Dielectric Properties of CuO Nanoparticles Prepared by Precipitation Method

JIJI KOSHY[1], SOOSEN SAMUEL[1], ANOOP CHANDRAN[1], POURNAMI VIJAYAN[1], K C GEORGE[1*]

[1]Department of Physics, SB College, Changanacherry, Kerala, India
[*]Corresponding author: drkcgeotge@gmail.com

Abstract

In spite of the high performance of dielectric materials in electronic industry, their strong temperature dependence and high loss creates problems in capacitive applications. Here we reports weak temperature dependence and very low loss factor of copper oxide nanoparticles. The copper oxide nanoparticles were prepared by a precipitation method. X-ray diffraction(XRD), scanning electron microscope (SEM) and Transmission electron microscope(TEM) were used to analyze the product. The dielectric properties of copper oxide nanoparticles have been investigated in the frequency range 100 Hz-1 MHz and in the temperature range 303K-463 K. The result revealed that copper oxide nanoparticles have high dielectric constant with weak temperature and frequency dependence. which makes them useful in the application of miniaturization of electronic devices It was also found that the high dielectric constant is due to the interfacial barrier layer capacitance (IBLC) effect. The dielectric constant and the loss factor decreased with increasing frequency of the applied field.

Keywords: CuO nanoparticles; dielectric properties; X-ray diffraction.

Introduction

Metal oxide nanomaterials have attracted increasing attention due to their physical properties arising from quantum confinement. Due to their special shape, composition, chemical and physical properties, metal oxide nanostructures are the focus of current research efforts in nanotechnology. They have now been widely used in many areas such as catalysis, sensors, transparent and conducting films and electro-optical devices **[1].** The electrical properties of nanomaterials are differing from those of their bulk counterparts. The high surface to volume ratio of grains, small size, enhanced contribution from grains and grain boundaries, quantum confinement of charge carriers, band structure modifications and defects in grains are some of factors that contribute to the electrical properties of nanostructured materials.

In recent years, high dielectric constant materials with low dielectric loss have been attracting much attention in wireless communication industry. There are large number of high dielectric constant materials like CCTO ceramic materials, metal doped NiO ceramics, cubic perovskite related ceramics etc**[2-4].** CuO is an important high dielectric constant p-type semiconductor with band gap in the range 1.8 eV-2.5 eV. They are suitable material for high efficiency solar cells because their band gap is close to the ideal energy gap for solar cells **[5-6].** Copper oxide materials are widely used for various applications such as magnetic storage media **[7],** solar cell technology **[8],** field emission **[6],** application in lithium ion batteries **[5],** gas sensing **[9],** catalysis and, magnetic resonance imaging[**10].** Various methods have been proposed to produce CuO nanomaterials. Some important methods are electrodeposition **[11],** hydrothermal**[12],** sputtering[**13],** chemical route**[14],** thermal evaporation **[15],** and precipitation method **[16].** Precipatation method attracts much interest because of its good yield and cost effective method for large scale production. Copper oxide nanostructures have attracted much attention, as they are very simple compound and easy to prepare in pure form.

The high dielectric constant is an inherent property of the material and study about this opens to wide application in electronic industry. The dielectric measurements can explain the underlying mechanism of relaxation in semiconductor materials. The aim of the present work is to explore the dielectric properties of copper oxide nanoparticles. In this work we studied the temperature and frequency dependence of dielectric constant. Also we discussed the dielectric loss of copper oxide nanoparticles with the help of hopping model.

To understand the absorption and dispersion in a dielectric material we were used the semi empirical complex Cole-Cole equation **[17].**

$$\varepsilon^* = \varepsilon' - i\varepsilon$$

$$= \varepsilon_\infty \left[\frac{\varepsilon_s - \varepsilon_\infty}{(1 + i\omega\tau)} \right] \qquad (1)$$

The real and imaginary part of the dielectric permittivity are written as

$$\varepsilon' = \varepsilon_\infty + \left(\frac{\Delta s'}{2} \right) \left\{ 1 - \frac{Sinh(\beta z)}{\left[Cosh(\beta z) + Cos\left(\beta \frac{\pi}{2} \right) \right]} \right\} \qquad (2)$$

$$\varepsilon'' = \left(\frac{\Delta s'}{2} \right) \left\{ 1 - \frac{Sinh(\beta \frac{\pi}{2})}{\left[Cosh(\beta z) + Cos\left(\beta \frac{\pi}{2} \right) \right]} \right\} \qquad (3)$$

where $z = \ln\left(\omega\tau\right)$, $\Delta\varepsilon' = \varepsilon_s - \varepsilon_\infty$, ε_∞ is the dielectric permittivity at high frequency, ε_s is the static dielectric permittivity, ω is the angular frequency, τ is the mean relaxation time, and $\beta = 1 - \alpha$

where α is a measure of distribution of relaxation time.

The dielectric loss of a dielectric material corresponds to the absorption of electrical energy when the material subjected to an ac field. The dielectric loss can be defined as the imaginary component of the complex dielectric susceptibility (χ'') is given by,

$$\chi(\omega) = \chi'\left(\omega\right) - \iota\chi''\left(\omega\right) \qquad (4)$$

The experimentally observed frequency dependence of dielectric loss can be expressed by the following empirical relation

$$\chi'' = \Lambda\left(T\right)\omega^{n-1} \qquad (5)$$

where $\Lambda\left(T\right)$ is weakly temperature dependent function and the value of n lies in the range $0 < n < 1$. The frequency dependence of all dielectric solids follows this universal law regardless of their physical and chemical nature. The traditional approach to dielectric loss is based on ideal Debye polarization in which the complex permittivity is given by

$$\chi(\omega) = \chi'\left(\omega\right) - \iota\chi''\left(\omega\right)$$

$$= \left[\varepsilon\left(\omega\right) - \varepsilon_\infty\right] / \varepsilon_0$$

$$= \left(1 + i\omega\tau\right)^{-1}$$

where $\varepsilon\left(\omega\right)$ is the complex dielectric permittivity at a frequency ω, ε_∞ is the limiting high frequency value of ε, ε_0 is the permittivity of free space and τ is the relaxation time. This produces a symmetric Debye loss peak at $\omega\tau = 1$ on a logω plot. But most of the solids does not obey the above relation, they deviates from ideal nature. Also the ratio of energy lost per cycle to the energy stored per cycle is independent of frequency.

Experimental

Highly purified Highly purified copper acetate [$Cu(CH_3COO)_2$] and glacial acetic acid [CH_3COOH] were used for the preparation of CuO nanoparticles. 300 mL of 0.02 M copper acetate aqueous solution was mixed with 1mL glacial acetic acid in a 500 mL beaker. The resulting solution was heated to 100 °C and NaOH was rapidly added until the pH of the mixture reached 6-7. The black precipitate formed was cooled to room temperature and centrifuged and washed well with distilled water and ethanol. The product was dried in air at room temperature and then ground well. The obtained powder was used for the analysis.

The X-ray diffractometry analysis of the obtained product was done using a Bruker AXS D8 Advance X-ray diffractometer with monochromated Cu-Kα radiation in the angular range 20^0-70^0 of 2θ. The morphology of the as prepared samples were examined using a FEI Quanta FEG 200 high resolution scanning electron microscope (HRSEM) and a Philips CM200 transmission electron microscope (TEM). For dielectric measurement the as synthesized product was shaped into cylindrical pellets of 10 mm diameter and 1 mm thickness in a hydraulic press by applying a pressure of 4.5 tons for 3 min. The prepared pellet was used as a dielectric medium by using silver pellets on both sides of the pellet as electrode. The frequency and temperature dependence of dielectric constant and dielectric loss were studied using a Hioki 3532-50 LCR meter in the temperature range of 303–463 K within the frequency range of 100 Hz – 1 MHz.

3. Results and discussion

The morphology and size of the nanoparticles were analyzed by SEM and TEM as shown in Figures 1 and 2. Figure 1 shows that the product consisted of nanoparticles with spherical shape, while Figure 2 clearly shows that the average size of the obtained product was about 6-8 nm.

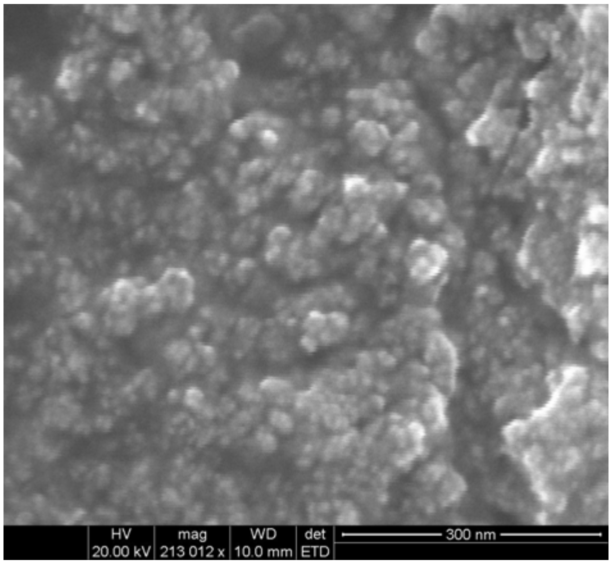

Fig. 1. The SEM image of CuO nanoparticles.

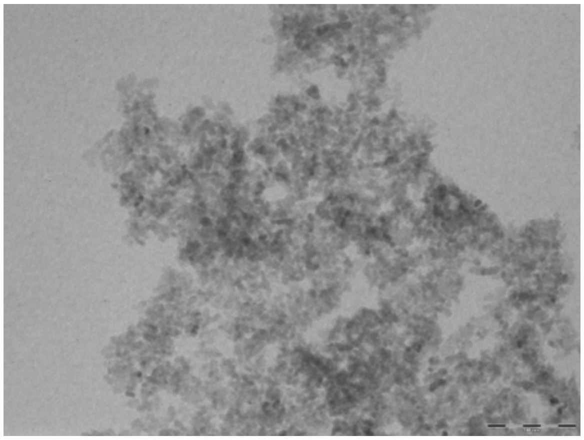

Fig. 2.The TEM image of CuO nanoparticles.

Figure 3 displays the XRD pattern of the as-prepared CuO nanoparticles. All the peaks of the samples in the XRD patterns were indexed based on the JCPDS card of CuO (JCPDS 80-1268) with monoclinic structure. The broadening of the peaks indicates the small size of the copper oxide nanoparticles. The average crystallite size of the nanoparticles was calculated using Scherrer's equation.

$$L = \frac{0.94\lambda}{\beta \cos\theta} \qquad (6)$$

where L is the average crystallite size, λ is the X-ray wavelength (1.5405 A°) and β is the full width at half maximum in radians **[18].** The average crystallite size of CuO nanoparticles was calculated to be 8 nm, in strongly agreement with that obtained from TEM observations.

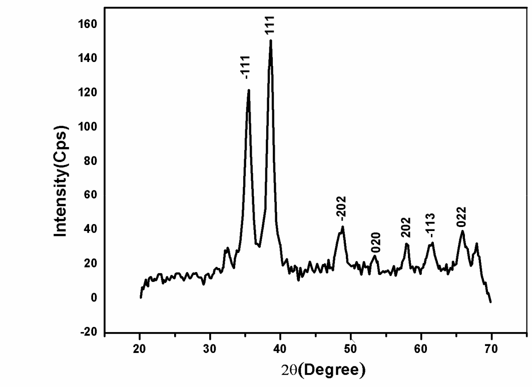

Fig. 3.XRD pattern of CuO nanoparticles

The variation of real part of dielectric constant with frequency at different temperature for copper oxide nanoparticles is shown in **figure 4.** The figure reveals the fact that the dielectric constant of CuO nanoparticles have weak frequency dependence at various temperatures. In the presence of an alternating field, nanomaterials possess different types of polarization, namely space charge polarization and rotation polarization owing to the presence of defects and large numbers of interfaces**[19].** These polarizations are closely related to the prevailing dielectric behavior of the nanomaterials. At low frequencies, the orientation of space charges creates a dipole moment in the direction of the field, which causes the space charge polarization, and the rotation of the existing dipoles causes the rotational polarization. Moreover, at low frequencies the dipoles are able to align with themselves, resulting in a total polarization and hence high dielectric constant.

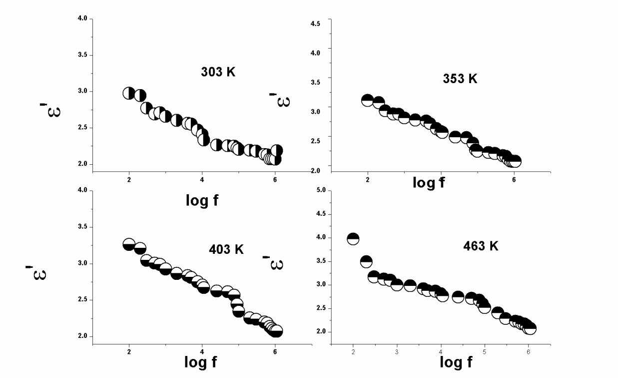

Fig. 4. The Variation of real part of dielectric constant with frequency at various temperatures.

When the frequency increases gradually, the relaxation time becomes low and the dipoles begin to lag the field so that dielectric constant decreases. At higher frequencies the dipoles can no longer follow the field, resulting in a decrease in polarization, which causes the dielectric constant to drop to a lower value. The value of the dielectric constant of CuO nanoparticles are much higher than that of bulk CuO. This is because the interfacial polarization of the CuO nanoparticles plays a significant role in their dielectric properties, which cannot occur in the bulk CuO. Moreover, copper oxide materials have micro quantity amount of Cu^{3+} ions which makes excess of holes in the material. The conduction process taken place by the hopping of holes between Cu^{2+} and Cu^{3+}. This hopping process makes more Cu^{3+} around Cu^{2+} and which makes copper oxide grains to be enriched with Cu^{3+}[20]. Here the grain boundaries act as an insulating wall which results an array of boundary barriers and grains ie, an internal barrier layer capacitance effect (IBLC), resulting a high dielectric value.

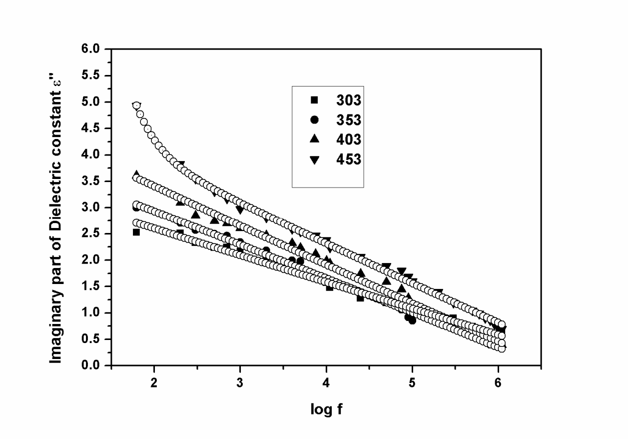

Fig. 5.Variation of imaginary part of dielectric constant with frequency at various temperatures.

Figure 5 shows the variation in the imaginary part of dielectric constant of CuO nanoparticles with frequency. The value of imaginary part of dielectric constant decreases with increasing frequency. We obtained the values of α, β and τ by fitting the experimental values with Cole- Cole equation. The resulting fits are also depicted in figure 5 and shows the experimental values are in good agreement with the theoretical values. The parameters obtained through the fitting are listed in Table 1. The variation in α reflects the fact that the dielectric relaxation behavior of the CuO nanoparticles deviates from Debye behavior. The value of β increased with temperature and the value of α decrease correspondingly. Thus, when the temperature was increased the dielectric relaxation behavior of the nanoparticles became very close to Debye behavior. Moreover, the dielectric relaxation time decreased with the increase in temperature.

To study the thermal effect on dielectrirc constant, we analyzed the temperature dependent dielectric constant at different frequencies as shown in figure 6 and 7. Figure shows a weak temperature dependence of dielectric constant. However at low frequencies there is slight increase in dielectric constant in accordance with the increase of temperature. Hence thermally activated mechanism and size induced grain and grain boundary effect also contribute to the dielectric enhancement.

Table 1. Parameters obtained by fitting the experimental data to the Cole-Cole equation at different temperatures.

Temperature (K)	β	α	τ(s)
353	0.646	0.354	0.00086
403	0.65	0.35	0.00049
453	0.661	0.339	0.00018

Also when temperature increases, the carriers attain enough energy and got the capacity to respond to the applied field. Thus this contribution makes an enhancement in dielectric value.

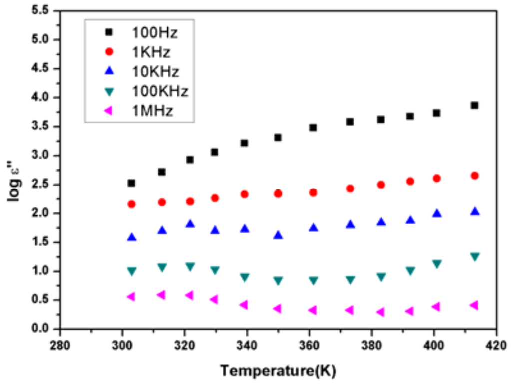

Fig.6. Variation of real part of dielectric constant with temperature at various frequencies.

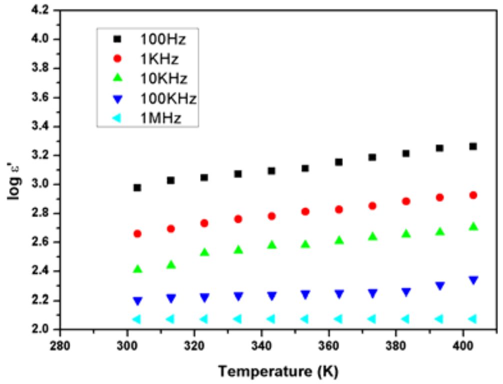

Fig. 7. Variation of imaginary part of dielectric constant with temperature at various frequencies.

The loss tangent (tan δ) value of copper oxide nanoparticles was very small (0.35) at room temperature. The variation of tan δ with respect to frequency is shown in **figure 8**. The dielectric loss tangent increased with temperature and decreased with increasing frequency. The dielectric loss attains a constant value at higher frequencies and exhibited frequency independent behavior. According to equation (6) the variation of loss with frequency must be flat in nature. Here loss becomes flat only at higher frequencies. The flat loss in CuO nanoparticles can be explained by the hopping model **[21].** The main feature of this model is that, it has a general applicability to a wide range of semiconducting and dielectric system. According to this model, the flat loss of CuO nanoparticles is due to the electronic hopping ie, the space charge hopping, which is due to the presence of low mobility carriers in the material. The hopping process occurs between two localised levels, each level is defined uniquely in space and in charge. At higher frequencies the space charge polarisation occurs very rapidly. But at lower frequencies the polarization of the medium responds relatively slowly in comparison with the tunneling time. This produces strong conductivity dispersion at low frequency region of CuO nanoparticles. This is another reason for the flat loss at lower frequency region for CuO nanoparticles. On applying varying electric field to the material, it shows an upper limit frequency of about 10 KHz, the equilibrium transiton frequency 1/τ, beyond this limit the polarization would cease to respond the applied field. Hence the space charge polarization occurs rapidly in this region. At lower frequency region the expected nature is that the loss must be tend to zero as ω goes to zero. But this is not happens in CuO nanoparticles because the onset dc conduction dominates the dielectric loss. The dielectric loss tangent of the present CuO nanoparticles was very small, which makes the material useful for HF, VHF, and microwave frequency applications.

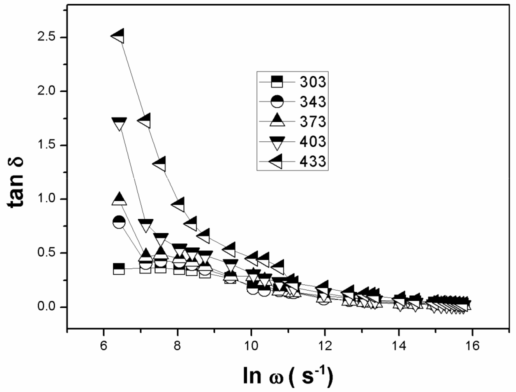

Fig. 8. Variation of loss tangent with respect to frequency at various temperatures.

Conclusion

The dielectric properties of CuO nanoparticles were investigated successfully within the frequency range of 100 Hz – 1 MHz and in the temperature range 303–463 K. The experimental results showed that the copper oxide nanoparticles have high dielectric constant, which is due to IBLC effect. It was also found that CuO nanoparticles exhibit non- Debye relaxation and loss tangent of the nanoparticles decreases with the increase in frequency.

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