

FTIR Spectroscopy and Structure of the Binary Glass $\text{Cu}_2\text{O} - \text{MoO}_3$ System

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FTIR transmission spectra have been carried out for glasses in composition form: $x\text{Cu}_2\text{O} - (100-x)\text{MoO}_3$, $x = 20, 25, 30, 35$ and 40 mole %. The most active peaks were observed in the region from 600 cm^{-1} to 1200 cm^{-1} . The first five peaks were centered in the ranges: $600 - 620 \text{ cm}^{-1}$, $696 - 699 \text{ cm}^{-1}$, $779 - 800 \text{ cm}^{-1}$, $837 - 862 \text{ cm}^{-1}$ and $894 - 929 \text{ cm}^{-1}$. The last three peaks were observed in the absorption regions: $940 - 953 \text{ cm}^{-1}$, $1058 - 1067 \text{ cm}^{-1}$ and $1094 - 1120 \text{ cm}^{-1}$ respectively. The magnetic susceptibility and density were also measured for the glasses under investigation. This work is dedicated to the memory of Prof. Dr. I. A. Gohar for his fruitful contribution and initiating pioneer work over a period of two decades with the glass research group.

1. Introduction:

The applications of the fast-ion conducting glasses in the solid state batteries and electrochemical devices have been examined by many investigators on various types of glasses [1 and refs.1-6 therein]. It is well known that V_2O_5 and MoO_3 oxides are network formers [2]. Ions like Ag^+ , Li^+ and Na^+ are well known as charge carriers in ion-conducting glasses with high conductivity in the range of $10 - 10^2 \text{ S.cm}^{-1}$ at room temperature [1].

Glasses containing Cu^+ ions are expected to show high conductivity [5,6,7 &8] because Cu^+ ions have the same electronic configuration [(Ar) 3d10] as Ag^+ [(Kr) 4d10] ions and smaller ionic radius (0.96 \AA) than Ag^+ ions (1.26 \AA) [3&4]. In spite of that the high conductivity [5,6,7&8] of Cu^+ ion in other

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glass containing oxides such as SiO₂, B₂O₃, GeO₂ could not be obtained, the cuprous ions was found to be stable in melts containing tungsten oxide, molybdenum oxide and /or phosphorous oxide with high acidity (9).

The effect of Cu²⁺ on the phase separation has been reported [11] for the glass Na₂O – B₂O₃ – SiO₂ system and it was found that Cu₂O took part as a network former. There was no tendency for Cu₂O or Cu²⁺ to be formed and conductivity occurred only by Cu⁺ ions [5, 10]. The optical absorption properties of Cu: (Ar) 3d¹⁰ 4s¹ and Mo: (Kr) 4d⁵ 5s¹ are immensely important since they are the coloring agents in the oxide glasses. The cuprous Cu⁺ ion does not produce coloring whilst Cu²⁺ ions create color centers with an absorption band in the visible, thus producing blue and green glasses. This absorption band is at or near 12500 cm⁻¹ (800nm) and occurs in alkali silicate and borate glasses [11,12].

Vanadium and molybdenum are expected to be the main glass forming substances in a system such as V₂O₅ – MoO₃ – Fe₂O₃ with two phases FeVMoO₇ and Fe₄V₂Mo₃O₂₀ [2]. The Mo-O bond in the molybdenum trioxide MoO₃ may be considered covalent. In mixed former molybdophosphate glasses, MoO₃ provides octahedral structural unit (MoO_{6/2}) that is necessary for the extensive network formation [13].

The present glasses were perfectly colorless and did not show any absorption band in the visible or near infrared region of the spectrum. This confirms that the existence of the copper in the glass is in the monovalent form.

The aim of the present study is to obtain an idea about the effect of Cu₂O on the structure of Cu₂O-MoO₃ glass system by using FTIR spectroscopy and some other physical properties such as density and magnetic susceptibility.

2. Experimental Procedure:

2.1. Samples Preparation:

Glasses under investigation are of the forms: {x Cu₂O – (100-x) MoO₃, x=20, 25, 30, 35 and 40 mole %} were prepared by the proper way using reagent grade Cu₂O and MoO₃ as starting materials.

The homogenized batches were melted in air in porcelain crucibles within the temperature range of 950-1100°C depending on the glass composition. The resulting samples were annealed at 350°C for about two hours and allowed to cool normally to room temperature (25–30°C). More details about sample preparation are given elsewhere [12 and 14-17].

2.2. IR Spectra:

Infrared transmission spectra were carried out using the same weight of the glass powder dispersed in KBr pellets. The data were recorded by Perkin Elmer 457 spectrophotometer from 600 cm^{-1} to 4000 cm^{-1} , the spectra were measured at room temperature with about 1 cm^{-1} resolution for the instrument. A 1.0 mg from each sample was mixed with 100 mg of KBr in an agate mortar and pressed into pellets.

2.3. Magnetic Measurements:

Magnetic measurements were obtained using Guay's method and Johnson Methly magnetic susceptibility balance, where the magnetic susceptibility (χ) is given by:

$$\chi = (1.305)(0.001)(R - R_0) L / m$$

where, R is the reading with the sample, R_0 represents the reading without the sample, L is the tube length and m is the sample weight in gram. The molar magnetic susceptibility $\chi_m = [\chi \cdot (\text{molecular weight})]$ and Bohr Magneton $\mu_{\text{eff}} = 2.84 \times 10^{-3} [\chi_m T]^{1/2}$, where $T = 25 + 273 = 298\text{ K}$.

2.4. Density Measurements:

The density of the glasses was measured by Archimedes' method, using xylene as the immersion fluid. Measurements were made in duplicate for each glass sample and the averages were taken.

3. Results and Discussions:

3.1. FTIR SPECTRA:

The infrared results of the glasses under investigation are shown in Fig.(1), where the spectra are shifted for the sake of clarity. The data have been drowning in such a way to get an idea about the replacement of MoO_3 by Cu_2O . In order to analyze the IR absorption spectra, many trials have been done to deconvolute them using the Peak Fit computer program [18], at last it was found that the Gaussian band is the best fit. The only input for fitting program was the number of bands and the initial values for the parameters describing the intensity, position and width of each band. Subsequently, the program using a least-squares fitting procedure adjusted these parameters [19].

Figure (3) shows, for example, the IR spectra for glass 35 mole % of Cu_2O along with the Peak Fit computer fitting in the wave number range from

1120 – 600 cm^{-1} . There were no characteristic absorption bands in the region $> 1120 \text{ cm}^{-1}$. From this figure the band deconvolution of IR spectra for the studied glass yielded the central position, amplitude, area and the full width at half maximum (FWHM) of each peak. The glasses show quite similar IR spectra with slightly shifting to the position of the main peaks this due to the Cu^{2+} ions. The main peaks were centered in the following absorption regions at 600 – 620 cm^{-1} , 696 – 698 cm^{-1} , 837 - 862 cm^{-1} , 940 – 953 cm^{-1} and 1094 – 1120 cm^{-1} . In addition there are very small peaks in the regions 779- 800 cm^{-1} , 894 - 929 cm^{-1} , and 1060 – 1067 cm^{-1} .

The results led to the conclusion that the glass is composed of discrete ions of Cu^+ and MoO_4^{2-} and condensed units of MoO_4 , probably $\text{Mo}_2\text{O}_7^{2-}$ ions. The condensed units of MoO_4 must be large because of the molar ratio of $\text{Cu}_2\text{O} / \text{MoO}_3$ ($= 0.25, 0.33, 0.43, 0.54$ and 0.667) deviates from unity [1]. This means that Cu_2O has an obvious effect on the IR spectra at $\text{Cu}_2\text{O} = 20, 25, 30$ and 35 mole %. While, the discrete ions of Cu^+ and MoO_4^{2-} might control the behavior of the spectrum at $x = 40$, (Fig.1).

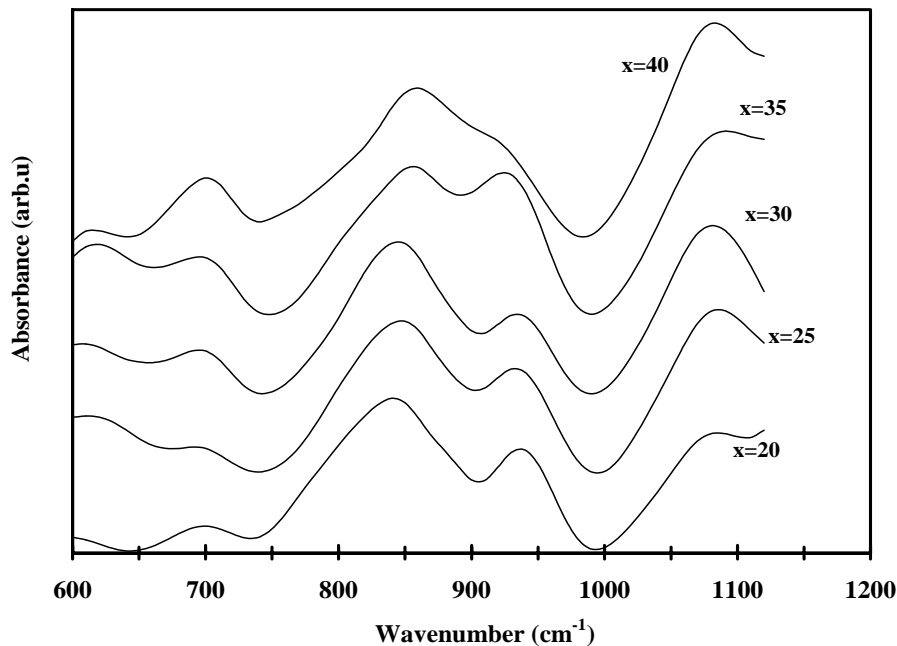


Fig. (1): Infrared absorption spectra of $x \text{ Cu}_2\text{O} - (100 - x) \text{ MoO}_3$ glass system with $x = 20, 25, 30, 35$ and 40 mole %

Nagano and Greenblatt [20], reported that the characteristic features of polymolybdate structure are MoO_6 octahedra sharing edges and usually have three nonequivalent type of oxygens: terminal O_t , bridging O_b and central

oxygen O_c . The basic elements of MoO_3 structure are similar to MoO_6 octahedra that form infinite sheet by edge and corner sharing. There also are terminal oxygen O_1 and bridging oxygens (O_2, O_3, O_3'). The unit cell of MoO_3 is shown in Fig. (2).

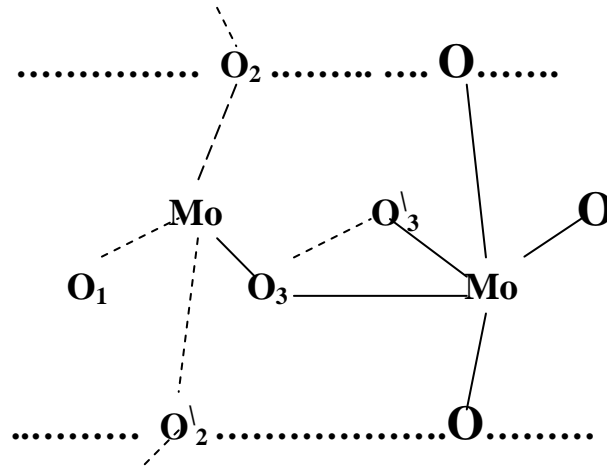


Fig. (2): A schematic diagram for a section of a unit cell of MoO_3 ,.....unit cell edges, - - - - Mo - O at $z = 3/4$ and solid lines Mo - O at $z = 1/4$ (after ref.[20]).

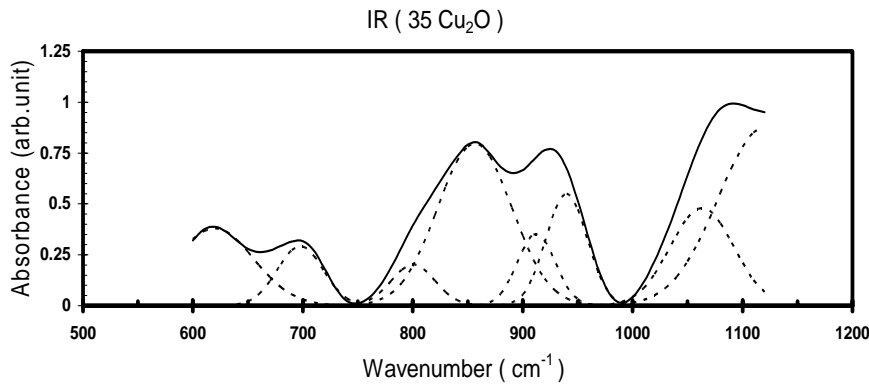


Fig. (3): The band deconvolution of IR spectra for glass of 35 Cu_2O content in the spectral region $600 - 1200\text{ cm}^{-1}$. where — denotes the experimental data, and - - - denotes the computer fit components.

From figure (1) one can give an explanation to the observed peaks as follows: The peaks at $600 - 620\text{ cm}^{-1}$ were assigned to asymmetric mode (ν_{as}) of the condensed ions of MoO_4 tetrahedral, probably MoO_7^{2-} [1]. The peaks were

seen in the range $696 - 698 \text{ cm}^{-1}$ were assigned to ν_4 mode of tetrahedral MoO_4^{2-} ions, the peaks observed in the absorption range $837 - 862 \text{ cm}^{-1}$ were assigned to ν_1 mode of tetrahedral MoO_4^{2-} ions [1] and the peaks noticed in the region from 940 to 953 cm^{-1} were assigned to the ν ($\text{Mo} - \text{O}_i$) stretching mode of MoO_3 [20]. The peaks observed in the region from 1094 to 1120 cm^{-1} might be due to either crystallinity of MoO_3 or / and Cu_2O .

It is so obvious that the central position of the peaks is not the same for each glassy sample, this is due to the Cu^{2+} ion.

Figure (4) shows the relation between the relative area of each peak (the relative intensity of each absorption band) and the content of Cu_2O . The relative intensity I_p has been calculated from the relation $I_p = A_p / A_T$, where A_p represents the area under the specific peak and A_T is the area under the whole spectrum in the selected region of the wave number $600 \text{ cm}^{-1} - 1200 \text{ cm}^{-1}$. It is obvious from this figure that the relative intensities for all Cu_2O contents have a maximum value at wavenumber 850 cm^{-1} , where the discrete ions of Cu^+ and MoO_4^{2-} have a strong effect on the relative intensity of each absorption band.

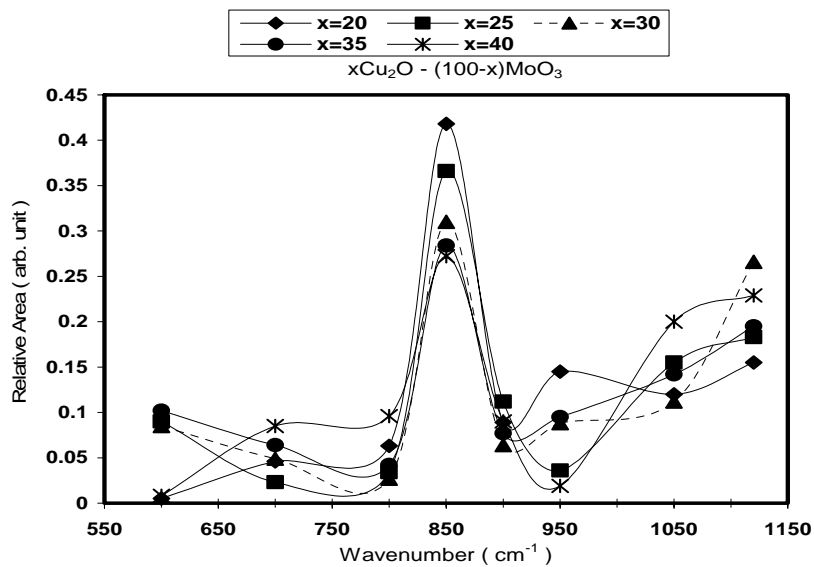


Fig. (4): The effect of Cu_2O content on the centre of the IR absorption bands for the studied glasses. Lines are drawn to guide eye.

Figure (5) represents the relation between the peak center and Cu_2O content. It is obvious from this figure that the value of the peaks center is approximately constant for different values of Cu_2O content (mole %). This means that the peak centers are approximately have the same values or almost

constant for different values of Cu_2O contents. This means there is no effect of either Cu_2O or MoO_3 on the position of the peak, but for constant values for either Cu_2O or MoO_3 there are about eight positions for different peaks. This due to the existence of the discrete ions Cu^+ and MoO_4^{2-} and condensed unit of MoO_4 .

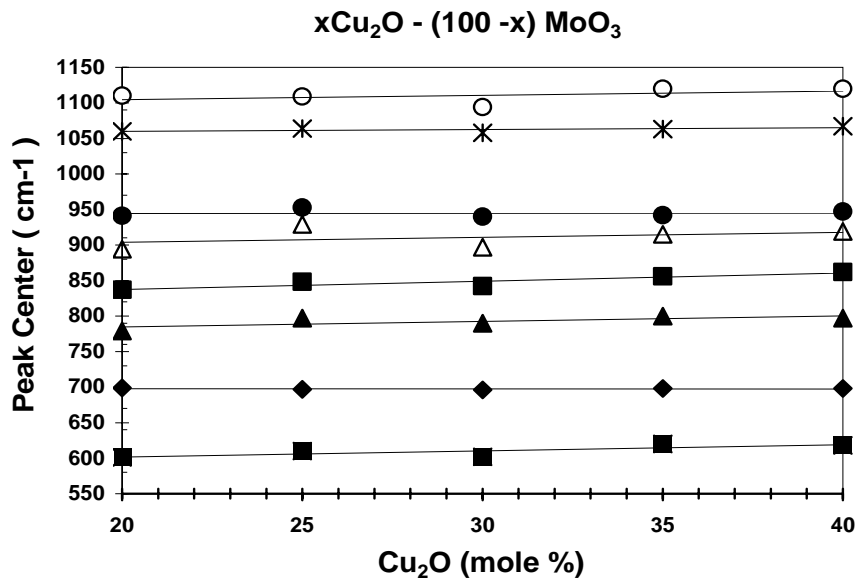


Fig. (5): Dependence of the peak centre (cm-1) on Cu_2O mole % for the studied glass. Lines are drawn to guide eye.

The relation between $\text{Cu}_2\text{O}/\text{MoO}_3$ and the data of magnetic susceptibility (χ), the molar magnetic susceptibility (χ_m) and the effective magnetic moment (μ_{eff}) is given in Fig. (6) from this figure one could observe that (χ), (χ_m) and (μ_{eff}) have maximum values at $\text{Cu}_2\text{O} / \text{MoO}_3$ or $\text{Cu}_2\text{O} = 30$ mole %. The main absorption band at $\text{Cu}_2\text{O} = 30$ mole % is in the region $790 - 940 \text{ cm}^{-1}$ and centered at 842 cm^{-1} . This band was assigned to the vibrational mode ν_1 mode of tetrahedral MoO_4^{2-} ions [1]. This means that the discrete ions of Cu^+ and MoO_4^{2-} and the crystallization of Cu_2O and MoO_3 control the behavior of χ , χ_m and μ_{eff} where their data yield the same shape with maximum values at 30 mole % of Cu_2O . This leads to the conclusion that the magnetic interaction between the Mo-Mo ions might be occurred through the cuprous ions.

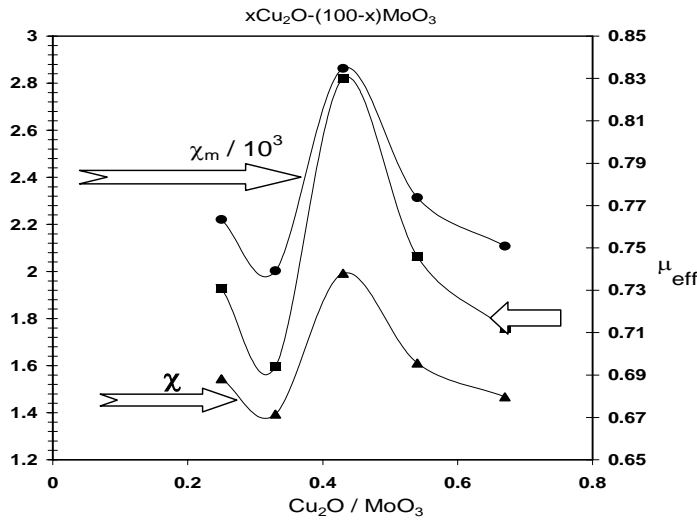


Fig. (6): Dependence of the magnetic susceptibility χ , molar magnetic susceptibility χ_m and the effective magnetic moment μ_{eff} on Cu₂O mole % . Lines are drawn to guide eye.

The relation between the density and Cu₂O (mole %) of the studied glasses is given in Fig. (7) which is almost straight line with error bars $\pm 0.3\%$, this means that more contents of Cu₂O increase the density and/or the solidity of the investigated glasses.

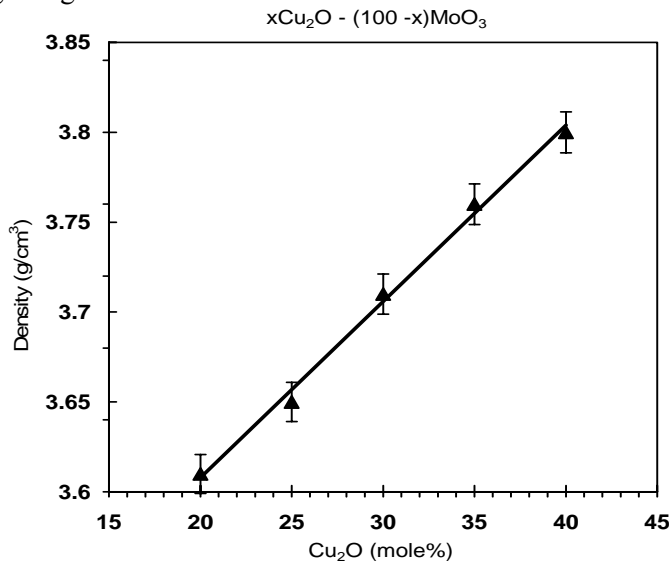


Fig. (7): The relation between the density; (with error bars = $\pm 0.3\%$) and the contents of Cu₂O mole %.

4. Conclusions:

The condensed units of MoO_4 , which are the results of the molar ratio of $\text{Cu}_2\text{O} / \text{MoO}_3$ have an obvious effect on the infrared spectra at $\text{Cu}_2\text{O} = 20, 25, 30$ and 35 mole %. The spectrum at $\text{Cu}_2\text{O} = 40$ mole % might be controlled by the discrete ions of Cu^+ and MoO_4^{2-} . The data of χ , χ_m and μ_{eff} leads one to conclude that the magnetic interaction between the Mo- Mo ions could be done through the Cu^+ ions (Mo-Cu-Mo). The addition of Cu_2O to $\text{Cu}_2\text{O} - \text{MoO}_3$ glasses increases the density of the glass and its solidity.

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