American Journal of Engineering Research (AJER)
e-ISSN : 2320-0847 p-ISSN : 2320-0936
Volume-03, Issue-05, pp-156-168
www.ajer.org

Research Paper Open Access

Mössbauer Spectra and Electric relaxation of some iron bismuth borate glasses.

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Abstract: **-** (65-x) mol% B_2O_3 - (15+x) mol % Bi_2O_3 - 20 mol% Fe_2O_3 glasses, where x = 0, 5, 10, 15 mol%, have been studied by using Mössbauer effect spectroscopy (ME), dielectric relaxation and electric conductivity σ_T. ME spectra indicated that iron ions acted as glass network formers (GNF). ME data showed an increasing in the glass formation ability and/or the homogeneity of the glassy state as the B_2O_3 the concentration increases. Dielectric dispersion was observed at a temperature nearly above 390 K. The loss factor was found to obey the power law $\varepsilon''=B\omega^m$. The electric modulus as a function of absolute temperature was observed to exhibit a relaxation peak at a temperature T_m, this peak shifted to a higher temperature as the frequency increases. The characteristic relaxation time was found to belong to that of ionic vibration. The measured conductivity σ_T (ω) increased with the increasing of B_2O_3 content. The AC conduction mechanism of the studied glasses was found to be belonging to the Correlated Barrier Hopping (CBH) model.

Keywords*:* **-** *ac conductivity; Dielectric relaxation; modulus; Mössbauer Effect; Oxide Glasses*

I. INTRODUCTION

In many applications, glass must serve as an electrical insulator or conductor; therefore, understanding the nature of its electrical conductivity is of a great importance. In most oxide glasses, the electrical conductivity results from the ionic motion. Virtually, the ionic conductivity of all oxide glasses results from the transport of monovalence ions. In many commercial glasses, the conducting ions are mainly due to iron ions which lead to the ionic nature of conduction process. Nowadays, transition metal ions are being greatly used to probe the glass structure. This is because the outer d-electron orbital's functions as a broad radial distribution having high sensitive response for the changes in the surrounding actions. Bismuth Silicate and Bismuth Borate oxide glasses have a lot of industrial applications [1- 2]. The applications of glasses containing both bismuth oxide and transition metal oxides are still completely unknown. Only a few works have been done on the physical properties of bismuth borate glasses [3- 4- 5], but many questions about its conductivity and structures are not answered yet. The purpose of this work is to examine the effect of increasing boric oxide (B_2O_3) on the structure of iron bismuth borate glasses. The samples were prepared and then the Mössbauer, electrical conductivity and dielectric measurements were performed at different temperature and frequency. The measured data have been carried out for iron bismuth oxide glass in its non-crystalline state.

II. EXPERIMENTAL

(65-x) mol% B_2O_3 - (15+x) mol% Bi_2O_3 - 20 mol% Fe_2O_3, with x = 0, 5, 10, 15 glass alloys were prepared, by the melting quenching method. The batches were melted in porcelain crucibles in an electric muffle furnace for two hours, at temperature 1050±20 ºC. Each melted alloy stirred several times during melting, then poured between two pre-cooled stainless steel plates in air. A constant acceleration spectrometer, with a radioactive source of ^{57}Co in Rh matrix, was used to obtain ME spectra of the studied glass alloys at room temperature. The spectra were analyzed by using the least square fitting of symmetrical Lorentzian shaped sextets and doublets. For the electrical measurements, the prepared alloys were polished to get a suitable shape of approximately constant area and thickness. Then both faces for each sample are coated with an air drying silver paste which acts as electrical electrodes. The measurements were carried out by using a computer controlled Stanford LCR bridge model SR 720 at four fixed frequencies [120, 10^3, 10^4, 10^5 Hz], and all measurements were performed in the temperature range from 300 to 550 K.

III. RESULTS AND DISCUSSION

Mössbauer effect (ME)

Room temperature ME spectroscopy was used to check the glassy phase formation for the samples under investigation. It is worth to mention that, ME-measurements were recorded by using the high velocity spectra (±10 mm/s) to check the possibility of any magnetic phase precipitation. Fig.1 shows the measured spectrum for studied alloys, where no magnetic phase was detected. ME analysis indicates that the studied alloys spectra can be interpreted as a broad paramagnetic doublet. According to the analysis parameters, table 1, this doublet is assigned to tetrahedral ferric ions (Fe^{3+}), which means that the iron ions act as glass network formers (GNF) [6-7-8]. Also, for all samples, the line width LW values of the measured spectra appeared to be highly broadened in comparison with the natural line width of iron ions [0.25 mm/s], indicating a good and homogenous glasses [9]. It was found, table (1), that there is a little decrease in the isomer shift (IS) energies of iron component by increasing B_2O_3 concentration on the expanse of Bi_2O_3. This behavior in IS energies may be due to the increase in the stability of the iron sites in the glass network and/or to a decrease in Fe-O bond lengths. The quadrupole splitting (Q.S) is known as the interaction between the nuclear quadrupole moment of the Mössbauer ions (iron) and the electric field gradient which results from the other charges in the structure. In other words, the quadrupole splitting expresses the charge distribution around the Mossbauer atom (iron), where the symmetric distribution has zero quadrupole splitting. Table (1) indicates that, there was a decrease in the Q.S values, with the increase in B_2O_3 concentration, which may be attributed to variations in the asymmetry around iron -ions in different owing to the electric field gradient of the lattice. Like behavior may indicate that, there was an increase in the glass formation ability and/or the homogeneity of the glassy state as the B_2O_3 concentration increases. To ensure this, a forth sample of a composition x=15 has been prepared and was investigated by ME spectroscopic analysis, Fig. (2). for this sample, participation on a magnetic field was clearly observed. In other word, a crystalline phase has been appeared in the structure when x is increased above 10 mole%.

Dielectric Relaxation

Dielectric relaxation is an expression refers to the dispersion that arises during a transition from full orientation polarization, at low frequencies, to the negligible orientation polarization, at high frequency [6-7]. The dielectric (relative permittivity), ε^*, is a complex quantity described by the relation: $\varepsilon^* = \varepsilon' - j\varepsilon''$; ($j^2 = -1$), where ε' and ε'' are the real part and the imaginary part (loss factor) of the dielectric constant respectively. The ratio between the two parts of relative permittivity is called the loss tangent $\tan\delta = \varepsilon''/\varepsilon'$. This quantity is a very useful quantity since its values does not depend neither on the type of the glass nor the shape of the studied samples. The real part of the dielectric constant ε' and the loss tangent, $\tan\delta$, were measured, for all studied samples, over a range of temperature 303–550 K and at four different frequencies (0.12, 1, 10 and 100 k Hz). Figures from 3a to 3c show the variation of ε' with the absolute temperature at four different frequencies (0.12, 1, 10, 100 kHz) in the temperature range (303–550 k). All samples showed similar behavior, since ε' increased gradually (exponentially) with temperature without any observable relaxation Peaks. Dielectric dispersion is observed at temperature nearly above 390 K, approximately. It was found that, the dispersion increased as the temperature increasing. Like behavior may be attributed to the fact that, in addition to the electronic, ionic and space charge (due to the bonding defects in the structure [10-11]) polarization types, the orientation polarization is the predominated one. This may explain why the dispersion of ε' increases as the temperature increasing. The increasing of temperature increasing the thermal vibration of the molecules which in terns increases the movement of the molecules [10-12]. It is noticed that, as the frequency decreases, the molecules will have sufficient time to follow up the frequency. This is clear from the values of ε' indicated in Figs. 3a, 3b and 3c. The variation of Ln ε'' as a function of Ln (ω) at constant different temperatures is indicated in Figs. 4a to 4c. For all studied samples, the plot of Ln (ε'') against Ln (ω) at different temperatures, showed straight lines with negative slope. This behavior is in an agreement with that of the predicted power law which has the formula $\varepsilon'' = B\,\omega^m$, where m has been described by Guintini equation [13-14]; $m = -4kT/w_m$, where, W_m is barrier height which defined as the energy required to remove an electron from its site to infinity. The effect of increasing of B_2O_2 content on the barrier height values, W_m, and on the loss factor ε'' at nearly room temperature are shown in Figures 5 and 6 respectively. Obviously, It is clear that, as the Bi_2O_2 content increasing, the vales of W_m decreasing while those of ε'' increasing. Such behaviors may give rise to the conclusion that, the electric conductivity increasing with gradual increasing in the concentration of Bi_2O_3.

Electric Modulus M*

The electric modulus M* formalism was developed by Macwdo for analysis of the electric relaxation data [15]. The electric modulus M* is a complex quantity described by the relations [16]; $M^* = M' + j M$ and related to the complex permittivity by the relation $M^* = 1/\varepsilon^*$, where $M' = \varepsilon'/(\varepsilon'^2 + \varepsilon''^2)$ while $M'' = \varepsilon''/(\varepsilon'^2 + \varepsilon''^2)$. Figs. 7a to 7c and Figs. 8a to 8c exhibit the temperature dependence of both M' and M'', respectively, for the studied samples. At a fixed frequency, M'' was observed to exhibits a relaxation peak at a certain temperature $T_{m,}$ this peak shifted to a higher temperature as the frequency increased. Such a character is known as the dielectric relaxation phenomena [17], which can be attributed to the frequency dependence of the dipolar dielectrics **[18].** This type of temperature dependence is generally observed in molecular solids where the Debye theory [19] for the viscosity dependence of relaxation time holds quite well. According to this theory, the dielectric constant ε' should increase exponentially with temperature, and such a relationship has been observed indeed for the studied samples. Like temperature peaks can be used to determine both the dielectric activation energy ΔE_D and the characteristic relaxation time $\tau_{o,}$($10^{-13} \leq \tau_o \leq 10^{-9}$ for ionic vibration, $10^{-15} \leq \tau_o \leq 10^{-14}$ for electronic motions) according to $\tau = \tau_o\, e^{(\Delta E_D/kT_m)}$, Where k is the Boltzmann constant and T is the absolute temperature [11, 6]. Both τ_o and ΔE_D can be calculated from the graph of Ln (1/f) against ($1/T_m$), which was found to be a straight lines for all samples, as indicated in Figs. 9a to 9c. The deduced values for both τ_o and ΔE_D have been summarized in table (2). The large values of ΔE_D indicate that the relaxation mechanism may be due to the dipolar model [7-19], which based on Elliott's idea [17] of hopping of charge carriers over a potential barrier between charged defect states D^+ and D^-. Each pair of sites D^+ and D^- is assumed to form a dipole attributed to the existence of a potential barrier over which the carriers hope [20-21-22]. Table (2) shows an increasing in ΔE_D with the increasing of B_2O_3 concentration which is in agreement with the barrier height W_m behavior. Also table (2) shows that the characteristic relaxation time belongs to that of the ionic vibration.

Measures conductivity σ_T (ω)

Figs. 10a to 10c show the dependence of σ_T (ω) on both absolute temperature and frequency. For all studied samples, it is clear that the conductivity σ_T (ω) increases with increasing the absolute temperature; such behavior refers to the thermal activated process (conduction) from different localized states in the energy gap [8]. Also, it is clear that the conductivity σ_T (ω) shows weak frequency dependence at high temperature range. Fig. 11 shows that, the effect of the variation of Bi_2O_3 content causes a change in σ_T (ω); it was found that σ_T (ω) increasing as Bi_2O_3 content increasing. Such a behavior may be attributed to the increasing in the free charge carriers in the structure as the result of increasing of Bi^{2+} ions [15]. For all amorphous and glasses materials the measured conductivity during any experiment follows the relations [22]; $\sigma_T(\omega) = \sigma_{dc}(0) + \sigma_{dac}$, $\sigma_{dc} = e^{\Delta E/kT}$ and $\sigma_{ac} = A\omega^s$, where σ_{dc} (0) is the frequency independent conductivity, A is a constant, s is the exponent factor and ω is the angular frequency. At a constant temperature both σ_{ac} and σ_T (ω) have the same behavior but with different values. Therefore by plotting Ln σ_T (ω) versus Ln ω, at constant temperature, the exponent factor s value was obtained. Fig. 12 shows s temperature dependence, where s decreasing with increase of temperature in away agrees with that of the correlated barrier hopping model CBH [23-24-25-26]. Hence, the CBH model can be used to describe the conduction mechanism in the studied glasses**.**

IV. CONCLUSION

ME spectroscopy appears that there is no magnetic phase was detected in the investigated alloys and the iron ions act as a glass network formers (GNF). All samples appear in good homogenous glassy state. Dielectric dispersion is observed at temperature above ≈ 390 K. At room temperature, the obtained W_m increased with gradual decrease in Bi_2O_3 concentration. value of the loss factor ε" increased with the increasing in the Bi_2O_3 concentration. At a fixed frequency M'' was observed to exhibits a relaxation peak, at a certain temperature $T_{m,}$ was shifted to the higher temperature as the frequency increased. The dielectric relaxation phenomena in the studied samples may be attributed to the frequency dependence of the dipolar dielectrics. The calculated values for τ_o and ΔE_D were found to be increasing by increasing the Bi_2O_3 content. The larger value of ΔE_D indicates that the relaxation mechanism is the dipolar model. It was observed that ΔED increasing with gradual increase of Bi_2O_3 concentration in an agreement with barrier height W_m behavior. While, τ_o found to belong to that of ionic vibration. All investigated samples, show that σ (ω) increases as the temperature increased, like behavior refer to thermal activated process from different localized states in the energy gap. Also σ (ω) increases as Bi_2O_3 content increased. The results, appears that the exponent factor s increasing with increasing the temperature in accordance to CBH model.

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Figures Caption

Fig.1 ME Spectra for X = 0, 5 and10 samples
Fig.2 ME Spectra for X = 15 sample
Fig.3 Dielectric constant temperature dependence for x =0
Fig.4 Dielectric constant temperature dependence for x =5
Fig.5 Dielectric constant temperature dependence for x =10
Fig.6 Loss factor frequency dependence for x=0
Fig.7 Loss factor frequency dependence for x=5
Fig.8 Loss factor frequency dependence for x=10
Fig.9 barrier height as a function of Bi_2O_3 content
Fig.10 the loss factor as a function of Bi_2O_3 content
Fig.11Real electric modulus temperature dependence for x =0
Fig.12 Real electric modulus temperature dependence for x =5
Fig.13 Real electric modulus temperature dependence for x =10
Fig.14 Imaginary electric modulus temperature dependence for x =0
Fig.15 Imaginary electric modulus temperature dependence for x =5
Fig.16 Imaginary electric modulus temperature dependence for x =10
Fig.17 relaxation time temperature dependence for x =0
Fig.18 relaxation time temperature dependence for x =5
Fig.19 relaxation time temperature dependence for x =10
Fig.20 Total conductivity temperature and frequency dependence for x =0
Fig.21 Total conductivity temperature and frequency dependence for x =5
Fig.22 Total conductivity temperature and frequency dependence for x =10
Fig.23 the Total conductivity as a function of Bi_2O_3 content
Fig.24 the exponent factor temperature dependence for x =0, 5 and 10

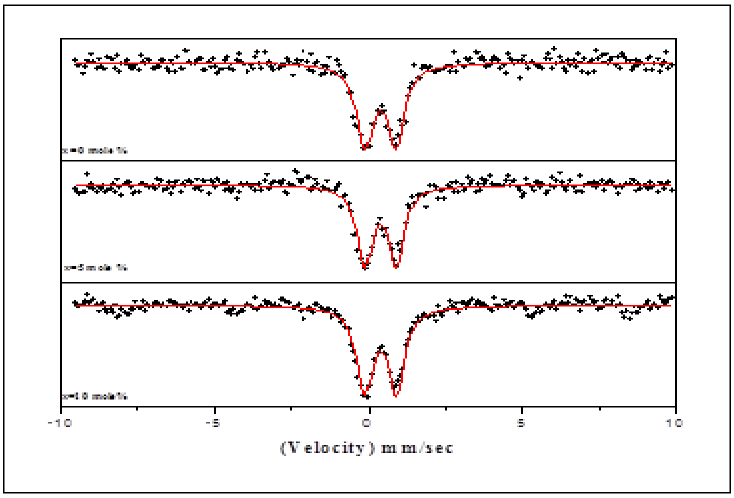
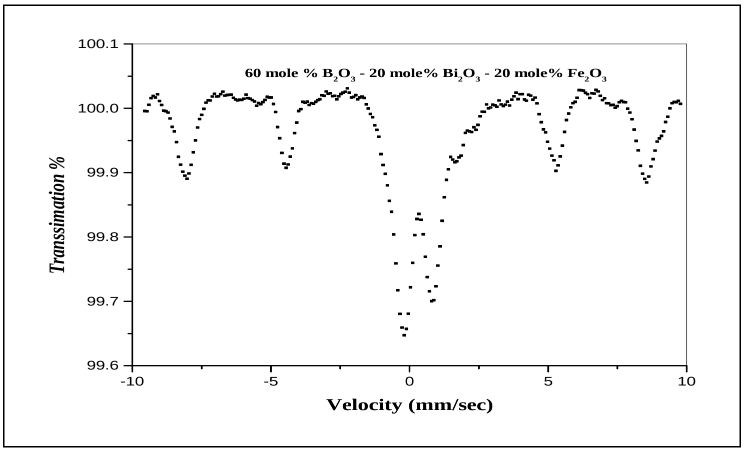


Fig.(1)



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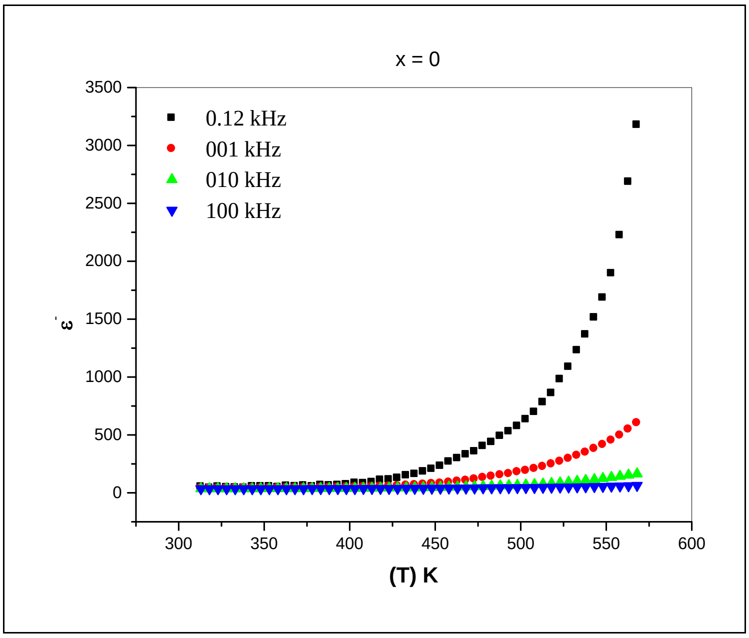

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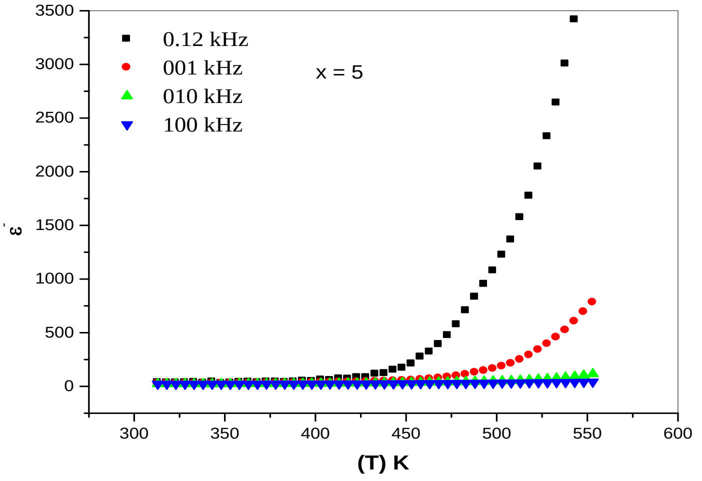

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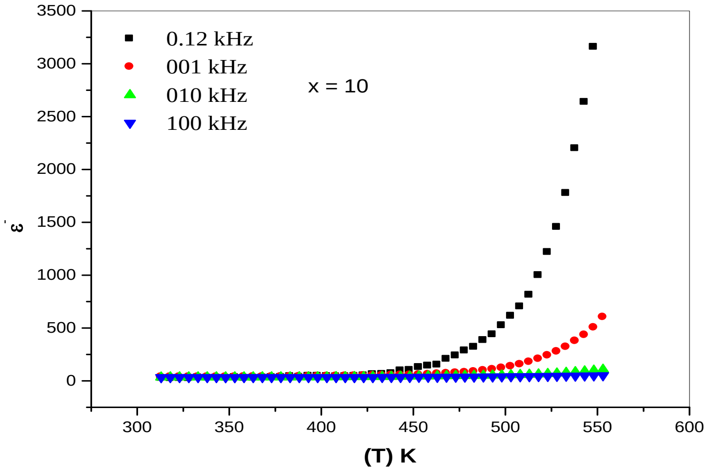

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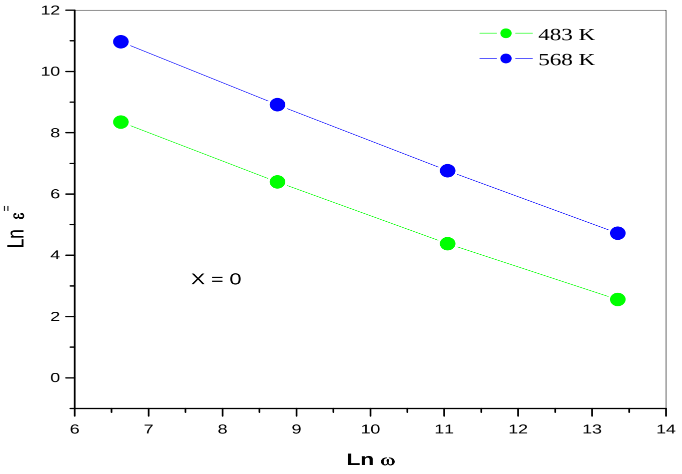

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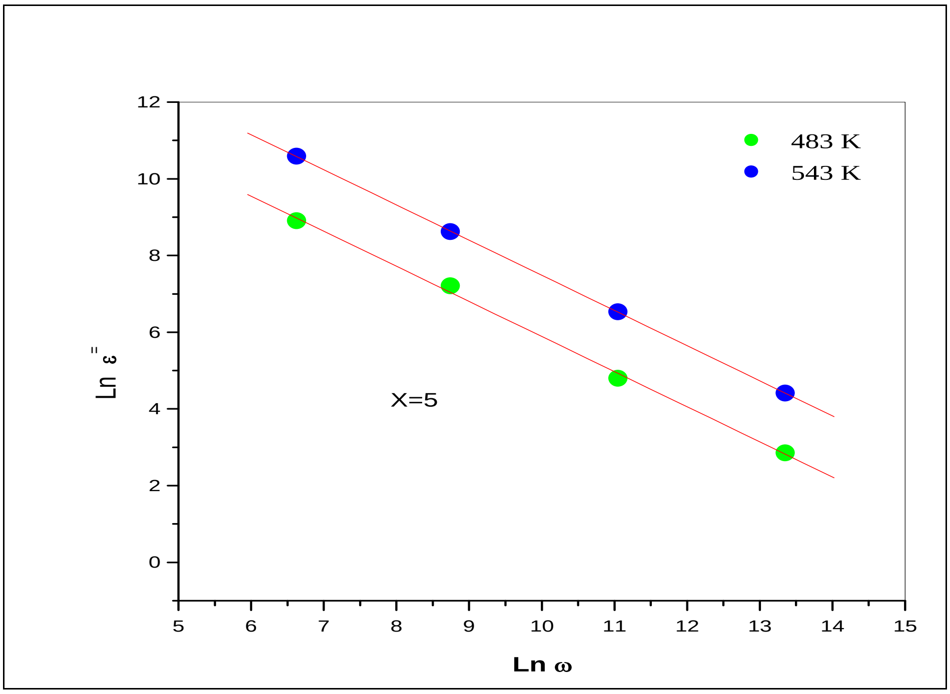
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Ln ω
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X=5
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Fig. (7)

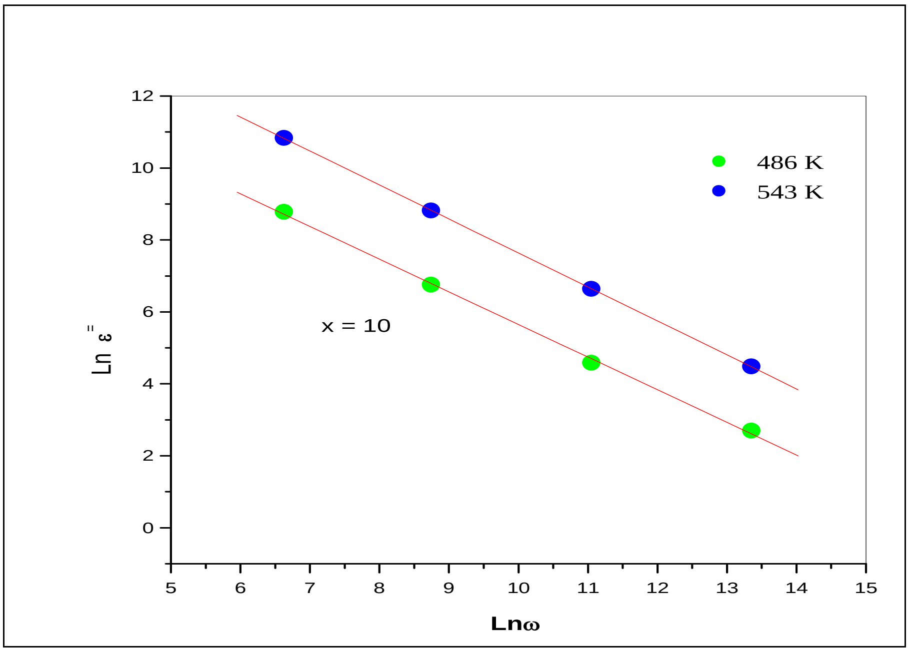
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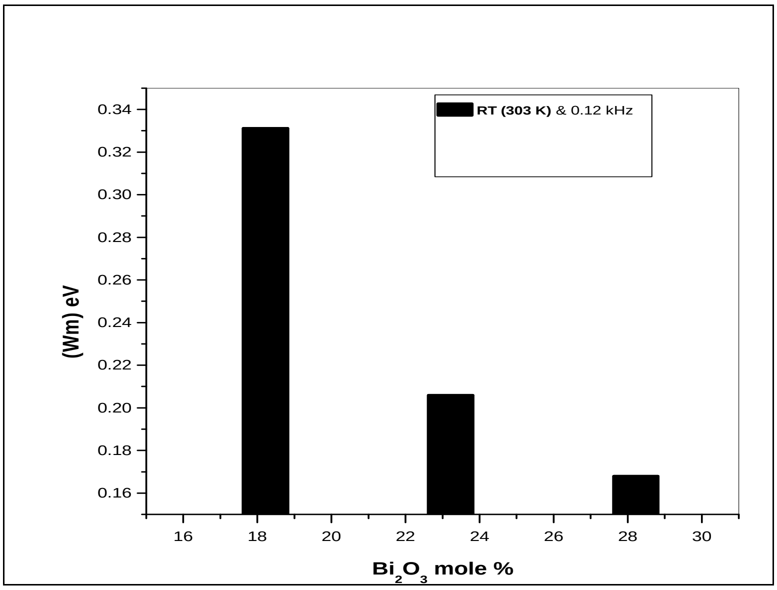
Fig. (8)



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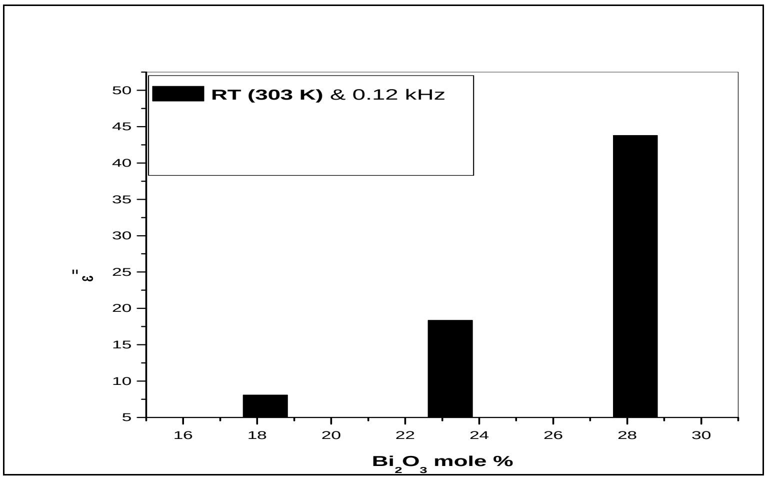

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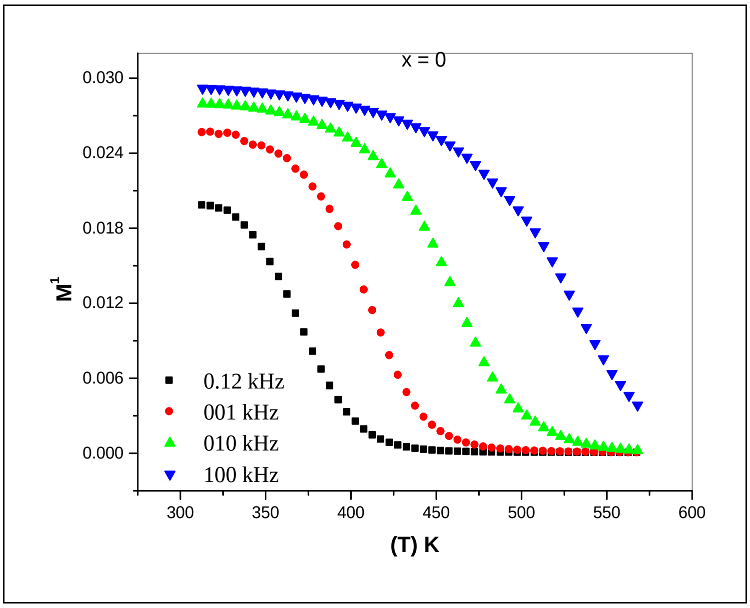

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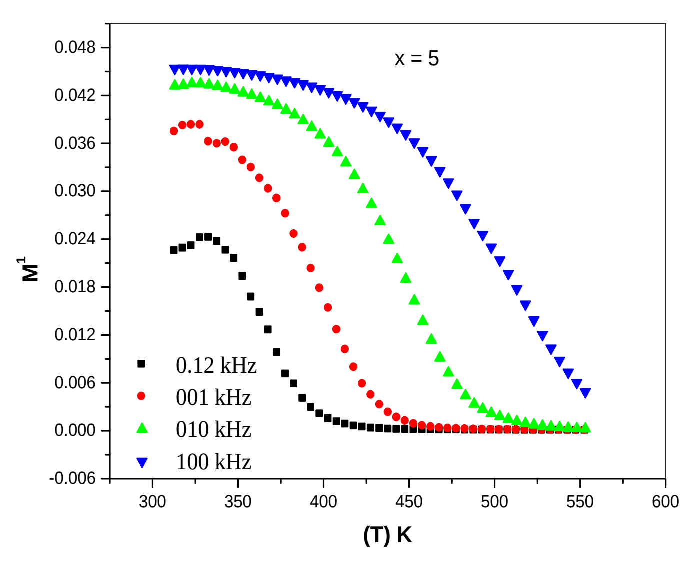

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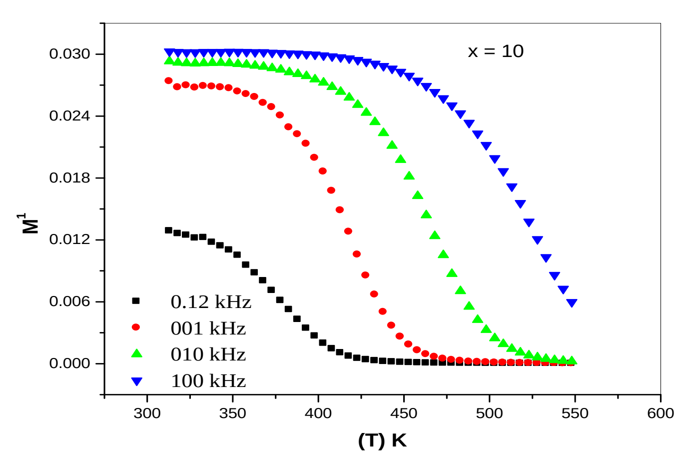

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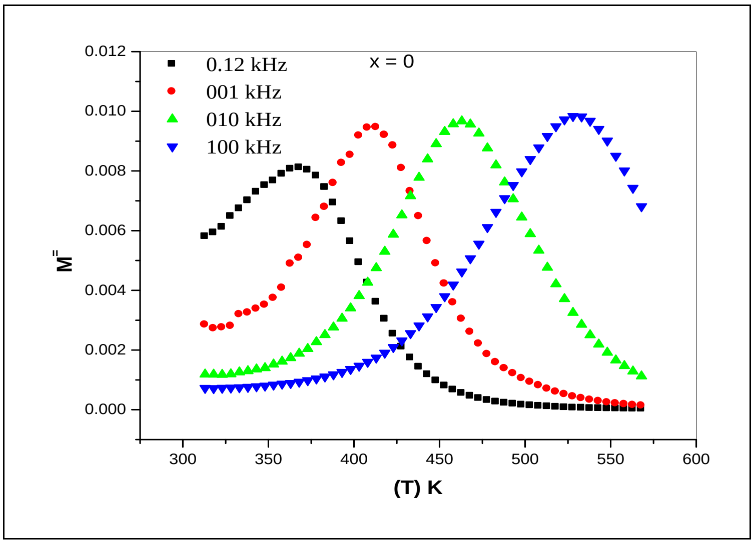

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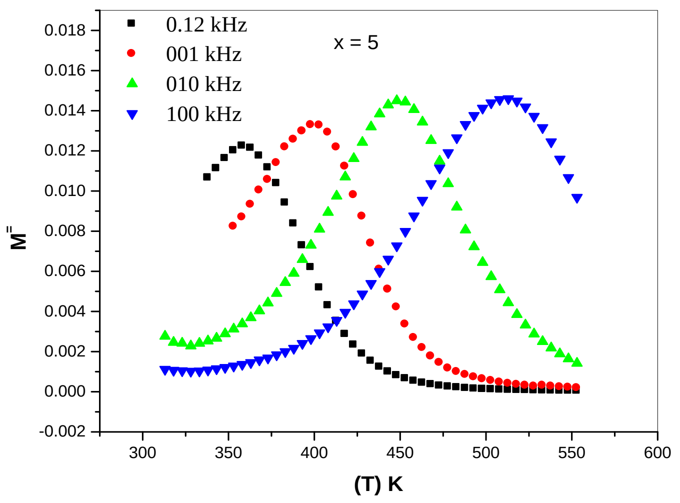

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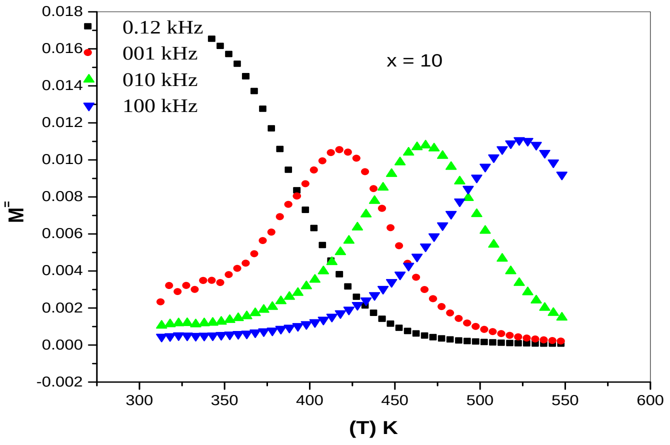

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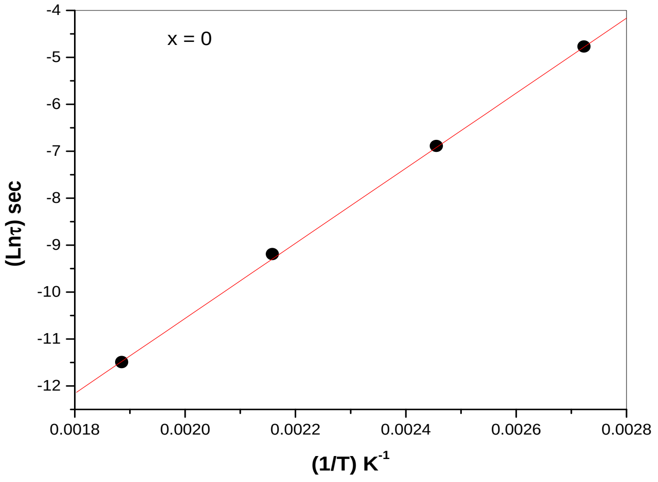

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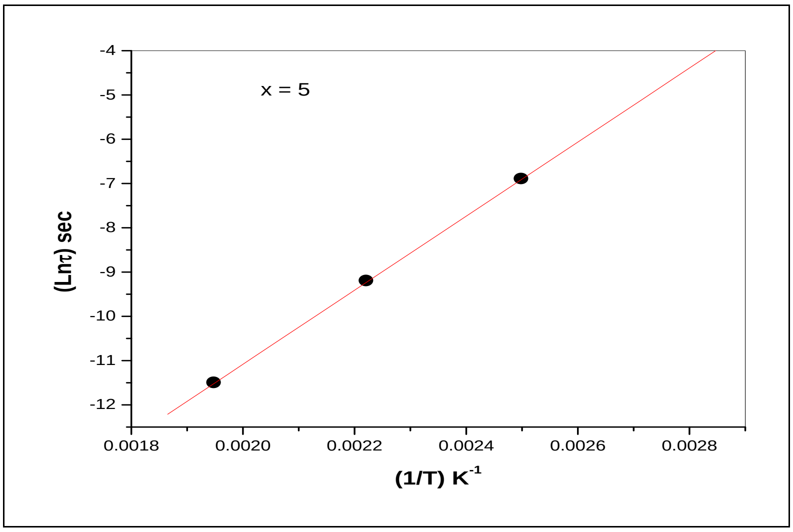

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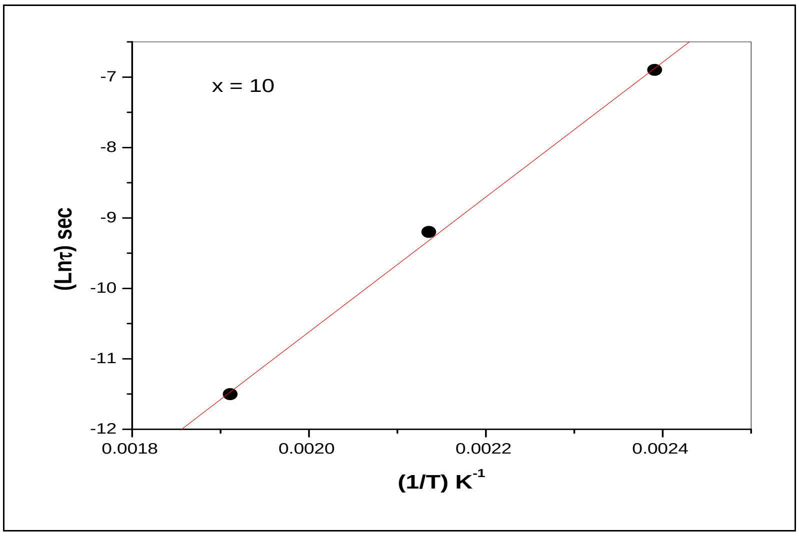

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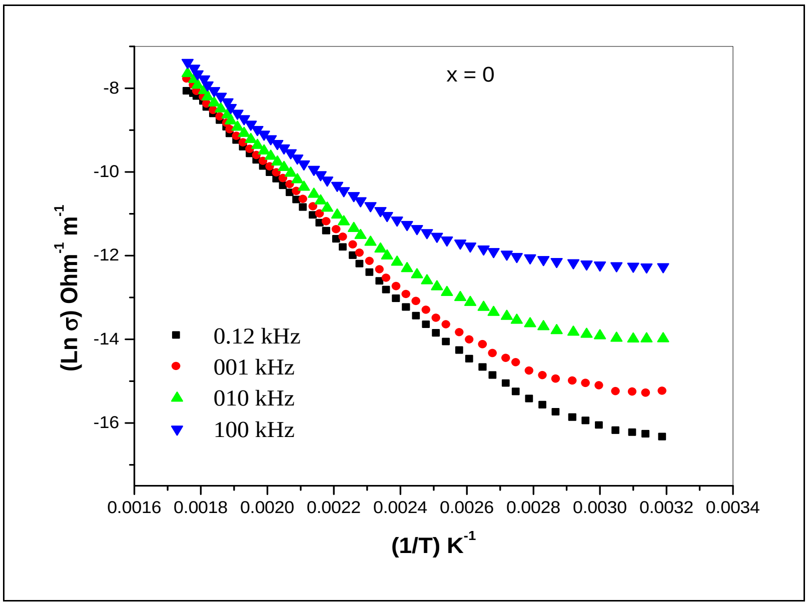
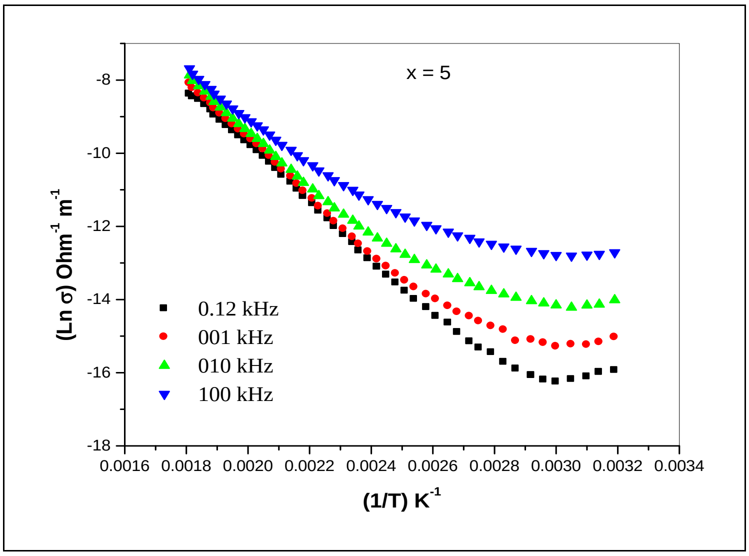


Fig.(20)



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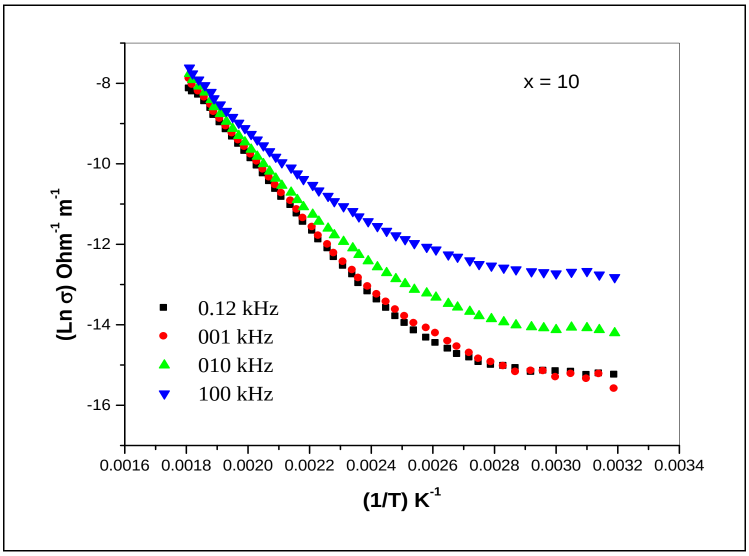

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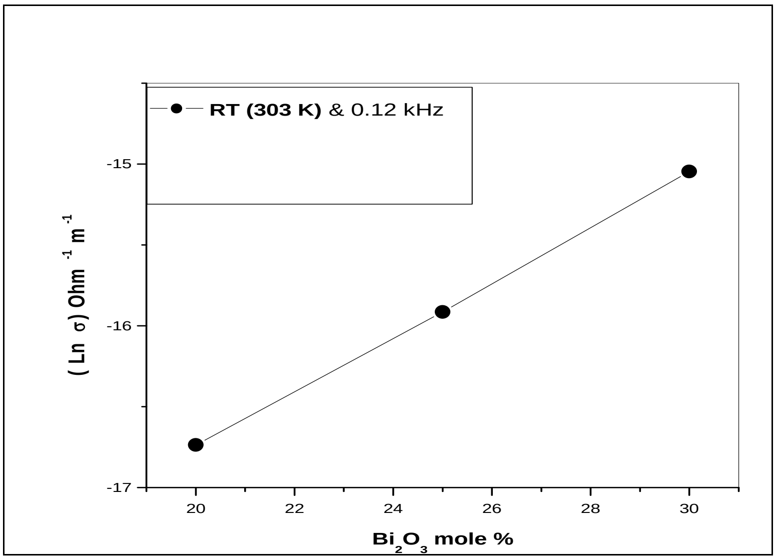

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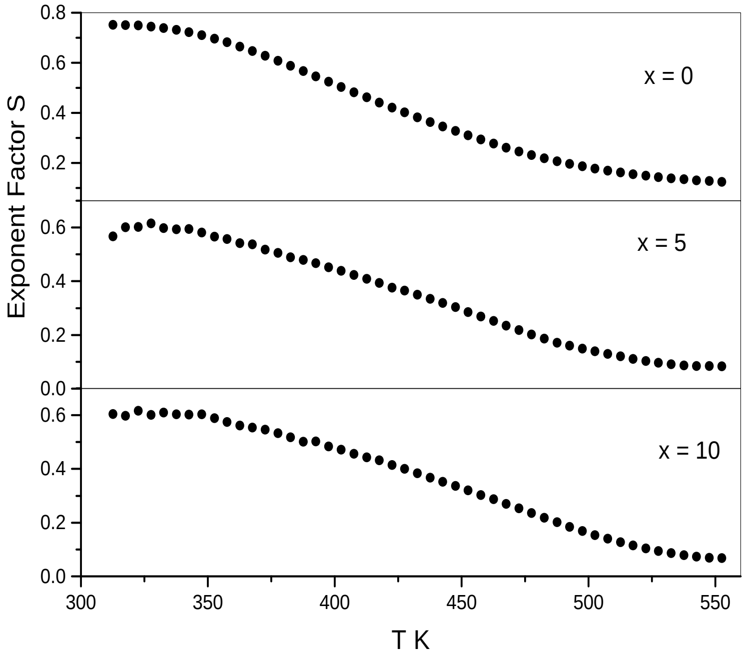

Fig. (24)

Table (1) ME Parameters

x mole%	Q.S (mm/sec)	I.S (mm/sec)	L.W (mm/sec)
0	1.017	0.395	0.627
5	1.005	0.392	0.592
10	0.985	0.389	0.653

Table (2) Calculated Activation energy and Characteristic relaxation time

x mole%	ΔE_D eV	τ_o sec
0	0.70	3×10^{-12}
5	0.74	8.4×10^{-13}
10	0.84	1.2×10^{-13}