42.5:27.5:30**	**0.47**	**S II.5**	**42.5:30:27.5**	**0.52**	**S III.5**	**55:22.5:22.5**	**0.82**

III. ELECTRICAL CONDUCTIVITY

The bulk conductivities calculated from the analyzed impedance data obtained at different temperatures for all the glasses. The conductivity data is fitted to the Arrhenius equation

$\sigma = \sigma_0 \exp(-E_a/k_BT)$,

where σ_0 is the pre exponential factor and E_a , k_B and T are the activation energy, Boltzman's constant and absolute temperature respectively. The activation energy for conduction (E_a) was calculated from the slope of the straight lines.

System wise electrical conductivity with activation energy at various temperatures is as follows;

Table 3.1 Electrical conductivity and activation energy for System SI, at various temperatures

σ for System I					
Temp (^{o}C)	**SI.1**	**SI.2**	**SI.3**	**SI.4**	**SI.5**
250 ^{O}C	**7.0275 e-4**	**5.5705 e-4**	**9.0469 e-3**	**4.6408 e-4**	**2.9349 e-4**
275^{O}C	**1.0363 e-3**	**7.8306 e-4**	**1.3832 e-3**	**5.9635 e-4**	**3.9382 e-4**
300^{O}C	**1.4204 e-3**	**1.0929 e-3**	**2.1862 e-3**	**8.1526 e-4**	**5.5705 e-4**
325^{O}C	**1.9257 e-3**	**1.3848 e-3**	**3.0067 e-3**	**1.1130 e-3**	**7.4920 e-4**
350^{O}C	**2.6418 e-3**	**1.8518 e-3**	**4.1572 e-3**	**1.5031 e-3**	**9.6272 e-4**
375^{O}C	**3.5059 e-3**	**2.3345 e-3**	**5.6781 e-3**	**1.9239 e-3**	**1.1984 e-3**
400^{O}C	**4.6547 e-3**	**3.1167 e-3**	**7.5318 e-3**	**2.5438 e-3**	**1.5638 e-3**
Ea (eV)	**0.54 ev**	**0.239 ev**	**0.421 ev**	**0.329 ev**	**0.304 ev**

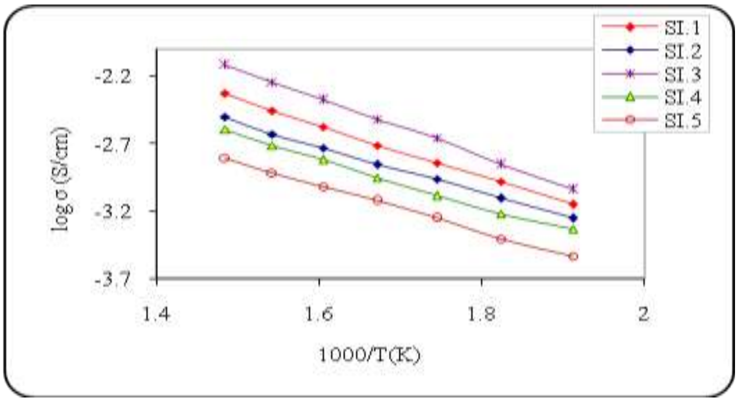

Figure 3.1 Variation of electrical conductivity with temperature for SI.

Table 3.2 Electrical conductivity and activation energy for System SII, at various temperatures

σ for System SII					
Temp (^{o}C)	**SII.1**	**SII.2**	**SII.3**	**SII.4**	**SII.5**
250 ^{O}C	**1.0306 e-4**	**5.2251 e-5**	**7.8126 e-5**	**3.7085 e-5**	**1.5149 e-4**
275^{O}C	**2.0007 e-4**	**9.1685 e-5**	**1.3185 e-4**	**6.2618 e-5**	**2.8392 e-4**
300^{O}C	**3.3113 e-4**	**1.9892 e-4**	**2.5205 e-4**	**1.2691 e-4**	**4.6291 e-4**
325^{O}C	**5.4075 e-4**	**3.4881 e-4**	**4.4781 e-4**	**2.2709 e-4**	**7.6612 e-4**
350^{O}C	**9.0427 e-4**	**5.9047 e-4**	**7.8741 e-4**	**4.0105 e-4**	**1.2288 e-3**
375^{O}C	**1.4434 e-3**	**9.4929 e-4**	**1.2959 e-3**	**6.8328 e-4**	**1.9182 e-3**
400^{O}C	**2.2656 e-3**	**1.5000 e-3**	**2.1712 e-3**	**1.1081 e-3**	**2.134 e-3**
Ea (eV)	**0.534 ev**	**0.514 ev**	**0.511 ev**	**0.584 ev**	**0.5 ev**

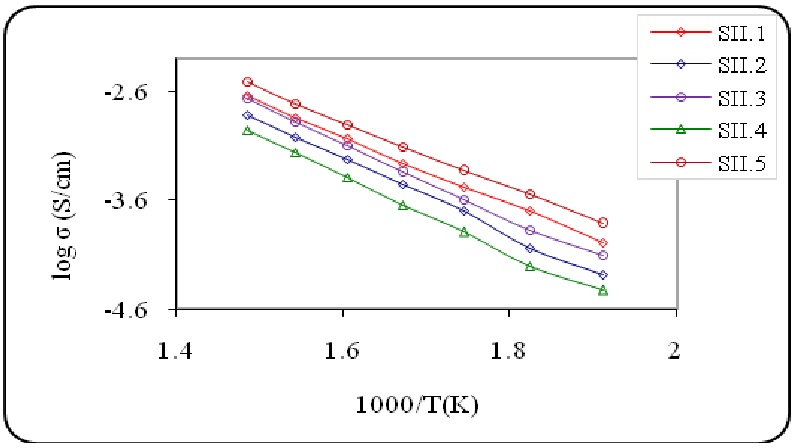

Figure 3.2 Variation of electrical conductivity with temperature for SII

Table 3.3 Electrical conductivity and activation energy for System SIII, at various temperatures

σ for System III					
Temp (^{O}C)	**SIII.1**	**SIII.2**	**SIII.3**	**SIII.4**	**SIII.5**
250 ^{O}C	**1.6485 e-4**	**2.1321 e-4**	**4.9181 e-5**	**1.0076 e-4**	**2.8582 e-4**
275^{O}C	**2.7346 e-4**	**3.4119 e-4**	**8.5153 e-5**	**1.6726 e-4**	**4.7632 e-4**
300^{O}C	**4.7643 e-4**	**6.1432 e-4**	**1.5728 e-4**	**2.9369 e-4**	**8.5075 e-4**
325^{O}C	**8.0686 e-3**	**1.0524 e-3**	**2.7189 e-4**	**5.3456 e-4**	**1.4295 e-3**
350^{O}C	**1.4061 e-3**	**1.6853 e-3**	**4.4411 e-4**	**8.0853 e-4**	**2.2966 e-3**
375^{O}C	**2.3275 e-3**	**2.8701 e-3**	**7.0355 e-4**	**1.3203 e-4**	**3.7462 e-3**
Ea (eV)	**0.557 ev**	**0.58 ev**	**0.537 ev**	**0.578 ev**	**0.558 ev**

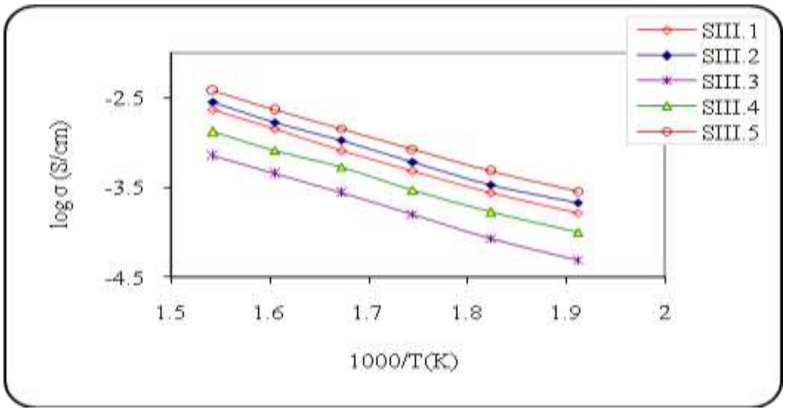

Figure 3.3 Variation of electrical conductivity with temperature for SIII

IV. THERMAL CONDUCTIVITY

Thermal conductivity for each sample was determined by using the Fourier's law,

$$\Delta Q/\Delta tA = -K\ \Delta T/\Delta x$$

where $\Delta Q/\Delta tA$ = power per unit area transported, $\Delta T/\Delta x$ = temperature gradient, and
$-K$ = Thermal conductivity

For metals, the thermal conductivity is quite high, and those metals which are the best electrical conductors are also the best thermal conductors. At a given temperature, the thermal and electrical conductivities of metals are proportional, but raising the temperature increases the thermal conductivity while decreasing the electrical conductivity. This behavior is quantified in the Wiedemann-Franz Law:

$$K/\sigma = LT \qquad \text{or} \qquad L = K/\sigma T$$

Where K = Thermal conductivity, σ = Electrical conductivity and L = Lorenz number

Qualitatively, this relationship is based upon the fact that the heat and electrical transport both involve the free electrons in the metal.

Table 4.1 Thermal conductivity and activation energy for System SI, at various temperatures

K for System I					
Temp °C	**SI.1**	**SI.2**	**SI.3**	**SI.4**	**SI.5**
250	**2.6018 e-4**	**3.4402 e-4**	**8.8168 e-4**	**6.5248 e-4**	**4.7727 e-4**
275	**2.2634 e-4**	**3.0307 e-4**	**7.6652 e-4**	**5.8973 e-4**	**4.1720 e-4**
300	**1.9668 e-4**	**2.6398 e-4**	**6.7722 e-4**	**5.0976 e-4**	**3.7037 e-4**
325	**1.7569 e-4**	**2.2992 e-4**	**6.0165 e-4**	**4.5414 e-4**	**3.2380 e-4**
350	**1.5540 e-4**	**2.0771 e-4**	**5.4148 e-4**	**3.9900 e-4**	**2.8752 e-4**
375	**1.3992 e-4**	**1.8702 e-4**	**4.9252 e-4**	**3.6668 e-4**	**2.6040 e-4**
400	**1.2684 e-4**	**1.7043 e-4**	**4.4697 e-4**	**3.3078 e-4**	**2.3821 e-4**
425	**1.1625 e-4**	**1.5504 e-4**	**4.0711 e-4**	**3.0329 e-4**	**2.1165 e-4**
Ea (eV)	**0.752**	**0.719**	**0.702**	**0.708**	**0.732**

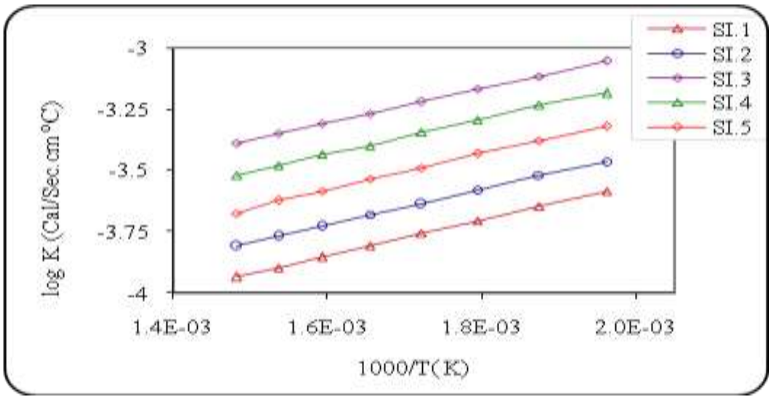

Figure 4.1 Variation of thermal conductivity with temperature for SI.

Table 4.2 Electrical conductivity and activation energy for System SII, at various temperatures

K for System II					
Temp °C	**SII.1**	**SII.2**	**SII.3**	**SII.4**	**SII.5**
250	**1.9971 e-3**	**1.1725 e-3**	**4.4822 e-3**	**6.9087 e-4**	**3.2047 e-3**
275	**1.5977 e-3**	**9.2405 e-4**	**3.6492 e-3**	**5.7213 e-4**	**2.5194 e-3**
300	**1.2879 e-3**	**7.4524 e-4**	**2.9417 e-3**	**4.6206 e-4**	**2.0197 e-3**
325	**1.0176 e-3**	**6.1023 e-4**	**2.4700 e-3**	**3.7239 e-4**	**1.7084 e-3**
350	**8.1808 e-4**	**5.1227 e-4**	**2.0165 e-4**	**3.2181 e-4**	**1.3915 e-3**
375	**6.9871 e-4**	**4.2102 e-4**	**1.7398 e-3**	**2.7580 e-4**	**1.2425 e-3**
Ea (eV)	**0.26**	**0.24**	**0.22**	**0.202**	**0.309**

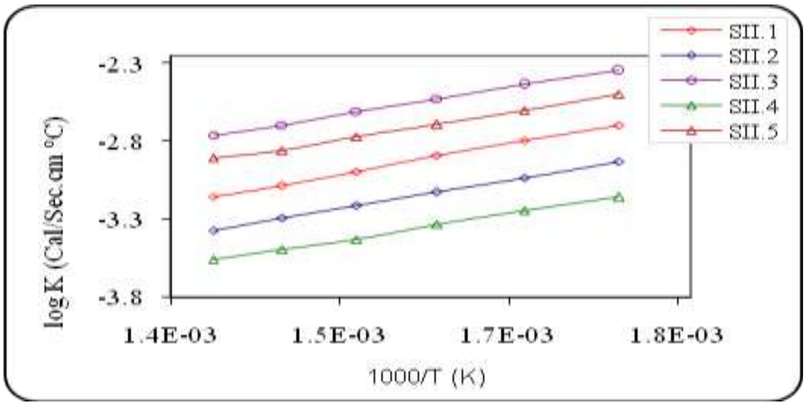

Figure 4.2 Variation of thermal conductivity with temperature for SII.

Table 4.3 Electrical conductivity and activation energy for System SIII, at various temperatures

K for System III					
Temp ^{o}C	**SIII.1**	**SIII.2**	**SIII.3**	**SIII.4**	**SIII.5**
250	**2.7949 e-4**	**4.6706 e-4**	**4.2115 e-4**	**3.6541 e-4**	**3.2107 e-4**
275	**2.4642 e-4**	**4.1418 e-4**	**3.7362 e-4**	**3.2087 e-4**	**2.7912 e-4**
300	**2.1665 e-4**	**3.6855 e-4**	**3.2973 e-4**	**2.8548 e-4**	**2.4797 e-4**
325	**1.9434 e-4**	**3.2979 e-4**	**2.9082 e-4**	**2.5266 e-4**	**2.2085 e-4**
350	**1.7210 e-4**	**2.9429 e-4**	**2.6502 e-4**	**2.3001 e-4**	**1.9665 e-4**
375	**1.2958 e-4**	**2.5424 e-4**	**2.3621 e-4**	**2.0908 e-4**	**1.6477 e-4**

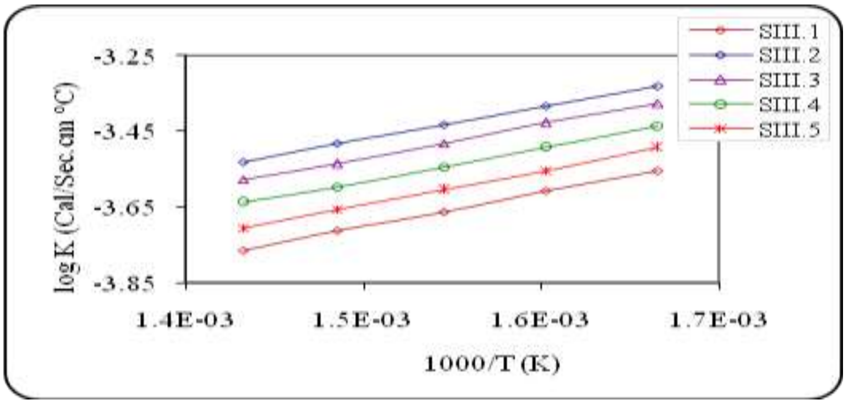

Figure 4.3 Variation of thermal conductivity with temperature for SIII.

The thermal conductivity increases with the average particle velocity since that increases the forward transport of energy. However, the electrical conductivity decreases with particle velocity increases because the collisions divert the electrons from forward transport of charge. This means that the ratio of thermal to electrical conductivity depends upon the average velocity squared, which is proportional to the kinetic temperature.
Electrical and thermal conductivity are closely related. For the most part good electrical conductors are also good thermal conductors. Many products will contain both conductors and insulators- the conductors take the electricity or thermal energy where it is wanted and the insulators prevent it from getting where it isn't wanted.

V. RESULTS AND DISCUSSION

Table 3.1, 3.2 & 3.3 shows the values of electrical conductivity for various temperatures and Figures 3.1, 3.2 & 3.3 shows the variation of electrical conductivity with temperatures for system I, II & III respectively. Similarly Tables 4.1, 4.2 & 4.3 shows the values of thermal conductivity for various temperatures and Figures 4.1, 4.2 & 4.3 shows the variation of thermal conductivity with temperatures for system I, II & III respectively.

The system wise maximum values of electrical conductivities are 9.0469 e-^{3}S/cm, 2.2656 e-^{3}S/cm, and 8.0686 e-^{3}S/cm where as, maximum thermal conductivities are 8.8168 e^{-4}Cal/sec cm^{o}C, 4.4822 e-^{3} Cal/sec cm^{o}C, and 4.6706 e-^{4} Cal/sec cm^{o}C.

It is well known that the glass is a bad conductor of heat. In such materials (insulators) conduction of heat is due to phonon-phonon interaction. Atomic vibration represents phonons when heat energy in a given solid expands and due to expansion amplitude of atomic vibration also increases, which is responsible for increasing coefficient of thermal conductivity. In amorphous solids factors like randomness in structure and presence of short range ordering lowers down thermal conduction.

Table 4.4 Electrical conductivity, thermal conductivity, activation energyand Lorenz number For Sample SI.3, at various temperatures

SI.3						
T in °C	**σ**	**K**	**L=K/σT**	**SI**	**E_σ**	**E_K**
250	9.0469 e-4	8.8168 e-4	3.898 e-3	SI.1	0.63	0.752
275	1.3832 e-3	7.6652 e-4	2.015 e-3	SI.2	0.69	0.719
300	2.1862 e-3	6.7722 e-4	1.032 e-3	SI.3	0.74	0.702
325	3.0067 e-3	6.0165 e-4	6.157 e-4	SI.4	0.73	0.708
350	4.1572 e-3	5.4148 e-4	3.721 e-4	SI.5	0.69	0.732
375	5.6781 e-3	4.9252 e-4	2.313 e-4			
400	7.5318 e-3	4.4697 e-4	1.483 e-4			

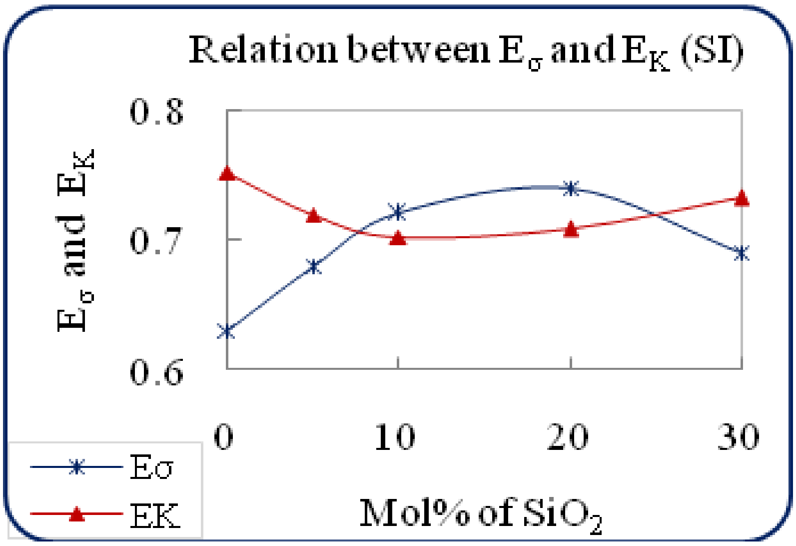

Figure 4.4 Relations between activation energies of thermal conductivity and electrical Conductivity for SI.

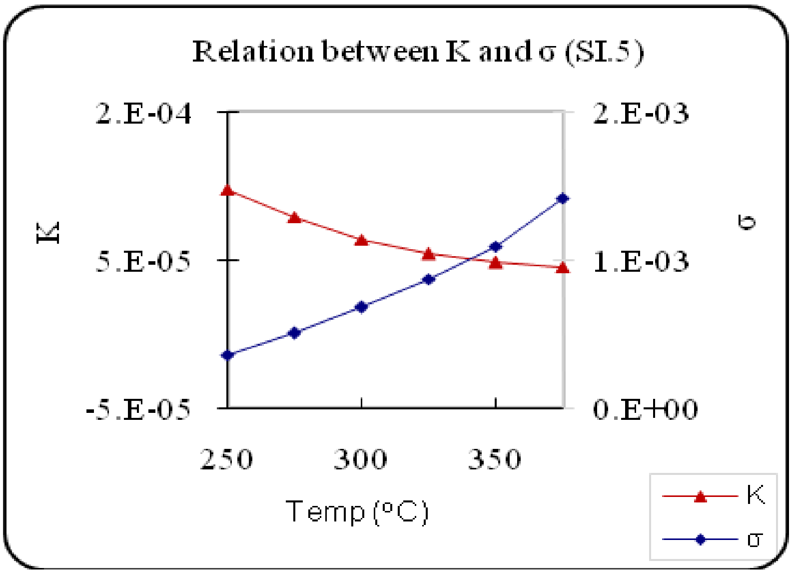

Figure 4.5 Relations between thermal and electrical conductivities for sample SI.5.

Table 4.5 Electrical conductivity, thermal conductivity, activation energy and Lorenz number for Sample SII.1, at various temperatures

SII.1						
T in ^oC	σ	K	L=K/σT	SII	E_σ	E_K
250	1.0306 e-4	1.9969 e^{-3}	7.751 e-2	SII.1	0.24	0.26
275	2.0007 e^{-4}	1.5975 e^{-3}	2.903 e-2	SII.2	0.42	0.24
300	3.3113 e^{-4}	1.2878 e^{-3}	1.296 e-2	SII.3	0.5	0.22
325	5.4075 e^{-4}	1.0176 e^{-3}	5.790 e-3	SII.4	0.36	0.202
350	9.0427 e^{-4}	8.1821 e^{-4}	2.207 e-3	SII.5	0.3	0.309
375	1.4434 e^{-3}	6.9863 e^{-4}	9.717 E-4			
400	2.2656 e^{-3}	6.5854 e^{-4}	5.804 E-4			

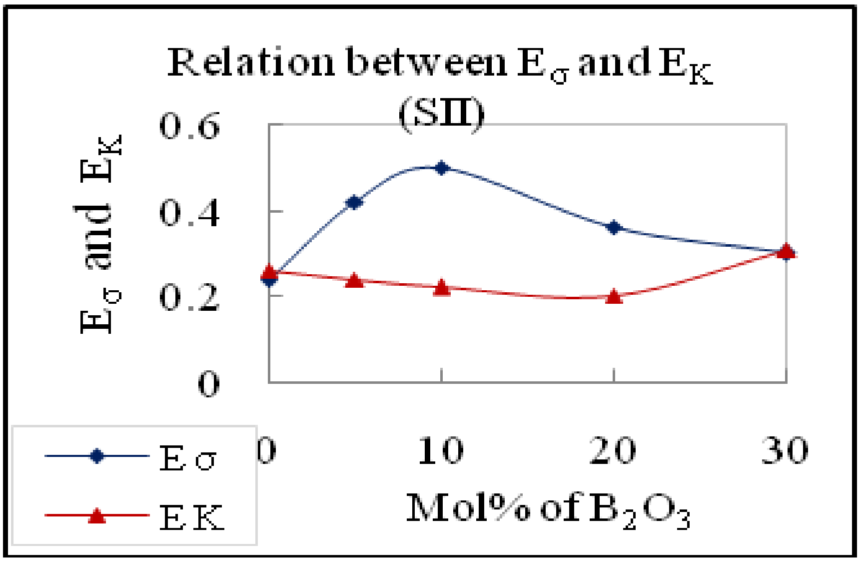

Figure 4.6 Relations between activation energies of thermal conductivity and electrical conductivity for SII.

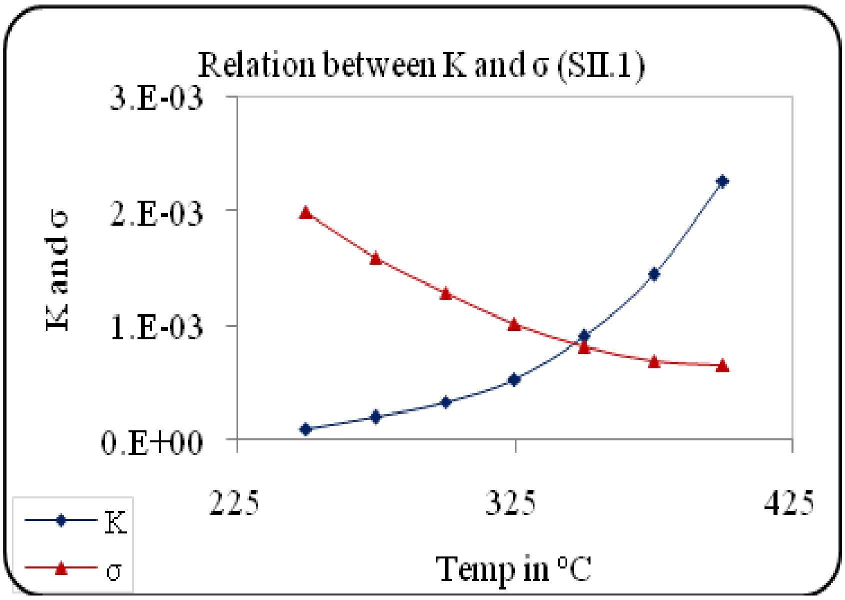

Figure 4.7 Relations between thermal conductivity and electrical conductivity. For sample SII.1

Table 4.6 Electrical conductivity, thermal conductivity, activation energy and Lorenz number For Sample SIII.3, at various temperatures

SIII.3						
T in °C	**K**	**σ**	**L=K/σ T**	**SIII**	**E_σ**	**E_K**
250	4.2115 e-4	4.9181 e-5	3.425 E-2	SIII.1	0.557	0.901
275	3.7362 e-4	8.5153 e-5	1.595 E-2	SIII.2	0.62	0.872
300	3.2973 e-4	1.5728 e-4	6.988 E-3	SIII.3	0.637	0.856
325	2.9082 e-4	2.7189 e-4	3.291 E-3	SIII.4	0.578	0.864
350	2.6502 e-4	4.4411 e-4	1.704 E-3	SIII.5	0.558	0.887
375	2.3621 e-4	7.0355 e-4	8.953 E-4			

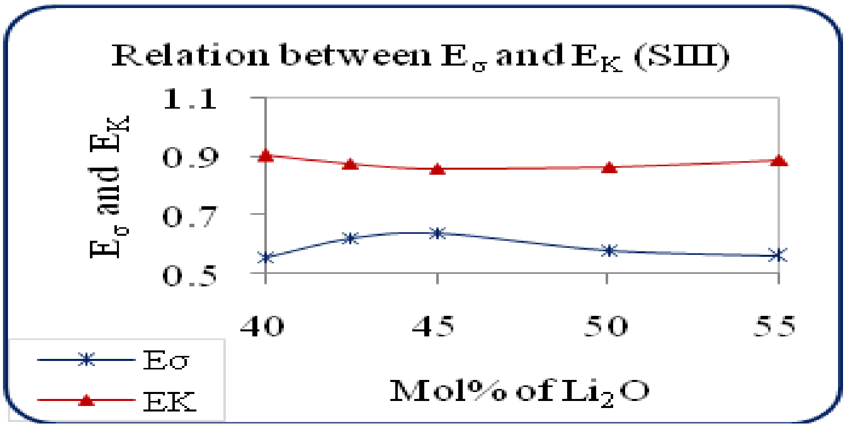

Figure 4.8 Relations between activation energies of thermal conductivity and electrical conductivity for SIII.

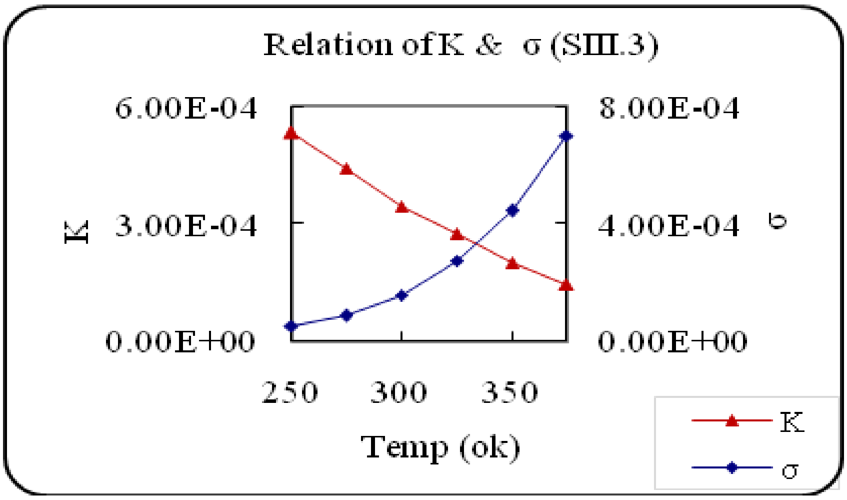

Figure 4.9 Relations between thermal conductivity and electrical conductivity. For sample SIII.3

Tables 4.4, 4.5 and 4.6 shows the values of electrical conductivity, thermal conductivity, activation energy and Lorentz number (L). It is observed that Lorentz number goes on decreasing with increasing in temperatures. The system wise maximum value of Lorentz numbers are 6.504 e^{-3} Watt-ohm/deg^2, 2.294 e^{-1} Watt-ohm/deg^2, and 3.425 e^{-2} Watt-ohm/deg^2 for 250 °C temperatures respectively.

Figure 4.4, 4.6, and 4.8 shows relations between activation energies of thermal and electrical conductivity for system SI, SII and SIII respectively. Activation energy of electrical and thermal conductivities is lie opposite in nature. Since the activation energy does not show the non linear behavior of conductivity; suggests that the conductivity enhancement is directly related to the increasing mobility of the charge carriers [18].

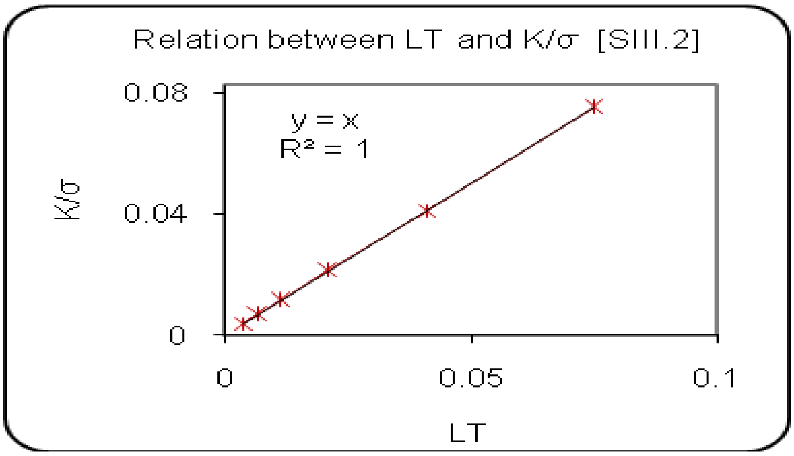

Figure 4.9 Relations between K/σ and LT

It is observed that for three system relations between K/σ and LT shows a straight line passing through origin therefore it gives y=x and the value of R^2=1.

Electricity and heat are not conducted in the same manner. Metals are good conductors of electricity because metallic bonding does not tie up their electrons and therefore they are free to move around. Electrons also carry heat, so the thermal conductivity of metals is also very large.

VI. CONCLUSION

Concluded that thermal conductivity depends on an-harmonic coupling. The magnitude of the an-harmonic coupling increases with increase in the vibration amplitude, decreases thermal conductivity. In amorphous solids due to randomness in structure and presence of short range ordering lowers down thermal conduction. Hence Thermal conductivity of different compositions of glasses decreased with increasing temperature and hence the Lorenz number also decreases.

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