

Structure and electrical transport properties of pure and Li₂O-doped CuO/MgO solid solution

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Abstract

The different electrical properties, σ , ε' , $\tan \delta$ and E_σ of pure and Li₂O-doped CuO/MgO solid solution were investigated. The mole fraction of CuO (MF) was varied between 0.048 and 0.2. Pure and doped samples were subjected to heat treatments at 673 and 1073 K. The results revealed that the amount of CuO dissolved in MgO lattice increases progressively by increasing the MF as evidenced from the progressive decrease in the intensity of all diffraction lines of undissolved CuO phase. The dissolution process of copper ions in MgO lattice was accompanied by progressive increase in its lattice parameter. This process being conducted at 1073 K was accompanied by a significant progressive increase in the values of σ , ε' and $\tan \delta$ with subsequent decrease in the value of E_σ . The increase in the MF value of CuO from 0.048 to 0.2 led to a significant increase in the value of σ_{DC} , measured at room temperature, from 6.33×10^{-12} to $9.9 \times 10^{-10} \Omega^{-1} \text{cm}^{-1}$ and E_σ decreases from 0.76 to 0.58 eV.

Li₂O doping of the investigated system followed by calcination at 1073 K resulted in a measurable increase in values of σ , ε' and $\tan \delta$ with subsequent decrease in E_σ . These results were discussed in the light of the possible effective increase in the charge carriers concentration (Cu²⁺ ions dissolved in MgO lattice) and also to an effective increase in mobility of these charge carriers by Li₂O doping.

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1. Introduction

Recently, transition metal oxides were the object of many investigations leading to the discovery of a large number of these compounds exhibiting a wide spectrum of physical properties including electrical and dielectric properties. Transition metal oxides supported on finely divided support material are successively used in catalyzing different reactions [1–6]. These supported solids can be used for different applications including closed cycle carbon dioxide laser and air purification devices besides their applications as oxygen and semiconducting electrodes [7,8].

The surface, catalytic and electrical properties of some transition metal oxides and their solid solutions in MgO were the focus of interest of our research program devoted to characterization of such system [9–14]. MgO can be used as a host matrix for dissolving different amounts of metal oxides such as NiO, Fe₂O₃, CoO, V₂O₅ and MnO in its lattice to forming solid solutions. The dissolution of transition metal oxide in MgO lattice depends, mainly, on the nature of these oxides, calcination conditions and doping with certain foreign cations such as Li₂O [13,14]. Study of the effect of temperature, composition and frequency as well as Li₂O doping on DC and AC electrical conductivity offers much valuable information on the behaviour of the localized electric charge carriers which can lead to a good explanation and understanding of the mechanism of electric conduction and dielectric properties in mixed metal oxide systems.

The present work aims to study structure, effect of temperature, frequency and Cu ions substitution on DC and AC electrical conductivity and dielectric behaviour of CuO/MgO solid solutions prepared by usual ceramic techniques. The effect of Li₂O doping effect on formation of CuO/MgO solid solutions was also investigated.

2. Experimental

2.1. Materials

Pure CuO/MgO mixed solids were prepared by wet impregnation of finely powdered magnesium basic carbonate solid with calculated amount of copper nitrate dissolved in the least amount of distilled water sufficient to make pastes. The pastes were dried at 383 K and then followed by calcination at 673 and 1073 K for 6 h. The molecular formulae of the calcined solid samples were 0.05 CuO/MgO, 0.15 CuO/MgO, 0.20 CuO/MgO and 0.25 CuO/MgO. Two Li₂O-doped samples were prepared by treating CuO/MgO sample having the formula 0.2 CuO/MgO with calculated amount of lithium nitrate followed by drying the calcination at 1073 K for 6 h. The amounts of Li₂O dopant were 2.5 and 5 mol%. All the chemicals employed were of analytical grade and supplied by Merck Company.

2.2. Techniques

An X-ray investigation of pure and doped mixed solids precalcined at 1073 K was conducted using a Philips diffractometer (type PW1390). The patterns were run with nickel filtered copper radiation ($\lambda = 1.5405 \text{ \AA}$) at 36 kV and 16 mA with a scanning speed of 2° in $2\theta \text{ min}^{-1}$.

The conductivity measurements of pure and Li₂O-doped samples in the temperature range 307–573 K were carried out by conventional electric circuit using high impedance electrometer (Keithely 614). The

real dielectric constant, ϵ' , dissipation factor, $\tan \delta$, and AC electrical conductivity, σ_{AC} , were measured in the frequency range 10^2 – 10^6 Hz using an RLC meter (type Hioki 3531 Z Hitester). The electric capacity, C , dissipation factor, $\tan \delta$, and the resistance, R , were obtained directly from the bridge from which ϵ' and σ_{AC} were calculated. The electrical measurements were carried out on samples in the form of discs having a radius of 0.6 cm and thickness of 0.25 cm obtained by compressing a fixed weight of powdered samples under hydraulic pressure of 5 tonnes/cm². The surfaces of the samples were well polished and rubbed with silver paste as a contact material for electrical measurements.

3. Results and discussion

3.1. X-ray diffraction analysis of pure and Li₂O-doped samples

XRD investigation of pure and Li₂O-doped CuO/MgO solid samples precalcined at 673 and 1073 K were determined. Fig. 1 depicts the diffractograms of pure samples precalcined at 1073 K. The diffractograms consist of all diffraction lines of MgO and CuO phases. It can be seen from this figure

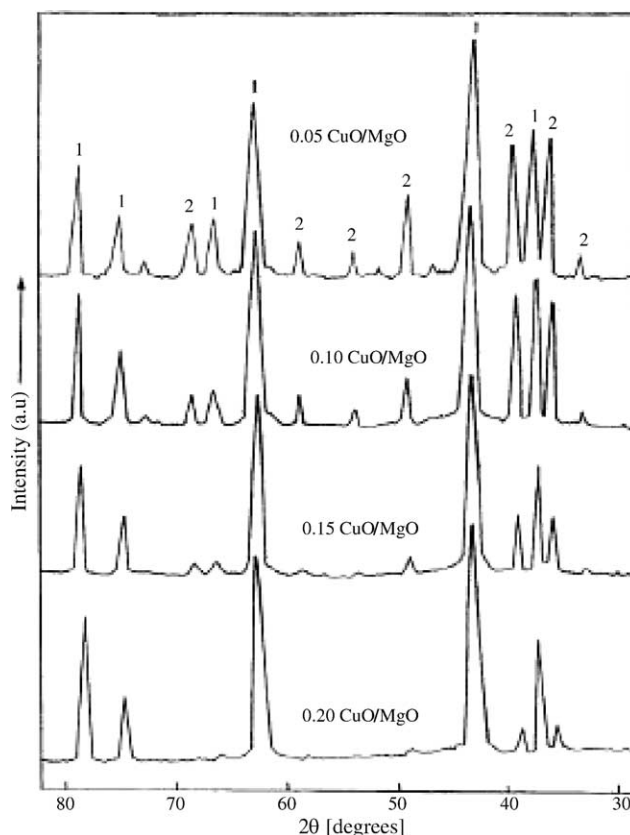


Fig. 1. X-ray diffractograms of different CuO/MgO solids precalcined at 1073 K, lines (1) refer to MgO and lines (2) refer to CuO.

that the peak height of the diffraction lines of CuO as a separate phase decreases progressively by increasing the mole fraction, MF, of CuO present. This finding suggested that the amount of CuO remained in the separate phase decreases by increasing the MF of the CuO or the amount of copper dissolved in MgO lattice increases as a function of MF of CuO added. This conclusion comes from the assumption that the height of the main diffraction peak of CuO phase might be taken as a measure for the abundance of CuO present as a separate phase.

The diffractograms of different pure solid samples precalcined at 1073 K were similar to those precalcined at 673 K (not given). The relative intensity of the peak height of diffraction lines of CuO separate phase decreases also as a function of MF of copper oxide added. This finding, similar to that observed in the case of solids calcined at 673 K, indicates also that the amount of copper species dissolved in MgO lattice increases by increasing the MF of CuO added.

Fig. 2 depicts the XRD diffractograms of pure and Li₂O-doped samples precalcined at 1073 K. Inspection of Fig. 2 shows that the peak height of CuO separate phase decreases effectively by Li₂O doping. The peak height of the main diffraction peak of CuO separate phase measured 210, 75 and 30 a.u. for pure sample and those doped with 2.5 and 5.0 mol% Li₂O, respectively. This finding might reflect the important role of Li₂O dopant in increasing the amount of CuO dissolved in MgO lattice. This behaviour

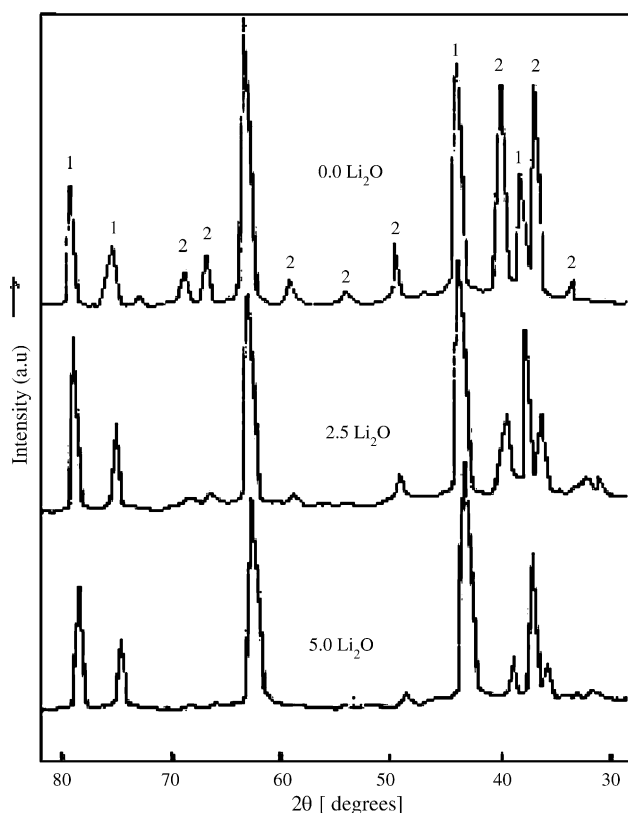


Fig. 2. X-ray diffractograms of pure and Li₂O-doped 0.2 CuO/MgO precalcined at 1073 K, lines (1) refer to MgO and lines (2) refer to CuO. The sensitivity of measuring the X-ray diffractograms given in this figure is different from that used in those given in Fig. 1.

might be attributed to an effective increase in the mobility of copper ions facilitating thus their diffusion in MgO lattice [14–16].

The dissolution of copper ions in MgO lattice yielding CuO/MgO solid solution having the formula $\text{Cu}_x\text{Mg}_{(1-x)}\text{O}$, where $0.048 < x < 0.200$. The formation of such a solid solution could be checked by determination of the lattice parameter, “ a ”, of MgO solvent and that in CuO/MgO solid solutions. In fact, the ionic radii of Mg^{2+} , Cu^{2+} and Cu^{1+} are 0.62, 0.69 and 0.96 Å, respectively [15]. So, the dissolution of copper ions in MgO lattice might be accompanied by an effective increase in the lattice parameter of MgO solvent. This has been successively done and the computed values of “ a ” of MgO were 4.2129, 4.2201, 4.2224, 4.2230 and 4.2242 Å for an individual MgO solid and those treated with 0.048, 0.091, 0.13, 0.17 and 0.2 MF CuO, respectively. The observed progressive increase in the “ a ” values of MgO by increasing the amount of CuO present in CuO/MgO solid solution might reflect a corresponding increase in the amount of copper ions that substitute some host Mg^{2+} of MgO lattice. This conclusion agrees with the results of XRD measurement previously mentioned in the present work.

3.2. Electrical properties of different investigated solids

3.2.1. DC electrical conductivity

The DC electrical conductivity of different pure solids precalcined at 1073 K was determined. Fig. 3a shows the variation of $\log \sigma_{\text{DC}}$ as a function of $1/T$ for CuO/MgO having different MF values of CuO. It can be seen from Fig. 3a that $\log \sigma_{\text{DC}}$ varies linearly as a function of $1/T$ for different investigated solids indicating one and the same conduction mechanism at temperatures between 303 and 573 K. Fig. 3b depicts the variation of $\log \sigma$ as a function of the values of the mole fraction, MF, of CuO measured at two different selected temperatures (303 and 573 K). The figure shows clearly that the conductivity increases progressively by increasing the MF value of CuO. σ_{DC} measured at room temperature increases from 6.3×10^{-12} to $9.9 \times 10^{-10} \Omega^{-1} \text{cm}^{-1}$ upon increasing the MF value of CuO from 0.048 to 0.2. This finding clearly indicates that this treatment resulted in a significant increase in the concentration of charge carriers (Cu^{2+} ions dissolved in MgO lattice). It is worth mentioning to report, here, that CuO and MgO behave as electric insulators [16], while CuO–MgO solid solution behaves as a semiconductor as being shown from their electrical conductivity. So, the presence of CuO as a separate phase and MgO (not containing any dissolved Cu^{2+} ions) did not contribute directly to the electrical conductivity of the system investigated. The higher the concentration of Cu^{2+} ions dissolved in MgO lattice the higher the concentration of charge carriers and the higher the electrical conductivity of the produced solid solution. It has been reported in the present work in the previous section that the greater the amount of CuO added to the investigated system the greater the amount of Cu^{2+} dissolved in MgO. So, the observed increase in the electrical conductivity values as a function of MF of CuO reflects the corresponding increases in the concentration of the Cu^{2+} (charge carriers) that can be dissolved in MgO lattice. It has been reported in a recently published work by one of the authors [12] that the electrical conductivity of CoO–MgO solid solution increases as a function of MF of CoO reaching to a maximum limit at MF = 0.1 and decreases by further increases the MF value above this limit. The decrease in the conductivity values upon increasing the MF value of CoO above 0.1 had been attributed to a possible decrease in the mobility of charge carriers (Co^{2+} ions dissolved in MgO lattice). In the present work, no maxima in the curve relating to electrical conductivity, σ , versus the MF of CuO through mole fraction ranged between 0.048 and 0.2. So, it seems that MgO can dissolve more CuO than CoO.

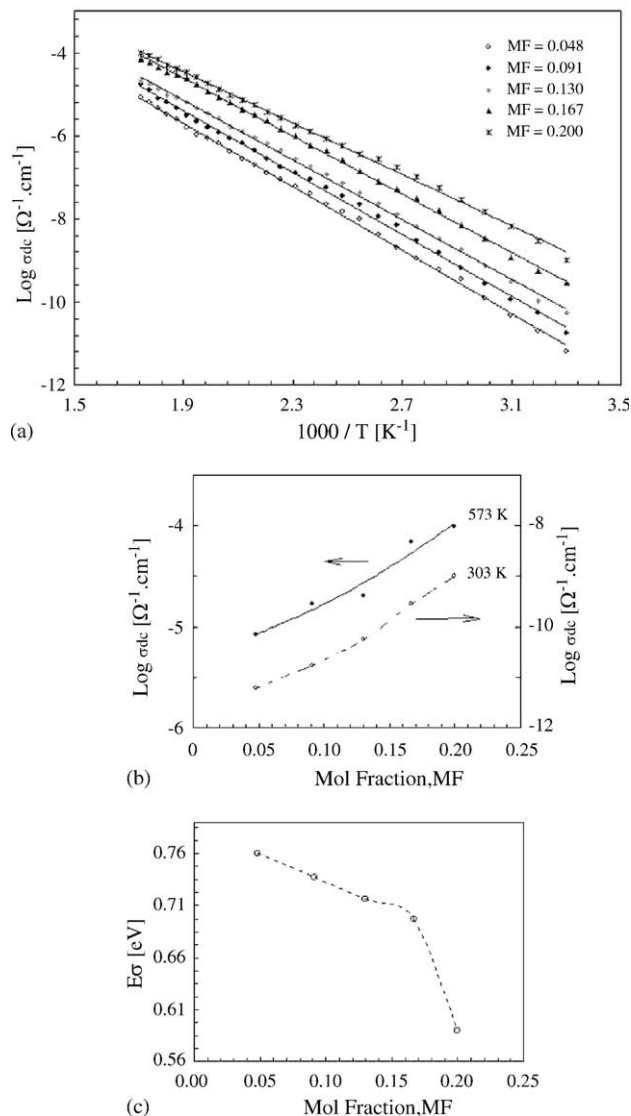


Fig. 3. (a) Variation of DC electrical conductivity with temperature for pure CuO/MgO solid solutions for the same samples shown in Fig. 1. (b) Mole fractional dependence of the DC electrical conductivity at temperatures 303 and 573 K, respectively, for the samples shown in (a). (c) The effect of mol fraction on the activation energy calculated from the samples shown in (a).

Fig. 3c depicts the variation of the activation energy, E_σ , as a function of mole fraction of CuO of various solids precalcined at 1073 K. It can be seen from this figure that E_σ decreases progressively by increasing the value of MF of CuO in the MF range 0.048–0.167. The increase of MF above this limit brought about further sudden drop in E_σ value. The increase in the MF of copper from 0.048 to 0.2 affected a decrease of about 0.2 eV in the E_σ value. It has been reported in the XRD section given previously in the present work that the increase in the MF of CuO up to 0.2 resulted in a significant increase in the amount of CuO that can be dissolved in MgO lattice, and the amount of CuO remained as a separate phase was negligibly small (cf.

Fig. 1). So, the observed significant decrease in E_σ as a function of MF of CuO (at MF = 0.2) can reflect a significant increase in the concentration of the charge carriers (Cu^{2+} ions dissolved in MgO lattice). This finding is in a good agreement with the results of XRD measurements given previously which showed clearly that the increase in the MF of CuO up to 0.2 resulted in an effective decrease in the peak height of diffraction peaks of CuO present as a separate phase.

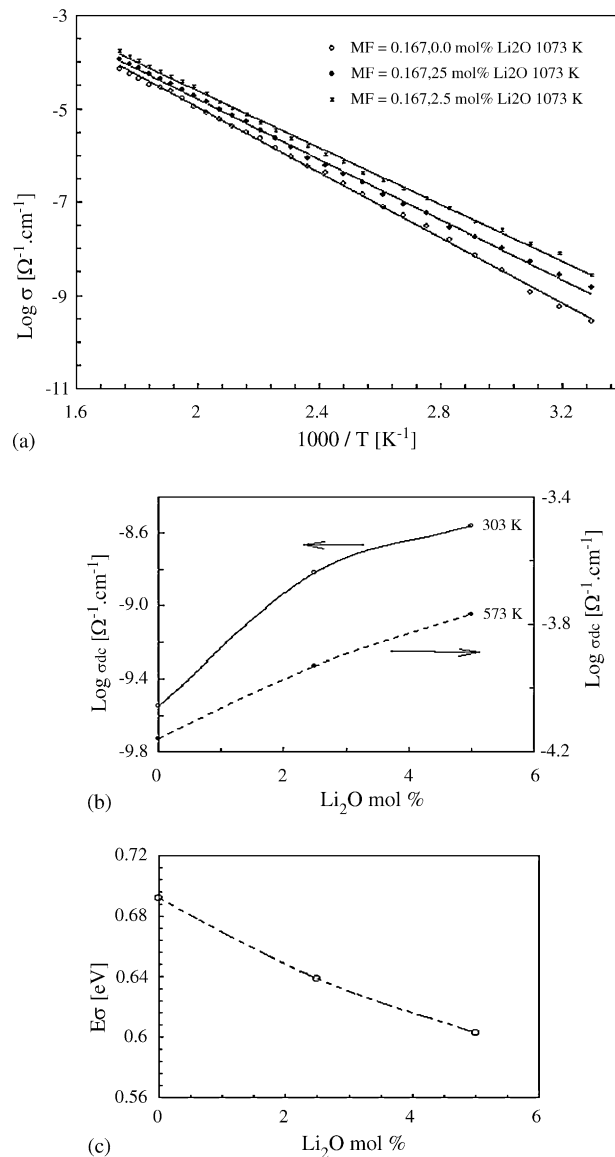


Fig. 4. (a) Variation of DC electrical conductivity with temperature for pure CuO/MgO solid solutions and those doped with 2.5 and 5.0 mol% Li₂O, for the same samples shown in Fig. 2 (MF = 0.167). (b) Li₂O doping effect on the DC electrical conductivity at temperatures 303 and 573 K, respectively, for the investigated samples shown in (a). (c) Li₂O vs. the activation energy calculated from the samples shown in (a).

The electrical conductivity of CuO/MgO solid solution having a mole fraction of 0.167 was treated with 2.5 and 5.0 mol% Li₂O and then subjected to heat treatment at 1073 K. Fig. 4a shows the variation of $\log \sigma_{DC}$ versus $1/T$ for pure sample and those doped with 2.5 and 5.0 mol% Li₂O. Similar to different pure CuO–MgO solid solutions, Li₂O-doped samples show conductivity that varies linearly with temperature showing one and same conduction mechanism of electrical conductivity within the temperature range 303–573 K. Fig. 4b shows the variation of $\log \sigma$ measured at 303 and 573 K as a function of dopant concentration. The electrical conductivity, σ_{DC} , measured at 303 K increases from 2.8×10^{-10} to $2.6 \times 10^{-9} \Omega^{-1} \text{cm}^{-1}$ upon doping with 5.0 mol% Li₂O.

Fig. 4c shows the variation of E_σ as a function of the amount of Li₂O added for solids precalcined at 1073 K. This figure shows clearly that E_σ decreases progressively as a function of the amount of dopant added. This finding might reflect an increase in the concentration of charge carriers involved in the electrical conduction of Li₂O-doped system. It has been shown in the XRD section given previously in the present work that Li₂O doping of the investigated system resulted in an effective increase in the amount of Cu²⁺ ions dissolved in MgO lattice (cf. Fig. 2); similar results have been reported in the case of Li₂O-doped NiO/MgO system [14].

3.2.2. AC electrical conductivity

Fig. 5 depicts the variation of room temperature AC electrical conductivity, σ_{AC} , versus the angular frequency, ω , for pure CuO/MgO solids solutions having different MF values of CuO and precalcined at 1073 K. It is clear from this figure that, $\sigma_{AC}(\omega)$ increases as the frequency increases. The real AC electrical conductivity $\sigma_{AC}(\omega)$ consists of two terms [17]

$$\sigma_{AC} = \sigma_1(T) + \sigma_2(\omega). \quad (1)$$

The first term, $\sigma_1(T)$, is the temperature-dependence or DC electrical conductivity, which is related to the drift mobility of the charge carriers and follows an Arrhenius relation. The second term, $\sigma_2(\omega)$, is the frequency-dependence. It is related to the dielectric relaxation caused by the localized electric charge carriers; it can be written as [17,18]

$$\sigma_2(\omega) = B\omega^n \quad (2)$$

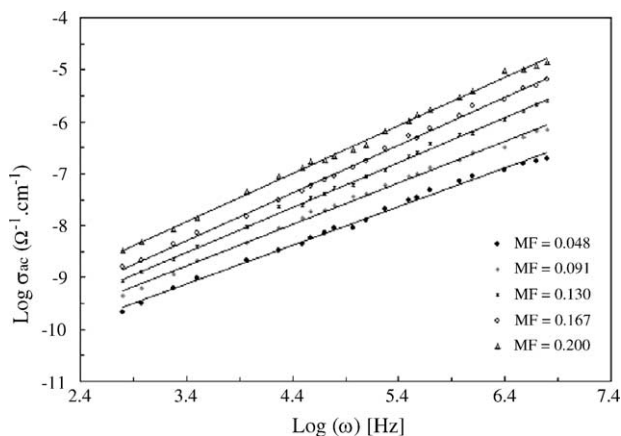


Fig. 5. Effect of $\log(\omega)$ on AC electrical conductivity, σ_{AC} , for pure CuO/MgO solid solutions, for the same samples shown in Fig. 1.

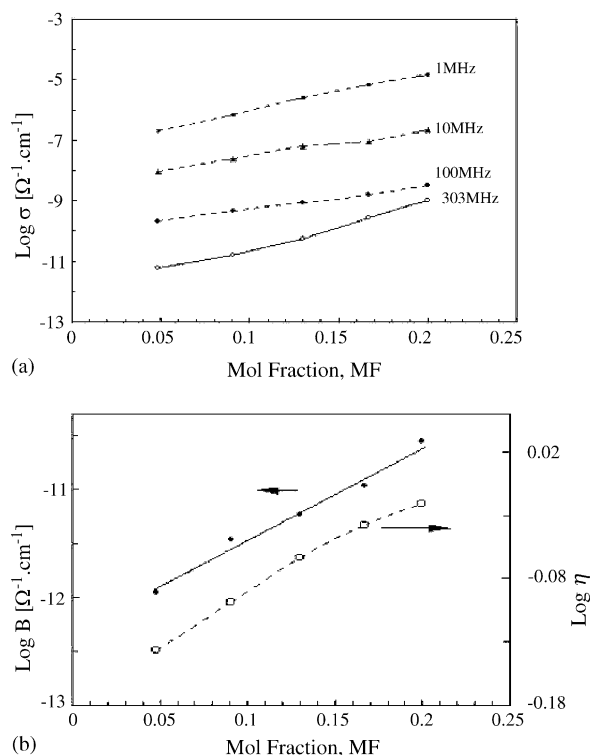


Fig. 6. (a) Mole fractional effect on the DC and AC electrical conductivity and (b) mole fractional effect on the parameters, n and B , calculated from Fig. 5, respectively.

where B and n are the composition-dependent parameters, n is dimensionless whereas B has the electrical conductivity units ($\Omega^{-1} \text{cm}^{-1}$) and $\omega = 2\pi f$ is the angular frequency. It was reported that n has values between 0 and 1 [17]. For $n = 0$, the electrical conductivity is frequency-independent or DC conduction but, for $n \leq 1$, the conduction is frequency-dependent. The values of n in the present work were found in the range 0.702–0.955 or in frequency-dependence range. Fig. 6a depicts the effect of mole fraction, MF, on the DC and AC electrical conductivity, σ_{DC} (at 303 K) and $\sigma_{\text{AC}}(\omega)$ at different selected frequencies. The figure shows that the DC electrical conductivity is smaller than the real AC electrical conductivity. This could be related to the fact that the $\sigma_1(T)$ is a part of $\sigma_{\text{AC}}(\omega)$ according to Eq. (1). The figure shows also that both σ_{AC} and σ_{DC} increase on increasing the mole fraction. Fig. 6b shows the variations of the parameters n and B (determined from Fig. 5) versus the MF values, where both n and B increase with increasing the amount of Cu^{2+} ions dissolved in MgO lattice. The increase in the amount of MF resulted in an increase of the AC electrical conductivity (Fig. 5) and, according to Eq. (2), the values of the exponents n and B (which has conductivity units) must also increase.

Graphical representation of frequency-dependence of the real dielectric constant, ϵ' , and dielectric loss, $\tan \delta$, for pure CuO/MgO solid solutions precalcined at 1073 K are shown in Figs. 7 and 8, respectively. Both ϵ' (Fig. 7) and $\tan \delta$ (Fig. 8) decrease with increasing the angular frequency. Fig. 8 for $\tan \delta$ shows a steep relaxation appearing for all the investigated samples within the frequency range

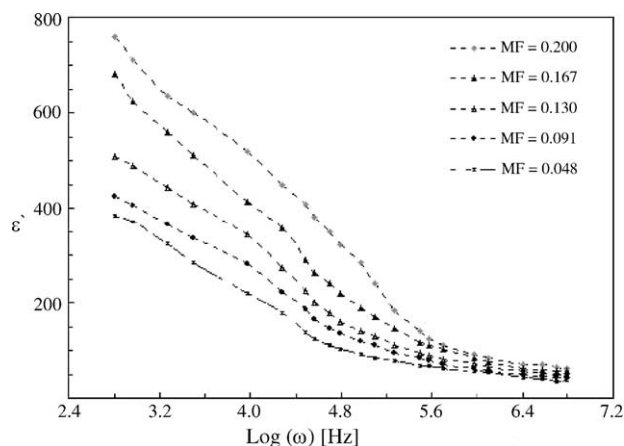


Fig. 7. Effect of $\log(\omega)$ on ϵ' for the samples shown in Fig. 1.

5–8 kHz. This steep relaxation is slightly shifted towards higher frequency range with increasing the MF value. The relaxation frequency $f_{\text{relx.}}$ determined from Fig. 8 was used to calculate the corresponding relaxation time, τ_D (where $\omega_D \tau_D = 1$). The calculated values of τ_D were found to vary within the range 2×10^{-5} to $32 \times 10^{-5} \text{ s}^{-1}$ for the samples having different MF values. These values reflect a limited change in the mobility of charge carriers in different investigated solid solutions. So, the observed increase in the electrical conductivity of the system investigated as a function of MF of CuO is directly related to the corresponding increase in the concentration of charge carriers.

It is worth mentioning, to report here, that the effect of frequency on σ_{AC} (Fig. 5), ϵ' (Fig. 7) and $\tan \delta$ (Fig. 8) had been studied theoretically [19] and verified experimentally for various mixed oxide systems [12,20]. The simplest expression predicted that the real AC electrical conductivity, σ_{AC} ,

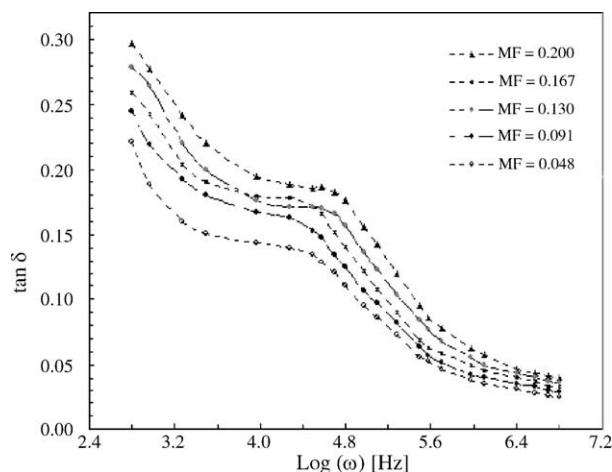


Fig. 8. Effect of $\log(\omega)$ on $\tan \delta$ for the samples shown in Fig. 1.

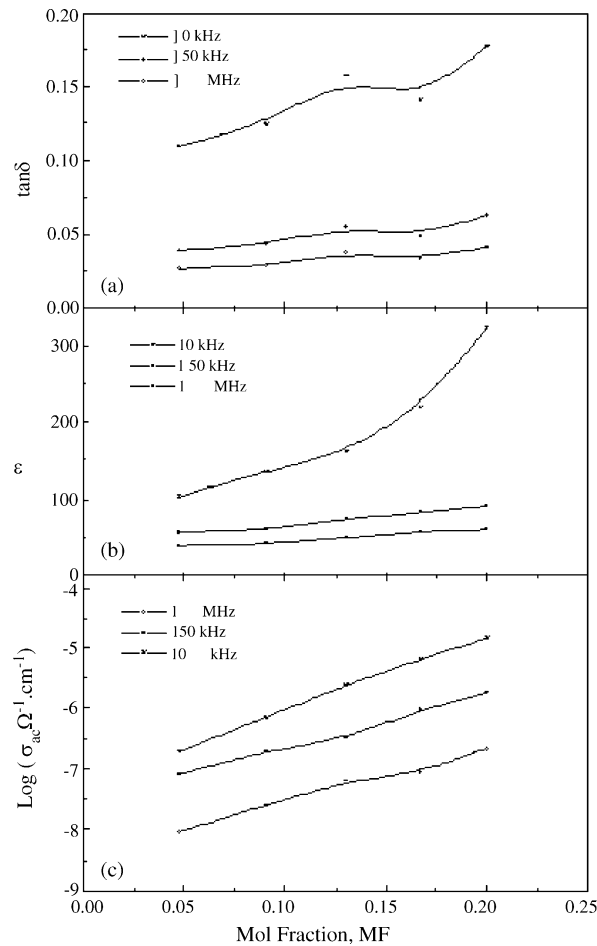


Fig. 9. Mole fractional dependence of (a) σ_{AC} , (b) ϵ' and (c) $\tan \delta$ at different selected frequencies.

is directly proportional to the angular frequency, ω , while ϵ' and $\tan \delta$ is inversely proportional to ω [17].

$$\epsilon' = \frac{4\pi\sigma_{AC}}{\omega \tan \delta} \quad (3)$$

The mole fraction dependence of σ_{AC} , ϵ' and $\tan \delta$ is shown in Fig. 9a–c, respectively, at selected frequencies. It was found that σ_{AC} , ϵ' and $\tan \delta$ increase as the MF increases. This is another reason supporting the possible increase of the charge carriers concentration with increasing the MF value as mentioned before.

The variation of $\log \sigma_{AC}$ as a function of $\log(\omega)$ for pure and LiO_2 -doped solids precalcined at 1073 K, not given, shows that σ_{AC} increases linearly as a function of ω and also by increasing the dopant concentration. The observed increase in the magnitude of σ_{AC} due to increase in the amount of LiO_2 added could be attributed to a possible increase in the mobility of charge carriers. Previous works have been reported and showed that Li_2O doping much enhanced the mobility of a big variety of solids such as $\text{MoO}/\text{Al}_2\text{O}_3$, $\text{V}_2\text{O}_5/\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3/\text{NiO}$, $\text{CoO}/\text{Fe}_2\text{O}_3$ and $\text{CuO}/\text{Fe}_2\text{O}_3$ [12,20,21].

4. Conclusions

The following main conclusions may be derived from the obtained results:

- (1) MgO solid dissolved increasing amounts of CuO forming $\text{Cu}_x\text{Mg}_{(1-x)}\text{O}$ solid solutions, where $0.05 < x < 0.20$. The fraction “ x ” increases by increasing the precalcination temperature (673–1073 K) of the investigated solids and also by increasing the amount of CuO added.
- (2) Li_2O doping of the investigated system enhanced the dissolution of CuO into MgO lattice.
- (3) The σ_{AC} , σ_{DC} , ε' and $\tan \delta$ were found to increase with increasing the amount of Cu^{2+} ions (charge carriers) dissolved in MgO lattice. E_σ decreases as a function of the MF (mole fraction of CuO). These results were discussed in terms of an effective progressive increase in charge carrier concentration.
- (4) Li_2O doping of CuO/MgO followed by calcination at 1073 K resulted in a measurable increase in the values of σ , ε' and $\tan \delta$ with subsequent decrease in the E_σ value.

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