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Dielectric Properties and Dispersion Parameters of Magnesium Oxide Nanoparticles with Temperature

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ABSTRACT

Magnesium oxide (MgO) nanoparticles were synthesized through chemical coprecipitation followed by thermal treatment. Structural, optical and luminescence properties along with dielectric properties were studied and relaxation mechanisms were explored. The structural characterization studies confirmed the formation of nano sized MgO particles with hierarchical structures and high purity. The dielectric properties were studied in different frequency range at different temperatures. In addition, the Cole –Cole plot are used to explore the relaxation mechanism prevalent in nanostructured MgO. In dielectric materials there are multiple dipole relaxation mechanisms which give rises to spreading of relaxation time on the average relaxation time.

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Introduction

Metal oxides constitute a versatile and truly fascinating class of materials spanning the entire range from superconductors to insulators. They find use in various technological applications such as thin film coatings for corrosion, sensors, medical implants, and energy conversion in fuel cells, catalyst support in heterogeneous catalysis and many more. Magnesium oxide is basically an insulator material and has several applications in the field of dielectrics. Magnesium Oxide (pericalse) is an exceptionally important material, with uses in catalysis, toxic waste remediation etc. These nanoparticles find use in electronics, ceramics, petrochemical products, coatings and many other fields. It isalso used as electric insulating material high-frequency magnetic-rod antenna, magnetic device filler, insulating material filler and various carriers used in radio industry. In the nanoform its properties changes making it an inseparable part of many electrical devices .It is a white hygroscopic solid mineral and is generally produced by the calcination of magnesium hydroxide $Mg(OH)_2$ or magnesium carbonate $MgCO_3$. In the nano form it's very easy to tailor its properties as different structures like nano flower, tubes etc are formed easily. One of the main aim of the study is to probe the optical properties and dielectric properties of fluffy magnesium oxide nanoparticles synthesized through chemical co precipitation. This is another binary oxide wide semiconductor in II-VI group which crystallizes in cubic structure. It is also used as a fire retardant fuel additive, cleaner, antistatic agent and corrosion inhibitor.

1) Synthesis

Magnesium Oxide nanoparticles were a prepared using solutions of Magnesium Acetate, Ammonium Carbonate, EDTA and Sodium Hydroxide . All solutions were prepared in distilled water. The nanoparticles were made from solutions of Magnesium Acetate and Ammonium Carbonate being dropped slowly into 0.01 molar solution of EDTA and 1 molar sodium hydroxide at the rate of 5ml/hr. under constant stirring using a magnetic stirrer. The molar concentration of EDTA and Sodium Hydroxide were optimized as a compromise between yield and particle size. The speed of stirring as well as time taken for dropping greatly influence the size of nano particles formed. All these parameters were optimized "one at a time" approach. The final product was filtered, dried and then finely ground using an agate mortar. The homogenously ground powder was annealed for three hours at 500^0C to obtain oxide particles.

Chemical properties and surface composition of magnesium oxide are greatly influenced by the calcination procedure, temperature, medium, i.e., air or vacuum and by the source of the precursors. Based on the various results it is observed that physical adsorption of water only occurs if MgO contains large surface defects, such as high quantity of pores. The samples named M1,M2,M3 and M4 are prepared from increasing strength of precursors starting from 0.05 M to 0.2M.

Table 1. EDAX data showing content percentage of Magnesium Oxide samples

Samples	Mg		O	
	Mass%	Atom%	Mass%	Atom%
M1	50	39.69	50	60.31
M1	52.73	42.26	47.27	57.74
M3	58.1	47.72	41.9	52.28
M4	58.48	48.1	41.52	51.9

The results obtained from EDAX shows the purity of samples and SEM micrographs indicate the tendency of magnesium oxide to form flake like structures.

2) Absorption studies and band gap variations

The variations in the absorption spectra of Magnesium Oxide nanoparticles are studied for all synthesized samples. i.e. Samples prepared from different molarity of the reagents. The effect of annealing on the bandgap is also studied and it is seen that the band gap decrease with annealing which can

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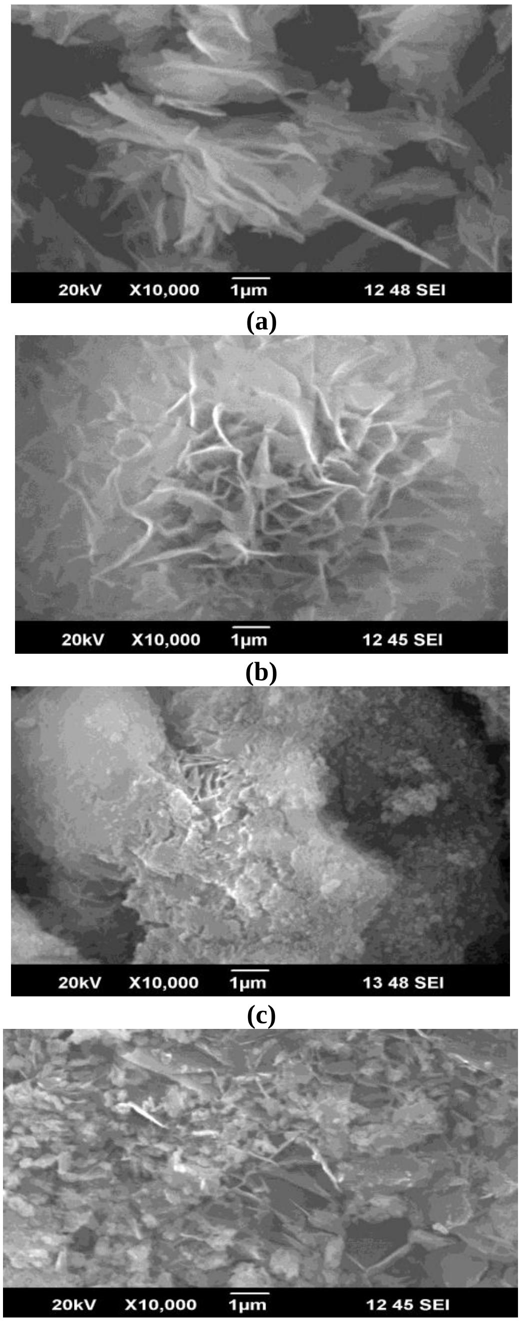
be attributed to an increase in the particle size due to agglomeration at high temperature. The bandgap variations of the samples obtained are form 4.43 eV to 5.1 eV, but less than its bulk value 7 eV.



(a)

(b)

(c)

(d)

Figure1. SEM micrographs of MgO nanoparticles a) M1, b) M2, c) M3, d) M4

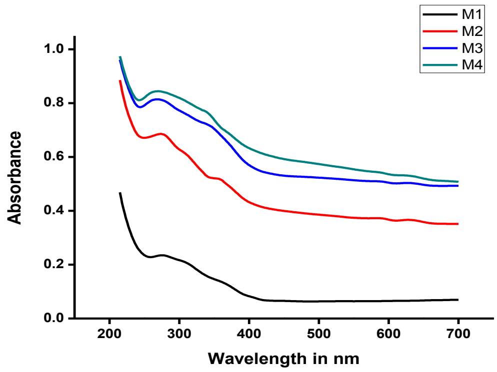
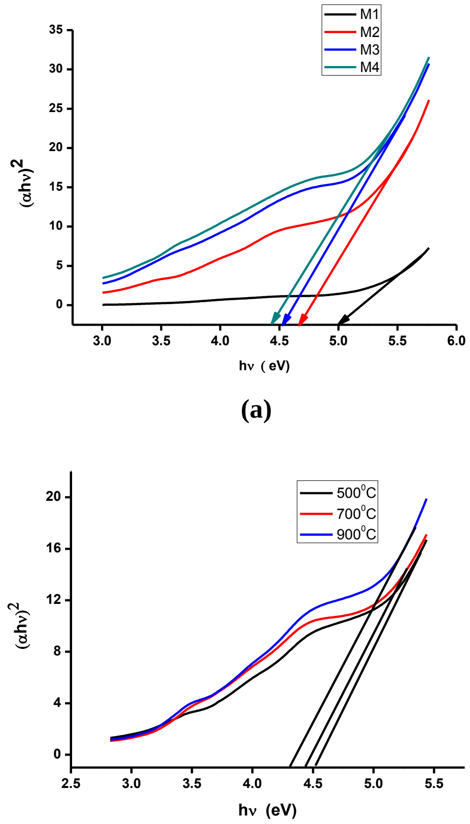


Figure 2.absorption spectra obtained for samples of Magnesium Oxide nanoparticles

The band gap of annealed nanoparticles of sample M3 at temperature 700^{0}C is 4.44eV which further reduced to 4.29 eV when annealing temperature increased to 900^{0}C.

The optical conductivity is one of the fundamental properties of metal oxides and can be experimentally obtained from reflectivity and absorption measurements. Due to quantum-size confinement, absorption of light becomes both discrete-like and size-dependent. For nano-crystalline semiconductors, both linear (one exciton per particle) and non-linear optical (multiple excitons) properties arise as a result of transitions between electron and hole discrete or quantized electronic levels.



(a)

(b)

Figure 3 a) Tauc plot for the MgO samples b) Tauc plot for the sintered sample (M3)

The electronic properties of Magnesium Oxide in the bulk form are governed by the long-range effects of the Madelung field, but this field is very limited in the nanostructured oxide. Theoretical studies for oxide show a redistribution of charge when going from large periodic structures to small clusters or aggregates which must be roughly considered to be relatively small for ionic solids while significantly larger for covalent ones.

Table 2. Bandgap of MgO nanoparticles

Sample name	Particle size(nm)	Band gap(eV)
M1	7±1	5.1
M2	10± 1	4.68
M3	12±2	4.53
M4	14±1	4.43

In its bulk state, MgO is a highly ionic compound and a wide bandgap (~ 7 eV) insulator. The bandgap obtained for the synthesized nanoparticles varied between 5.1 eV to 4.43 eV with variation in particle size. For small nanoparticles of MgO, a reduction in the bandgap could be measured by using optical absorption techniques and the effects of the electrostatic Madelung potential could not be as strong as those in bulk MgO [1] and hence a reduction in the bandgap occurs in nanostructured MgO. Our results are in good agreement with this fact.

3) **Photo-luminescence studies:** The PL emission from the Magnesium Oxide nanoparticles due to an excitation wavelength 250 nm, are given in Figure 4.

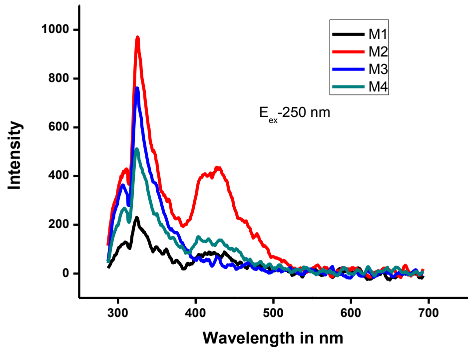


Figure 4. PL emission spectra of Magnesium Oxide nanoparticles

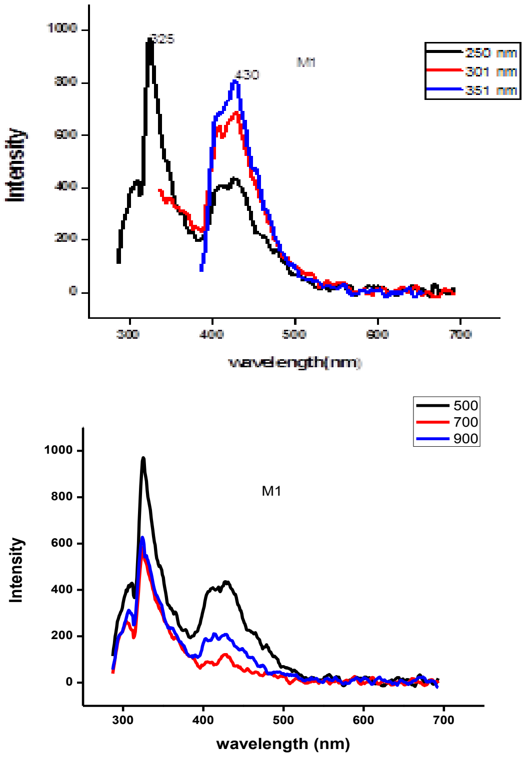


Figure 5 a) Dependence on excitation wavelength (M1) b) Dependence on annealing temperature

There are two peaks in the spectrum of all the synthesized samples, one between 320-350nm and another between 410-450 nm. The emission in the 320 range is sharp but the other peak is very broad. This emission can be attributed to the displacement of oxygen ions and subsequent electron trapping resulting in the formation of F centres [2].

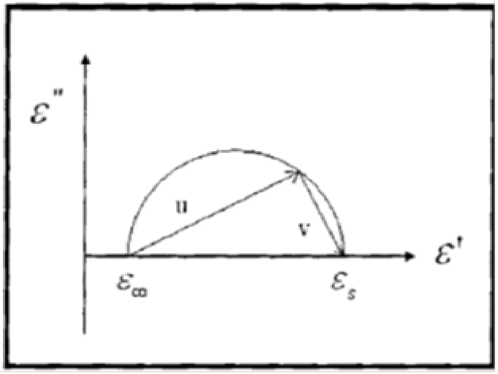
The maximum intensity of emission was obtained for the sample M2. The dependence of emission on the excitation wavelength is also probed and it is seen that the sharp emission at 325 nm disappears with increase in the excitation wavelength to 300 nm and the band at 430 nm became sharper with a corresponding increase in intensity. The inefficient energy transfer between the upper and the lower vibrational levels of the excited state of these particles owing to short fluorescence lifetime is primarily responsible for the excitation wavelength dependent spectral shift of Magnesium Oxide colloids.

The luminescence spectra also changed with annealing temperature and the changes are given in figure 5 b. Here the intensity of both peaks is found to decrease with increase in temperature.

4) Cole- Cole method to find dispersion parameters

In order to study the dielectric behaviour, it is customary to plot ε', ε" or *tanδ* against frequency. A more convenient method is the Argand diagram or complex locus diagram in which the imaginary part of the complex dielectric constant is plotted against the real part at the same frequency. Kenneth S. Cole and Robert H. Cole applied this method to dielectric and hence it is often called Cole-Cole plot [3,4,5,6].

The Cole–Cole model has been used successfully to describe the experimental data for the dielectric constant of many materials as a function of frequency [7,8,9,10,11]. In this model the dielectric constant depends mainly on four parameters, the static dielectric constant ε_s, the dielectric constant at infinite frequency ε_∞ , the relaxation time τ_0 and an exponent factor α. In principle, ε_s and ε_∞ can be experimentally measured and the other two parameters τ_0 and α have to be treated as fitting parameters whose values can be retrieved from the best fit to the experimental data. In most of the cases, however, ε_s and ε_∞ cannot be obtained directly from the experimental data since it is difficult to perform the measurements at very low and very high frequencies and to detect the saturated values in the two limits. The present work is concerned with presenting a simple method to extract ε_s and ε_∞ from the available measurements and to obtain subsequently the other two parameters.



For a dielectric with single relaxation time, the Cole-Cole plot is a semicircle with its centre on the real axis and intercepts ε_∞ and ε_s, on the same axis.

From the figure, we can write

$$U + V = \varepsilon_s - \varepsilon_\infty \qquad (5.7)$$

where the quantities U and V considered as vectors in the complex plane are perpendicular, their vector sum being the constant real quantity (ε_s - ε_∞) The right angle included by these vectors is therefore inscribed in a semicircle of (ε_s - ε_∞) as shown in figure. This semicircle is then locus of the dielectric constant ω varies from 0 to ∞.

Many materials, particularly long chain molecules and polymers shows a broader dispersion curve and lower maximum loss than would be expected from the Debye's relationship. K.S Cole and R.H Cole suggested that in this case the permittivity might follow the empirical relation,

$$\varepsilon^* - \varepsilon_\infty = \frac{\varepsilon_s - \varepsilon_\infty}{\left(1 + j\omega\tau_0\right)^{1-\alpha}} \qquad (5.8)$$

Where $\varepsilon^* = \varepsilon' - \varepsilon''$ and $\omega = 2\pi f$, f is the frequency and ε' and ε'' are the real and imaginary part of complex dielectric constant. Here τ_0 is the average relaxation time and constant α is the spreading factor($0 \leq \alpha \leq 1$) of the actual relaxation time τ about its mean value τ_0.When $\alpha=0$, this equation reduces to Debye's equation

$$U + V = \left(\varepsilon^* - \varepsilon_\infty\right)\left(1 + j\omega\tau\right) \qquad (5.9)$$

From the expression for ε'', it is clear that at $\omega = 1/\tau$, it becomes maximum and the value is given by

$$\varepsilon''_{\max} = \frac{\left(\varepsilon_s - \varepsilon_\infty\right)}{2} \tan \frac{(1-\alpha)\pi}{4} \qquad (5.10)$$

The average relaxation time τ_0 can be estimated from the expression

$$\frac{(\varepsilon_0 - \varepsilon)^2 - \varepsilon'^2}{(\varepsilon' - \varepsilon_\infty)^2 + \varepsilon''^2} = (j\omega\tau_0)^{2(1-\alpha)} \qquad (5.11)$$

The molecular relaxation time can be estimated using the following equation by substituting the value of τ_0

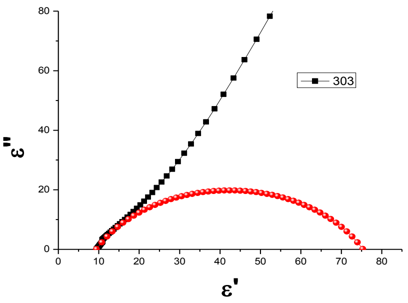
$$\tau = \frac{(2\varepsilon_s - \varepsilon_\infty)}{3\varepsilon_s}\tau_0 \qquad (5.12)$$

A detailed description of derivations of these equations is given elsewhere [4,5,6].

From the Cole-Cole plot, the dispersion parameters like static dielectric permittivity, optical dielectric permittivity and spreading factor α can be evaluated [12]. Using the dielectric values obtained from the LCR meter measurement, the Cole- Cole plots of the samples were drawn and using a non- linear least square fitting program (C-Ianguage) the different dispersion parameters were evaluated. In Cole - Cole plot analysis imaginary value of dielectric permittivity is plotted against real permittivity and using non- linear least square fitting circular arcs can be completed above real permittivity axis. Dispersion parameters can be evaluated from the fitting parameters.

Cole- Cole analysis of MgO nanoparticles

The Cole-Cole analysis of the Magnesium Oxide nanoparticles are analysed using pellets made of sample M1. The results obtained from the non-linear least square fitting is given in the The value of spreading factor varied from 0 to 1, and the relaxation time and average relaxation time is obtained in the order 10^{-7} s. The relaxation time is found to increase with temperature except for a small anomaly at 323 K. In the dielectric studies also a peak is obtained at 323 K and this may have reflected in the relaxation time also. The Cole- Cole plots are drawn for temperature 303 K to 353 K and are given in Figure 5.18.



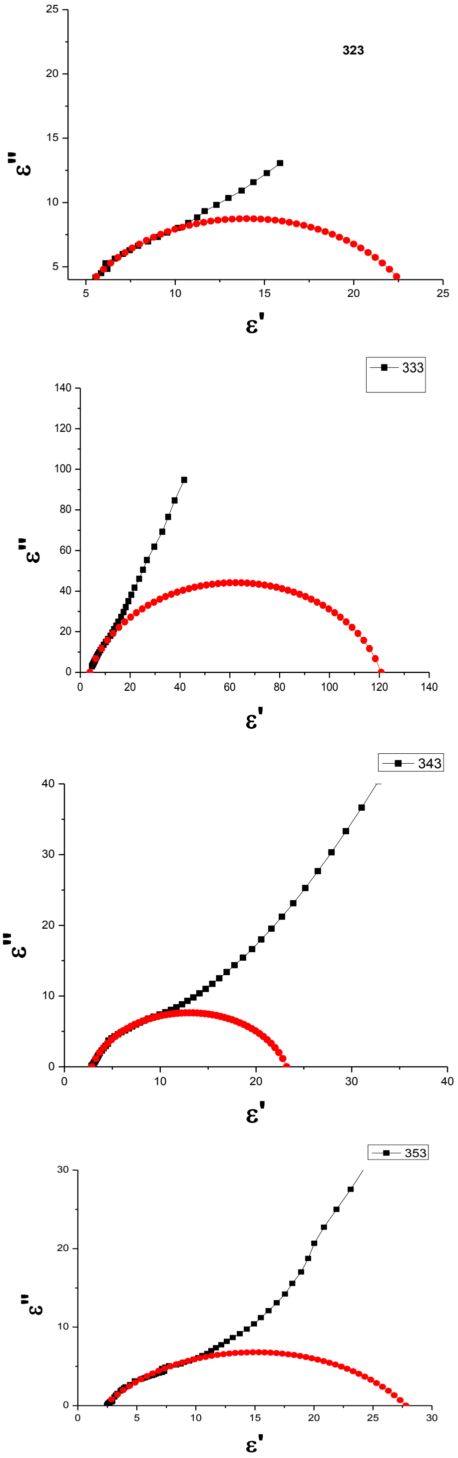


Figure 6. Cole –Cole plots of Magnesium Oxide nanoparticles

Table 3. The dispersion parameters obtained for the MgO nanoparticles

Temperature	$\varepsilon''_{\max}$	α	$\tau_0 (10^{-7}$ s)	τ (10^{-7} s)	ε_∞	ε_s
303	19.74	0.3125	0.176	0.125	9.432	76.625
323	8.743	0.0854	4.304	3.108	3.998	24.003
333	44.124	0.1768	3.421	2.317	3.834	120.76
343	7.632	0.180	6.299	4.459	2.873	23.216
353	6.7935	0.377	31.425	23.002	2.864	28.304

Dielectrics are used in fabrication of capacitors, filtering out noise from signals as part of a resonant circuit and in a camera flash system. Dielectric constant is helpful in determining other properties i.e. n, σ , $\varkappa_e$. This is useful for the study of resonance phenomena in dielectrics and critical phenomena at ferroelectric transitions. The ultralow dielectric constant is useful for high-frequency switching applications. Dielectric constant and loss plays a vital role in microwave technology and devices because of very high requirements to electric parameters. Dielectric loss is utilized to heat food in a microwave oven. Dielectric constant is a sensitive parameter in fabrication of sophisticated electronic equipment such as rectifiers, semiconductors, transducers and amplifiers. In short, the dielectric constant of materials is important in material processing, electronics & biomedical engineering. In this chapter dielectric properties of synthesized nanostructured materials are studied in detail. The Cole- Cole analysis is also done for all samples and dispersion parameters calculated.

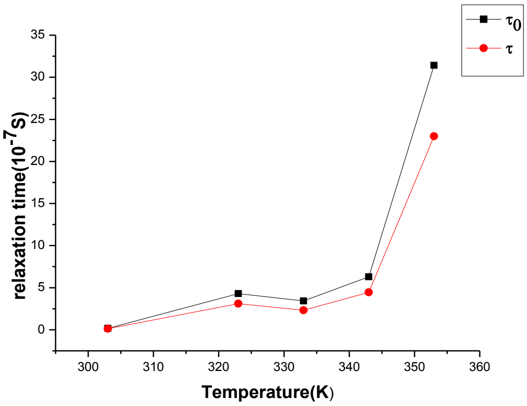


Figure 7. Variation in relaxation time of MgO nanoparticles with temperature

Conclusion

The method of precipitation is an easy method to prepare nano metal oxides and by changing the composition their properties change drastically. The optical and dielectric properties exhibited by them is closely related to synthesis method, defects in the lattice and composition. The frequency dependence of the dielectric constant and dielectric loss is found to decrease with increase in frequency at different temperatures. Applications of magnesium oxide includes various industry sectors. For their refractory properties, it is a valuable fireproofing ingredient in construction materials. Also in applications where corrosion is not acceptable such as nuclear, chemical or superalloy industries. It has a usage in medical applications, where MgO is used for relief of heartburn and sour stomach, as an antacid, magnesium supplement, and as a short-term laxative. Other applications include insulators, fertilizers, water treatment, protective coating, etc. The Cole-Cole plots are found to be a good tool to understand the relaxation mechanism and relaxation time in the dielectric oscillations.

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References

1. Stener M., Fronzoni G., De Francesco R., " Core excitations in MgO: a DFT study with cluster models "Chem. Phys. 309, (2005), 49.
2. Caulfield Kevin J., Kooper Ronald, Boas John F., " Temperature effect in the luminescence emission from electron irradiated MgO", J.Chem.Phys, 92, (1990), 6441.
3. Debye P., Polar Molecules, Dover, New York (1929).
4. Cole K.S., and Cole R.H., "Dispersion and absorption in dielectrics." J Chem. Phys., 9, (1941), 314.
5. Daniel Veera V., Dielectric Relaxation, Academic, London (1967).
6. Hill N.E., Vaughan W. E., Price A. H., Mansel Davies, "Dielectric properties and Molecular Behaviour", Van Nostrand Reinhold, London (1969).
7. Barati M.R., Ebrahimi S.A.S., Badiei A., Non-crystallineSolids, 354(47-51), (2008), 5184.
8. Pradeep A., Priyadharsini P., Chandrasekaran G., "Production of single phase nano size NiFe2O4 particles using sol–gel auto combustion route by optimizing the preparation conditions ", Mater. Chem. Phys. 112 (2), (2008), 572.
9. Toksha B.G., Shirsath S. E., Patange S.M., Jadhav K.M., "Structural investigations and magnetic properties of cobalt ferrite nanoparticles prepared by sol-gel auto combustion method" ,Solid State Communications vol. 147, no. 11-12, (2008), 479.
10. Yuan Y., Liu C., Zhang Y., Shan X.," Sol-gel auto-combustion synthesis of hydroxyapatite nanotubes array in porous alumina template", Mater. Chem. Phys., 112(l), (2008), 275.
11. Mo Chi-mei, Zhang Lide, Wang Guozhong, "Characterisrtics of dielectric behaviour in nano structured materials", Nanostructured materials Vol 6, (1995), 823.
12. Sagar S., Saravanan S., Suresh Kumar S., Venkatachalam S. Anantharaman M. R., "Evidence for the existence of multiple equilibrium states in cobalt phthalocyanine tetramer: a study by dielectric spectroscopy", J Phys. D: Appl. Phys. 39, (2006), 1678.