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Dielectric Studies on CuO-Na_2O-B_2O_3 Glasses

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Abstract

This work is aimed to shed light on the dielectric behavior of CuO containing glasses, since no publications concerning this issue have been presented before. Different glasses in the binary Na_2O-B_2O_3 system were prepared by melt annealing technique. XRD spectra have shown that the amorphous structure is dominant in all glasses containing mixed concentrations from CuO and Na_2O. The crystalline phases appeared only in glass free from Na_2O. The dielectric spectroscopy is applied to shed some light on the conduction mechanisms in terms of changing both the dielectric constant and the electrical modulus of the investigated glasses. The ac conductivity increases with increasing frequency and decreases with increasing CuO concentration. Both the dielectric constant and dissipation loss is decreased with increasing frequency. Correlated barrier hopping (CBH) is considered an appropriate conduction mechanism results from the increase of frequency.

Keywords

Electrical Measurement, Cuo, Borate Glasses, Impedance Spectroscopy

1. Introduction

Most of the studied borate glasses are known to have different properties such as good transparency, appropriate structure stability and higher electrical resistivity compared with the other types of glasses [1] [2]. Many of the previous studies are concentrated on the effect of both alkali and alkali earth oxides on the structure and properties of phosphate and borate glasses [2]. This consideration may be due to the fact that alkali phosphate or borate glasses possess low melting temperature, low chemical durability, and high thermal expansion which are important in some specific applications such as sealing and soldering processes [3] [4]. Modifying with other types of modifier oxides is useful to enhance and improve the properties of glasses [5]. In this regard, it has long been known that

strontium oxide and cupper oxides can be added to improve the glass durability and make glass hard enough and more stable [6]. CuO is as well as Cr_2O_3 may contribute to enhance the glass structure via adding more bridging bonds [7]. Besides, a wide variety of technological applications is considered due to the improved both glass structure and properties. Moreover, their high solubility for rare-earth or metal ions makes them very useful for laser glasses [8] [9].

Transition metal ions including chromium or cupper can be easily dissolved in a modified borate glassy matrix. The different oxidation states of Cu ions and different coordinations are considered the main responsible factors affecting the physical properties [1] [10] [11]. Depending upon metal oxide concentrations, mechanical strength, chemical durability, and electrical conductivity are all affected [12] [13]. CuO is in general plays a dual role, it acts as a modifier and as a glass former, depending on the whole glass composition.

The present study aims to shed some light on the structural role of CuO in different glasses. The change of dielectric behavior of the studied glasses upon changing CuO concentration is also useful to be studied. The electrical conductivity and its relationship with the change in frequency, and concentration of metal oxide (CuO) is aimed to be reported, since, to our knowledge, limited studies on dielectric properties of copper borate glasses modified by lead oxide have been considered before.

2. Experimental Method

Glasses in the system $xCuO\text{-}(25\text{-}x)Na_2O\text{-}75B_2O_3$ were successfully synthesized using pure analytical grade chemicals via melt annealing route. Boric acid (99%) purchased from Sigma Aldrich is used as a source of B_2O_3. Sodium carbonate is the source for Na_2O and CuO was added as received. All components were weighted and mixed together; then they melted in porcelain crucibles at 1150˚C for approximately 1 h depending on the composition of the glasses). The melt is swirled several times to obtain homogenous synthesized samples. The melted samples were poured onto a heated stainless steel mold to obtain the desired samples. They were annealed in a muffle furnace regulated at 300˚C, after some minutes, the furnace was turned off.

X-Ray measurements were carried out to check the state of orderings of phases. XRD patterns were carried out (Metallurgical Institute—Helwan-Cairo) using a Brucker Axs-D8 technique. Data was accumulated steeply with an interval of 0.2˚ over 2˚ range 4˚ - 65˚.

The cylindrical-shaped pellets were polished to smoothen their both the surfaces and coated with conductive silver on both sides to serve as good electrodes, were used for electrical conductivity measurement in the frequency range (0.1 Hz - 20 MHz) at room temperature.

3. Results and Discussion

It was known that boron oxide is considered as an ideal strong amorphous

forming material. This is because B_2O_3 cannot be crystallized at normal circumstances or at ambient pressure. This property can be reflected from Figure 1 which shows XRD spectra of B_2O_3 modified by Na_2O and CuO (Table 1). It can be observed that, the crystallization cannot be occurred because of completion between several borate units or phases which eventually induce the amorphization of the system. The XRD spectra presented by Figure 1 leads that the most of the investigated B_2O_3 samples consist only of the stable amorphous structure which may involve boroxol borate rings [$BO_{3/2}$] units in hexagonal arrangement.

A dielectric material is considered as an electrical insulating solids that can be polarized by an applied external electric field. When placing the dielectric material in an electric field, electric charge carriers do not flow through the material as they do in an electrical conductor but only slightly shift from their average equilibrium positions causing dielectric polarization. Because of polarization, the positive charges are displaced in the direction of the field and negative charges shift in the direction opposite to the field. This creates an internal electric field that reduces the overall field within the dielectric itself. If a dielectric is composed of weakly bonded molecules like Na, those molecules not only become polarized, but also reorient so that their symmetry axes align to the field.

Table 1. Sample nomination and composition.

Sample	CuO	B_2O_3	Na_2O
	mol%		
Parent (Base)	0	75	25
Cu_1	2.5	75	22.5
Cu_2	5	--	20
Cu_3	7.5	--	17.5
Cu_4	10	--	15
Cu_5	15	--	10
Cu_6	20	--	5
Cu_7	22.5	--	2.5
Cu_8	25	--	0

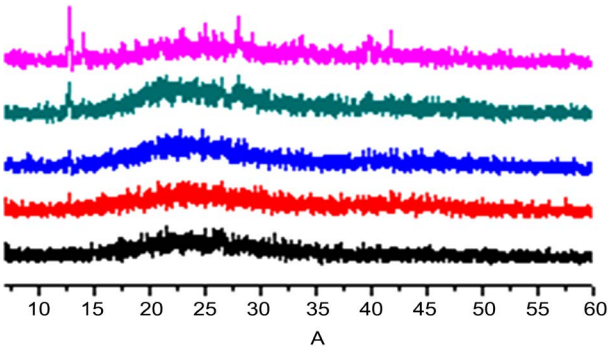

Figure 1. XRD spectra of CuO-Na_2O-B_2O_3 glasses.

The dielectrics measurements are important for explaining various phenomena throughout changing both the real and imaginary parts of its complex conductivity.

3.1. Ac Measurements

The effective complex conductivity of real and imaginary part [14] of ac conductivity is presented as:

$$\sigma^*(\omega) = \sigma'(\omega) + j\sigma''(\omega) \tag{1}$$

The real part of the measured conductivity σ', at a given frequency range, is separable into dc and ac components and can be given by Jonscher's power law [14]:

$$\sigma'(\omega) = \sigma_{dc} + A\omega^S \tag{2}$$

where; σ_{dc} represents the direct current resulting from drift mobility of Na^+ as the main charge carriers and in most cases is temperature-dependent. $\sigma_{ac} = A\omega^S$ is the "true a.c." conductivity which may be obtained through subtraction of the measured dc conductivity (σ_{dc}) from the total conductivity ($\sigma'(\omega)$) measured at the frequency ω. The pre-factor constant A can be assumed as

$$A = \pi N^2 e^2 / 6K_B T(2\alpha) \tag{3}$$

where; α is the polarizability of a pair of sites.

n is the number of sites per unit volume at which the hopping process takes place

s is the exponent of frequency and differs between 0.5 and 1 that characterize the interaction between charged species to be determined as the slope of curves at variable temperatures.

ω is the angular frequency of the applied electric field,

$$\omega = 2\pi f \tag{4}$$

Figure 2 presented the frequency dependence of ac conductivity at different concentrations of CuO in the ternary CuO-Na_2O-B_2O_3 glass system. The sodium borate glasses containing different CuO concentrations have shown nearly like behavior with minor changes. Electrical conductivity was calculated as a function of frequency within the range (0.1 Hz - 20 MHz) at room temperature. It was observed that the values of ac conductivity increase with monotonic manner with increasing frequency especially in the high-frequency region. The rate of change is lower in the lower frequency region (≤2 KHz) which can be attributed to the effect of space charges [13] [14]. The effect of space charge was disappeared at higher frequencies, since the conductivity is increased with a higher rate than that detected in lower frequency region. It can also be shown from **Figure 2** that increasing CuO leads to an obvious decrease in ac conductivity.

The decrease of conductivity with increasing CuO contents, **Figure 3** leads one to suggest that the main portion from CuO can share in the constructing of the glass network and as a consequence CuO plays the role of a network forming

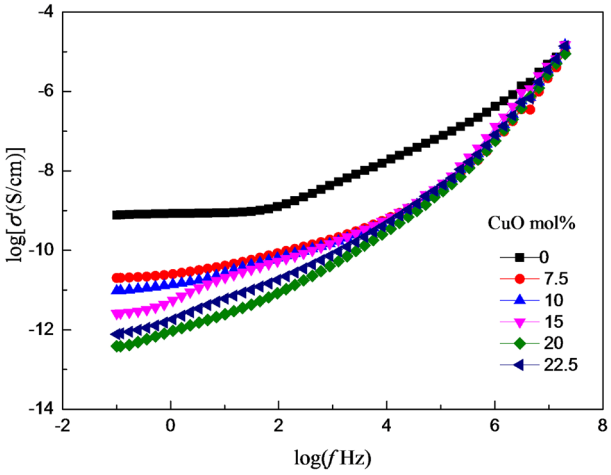

Figure 2. Logarithm of ac conductivity versus frequency, at different CuO concentrations.

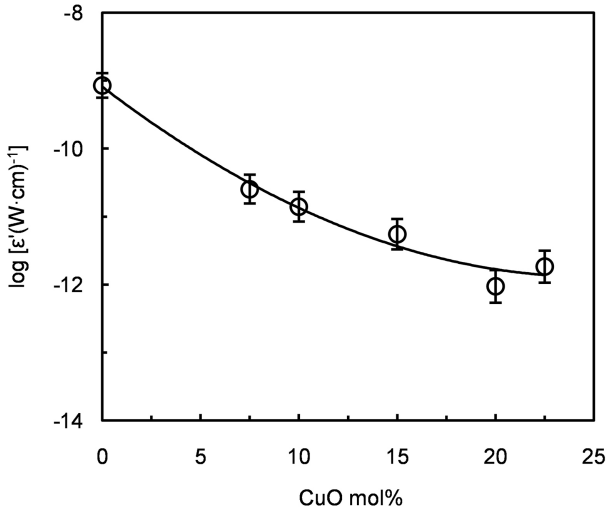

Figure 3. Change of room temperature conductivity of modified borate glasses with CuO concentration.

species (CuO_4). The formation of the latter structural units causes a reduction in the concentration of Na_2O which required for transformation of BO_3 to BO_4 groups. Then part of Na_2O can modify CuO to form CuO_4 tetrahedral units. Then more CuO_4 and BO_3 units are formed with more addition of CuO at the expense of tetrahedral BO_4 groups. As a result more bridging oxygen atoms are formed and consumed to bridge Cu and B forming Cu_4-O-B_3 species. Therefore, some of the well formed BO_4 units are replaced with CuO_4 ones.

The above arguments are in the same lines suggested upon analysis based on NMR spectroscopy of ^{11}B data (**Figure 4**). The total result extracted from **Figure 3** is that the main role played by CuO is forming CuO_4 through presenting more bridging units in the glass structure and their abilities to shield and coordinate with BO_3 units. Therefore, increasing of CuO results in increasing of Cu-O-Cu and B_3-O-Cu bonds at the expense of BO_4 units. The glass structure is then

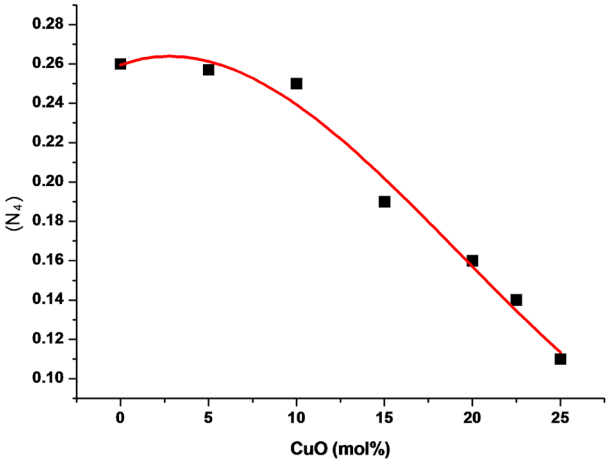

Figure 4. Change of the fraction of tetrahedral boron (N_4) with CuO content.

mainly consisting of Cu-O bond in CuO_4 groups. In such a case, the linkage between CuO_4 and BO_3 groups is being the most abundant within the glass network. The possibility for the cross linking of these CuO_4 units with BO_3 groups to form Cu-O-B bonds in the glass network obviously reduce the mobility and the number of the charge carriers which leads to decrease in the values of ac conductivity of the study samples with increasing CuO contents as presented by **Figure 3**. The conductivity is decreased by more than 3 orders of magnitudes upon increasing CuO from 0 to 22.5 mol%.

Change of dynamic ionic conductivity of Na_2O containing CuO borate glasses, xCuO-(25-x)Na_2O-75B_2O_3 versus frequency can be represented by three distinct regions in the conductivity spectrum see **Figure 2**. Lower frequency region in which the change in conductivity is relatively small with changing frequency (low frequency plateau). This limited change is clearly observed in glass free from CuO and in a glass contains 7.5 mol% CuO. The plateau length is decreased with increasing CuO content. On the other hand, glasses containing lower concentration of Na_2O (high CuO) did not show the low frequency plateau, where steeply increase in the conductivity is observed. In the second region, the conductivity increases with higher rate with increasing frequency (jump relaxation) [15]-[23]. Finally, at certain value of frequency (log f = 6.5), the conductivity tends to be fixed around a specific maximum single value for all composition (higher frequency limit). Comparing the experimental data of conductivity of sodium rich glass with the dispersion of the conductivity according to the jump relaxation model reflects a good resemblance [23] [24] [25] [26].

Actually, several models [24] [25] [26] have been proposed claiming that some glass systems contain small clusters or micro domains. These clusters are formed during the cooling process and are surrounded by a residual phase or connective tissue. In these clusters the ions can move more freely and more easily depending only on the effective frequency value which required for charge carriers to gain the highest mobility. The ion mobility is therefore higher than that of hop-

ping process in connective tissue between the well formed clusters. Then the highest conductivity is found to depend only on the specific value of frequency frequency regardless changing composition.

3.2. Dielectric Properties

Dielectric materials are characterized by their ability to store energy when they exposed to an external electric field. In all cases there is an induced polarization due the interaction between the external electric field and the field produced by the investigated sample. The behavior of dielectric materials generally described by the complex permittivity that formulated with two parts [23]:

$$\varepsilon^* = \varepsilon' - j\varepsilon'' \tag{6}$$

where $\varepsilon'$and $\varepsilon''$are real and imaginary components of the complex permittivity respectively, and can be calculated using the following equations:

$$\varepsilon' = \frac{Cd}{A\varepsilon_0} \tag{7}$$

$$\varepsilon'' = \varepsilon' \tan\delta \tag{8}$$

where (C) is the sample capacitance measured in parallel mode in farads, d is the thickness of the glass samples in meters, A represents the cross-sectional area of the sample in square meters and ε_0 ($\varepsilon_0 = 8.85 \times 10^{-12}$ F/m) is the permittivity of free space, ε'represents the amount of electrical energy stored in the material in response to an external electric field. The imaginary part of permittivity ε'' represents energy dissipated in the heat form. $\varepsilon''$is usually much smaller than ε' ($0 < \varepsilon'' < \varepsilon'$).

When the alternating voltage is applied to the dielectric materials, the material will absorb an electrical energy and dissipated in the form of heat which may be represented by the term (tan δ) which includes the influence of both dielectric loss and conductivity. Based on the values of ε' & ε'', the term tan δ gives the phase difference due to the loss of energy within the structure. This means that tan δ is a dissipation factor (tangent loss) which represents the electrical loss. Dissipation factor, tan δ is equal to the ratio between the electrical energy dissipated in heat to the total electrical energy stored per cycle in the dielectric materials, which is given by the following relation:

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} \tag{9}$$

Figure 5 and **Figure 6** show dependence of the real (ε') and an imaginary (ε'') parts of the dielectric permittivity on the frequency respectively. All samples of $CuO\text{-}Na_2O\text{-}B_2O_3$ showed the same trend except the composition free from CuO.

Obviously, the dielectric constant and losses both are decreased with increasing the CuO concentrations (**Figure 7** and **Figure 8**). The decreasing trends may be related to the hopping process of the charge carriers' species. The change in CuO concentrations leads to increasing $Cu\text{-}O\text{-}B_3$ which makes the charge carrier unable to follow such change in the electric field. This leads to a decrease in the dielectric constant and losses (ε'& ε'').

3.3. Electric Modulus

The electric modulus approach was used to assist in understanding the response of bulk materials to the electrode polarization effect. The latter is negligible and enables the relaxation processes to be assessed at the lower frequency range of dielectric spectra [25] [26]. The complex electric modulus M^* is related to the complex dielectric constant as described in the following expressions:

$$M^* = \left(\varepsilon^*\right)^{-1} \tag{10}$$

$$M^* = M' + iM'' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} + \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \tag{11}$$

where M' and M'' are the real and imaginary parts of dielectric modulus respectively.

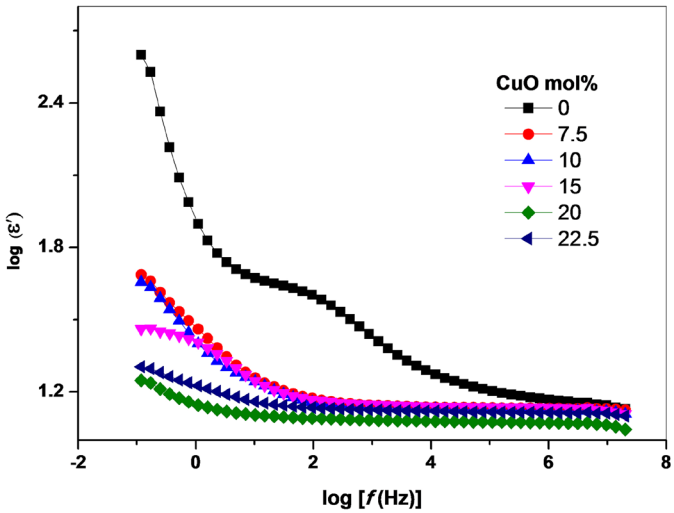

Figure 5. Dielectric constant (ε') versus frequency for different concentration of CuO.

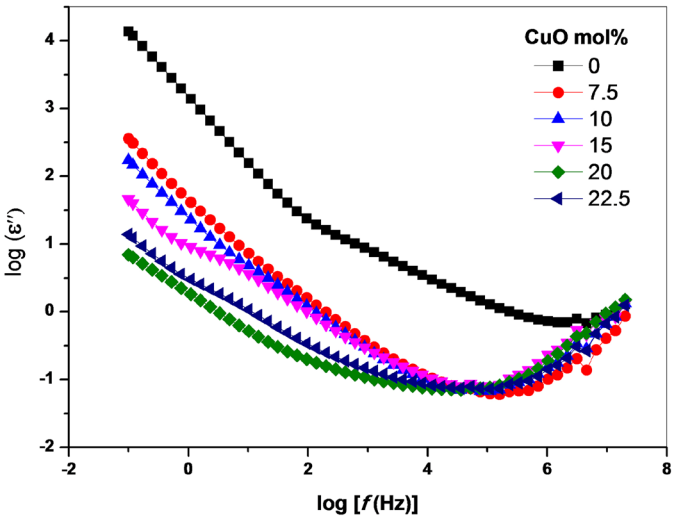

Figure 6. Dielectric loss (ε'') versus frequency for different concentration of CuO.

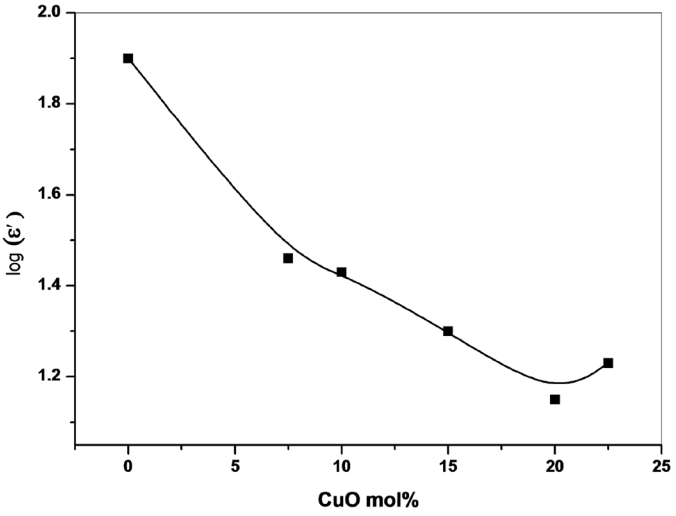

Figure 7. Change of dielectric constant (log ε') with different concentration of CuO.

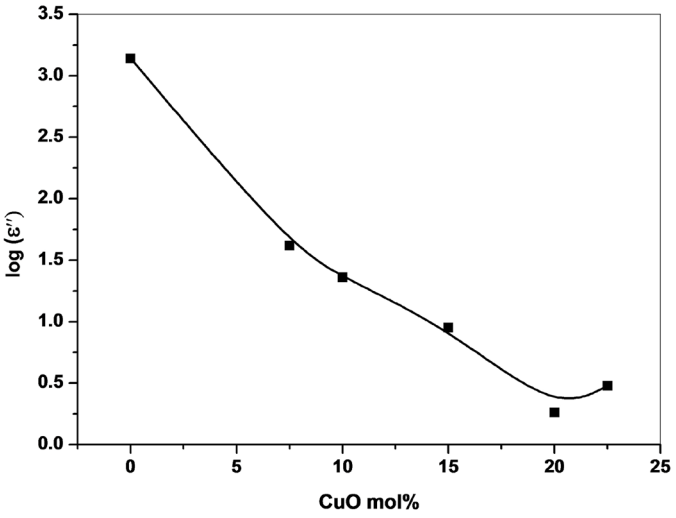

Figure 8. Change of dielectric loss (log ε'') with different concentration of CuO.

All investigated samples have showed the same behavior (**Figure 9** and **Figure 10**) except the sample which free from CuO. It can be observed from **Figure 9** that the values of M' at low frequencies are small ($M' \approx 0$) for CuO = 0 which is attributed to the negligible contribution of electrode polarization. With increasing frequency, M' increases gradually and tends to approach maximum constant values M_∞ due to the relaxation process. This is attributed to the reduced space charge effects. The frequencies dispersion may be attributed to the conductivity relaxation processes. The graph also clearly shows that the M' increases with a rise of CuO contents which indicates that the conduction in the investigated samples can be attributed to the long-range mobility of charge carriers. It is observed that the normalized plot does not overlap on a single curve, which indicates that the conductivity relaxation depends on the glass composition.

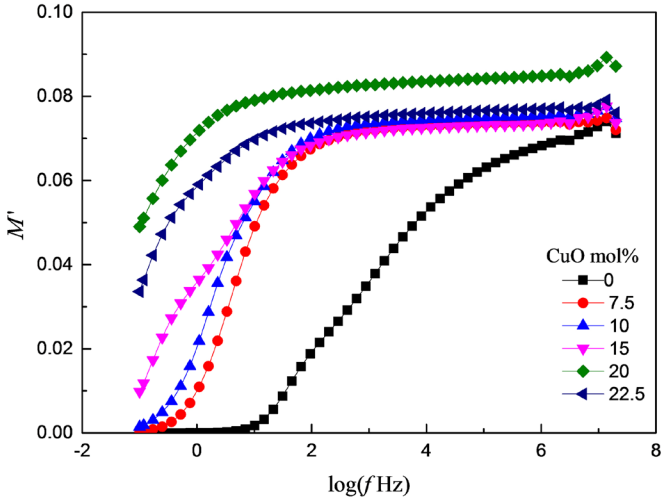

Figure 9. The dependency of M' with the applied frequency for different CuO concentrations.

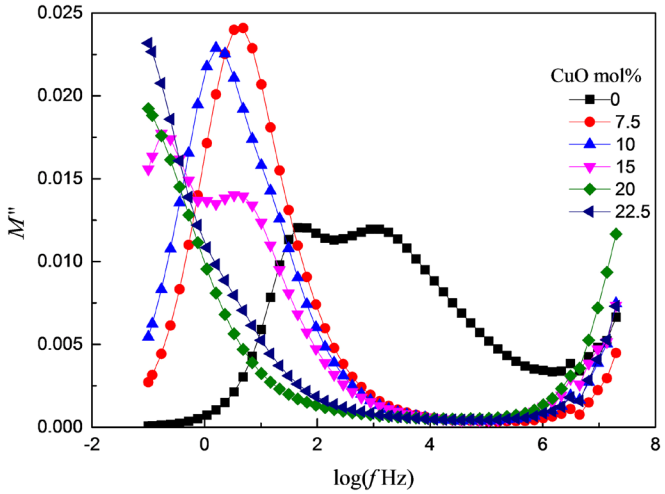

Figure 10. The dependency of M'' with the applied frequency.

4. Conclusion

Sodium borate glasses containing CuO were successfully prepared via melt annealing-technique. The ac conductivity was found to be directly proportional to frequency. The decreasing values of the real and complex parts of the dielectric constant (ε' & ε''), loss tangent (tan δ), and the increasing value of the activation energy (E_a) for ac conduction have been observed with the incorporation of CuO. These changes are attributed to the presence of main part of CuO as the glasses former. The ac conductivity mechanism is reasonably well interpreted in terms of the correlated barrier hopping (CBH) according to the behavior of the exponent(s).

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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