

(FeNaP)₂O₉ Glasses Doped with Different TM Ions

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To cite this article:

Hossam Mohamed Gomaa, Ahmed Hamdy El-Dosokey, Khaled Hamoda Idress. (FeNaP)₂O₉ Glasses Doped with Different TM Ions. *International Journal of High Energy Physics*. Vol. 4, No. 6, 2017, pp. 75-87. doi: 10.11648/j.ijhep.20170406.12

Received: September 15, 2017; **Accepted:** October 27, 2017; **Published:** November 27, 2017

Abstract: In an attempt to check the effect of the transition metal ions on the glass network, the following chemical formula was used to prepare some of Iron sodium phosphate glasses doped with different transition metal (TM) ions. 50 mol% P₂O₅ + 20 mol% Na₂O + 15 mol% Fe₂O₃ + 15 mol% M_nO_m, where M_nO_m represents V₂O₅, MnO, Co₃O₄, CuO and ZnO. Mossbauer Effect (ME) spectroscopic analysis showed that, the iron ions are located in two different oxidation states Fe³⁺ and Fe²⁺. A fraction of Fe³⁺ ions act as glass network formers (GNFs), whereas the other in addition to all Fe²⁺ ions act as glass network modifiers (GNMs). The electrical properties for all samples have been measured and then studied as a function of the TMIs atomic number. The D.C. conductivity showed a gradual decreasing with increasing the atomic number of TMIs, while the A.C. conductivity has a similar behavior as predicted by CBH model.

Keywords: Transition Metal Ions, Mossbauer Effect, Amorphous Materials, Structural Properties and Electrical Properties

1. Introduction

Phosphate glasses technologically considered as an important materials, because they have generally higher thermal expansion characteristic and lower transition temperatures comparing with silicate and borate glasses. Oxide glasses such as boron oxide, lead oxide and silicon oxide are characterized by a hard stability and a chemical durability. Also, phosphate glasses were found to be electronically conductors or semiconductors, due to the addition of transition metal oxides. Nowadays Oxide glasses containing large amounts of transition-metal ions exhibit interesting electrical properties, since their behaviors are strongly influenced by the presence of their ions in more than one valence state [1]. These states appeared in the glass networks as a result of the redox processes occurring during melting process. The majority of the experimental measurements have carried out on vanadate glasses [2]. Oxide glasses containing high percentages of iron [3] and copper [4], [5] have a great interesting because copper ions serve not only as a shopping center, but they also contribute in the ionic conductivity. Iron phosphate glasses were found

to behave as a typical semiconductor and exhibit unusually a good chemical durability. This work aims to show the effect of the different transition metal ions on both structural and electrical properties of the phosphate glasses.

2. Experimental

Glasses of the composition 50 mol% P₂O₅, 20 mol% Na₂O, 15 mol% Fe₂O₃, 15 mol% M_nO_m where M_nO_m represents V₂O₅, MnO, Co₃O₄, CuO and ZnO were prepared by the melting quenching method. All glass samples were prepared from chemicals with 99.99% purity as starting materials. Each batch was grounded and mixed well by using agate mortar and then transferred to porcelain crucible. The crucible of all batches inserted, at the same time, for two hours in an electric muffle furnace which had reach fixed temperature about 1000°C. Melts were stirred from time to time to get a complete homogeneity for melts. After duration of time, they were poured between two precooled stainless-steel plates. Mossbauer Effect spectroscopy have been

performed for all samples at room temperature using 20 mCi ⁵⁷Co radioactive source in Rh matrix. For AC conductivity measurements, each sample was cut in the form of a square plane of area in the order of 1 cm² and of a constant thickness. All AC measurements carried out by using RLC bridge (Stanford model SR 720 RLC meter) in the temperature range from 303 K up to 417 K and at four fixed different frequencies (0.12, 1, 10 and 100 kHz).

3. Results and Discussion

3.1. ME Spectra

Mossbauer Effect spectra give very useful information about hyper fine structure of the solid compounds. ME parameters carried out a good description for type, length and energy of chemical bonds within the solid internal structure. For all samples ME spectra and their treatment by a computer analysis software have been displayed separately in Figures 1, 2, 3, 4 and 5. All these spectra showed clearly that, each sample exhibits three different paramagnetic doublets, without participation of any crystalline phases. The thing which indicates the formation of pure and good glassy/amorphous phase in all samples. As a result to computer treatment, for ME spectra, some valuable Quantities was obtained. Such Quantities called ME parameters and defined as (i) the quadrupole splitting Q.S, (ii) the isomer shift I.S, (iii) spectra Line width W and finally (iv) the relative area. These parameters are very important since the Q.S reflects the local environment for iron ions symmetrical/asymmetrical, while the I.S helps in determining both oxidation states and coordination of iron ions in the structure. Generally the values of both Q.S. and I.S, for all samples, have revealed that iron ions have two different oxidation states Fe³⁺ and Fe²⁺. Such that some of Fe³⁺ ions

have tetrahedral configuration and shared in the glass network formation, whereas the rest in addition to all Fe²⁺ ions have an octahedral configuration and occupied some interstitial spaces throughout the glass network. In other words, a fraction of Fe³⁺ ions acts as glass network former (GNF), whereas the other in addition to all Fe²⁺ ions act as glass network modifiers (GNMs). Figure 6a showed that the Q.S of Fe³⁺O₄ increased as the TM atomic number increased, such behavior refers to an increase in the asymmetry (Q.S ≠ 0) of the local environment around the Fe atom within the chain layers of the phosphate glass. Figures 6, 7 and 8 showed that the Q.S of both Fe³⁺O₆ and Fe²⁺O₆ decreased as the atomic number of the transition metal increased, this action refers to an increase in the symmetry (Q.S = 0) of the local environment around the Fe atom within the interstitial vacancies among the chain layers of the phosphate glass. In other word the transition metal ions (d-electrons rich) cause non-spherical charge distribution around Fe ions that shared the glass network and improve the spherical charge distribution around Fe ions that occupied the interstitial positions. Figures 9, 10 and 11 showed that as the increasing of TM atomic number cause an increasing in the I.S values of Fe (III) ion in both tetrahedral and octahedral configurations. While figure 7c showed the I.S value of Fe (II) decrease with increasing the atomic number. These observations may due to screening effect of 3d-electrons of the transition metal ions on s-electrons of Fe (II) ions. As seen in figures 12 and 13 the relative concentration of Fe (II) increase while that of Fe (III) decrease with increasing of the TM atomic number. This action indicates that the increase of TM ions convert both tetrahedral and octahedral Fe (III) to octahedral Fe (II). The result may give expectation to decrease in the electric conductivity of these glasses.

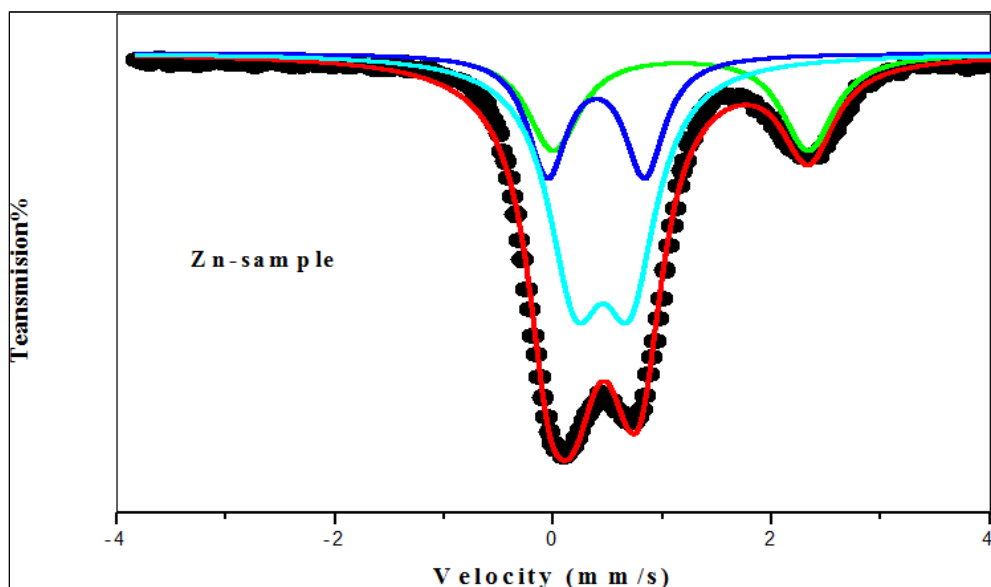


Figure 1. Mossbaure spectrum and its analysis for Zn-sample.

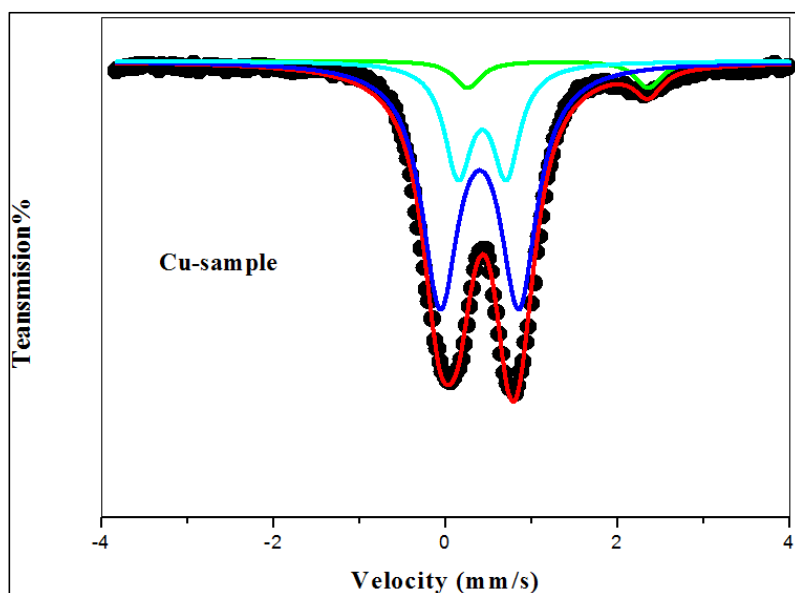


Figure 2. Mossbaure spectrum and its analysis for Cu-sample.

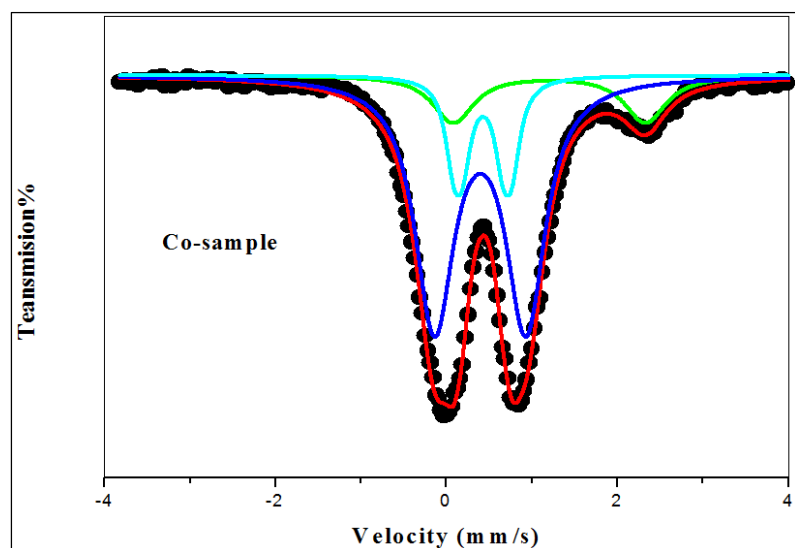


Figure 3. Mossbaure spectrum and its analysis for Co-sample.

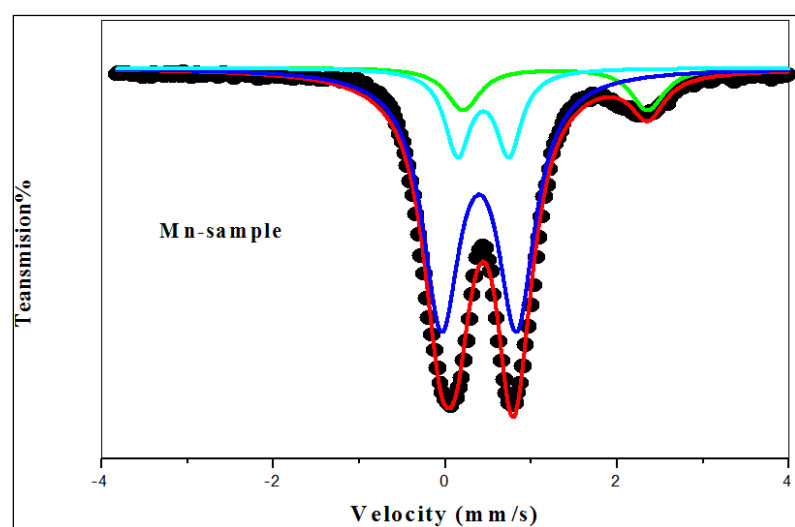


Figure 4. Mossbaure spectrum and its analysis for Mn-sample.

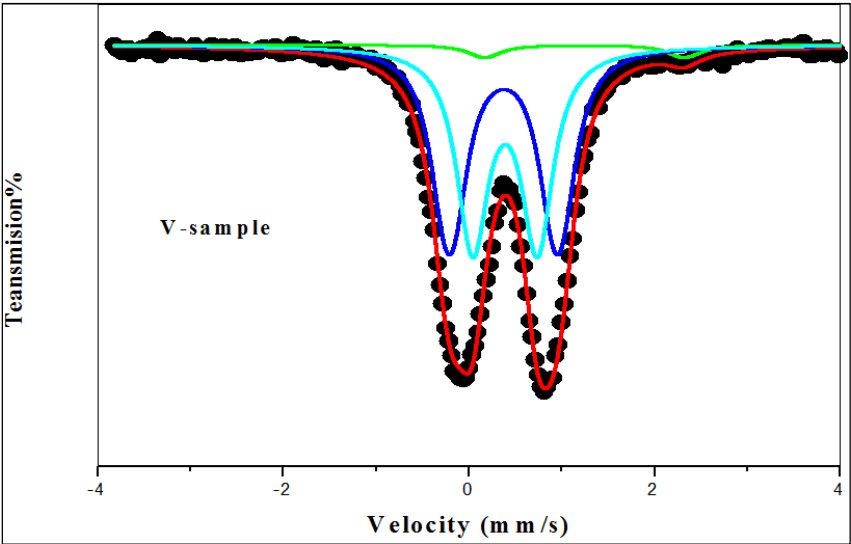


Figure 5. Mossbaure spectrum and its analysis for V-sample.

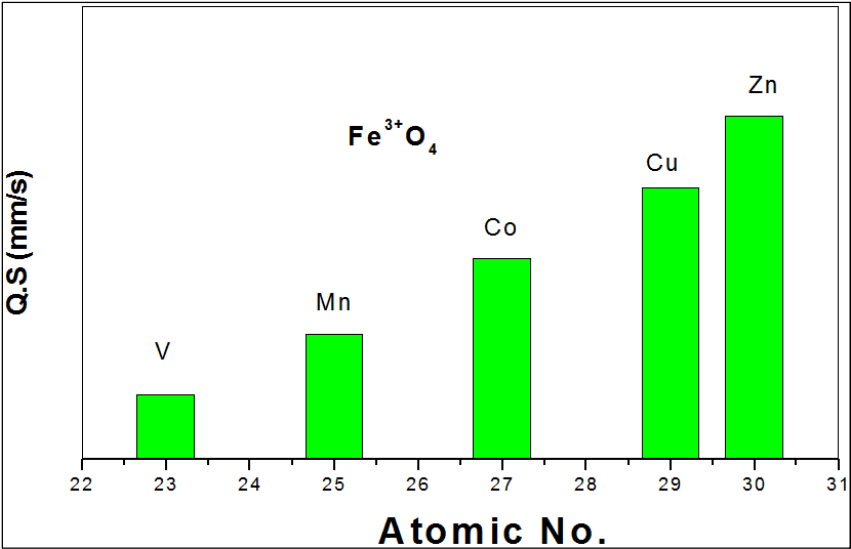


Figure 6. Quadruple splitting Values of Fe³⁺O₄ for all samples.

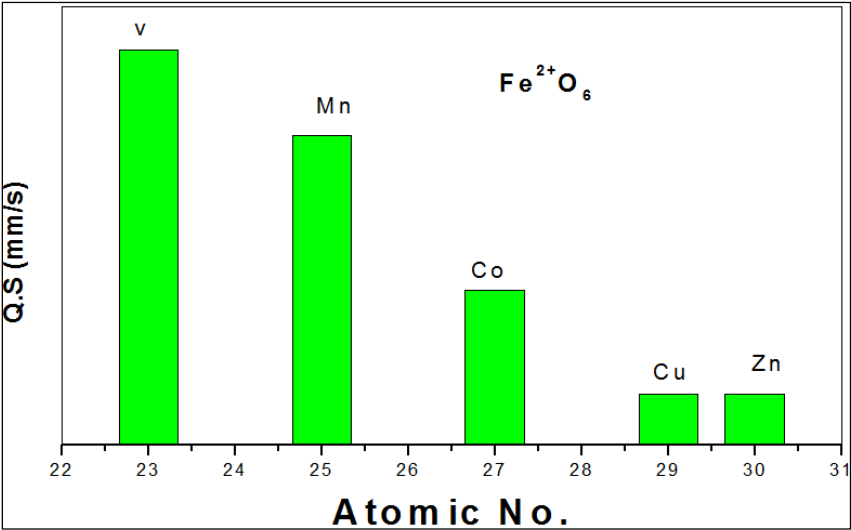


Figure 7. Quadruple splitting Values of Fe²⁺O₆ for all samples.

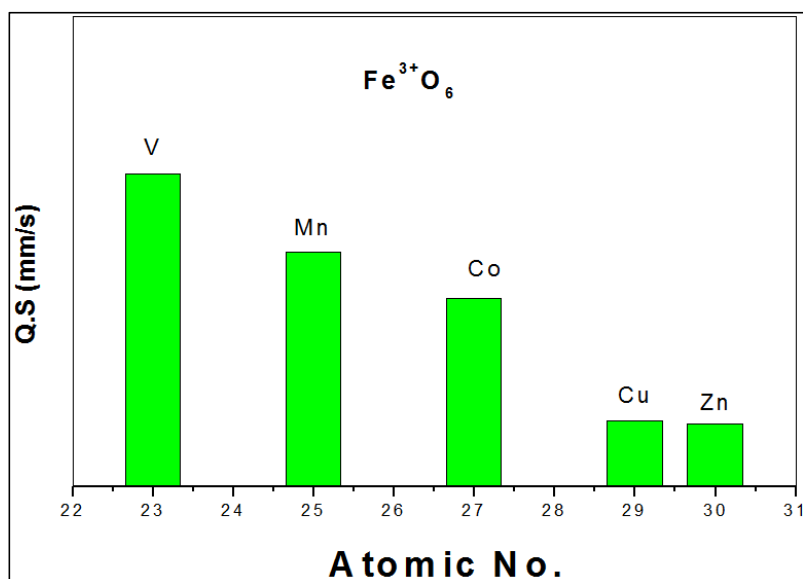


Figure 8. Quadruple splitting Values of Fe^{3+}O_6 for all samples.

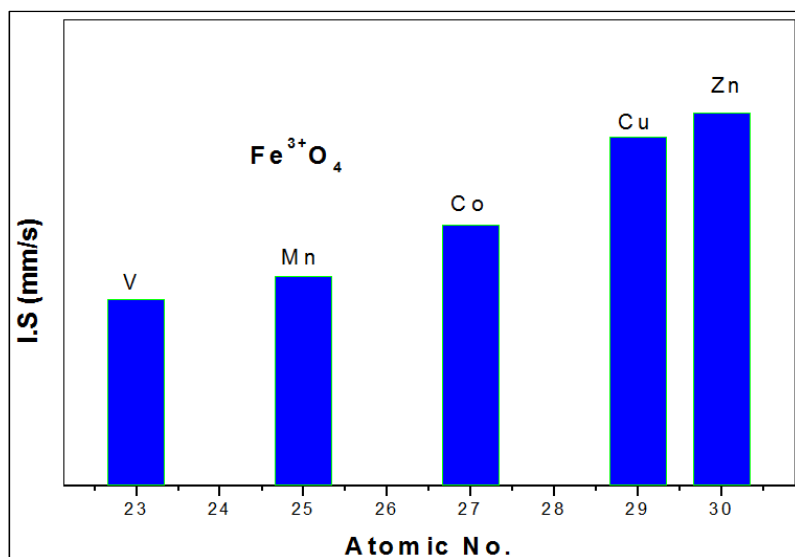


Figure 9. Isomer shift Values of Fe^{3+}O_4 for all samples.

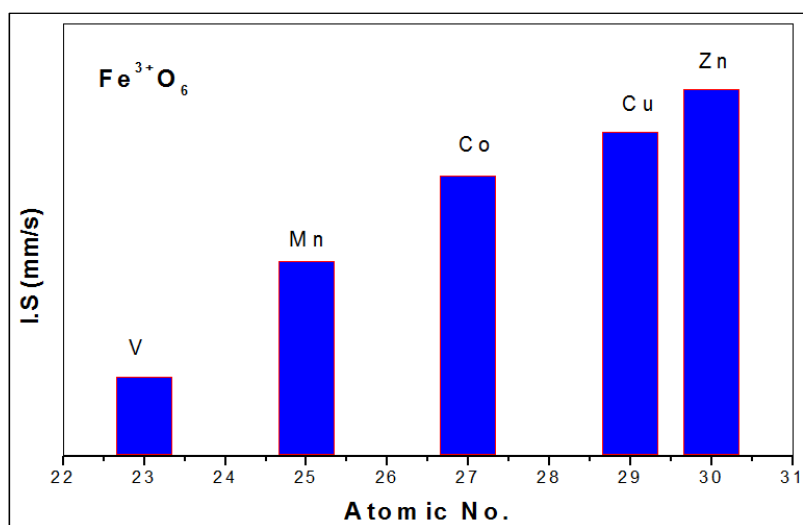


Figure 10. Isomer shift Values of Fe^{3+}O_6 for all samples.

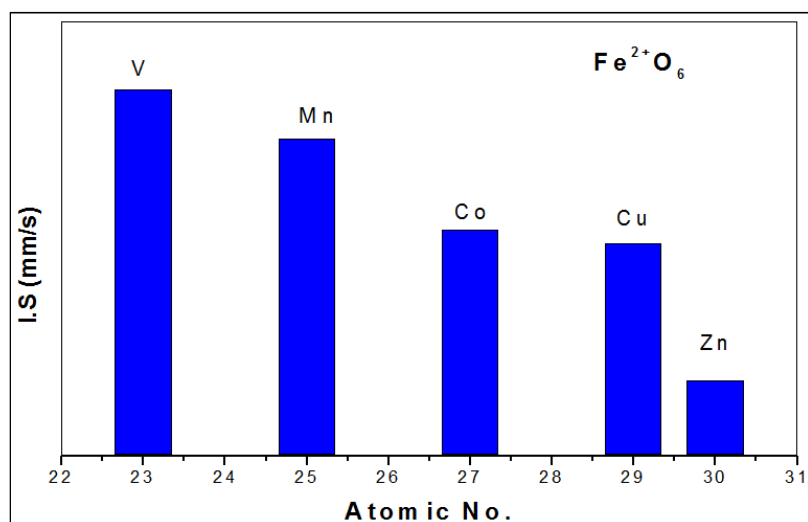


Figure 11. Isomer shift Values of Fe^{2+}O_6 for all samples.

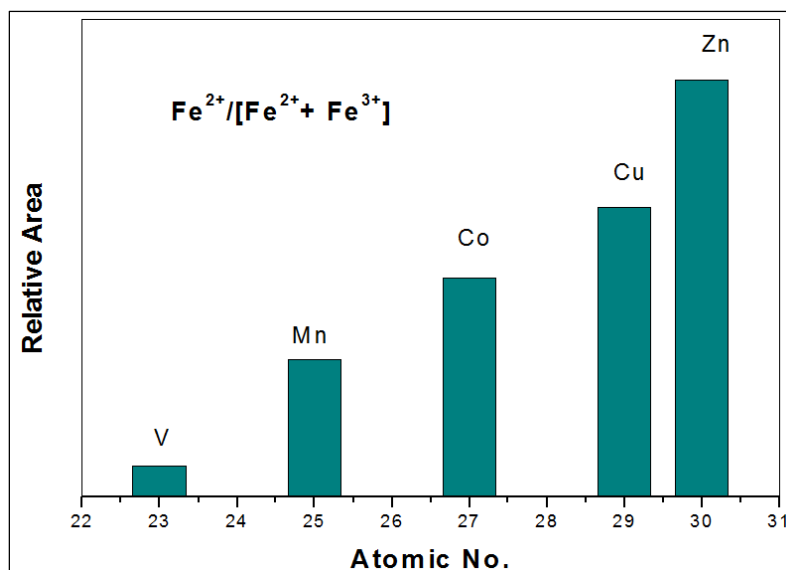


Figure 12. Relative area of Fe (II) for all samples.

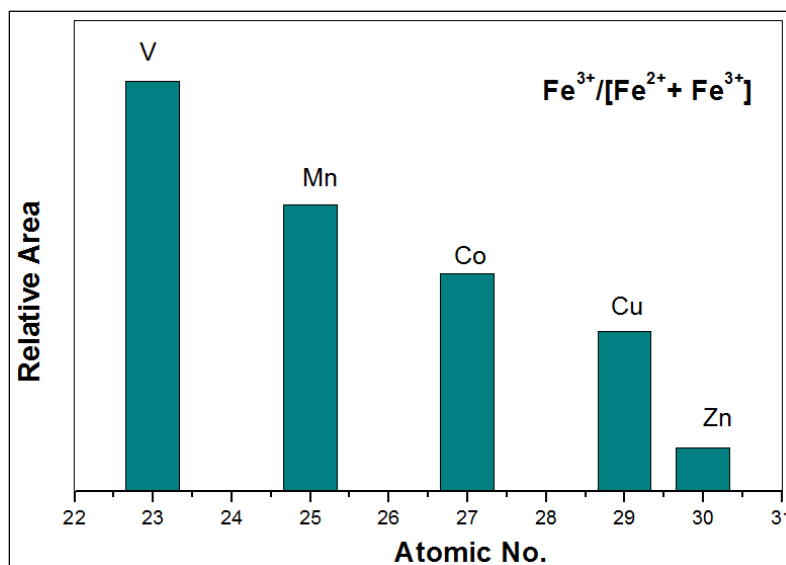


Figure 13. Relative area of total Fe (III) for all samples.

3.2. Electric Conductivity

Electric properties are very helpful for check any precise changes in the internal structure of the solid. Therefore, the electrical conductivity has been measured as a function of both temperature and frequency.

The measured electrical conductivity $\sigma_T(T, \omega)$ can describe by the following relation [7]

$$\sigma_T(T, \omega) = \sigma_{d.c}(T) + \sigma_{a.c}(T, \omega) \quad (1)$$

$$\sigma_{d.c}(T) = \sigma_o e^{-\Delta E/kT} \quad (2)$$

$$\sigma_{a.c}(T, \omega) = A \omega^s \quad (3)$$

where, $\sigma_{d.c}(T)$ is the d.c conductivity, $\sigma_{a.c}(T, \omega)$ a.c conductivity, σ_o is a pre-exponential factor, A is a weakly

temperature dependent constant, ω is the angular frequency, T is the absolute temperature and s is the exponent factor. “Figures 14, 15, 16, 17 and 18” show the variation of the Logarithmic measured conductivity [$\ln(\sigma_T)$] with the reciprocal absolute temperature [$1000/T$] for all samples. The measurements carried in the temperature range from 300K up to 417K at the three fixed frequencies 1, 10 and 100 kHz. These figures showed that for each sample the electric conductivity has increased regularly with increasing of the absolute temperature. This may be attributed to the thermally activated process from different localized states in the energy gap [8]. On the other hand, it is easy to observe that, the electric conductivity displays a weak dependence on the frequency at high temperature, whereas at low temperature it depends strongly on the frequency

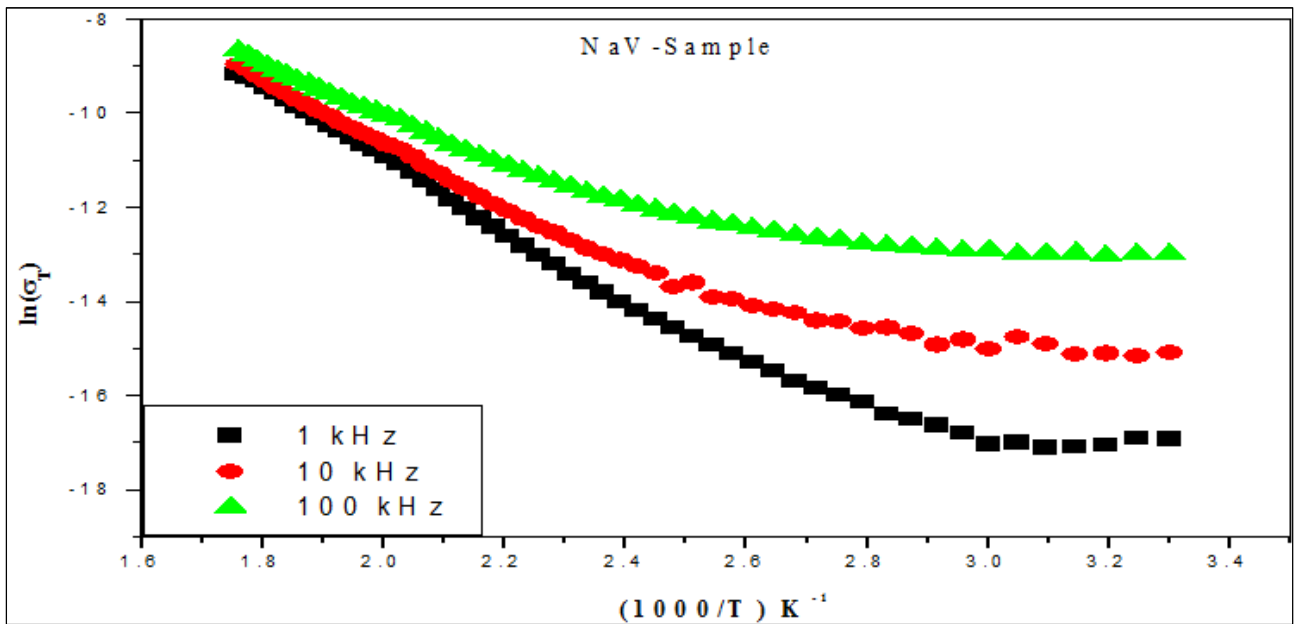


Figure 14. The variation of logarithmic a.c. conductivity with $(1000/T)$ for V-sample.

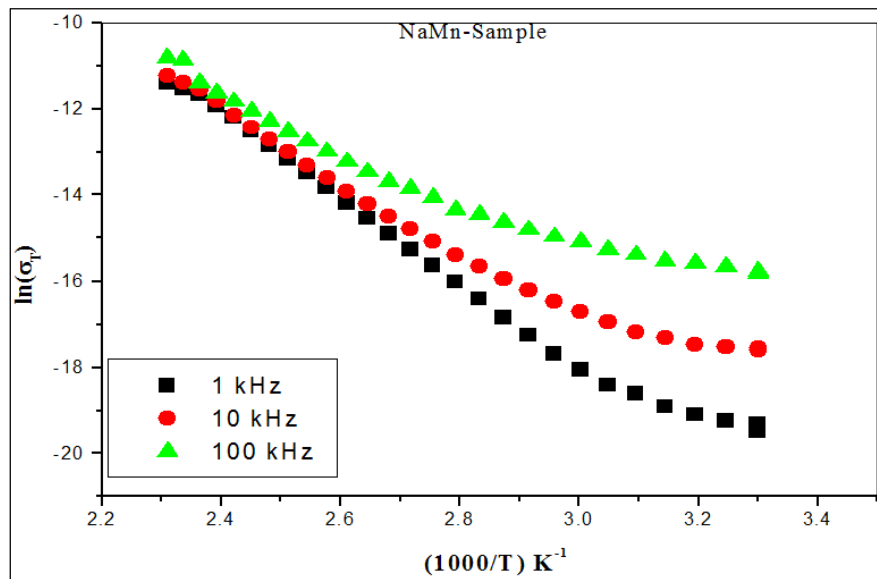


Figure 15. The variation of logarithmic a.c conductivity with $(1000/T)$ for Mn-sample.

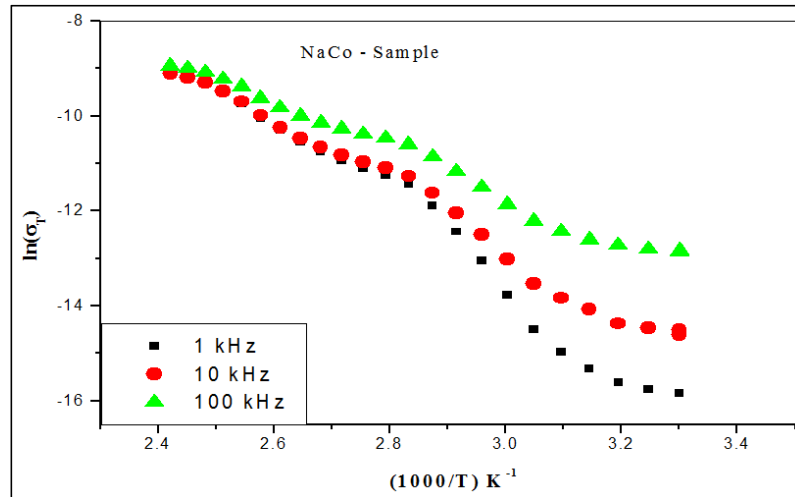


Figure 16. The variation of logarithmic a.c. conductivity with $(1000/T)$ for Co-sample.

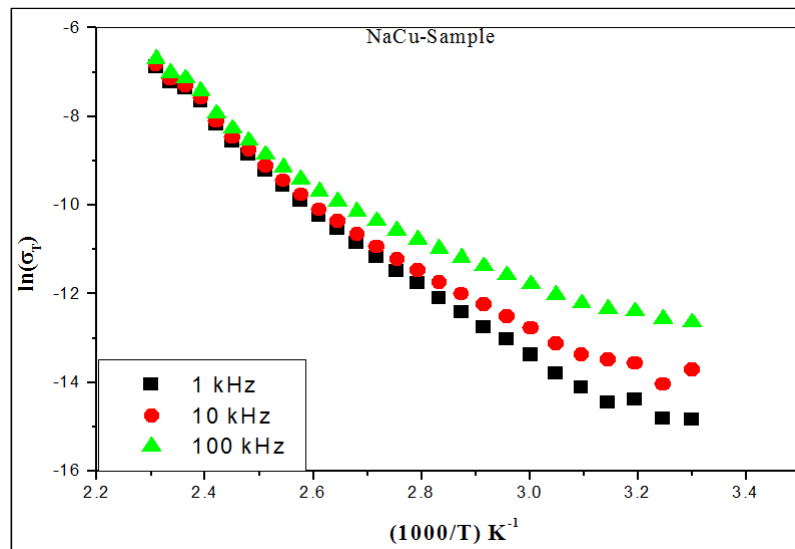


Figure 17. The variation of logarithmic a.c. conductivity with $(1000/T)$ for Cu-sample.

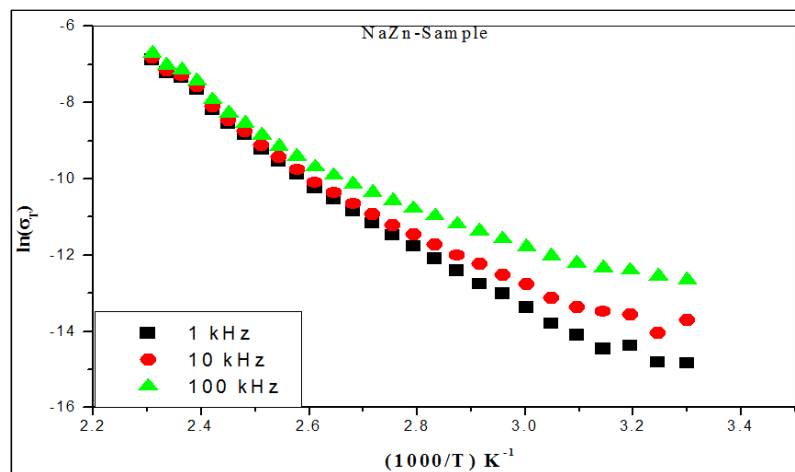


Figure 18. The variation of logarithmic a.c. conductivity with $(1000/T)$ for Zn-sample.

There are some basic models that have been proposed for describe the ac conduction mechanism in amorphous solids, like glasses. These models can be distinguished using the

dependence of the exponent factor (s) on the frequency and temperature or on both of them. Therefore, the Exponent factor (s) is very important parameter to recognize the type of

ac conduction mechanisms. According to relation (1), at a fixed temperature, both σ_T and $\sigma_{a.c}$ will have the same behavior with the frequency changing. Therefore, the following relation can be used to determine the value of the exponent factor s , for each sample,

$$s = \frac{\delta[\ln \sigma_T]}{\delta[\ln \omega]} \quad (4)$$

By plotting $\ln \sigma_{(T, \omega)}$ against $\ln \omega$ at fixed temperatures the exponent factor (s) will be equal to the slope of the segment straight line, while the extrapolated segment line can be used to calculate the D.C. conductivity at the same temperature. Figures 19, 20, 21, 22 and 23 show $\ln \sigma_{(T, \omega)}$ versus $\ln \omega$ at a constant temperature 373 K, for all samples, respectively. Each sample manifests many values for (s) that have been obtained at different temperatures.

For all samples, the measured conductivity as a function of the frequency at temperature $T = 373$ K, have been fitted to the relations 1, 2 and 3 to achieved the D.C. conductivity at

this temp., as shown in “Figures from 14 to 18”, where dots refer to the experimental data and the solid lines refer to the theoretical one. “Figure 24” shows the calculated d.c. conductivity as a function of the atomic number of the TMIs. The D.C. conductivity decreased approximately linearly as the atomic number of the introduced TMIs increased. Like, this behavior may be attributed to the decreasing of the polaron radius with the increasing of the atomic number of TMIs [8-10]

The exponent factor (s) has been calculated and then plotted as a function of temperature as in “Figures 25, 26, 27, 28 and 29”. These figures show that (s) decreasing gradually with increasing the temperature. Such behavior resample to the mechanism predicted by the correlated barrier hopping C.B.H. model [9]. This model proposed that, the charge carrier transfer by thermal activated over the barriers between two sites, each of individual potential well. If these sites are neighbor to each other their potential wells will overlap.

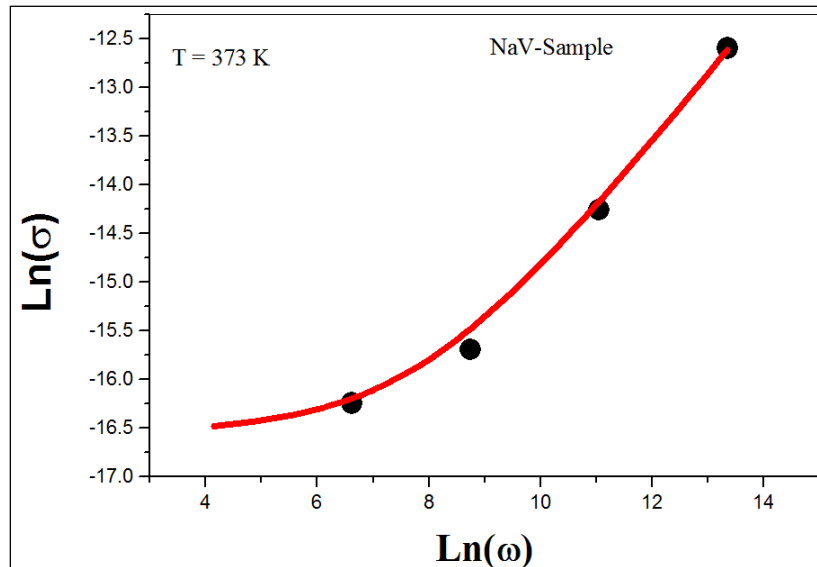


Figure 19. The variation of logarithmic d.c. conductivity with $(1000/T)$ for V-sample.

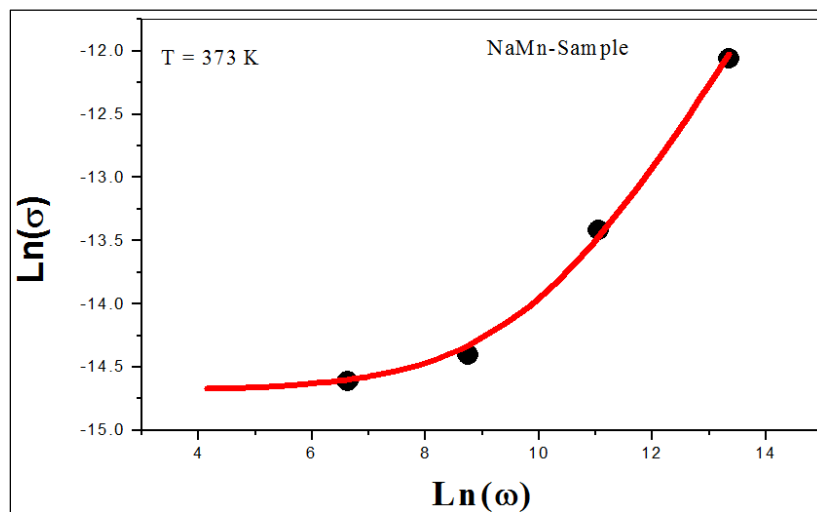


Figure 20. The variation of logarithmic d.c. conductivity with $(1000/T)$ for Mn-sample.

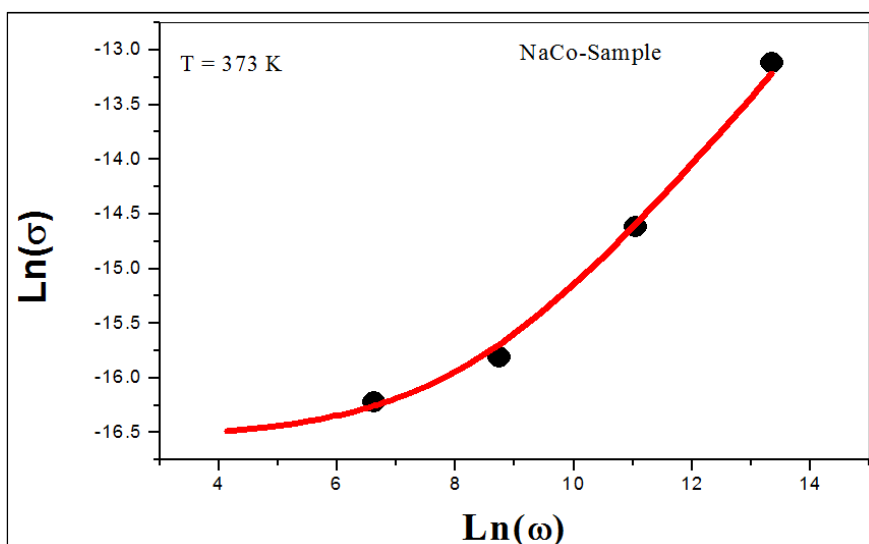


Figure 21. The variation of logarithmic d.c. conductivity with $(1000/T)$ for Co-sample.

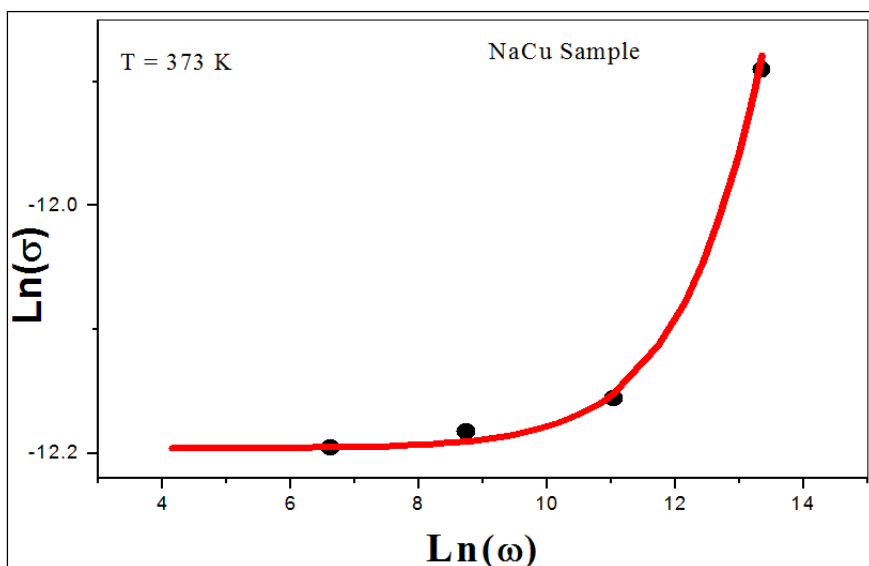


Figure 22. The variation of logarithmic d.c. conductivity with $(1000/T)$ for Cu-sample.

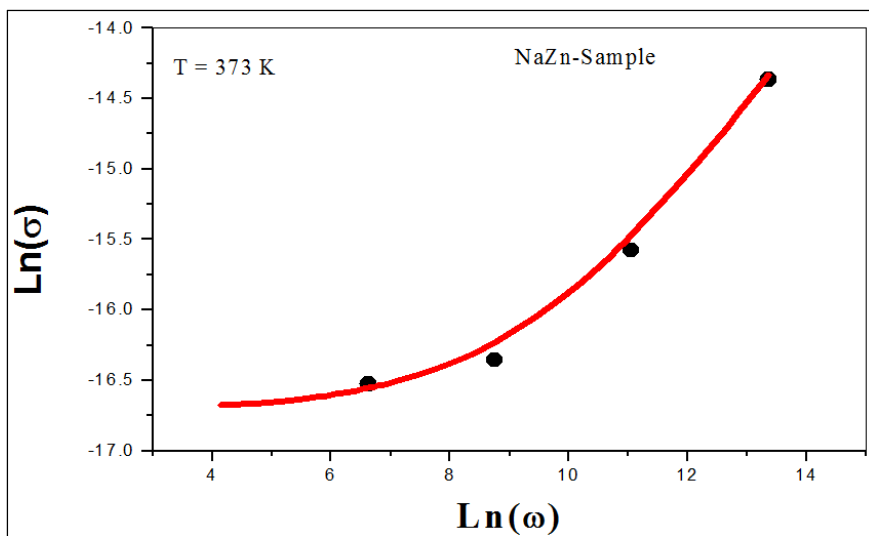


Figure 23. The variation of logarithmic d.c. conductivity with $(1000/T)$ for Zn-sample.

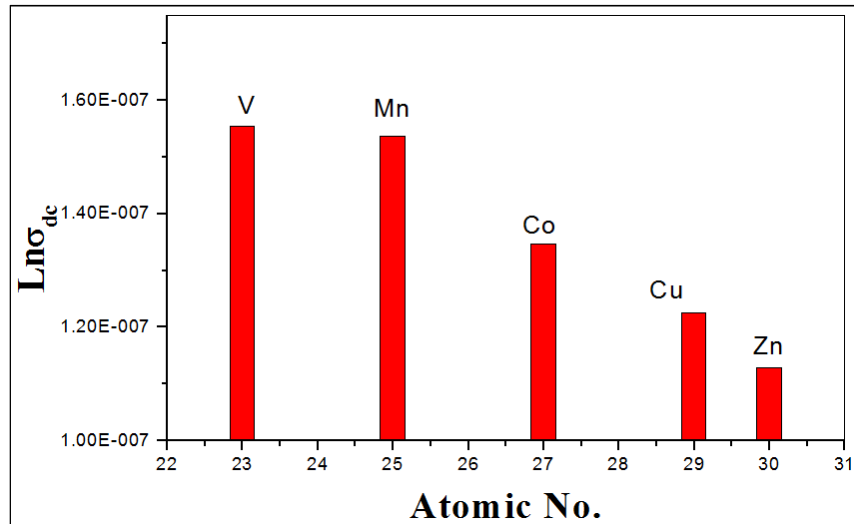


Figure 24. The variation of logarithmic d.c. conductivity with atomic number of TMI.

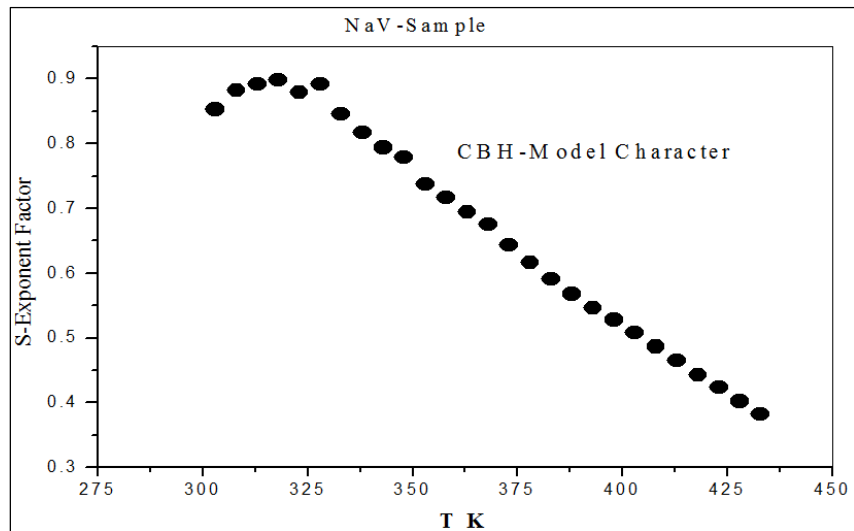


Figure 25. The variation of Exponent factor with T for V-sample.

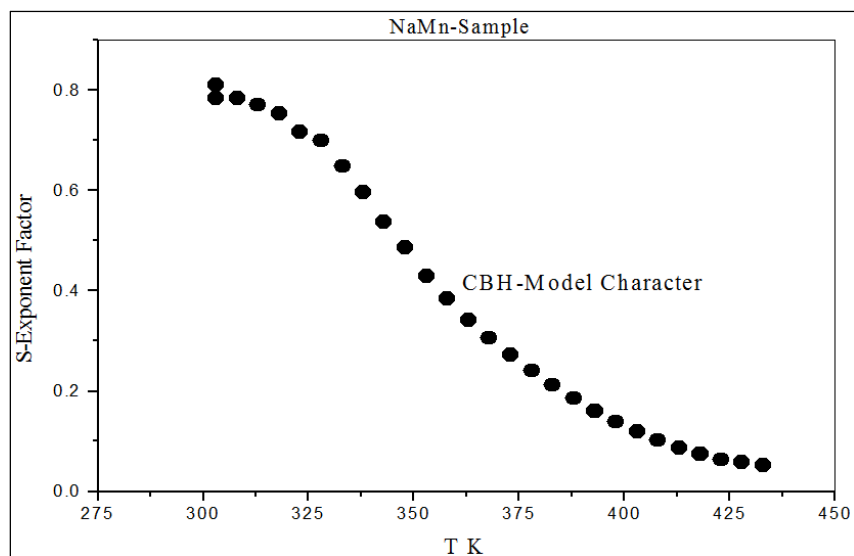


Figure 26. The variation of Exponent factor with T for Mn-sample.

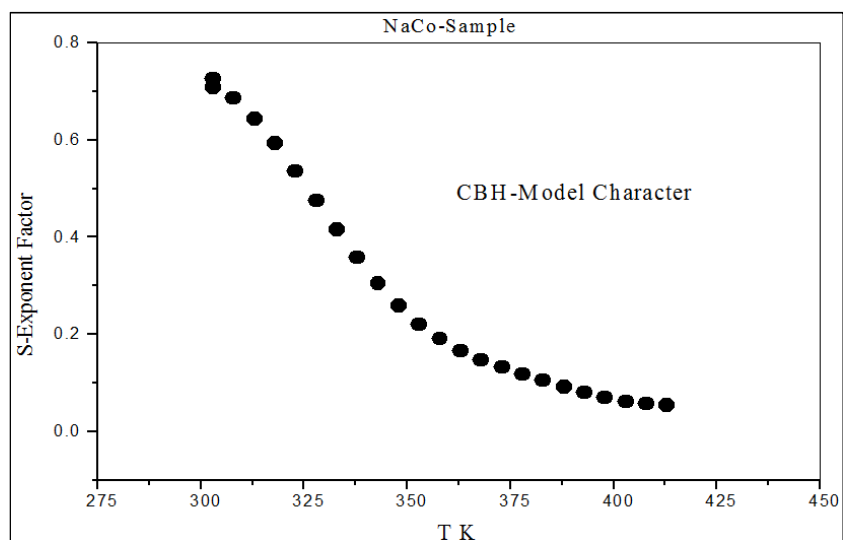


Figure 27. The variation of Exponent factor with T for Co-sample.

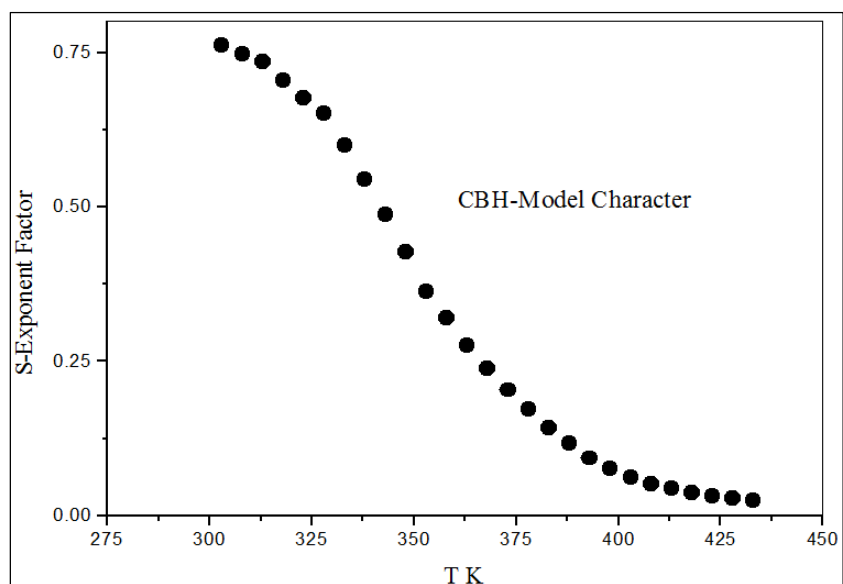


Figure 28. The variation of Exponent factor with T for Cu-sample.

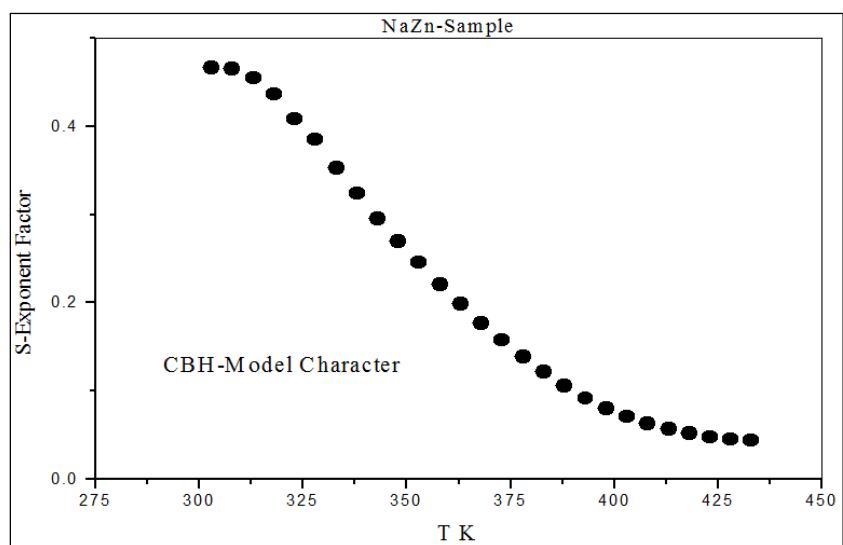


Figure 29. The variation of Exponent factor with T for Zn-sample.

4. Conclusion

Some Iron sodium phosphate glasses doped with different transition metal ions have been prepared by fast cooling method. The prepared glasses based on the following chemical formula: 50 mol% P_2O_5 + 20 mol% Na_2O + 15mol% Fe_2O_3 + 15 mol% M_nO_m , where M_nO_m represents V_2O_5 , MnO , Co_3O_4 , CuO and ZnO .

Mossbauer spectra showed that all studied samples are in a pure glassy state and are of pure paramagnetic character. The increase of the transition metal cause a reduction of Fe (III) to Fe (II). Electric Conductivities of all samples are in the semiconductors range. Whereas, the conductivity behavior is inversely with the atomic number. The AC conduction mechanism was found to belong to the correlated barrier hopping (CBH) model.

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