Structural, microstructural, magnetic and dielectric properties of Fe₂O₃ modified CuO composite

ABSTRACT

1-xCuO-xFe₂O₃ composites where x = 0.05, 0.10, 0.15 and 0.20 have been synthesized using ball milling mixing method. The structural, microstructural, elemental analysis, magnetic and dielectric properties of prepared ceramic composites have been investigated using the advanced characterization techniques. The influence of sintering temperature on structural, dielectric and magnetic properties have been investigated. The structural phase analysis has been carried out using X-ray diffraction and effect of sintering temperature clearly depicted in graphs. As increase in sintering temperature from 700 °C to 900 °C, diffraction peaks shift towards higher angles, indicating changes in crystal lattice parameters and potential crystal structure distortions. However, after careful consideration of the XRD results and a comprehensive analysis, we concluded that a synthesis temperature of 700 °C is preferable. The SEM micrographs show an increase in grain size of ceramic composites as concentration of Fe₂O₃ increases. The Energy Dispersive X-Ray spectroscopy affirms presence of elements according to stoichiometric proportion whereas S-shaped M vs. H. loop confirms presence of magnetic ordering. Variation of Real (ε') and Imaginary (ε'”) parts of dielectric permittivity with frequency shows general dielectric behavior.

Keywords: Composites, Ball milling mixing method, Dielectric properties, Magnetic properties

1. INTRODUCTION

Semiconducting nano crystalline materials draw attention for their vast usage in microelectronics industry due to their small band gap. Transition metal oxide (CuO) based semiconductor having small band gap (1.2-1.5 eV) become important candidates for their usage in digital as well as in electronic industry. CuO is unique and important for wide range applications such as including photochemical cells, gas sensors, biosensors, solar cells, and photocatalytic properties. Current research on pure and modified CuO provides significant potential in realm of microelectronics because of its extraordinarily high dielectric constant. It has been reported in literature that synthesis methods impact on particle size as well as on dielectric behavior of CuO.

These are so many synthesis methods to synthesize CuO reported in literature such as sol-gel and sono-chemical method, thermal decomposition method and precipitation method [1-8].

According to Zhu et. al.’s investigation into structural characterization of CuO nano-particles created by microwave irradiating copper (II) acetate and sodium hydroxide as starting material. The particles have a regular shape and limited size distribution as well as high degree of purity. Kim et al. investigated structural, optical, and electrical characteristics of CuO nano-particles with a monoclinic structure phase [9]. From x-ray photoelectron spectroscopy profile, O is 1s and Cu 2p peaks corresponding to the CuO nano-particle were seen. The band gap of CuO nano-particle at room temperature was discovered to be 3.63eV [9].

In this paper, we report structural, elemental, magnetic as well as dielectric properties of Fe₂O₃ modified CuO composites (1-xCuO-xFe₂O₃ where x=0.05, 0.10, 0.15 & 0.20) synthesized using Ball mixing method. The major aspect of choosing Fe₂O₃ is modification in magnetic and dielectric properties of CuO ceramics.
2. EXPERIMENTAL

1-xCuO-xFe₂O₃ composites where \( x = 0.05, 0.10, 0.15 \) & 0.20 have been successfully synthesized using ball mixing method. For synthesis of composites, CuO & Fe₂O₃ mixed in required stoichiometric proportion. The CuO and Fe₂O₃ purchased from Sigma Aldrich. The weighed powders of oxides (CuO & Fe₂O₃) transferred in a plastic bottle contains zirconia ball and ball milled in high-energy ball milling machine for 12 hours. After 12hours, mixture of powder and acetone has been taken out from bottle and heated at 100 °C for ~1 hour so that acetone get evaporated and powder dried. Dried powder mixed with polyvinyl alcohol (2%wt) as binder and pressed into circular disc (Diameter ~ 12 mm, Thickness ~ 1 mm and Pressure ~ 1.5 ton).

The pallets have been sintered at 700° & 900°C for 2 hours for optimization of sintering temperature at which sample exhibits enhanced magnetic and dielectric properties. The presence of both phases (Structural Phase of CuO & Fe₂O₃) confirmed from X-Ray diffractograms whereas morphological analysis (Grain Growth as well as Grain Size) studied from SEM micrographs. The presence of elements as per stoichiometric proportion mentioned above confirmed using Energy Dispersive X-ray Dispersive spectroscopy whereas elemental mapping shows uniform distribution of different different metal ions. The density of sintered pellet was measured using lab made set up based on Archimedes principle. The magnetic ordering has been confirmed using Vibrating Sample Magnetometer. The \( \varepsilon', \varepsilon'' \) & \( \sigma_{ac} \) vs. Frequency measurements were carried out using impedance analyser.

3. RESULTS AND DISCUSSION

Room temperature structural phase formation has been studied using x-ray diffractograms of CuO, Fe₂O₃ & 1-xCuO-xFe₂O₃ composites where \( x = 0.05, 0.10, 0.15 \) & 0.20 sintered at 700°C and 900°C shown in figure 1. Sharp high intensity diffraction peaks reveal crystalline nature of prepared ceramic composites whereas noise in background data of Fe₂O₃ results due to fluorescence effect. The diffraction data (diffraction peaks) have been matched with reported JCPDS cards which gives crystallographic information of structural phase of CuO and Fe₂O₃.

![Figure 1. X-Ray Diffraction data of 1-xCuO-xFe₂O₃ where (a) = Sintered at 700°C & (b) 900°C for CuO, Fe₂O₃ and x = x = 0.05, 0.10, 0.15 & 0.20 ceramic composites](image-url)

_Slika 1. Podaci difrakcije rendgenskih zraka 1-xCuO-xFe₂O₃ gde je (a) = sinterovano na 700°C & (b) 900°C za CuO, Fe₂O₃ i x = x = 0.05, 0.10, 0.15 i 0.20 keramičkih kompozita_
The experimental data has been indexed according to JCPDS card no 80-1917 (ICDS # 069750) represent for Monoclinic phase space group Cc No. 9 for pure CuO and no. 73-2234 (ICDS # 024791) reports Hexagonal phase space group $\overline{R}3c$ for Fe$_2$O$_3$. No diffraction peak left unassigned shows that CuO and Fe$_2$O$_3$ exhibits its own phase reported in literature. In graphs, for $x = 0.05 \& 0.10$, diffraction peaks quiet well overlapped at both temperatures shows that sample exhibits similar phases but as 'x' increases up to $x = 0.15$ to 0.20, diffraction peaks shift towards higher $2\theta$ shows change in structural phase with sintering temperature and maximum in $x = 0.20$. This change in structural phase may result due to strain produced with increasing sintering temperature or increasing concentration of Fe$_2$O$_3$ in ceramic composites. Therefore it has been concluded that sample sintered at 700 °C demonstrated structural phase of CuO (Monoclinic Phase).

The microstructural analysis of CuO, Fe$_2$O$_3$ & 1-xCuO-xFe$_2$O$_3$ composites where $x = 0.05$, 0.10, 0.15 & 0.20 sintered at 700°C has been studied from FESEM micrographs and shown in figure 2. Micrographs clearly expresses presence grains with irregular in shape, size and randomly orientated with proper grain growth. All the micrographs were recorded using in-lens detector at 20k magnification & 10 kV accelerating voltage. The increase in grain size with increasing 'x' shows increase in grain growth with least porosity. The grain size has been calculated using Smart SEM software equipped with FESEM. The grain size increases from ~1.46 μm to ~2.26 μm as ‘x’ increases from 0.05 to 0.20. The density has also been increased from from 6.98 to 7.38 g/cm$^3$, respectively as ‘x’ increases.

The presence of elements as per stoichiometric formula have been confirmed from Energy Dispersive X-ray spectroscopy (EDS) analysis. The EDS spectra of pure CuO, Fe$_2$O$_3$ and 0.8CuO-0.2Fe$_2$O$_3$ ceramic composite sintered at 700 °C have been shown in Figure 3. The Binding Energy vs. Intensity electro micrographs shows that peak corresponding to 8.04 eV, 0.542 & 6.39 eV of Kα evident for presence Cu & O in CuO and Fe and O in Fe$_2$O$_3$. The presence of Cu, O & Fe in wt% as well as in mol% has been shown in Table shown in figure 4.
Figure 3. Energy Dispersive Spectral Micro Graphs of CuO, Fe$_2$O$_3$ and 0.8CuO-0.2Fe$_2$O$_3$ ceramic composites sintered at 700°C

Slika 3. Energetske disperzivne specmakralne mikrografije CuO, Fe$_2$O$_3$ i 0.8CuO-0.2Fe$_2$O$_3$ keramičkih kompozita sinterovanih na 700°C

Figure 4. Weight (%) and Mol (%) of CuO, Fe$_2$O$_3$ and 0.8CuO-0.2Fe$_2$O$_3$ ceramic composites sintered at 700°C

Slika 4. Težina (%) i mol (%) CuO, Fe$_2$O$_3$ i 0.8CuO-0.2Fe$_2$O$_3$ keramičkih kompozita sinterovanih na 700°C
The distribution of different metal ions as per stoichiometric formula. Elemental mapping in selected area has been carried out. The elemental mapped electron micrographs of CuO, Fe₂O₃ & 0.8CuO-0.2Fe₂O₃ ceramic composites sintered at 700 °C shown in figure 5. The different colours have been assigned to different metal ions. The micrographs with all coloured dot show that all metal ions distributed uniformly. The red colour assigned to Cooper (Cu) whereas Oxygen (O) and Iron (Fe) green and yellow colour. The micrograph in which all colour represents uniformly presence of all metal ions in selected area.

Figure 5. Elemental Mapping along with mixed micrograph of 0.8CuO-0.20Fe₂O₃ ceramic composites sintered at 700°C

Slika 5. Elementarno mapiranje zajedno sa mešovitim mikrografijom 0.8CuO-0.20Fe₂O₃ keramičkih kompozita sinterovanih na 700°C

Magnetization vs. Magnetic Field measurements of CuO, Fe₂O₃ & 1-xCuO-xFe₂O₃ composites where x = 0.05, 0.10, 0.15 & 0.20, sintered at 700°C have been shown in figure 6. The magnetic data clearly reveal that (a) Small remnant magnetization value and narrow coercivity of CuO results for superparamagnetic or week magnetic ordering as already reported (b) magnetic hysteresis of Fe₂O₃ sintered at 700 °C magnetically ordered behavior. The hysteresis in 1-xCuO-xFe₂O₃ samples sintered at 700 °C reveals dominance of ferromagnetic ordering over antiferromagnetic (Presence of Both Ferromagnetic as well as antiferromagnetic confirmed from unsaturated hysteresis curve). Such kind of behavior (Presence of both Ferromagnetic and Antiferromagnetic ordering) may be due to oxygen vacancies created which results in pinched hysteresis loop. The remnant magnetization (M_r) of prepared ceramic composites increases from 0.068 emu/g for x = 0.05 to 0.118 emu/g for x = 0.15 and then decreases to 0.099 emu/g for x = 0.20 whereas coercivity also varies from 393.8 Oe for x = 0.05 to 438.6 Oe for x = 0.15 and then decreases to 296.2 Oe for x = 0.20. Since CuO is exhibits weakly magnetic or superparamagnetic behavior. This increase in remnant magnetization may result due to increase in creation of oxygen, which create multi valance state of Fe (Fe²⁺ & Fe³⁺) during sintering in oxygen deficient environment. These
oxygen vacancies responsible for strong negative super exchange interaction between Fe$^{3+}$ and Fe$^{3+}$ through oxygen (O$^{2-}$) anion responsible for antiferromagnetic ordering whereas direct exchange interaction between Fe$^{3+}$/Fe$^{3+}$ and Fe$^{3+}$/Fe$^{2+}$ through vacancies (V$_{\text{O}}$) results in ferromagnetic ordering. The increase in value of $M_r$ may be due to increased effect of Fe$^{3+}$/Fe$^{3+}$ and Fe$^{3+}$/Fe$^{2+}$ through vacancies (V$_{\text{O}}$) which results in ferromagnetic ordering [10]. The value of remnant magnetization (emu/g) and coercivity (Oe) tabulated in Table 1. It is clear that direct exchange interaction between Fe$^{3+}$/Fe$^{3+}$ and Fe$^{3+}$/Fe$^{2+}$ through vacancies (V$_{\text{O}}$) dominates over strong negative super exchange interaction between Fe$^{3+}$ and Fe$^{3+}$ through oxygen (O$^{2-}$) anion up to $x = 0.15$ and then reverses responsible for increase in remnant magnetization up to $x = 0.15$ and then decreases.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_r$ (emu/g)</th>
<th>$H_c$ (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>0.007</td>
<td>276.6</td>
</tr>
<tr>
<td>(b)</td>
<td>0.262</td>
<td>2461</td>
</tr>
<tr>
<td>(c)</td>
<td>0.068</td>
<td>393.8</td>
</tr>
<tr>
<td>(d)</td>
<td>0.013</td>
<td>254.9</td>
</tr>
<tr>
<td>(e)</td>
<td>0.118</td>
<td>438.6</td>
</tr>
<tr>
<td>(f)</td>
<td>0.099</td>
<td>296.2</td>
</tr>
</tbody>
</table>

Figure 6. Magnetization vs. Applied Magnetic Field of CuO, Fe$_2$O$_3$ & 1-xCuO-xFe$_2$O$_3$ where (a) = CuO, (b) = Fe$_2$O$_3$(c) = 0.05, (d) = 0.10, (e) = 0.15 & (f) = 0.20 ceramic composites sintered at 700 °C

Slika 6. Magnetizacija u odnosu na primenjeno magnetno polje CuO, Fe$_2$O$_3$ i 1-CuP-Fe$_2$O$_3$ gde je (a) = CuP, (b) = Fe$_2$O$_3$(c) = 0.05, (d) = 0.10, (e) = 0.15 & (f) = 0.20 keramičkih kompozita sinterovanih na 700°C

Table 1. The Value of Remnant Magnetization & Coercive Field of CuO, Fe$_2$O$_3$ & 1-xCuO-xFe$_2$O$_3$ where (a) = CuO, (b) = Fe$_2$O$_3$(c) = 0.05, (d) = 0.10, (e) = 0.15 & (f) = 0.20 ceramic composites sintered at 700°C

Tabela 1. Vrednost preostale magnetizacije i koereticivnog polja CuO, Fe$_2$O$_3$ i 1-CuO-kFe$_2$O$_3$ gde je (a) = CuO, (b) = Fe$_2$O$_3$(c) = 0.05, (d) = 0.10, (e) = 0.15 & (f) = 0.20 keramičkih kompozita sinterovanih na 700°C

Room temperature variation of Real & Imaginary part of dielectric permittivity ($\varepsilon'$) & ($\varepsilon''$) of CuO & 1-xCuO-xFe$_2$O$_3$ composites where $x = 0.05$, 0.10, 0.15 & 0.20 in frequency range varies from 100Hz -1MHz have been shown in figure 7 & 8. It has been clearly revealed from graphs that value of both Real ($\varepsilon'$) and Imaginary ($\varepsilon''$) part of dielectric permittivity decreases as frequency increases up to a certain value and afterward varies linear. In lower frequency range, both Real & Imaginary part of dielectric permittivity ($\varepsilon'$) & ($\varepsilon''$) exhibits maximum value and decreases continuously with increasing frequency and become almost linear after certain value of frequency. Such types of behavior of represent general dielectric behavior of any dielectric, which follow either Debye, or Non-Debye behavior. In lower frequency range, maximum of all polarizations (Dipolar, Ionic, Electronic &
Interfacial) effectively contributes to dielectric permittivity resulting in maximum value of both Real ($\epsilon'$) and Imaginary ($\epsilon''$) part of dielectric permittivity [11,12].

\[
\epsilon'(\omega) = \epsilon_\infty + (\epsilon_1 - \epsilon_\infty) \left(1 + (\omega \tau_1)^{-\alpha} \sin \frac{\alpha \pi}{2}\right) \\
\epsilon''(\omega) = (\epsilon_2 - \epsilon_\infty) \left(1 + 2(\omega \tau_1)^{-\alpha} \sin \frac{\alpha \pi}{2} + (\omega \tau_1)^{-\beta}\right)
\]

Where $\epsilon_\infty$ is dielectric constant measured at high frequency, $\epsilon_1$ and $\epsilon_2$ are dielectric constants measured at low frequency, $\omega = 2\pi f$ is the angular frequency of applied field and $\tau_1$ is characteristic relaxation time of the medium. The exponent parameter $\alpha$ is usually a shape parameter that describes the shape of the spectral curves. It may be noted that for $\alpha = 0$, Cole-Cole model reduces to Debye model.

Room temperature $\sigma_{dc}$ vs. Frequency at room temperature CuO, Fe$_2$O$_3$ & 1-xCuO-xFe$_2$O$_3$ composites where $x = 0.05, 0.10, 0.15, & 0.20$, sintered at 700°C have been shown in figure 8. The ac conductivity calculated from recorded dielectric parameters using following formula

\[
\sigma_{ac} = \sigma_{dc} + A \omega^n
\]

Where the parameters have their usual meaning. Ac conductivity profile with frequency has been divided into two regions. First linearly varied region with frequency known as dc conductivity whereas dispersion region which corresponds to ac conductivity. Frequency varied ac conductivity in ceramics is generally analyzed by Jonscher’s power law;
According to Jonscher, origin of frequency dependence of conductivity may be due to relaxation phenomenon arising due to hoping of mobile charge carriers [13-16]. The conductivity also follows similar behavior like dielectric behavior. This may also due to variation in concentration of oxygen vacancies created which also effect magnetic properties means remnant magnetization first decreases and then increases may result due to processing of Fe$_2$O$_3$ with CuO in CuO-Fe$_2$O$_3$ composites as shown in figure 9.

![Graph showing σac vs. Frequency variation of CuO, Fe$_2$O$_3$ & 1-xCuO-xFe$_2$O$_3$ where (a) = CuO, (b) = Fe$_2$O$_3$, (c) = 0.05, (d) = 0.10, (e) = 0.15 & (f) = 0.20 ceramic composites sintered at 700°C.](image)

Figure 9. σac vs. Frequency variation of CuO, Fe$_2$O$_3$ & 1-xCuO-xFe$_2$O$_3$ where (a) = CuO, (b) = Fe$_2$O$_3$, (c) = 0.05, (d) = 0.10, (e) = 0.15 & (f) = 0.20 ceramic composites sintered at 700°C.

Slika 9. σac naspram varijacije frekvencije CuO, Fe$_2$O$_3$ i 1-xCuO-xFe$_2$O$_3$ gde je (a) = CuO, (b) = Fe$_2$O$_3$ (c) = 0.05, (d) = 0.10, (e) = 0.15 i (f) = 0.20 keramički kompoziti sinterovani na 700°C

4. CONCLUSION

CuO, Fe$_2$O$_3$ and 1-xCuO-xFe$_2$O$_3$ where x = 0.05, 0.10, 0.15 & 0.20 ceramic composites sintered at 700 °C & 900 °C where x = 0.05, 0.10, 0.15 & 0.20 have been successfully prepared using ball milling mixing method. X-ray diffraction pattern confirms that optimized sintering temperature for ceramic composites is 700 °C at which composites exhibits crystalline phase of both CuO and Fe$_2$O$_3$ as reported in JCPDS cards. Microstructural analysis gives densification as well as grain growth whereas energy dispersive x-ray spectroscopy and elemental mapping reveals presence of elements according to mentioned stoichiometric proportion and uniform distribution of metal ions.

Magnetic hysteresis data confirms that variation in magnetization directly follows competition of AFM and FM interaction whereas dielectric data follow similar behavior to magnetic ordering which results from creation of oxygen vacancies. The oxygen vacancies also play an important role in conduction behavior of dielectrics whereas interfacial polarization also plays effective role in dielectric properties of composites.

5. REFERENCES


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IZVOD

STRUKTURNA, MIKROSTRUKTURNA, MAGNETNA I DIELEKTRIČNA SVOJSTVA CuO-KOMPOZITA MODIFIKOVANOG Fe₂O₃

1-xCuOₓFe₂O₃ kompozit, gde je x = 0,05, 0,10, 0,15 i 0,20, su sintetizovani metodom mešanja sa kugličnim mlevenjem. Pripremljena keramika je okarakterisana po različitim osobinama kao što su struktura i mikrostruktura, elementarni sastav prema navedenoj stehiometrijskoj proporciji i magnetna svojstva. Takođe, istraživana su dielektrična svojstva pripremljenih keramičkih kompozita, sinterovanih na različitim temperaturama, na sobnoj temperaturi. Kako povećavamo temperaturu sinteze sa 700 °C na 900 °C, vrhovi difrakcije se pomeraju ka većim uglovima, što ukazuje na promene u parametrima kristalne rešetke i potencijalne izobličenja kristalne strukture. Ova primećena promena pokazuje na povećanu toplotnu energiju koja utiče na raspored atoma u materijalu. Međutim, nakon pažljivog razmatranja XRD rezultata i sveobuhvatne analize, zaključili smo da je temperatura sinteze od 700 °C poželjna, a ovoj nižoj temperaturi održava se željena kristalna struktura, minimizirajući rizik od strukturalnih promena ili faznih transformacija koje bi mogle uticati na svojstva i performanse materijala. Pored toga, izbor od 700 °C obezbeđuje ravnotežu između postizanja željenih karakteristika materijala i izbegavanja potencijalnih nedostataka povezanih sa višim temperaturama sinteze. SEM mikrografije pokazuju povećanje veličine zrna keramičkih kompozita. Energetska disperzivna rendgenska spektroskopija potvrđuje prisustvo elemenata u skladu sa stehiometrijskom proporcijom, dok S-oblika M protiv H. petlje potvrđuje prisustvo magnetnog uređenja. Realni (e') i imaginarni (e") delovi dielektrične perimitivnosti u odnosu na frekvenciju pokazuju dielektrično ponašanje.

Ključne reči: Kompoziti, metoda mešanja sa kugličnim mlevenjem, dielektrična svojstva, magnetna svojstva

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