Influence of Fe Doping on Structural, Optical, and Dielectric Properties of MgO nanoparticles

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Abstract. In this paper, we report the synthesis of pure MgO and Fe-MgO (Mg$_{0.90}$Fe$_{0.10}$O) nanoparticles (NPs) by co-precipitation method. The structural properties of the samples were characterized by X-ray diffraction (XRD) which reveal that the pure and Fe-MgO NPs have a cubic structure. The functional groups of the as-synthesized samples were analyzed by Fourier transform infrared spectroscopy (FTIR). Optical properties of the as-synthesized samples were studied by UV-vis spectroscopy in the range of 200-700 nm and the energy band gap was calculated by Tauc relation. The frequency dependence of dielectric constant, dielectric loss and ac conductivity were studied over a range of the frequency 42Hz to 5MHz at room temperature.

1. Introduction
In the last decade, a great attention has been payed on nano-sized materials because of their unusual physical, chemical and mechanical properties. The presence of defects and vacancies can have a strong impact on the optical and dielectric properties, when the dimensions of the material are reduced to nanometre scale [1]. Magnesium oxide (MgO) is an alkaline earth metal oxide which has a rock salt structure and has a large band gap 4-5 eV. MgO has many numerous properties for example light weight, high surface area, basicity, noncorrosivity, nontoxicity and high thermal stability. These properties are valuable in the several fields such as biosensing, water purification, automotive applications, aerospace, nanoelectronics, supercapacitors, photovoltaic devices and biomedical applications [2].

Various methodologies have been implemented to produce various kinds of MgO nanostructures like nanoparticles, nanosheets, nanorods, nanowires, nanotubes and nanobelts by different synthesis process such as precipitation method, wet chemical method, solvothermal method, sonication method, laser vaporization, chemical gas phase deposition, sol-gel process, solid state, etc. Recently many researches have been working on the production and characterization of nano-sized dielectric materials, since the present technology needs very small size particles for the fabrication of microelectronics devices which stores energy. Materials having high dielectric constant are used to design such materials [3]. Hence, the production and the study of these kinds of materials draws excessive attention to now-a-day research. Various metal doped MgO nanocomposites have been reported for various applications. Such as, Y Cai et al have reported the enhanced antibacterial activity of Ag-doped MgO [4]. S. Phokha et al reported room temperature ferromagnetism in Fe- MgO[5].
In this article we report the synthesis of pure MgO and Fe-MgO NPs by co-precipitation technique and investigation of the structural, optical and frequency dependence dielectric properties of MgO and Fe-MgO at room temperature.

2. Experimental Details

2.1. Sample Preparation

The synthesis of Fe-MgO NPs is done by co-precipitation method by using magnesium nitrate [Mg(NO$_3$)$_2$.6H$_2$O] and iron nitrate [Fe(NO$_3$)$_3$.9H$_2$O] as starting materials. A stoichiometric amount of magnesium nitrate and iron nitrate were dissolved in 100 mL of deionised water to make a homogenous solution. Then the solution was mixed thoroughly under magnetic stirring for 1 h. Then, the pH of the solution was maintained at 9 by adding a 0.1M aqueous solution of sodium hydroxide [NaOH] dropwise. The obtained solution was stirred further for 1 h on a magnetic stirrer. The precipitates were washed with deionised water and ethanol and the resultant product was dried in a vacuum oven at 100°C for 12 h. The obtained powder was calcined at 400°C for 3 h. For comparison, a similar procedure was adopted to prepare MgO without the addition of iron nitrate.

2.2. Characterization

The synthesized NPs of pure MgO and Fe-MgO were characterized by using XRD, FTIR, UV Visible and LCR meter. The crystal structure of the sample was inspected using powder XRD using a Bruker D8-Advance X-ray diffractometer with Cu Kα radiation in the 2θ range 20° to 80°. FTIR analysis of the samples was done by Perkin Elmer spectrophotometer in the range 400–4000 cm$^{-1}$. UVVisible measurement of the samples was performed with a Perkin Elmer Spectrophotometer (Lambda 45) in the range of 200–700 nm. The frequency dependence of the dielectric behaviour was studied by a parallel plate capacitor connected to a precision LCR meter (Agilent 4285 A).

3. Results and Discussion

3.1. Structural Analysis

The Fig.1 shows the XRD patterns of pure MgO and Fe-MgO NPs. The diffraction peaks of MgO and Fe-MgO can be indexed to the (111), (200), (220), (311) and (222) planes. The obtained diffraction peaks are in a good pact with the standard XRD data for the cubic phase of MgO (JCPDS no.05–0667). From the XRD patterns, no diffraction peak of Fe can be detected, due to the small amount of Fe doping. A minor change in the location of the (200) peak to the lower angle of 2θ value is detected for Fe-MgO. This shift is predominantly because of the substitution of Fe$^{3+}$ in the MgO lattice. A significant decrease in the lattice parameter is predictable for Fe-MgO because of the lattice shrinkage as Fe$^{3+}$ (63 pm) has a smaller radius as compared to Mg$^{2+}$ (72 pm). This may recommend that the Fe-MgO shows distorted lattice structure in comparison to pure MgO due to the substitution of Fe ions into MgO.

The Debye–Scherrer formula was used to evaluate the crystallite size for MgO and Fe-MgO NPs [6].

$$ D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1) $$

Table-1 lists the calculated value of the lattice parameter (a=b=c), cell volume, crystallite size and band gap for the most intense peak (200) for MgO and Fe-MgO.
Figure 1. X-ray diffraction pattern of Pure MgO and Fe-MgO NPs.

Table 1. Lattice parameters, crystallite size, cell volume and the band gap of samples.

| Parameters                        | MgO     | Fe-MgO  |
|-----------------------------------|---------|---------|
| Lattice parameter [a=b=c] (Å)     | 4.219   | 4.216   |
| Crystallite size (nm)             | 15.60   | 10.58   |
| Cell volume (Å$^3$)               | 75.10 x 10$^{-30}$ | 74.93 x 10$^{-30}$ |
| Band gap (eV)                     | 4.32    | 4.45    |

The Fig.2 shows the FTIR spectra of pure MgO and Fe-MgO NPs. The bands at 3443, 2878, 2442, 1638, 1413 and 1061 cm$^{-1}$ were allotted to the stretching vibrations of O-H, C–H stretching mode, C=O stretching vibrations, bending vibration of H$_2$O, asymmetric stretching of the carbonate ion (CO$_3^{2-}$) respectively. The bands at 884 and 530 cm$^{-1}$ were ascribed to different Mg-O-Mg vibration modes of MgO [7,8]. Fe-MgO also shows similar absorption peaks and no peaks of Fe were present due to its smaller percentage in Fe-MgO.
3.2. Optical Analysis

The absorption spectrum of pure MgO and Fe-MgO NPs are depicted in Fig.3. The pure MgO displays an absorption peak at 288 nm. The absorption peak at 279 nm of Fe-MgO shows a blue shift. This shift towards the lower wavelength can arise due to the creation of donor energy levels in the actual band gap of MgO.

Figure 2. FTIR spectrum of Pure MgO and Fe-MgO NPs

Figure 3. Absorbance spectra of Pure MgO and Fe-MgO NPs.
For determining the optical band gap of the pure MgO and Fe-MgO NPs the Tauc relation [9] was used:

\[ \alpha h \nu = K (h \nu - E_g)^n \]  

(2)

Where \( h \nu \) is the photon energy in eV, \( \alpha \) is the absorption coefficient, \( K \) is a constant, \( E_g \) is the band gap measured in eV and \( n \) is a constant which is taken as \( \frac{1}{2} \) for direct band gap semiconductors. From the Fig. 4, \( E_g \) can be estimated by extending the linear region of the plot of \( h \nu \) vs \((\alpha h \nu)^2\) on the x axis. The value of band gaps of all the samples is tabulated in Table-1 which shows that the band gap increases with Fe doping. The increase in optical band gap can be because of the decrement in the particle size. This can be explained with the help of Brass’s effective mass model [10]. The relation between band gap and particle size can be written as:

\[ E_{g}^* = E_{g, \text{bulk}} + \frac{h^2 \pi^2}{2 e r^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{4\pi\varepsilon\varepsilon_0 r} \]  

(3)

where \( E_{g, \text{bulk}}, r, \varepsilon, \varepsilon_0, e, m_e, m_h \) is the bulk energy gap, particle size, relative permittivity, permittivity of free space, charge of the electron, the effective mass of electrons and holes respectively.

![Figure 4. Tauc plots of Pure MgO and Fe-MgO NPs.](image)

3.3. Dielectric Analysis

The energy stored in the material in the presence of an applied field is described by the real part of the dielectric constant (\( \varepsilon' \)). The value of \( \varepsilon' \) for MgO and Fe-MgO were evaluated by using the relation [11]:

\[ \varepsilon' = \frac{C_p t}{A\varepsilon_0} \]  

(4)
Where $C_p$ is the parallel plate capacitance, $t$ is the thickness of the pellet, and $A$ is the area of the pellet. Fig. 5 shows the frequency dependence of $\varepsilon'$ for MgO and Fe-MgO samples in the frequency range from 42 Hz to 5 MHz.

From the Fig. 5 it can be observed that the dielectric constant of Fe-MgO has a higher value as compared to MgO, this behaviour can be clarified with the help of Maxwell–Wagner model [12] which is based on Koop’s theory [13]. According to this model, a dielectric medium has well-conducting grains which are detached by poor conducting grain boundaries. The grains are more operative at higher frequencies, whereas grain boundaries are operative at lower frequencies. When the external field is applied, the charge carriers can effortlessly migrate through grains and are assembled at the grain boundaries, which results in large polarization and high dielectric constant. With the increase in frequency, the polarization decreases and becomes constant at a higher value of frequency because beyond a definite value of frequency, the springing of electrons of different metal ions (Fe$^{2+}$, Fe$^{3+}$ and Mg$^{2+}$) cannot monitor the rapid ac field variations.

The amount of energy degenerated in the dielectric material can be explained by the dielectric loss. Dielectric loss occurs when the polarization lags behind the applied ac field and is caused by the impurities and defects in the crystal lattice. The room temperature variation of dielectric loss with frequency for MgO and Fe-MgO is shown in the Fig. 6. It can be noted that the dielectric loss falls noticeably with frequency and approaches a steady value. The larger value of dielectric loss at a lower frequency is because of the jumping between Mg$^{2+}$ and Fe$^{3+}$ leads and the electrons monitor the applied field. As frequency increases the electrons cannot track the applied high frequency which diminishes the jumping between Mg$^{2+}$ and Fe$^{3+}$. Therefore, the loss is minimum at greater frequencies of the applied field [14].

![Figure 5. The behaviour of dielectric constant with frequency.](image-url)
The variation of ac conductivity ($\sigma_{ac}$) with frequency in the range 42 Hz to 5 MHz at room temperature is shown in Fig. 7. The value of ac conductivity was estimated by the formula [15]:

$$\sigma_{ac} = 2\pi\varepsilon_0\varepsilon'\tan\delta$$  \hspace{1cm} (5)

where ‘$f$’ is the frequency of the applied field.
The Fig. 7 shows the variation of $\sigma_{ac}$ with frequency at room temperature which clearly depicts that the value of ac conductivity increases exponentially with frequency. Various conduction processes, for example jumping, tunnelling or free band conduction etc, contribute to the increment in the value of ac conductivity. In the whole frequency range, it is found that the addition of Fe increases the conductivity as compared to pure MgO. This happens because the addition of Fe increases the number of intrinsic donors and due to which the hopping between Mg$^{2+}$ and Fe$^{3+}$ is enhanced, which consequences in an increase in the ac electrical conductivity with Fe concentration.

4. Conclusion
The synthesis of pure MgO and Fe-MgO NPs was successfully done by co-precipitation technique. The crystallite size is found to decrease with the Fe doping in MgO. The increase in the band gap can be seen due to Fe doping in MgO. The signature functional groups present in pure MgO and Fe-MgO NPs are shown by FTIR spectra. The dielectric behavior has been studied over a wide range of frequencies at room temperature for of pure MgO and Fe-MgO. At room temperature the dielectric constant and dielectric loss exhibits the normal dielectric behavior and both show a declining tendency with increasing frequency, whereas the ac conductivity shows a growing tendency with an increase in frequency. The dielectric constant increases, while dielectric loss decreases with Fe doping. An increase in the ac conductivity is observed with Fe doping in MgO.

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6. References
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