

# Optimization of Optical and Dielectric Properties of $\text{CoFe}_2\text{O}_4/\text{CaTiO}_3$ Nanocomposites

Neelam Kumari<sup>a</sup>, Shivali Meena<sup>a</sup>, Deepshikha Rathore<sup>a</sup>, Rahul Singhal<sup>b</sup>, Umesh Kumar Dwivedi<sup>a\*</sup>

<sup>a</sup>Amity University Rajasthan, Jaipur 303002

<sup>b</sup>Malaviya Institute of Technology Jaipur, Rajasthan 302017

**Abstract :** The main aim of this article is to achieve excellent optical and dielectric properties. For this purpose,  $\text{CoFe}_2\text{O}_4/\text{CaTiO}_3$  nanocomposites have been synthesised using solid-state method. The optical properties and dielectric properties have been studied using UV-Vis Spectroscopy and LCR meter respectively. The absorbance with respect to wavelength has been illustrated through UV-Vis spectroscopy which evidenced the absorption of UV-C rays and Violet visible rays. The dielectric properties of  $\text{CoFe}_2\text{O}_4/\text{CaTiO}_3$  nanocomposites have been studied in the frequency range from 40 Hz to 8 MHz at room temperature ( ). The dielectric permittivity and dissipation factor has been found to be highest at 40 Hz and observed to be decreasing with increasing frequency.

**Keywords:** Nanocomposites; UV-Vis spectroscopy; Dielectric constant; Dissipation factor; Optical properties.

## Introduction

The combination of ferroelectric and ferromagnetic materials in the same environment can open up a slew of new possibilities in the fields of sensors, memory, and EMI shielding etc. the pace of polarization and magnetization can be controlled by ferroelectric and ferromagnetic materials used in formation of resultant nanocomposites [1].  $\text{ABO}_3$  type perovskites oxides have attracted much attention from researchers due to their excellent properties. Among various kinds of perovskites, calcium titanate (CTO)-an orthorhombic alkaline earth titanate has gained a lot of attention due to its ferroelectric, semi conductive and photorefractive properties. Electrical and dielectric properties of  $\text{CaTiO}_3$  have been mostly investigated by researchers and found that  $\text{CaTiO}_3$  is a good candidate for industrial and technical applications such as in capacitor, oscillator, and filters etc [2, 3]. Generally, incorporation of transition elements in metal oxides elevated the ionic conductivity due to oxygen vacancies. In addition, introduction of second phase into oxide ions has been greatly explored by the scientific community due to creation of grain boundaries and therefore resulted in better properties [4, 5].

As regards nanoferrites have created much interest among the researchers because of their

excellent electrical and magnetic properties and hence count it in the list of suitable candidate for memory devices, magnetic tapes, biomedical, recording devices, solar cells, and gas sensors. Several techniques such as sol gel, co-precipitation, hydrothermal, and auto combustion have been efficiently explored to synthesize nanoferrites [6]. The combination of nanoferrites ( $\text{CoFe}_2\text{O}_4$ ) with ferroelectric material ( $\text{ABO}_3$  perovskites) in nanocomposites may improve the overall characteristics of resultant product collectively. Composition of individual materials can directly tune the optical and dielectric properties of nanocomposite. Investigation of several properties has been reported for Cobalt ferrite (CFO) and barium titanate (BTO) nanocomposites.

Hkiri et al. [7] synthesized the mono-phased calcium zirconate ( $\text{CaZrO}_3$ ) and  $\text{CaZrO}_3\text{-CaTiO}_3$  composites by using conventional dry route method. They studied electrical and dielectric characteristics of  $\text{CaZrO}_3\text{-CaTiO}_3$  composites and found that the ionic conductivity of prepared composites is higher as compare to mono-phase  $\text{CaZrO}_3$ . The dielectric response of  $\text{CaZrO}_3\text{-CaTiO}_3$  composites has been found to be enhanced due to interfacial polarization between hetero-phases. Cherdchom el al. [8] synthesized calcium titanate from waste egg shells of duck considering them a high calcium source and white calcium titanate

\*Corresponding author:(E-mail: umeshkudwivedi@gmail.com)

powder has been prepared by using high temperature combustion method. The prepared powder composites exhibited dielectric constant of about 78 and minimum dielectric loss of about 0.02 due to space charge polarization. Dhabekar et al. [9] employed co-precipitation method to synthesised cobalt ferrite nanoparticles and combined it with ferrites of strontium and barium. Identification of structural properties and dielectric properties with temperature has been studied.

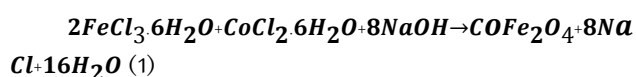
## Experimental Procedure

### Materials

In present work, Ferric chloride hexahydrate, cobalt chloride hexahydrate (98+% purity), and NaOH chips have been used. Distilled water has been used as a solvent. All the materials are reagent grade and used without further purification. Commercially available  $\text{CaCO}_3$  and  $\text{TiO}_2$  have been used for preparation of  $\text{CaTiO}_3$  powder.

### Synthesis of Cobalt ferrite

Ultra fine particles of cobalt ferrite have been prepared by co-precipitation method shown in Fig.1 (a). Iron (II) chloride ( $\text{FeCl}_2$ ) precursor has been used to prepare cobalt ferrite nanoparticles. Whereas  $\text{CoCl}_2$  and NaOH has been used as a reducing and precipitating agent. Distilled water has been used as a solvent to minimize the impurities in final product. 0.1M of cobalt chloride has been dissolved in 100 ml distilled water by magnetic stirrer to form homogeneous solution. 0.2 M of ferric chloride has been dissolved in 100 ml of distilled water and continuously stirred for about 10–15 min. Cobalt based solution has been poured into iron based solution and stirred continuously about 10–15 min. After that 0.8M of sodium hydroxide has been dissolved in 100 ml of distilled water. The aqueous solution of ferric chloride (0.2M) and cobalt chloride (0.1M) have been added drop by drop to the 0.8M of NaOH solution under dynamic stirring with constant speed, respectively. With the dropping of solution to the alkaline medium, the precipitation start forming instantly from reddish brown colour in initiation to dark brown colour in the end.

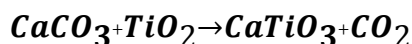


Suspension has been kept stirring for 30 min. Reaction time of 30 min was sufficient for dehydration and atomic rearrangement. The sufficient amount of

particles has been formed by using magnetic separation. The precipitation thus formed was washed several times by distilled water and centrifuged to extract nanoparticles and ground into mortar pestle then sintered at 250°C for 2 h.

### 2.3 Preparation of $\text{CaTiO}_3$

The preparation of  $\text{CaTiO}_3$  by conventional dry route depicted by Fig.1 (b) relies on the reaction expressed as



To the successful formation of friable  $\text{CaTiO}_3$  powder, an appropriate amount of calcium carbonate ( $\text{CaCO}_3$ ) and titanium oxide ( $\text{TiO}_2$ ) has been used. These compounds then mixed and ground thoroughly in mortar pestle with few drops of ethanol in order to remove inhomogeneity of mixture. For the proper formation of pure compound, the fine powder sintered at 1100°C temperature.

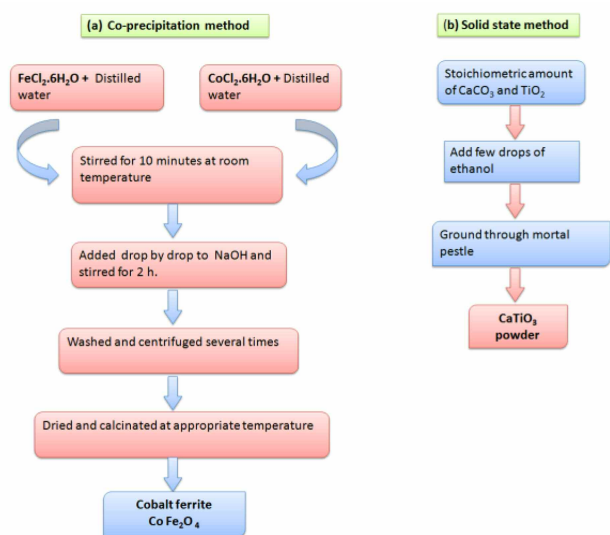


Fig.1 Flowchart of (a) Co-precipitation and (b) Solid state method.

### Preparation of specimens

The  $\text{CaFe}_2\text{O}_4$ /  $\text{CaTiO}_3$  composites have been developed by conventional solid state method. In order to form composites, both the powders in ratio 1:1 mixed via mortar pestle with few drops of ethanol into it. At last, CTO, and CFO/CTO powder have been compressed to disk form using hydraulic press at appropriate pressure. The prepared pellets calcinated at 1000°C for successful formation of compact disks with reduced porosity.

### Characterization

The optical properties of ceramics have been investigated by BIOMATE 3S UV-Vis spectrophotometer of Thermo Scientific model. The

dielectric properties of composites have been examined by LCR meter (HIOKI IM-3536) at 40 Hz to 8 MHz frequency range at room temperature.

## Results and discussion

### Optical analysis

UV-Vis absorption and transmittance spectra of CTO and CFO/CTO composites have been shown in Fig.2 (A) and (B) in wavelength of 200 nm to 900 nm range. The absorption spectra of CTO and CFO/CTO confirmed the absorption of 284 nm (UV-B rays) and 256 nm (UV-C rays) wavelength, respectively.

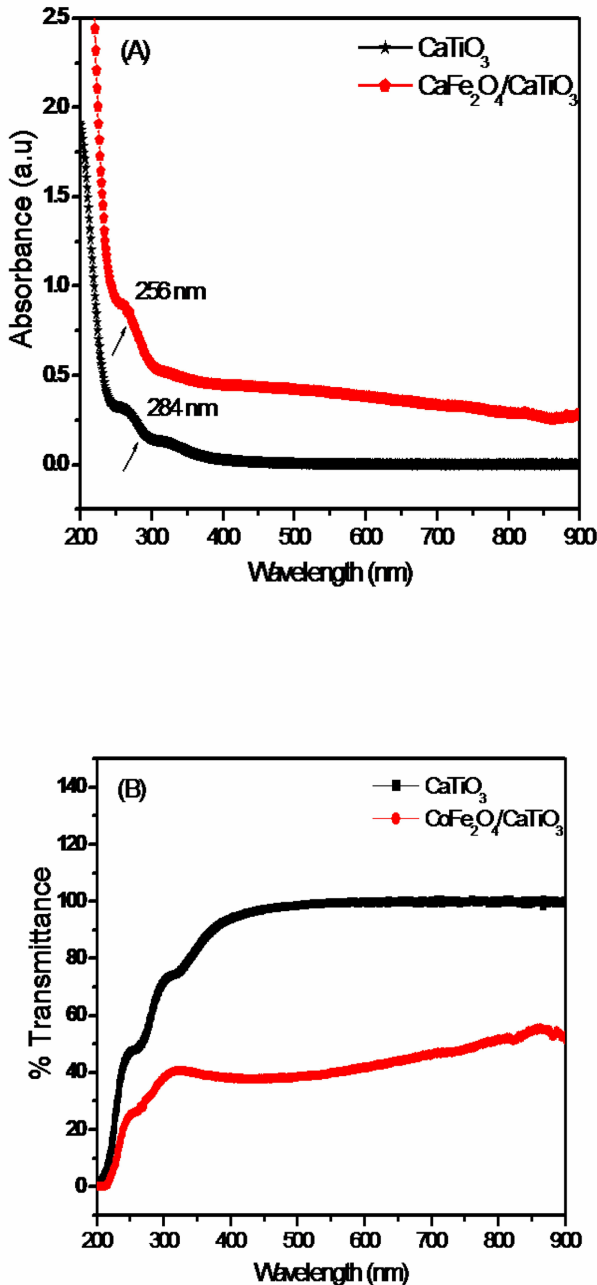


Fig.2 (A) depicted the UV-Vis absorption and (B) transmission spectra of  $\text{CaTiO}_3$  and  $\text{CaFe}_2\text{O}_4/\text{CaTiO}_3$  composites.

The UV-C rays (100 nm-279 nm) are shortest wavelength of UV radiation and can cause severe effect on human eyes and skin. Whereas, these short wavelength rays can be used in water and air disinfection. From the decades, ultraviolet C rays have efficiently been used in germicidal lamps to diminish the spread of bacteria. Therefore, detection of these UV-C rays is important for human benefit and hence incorporation of CFO nanoparticles in CTO particles makes the composites to absorb harmful UV rays and can also be used in germicidal lamps due to UV-C rays disrupts DNA pairing of several bacteria and germs and hence lower the chances of spreading diseases.

From the transmittance spectrum, only 20% of ultraviolet light has been transmitted through CFO/CTO composites as shown in Fig.2 (B) that means 80% of harmful rays can be blocked by CFO/CTO composite. The band gap between electronic energy levels has been calculated by formula [10].

$$ah\nu = A (h\nu - E_g)^{1/2}$$

Where,  $h\nu$  is energy of light,  $A$  is energy constant,  $E_g$  is band gap between energy levels, and  $a$  is absorption coefficient. The energy band gap of 4.95 eV for CTO, and 5.70 eV for CFO/CTO composites have been estimated using Fig.3. This wide energy gap makes the devices to operate at high voltage and high frequency.

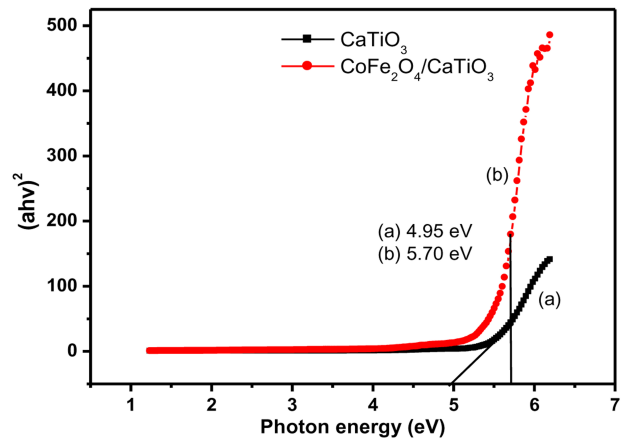


Fig.3 Energy band gap of (a)  $\text{CaTiO}_3$  and (b)  $\text{CaFe}_2\text{O}_4/\text{CaTiO}_3$  composites.

### Dielectric properties

The dielectric measurements of  $\text{CaFe}_2\text{O}_4/\text{CaTiO}_3$  composites have been carried out up to 8 MHz frequency at room temperature. The measured value of capacitance ( $C$ ) has been used to calculate relative

permittivity ( $\hat{\epsilon}$ ), using the following expression [11]

$$\hat{\epsilon} = \frac{C d}{\epsilon_0 A}$$

Where, d is sample thickness, A is area of the sample, and  $\epsilon_0$  is permittivity of free space. Whereas the dielectric loss  $\epsilon''$  has been calculated by equation (5)

$$\epsilon'' = \epsilon' \times \tan\delta$$

Where,  $\tan\delta$  is dissipation factor.

Data collected from the set up of the dielectric constant versus frequency and the dielectric loss versus frequency at room temperature has been obtained on silver electrode. Fig.4 (a) demonstrated the variation of the dielectric constant of composite as a function of frequency at room temperature. It is quite evident that the dielectric constant decreases gradually with increase of frequency. At resonance frequency, dielectric constant attains a constant value that means at that point the orientation polarization get captured due to no response of Ti ions with high frequency and Debye type behavior is shown by the materials [8]. This behavior shows the lagging of dipoles behind the E field and hence reduces the relative permittivity and at higher frequency polarization is stopped. The maximum values of dielectric constant for  $\text{CaTiO}_3$  &  $\text{CaFe}_2\text{O}_4/\text{CaTiO}_3$  composite found to be 74 and 103, respectively at initial frequency which is evident from Fig. 4 (a). So, the slight enhancement of dielectric constant with addition of  $\text{CaFe}_2\text{O}_4$  is due to introduction of interfacial polarization in hetero interfaces. The stresses in

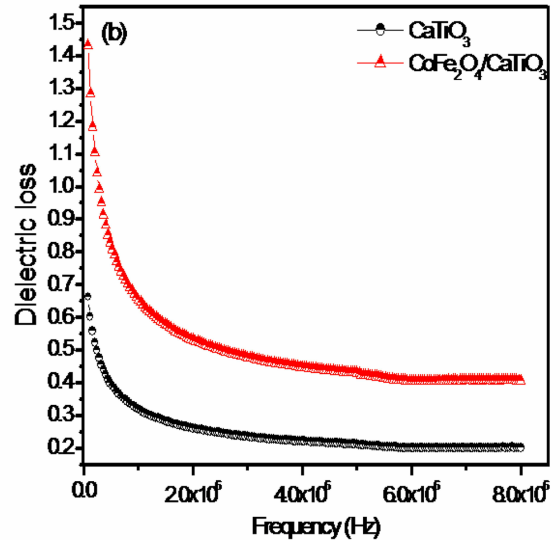
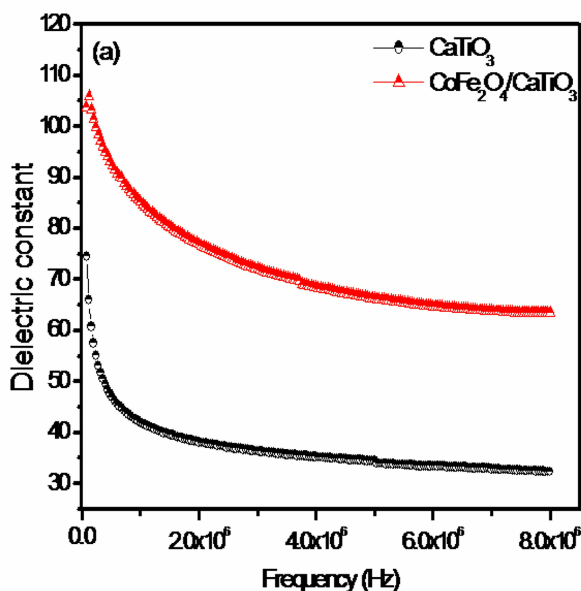


Fig.4 Variation of dielectric constant (a) and dielectric loss (b) with frequency.

$\text{CaFe}_2\text{O}_4$  nanoparticles and  $\text{CaTiO}_3$  interface produce lattice distortion and further cause lattice vibration and hence improve the polarization. Crystalline size of CFO nanoparticles also plays a prominent role in improvement of dielectric

properties [12]. In proposed composition, single domain CFO nanoparticles are responsible for enhanced value of dielectric constant.

Table.1 Dielectric constant and Dissipation factor with frequency.

Material Composition	Frequency	Dielectric Constant	Dissipation Factor
$\text{CaTiO}_3$	80 KHz	74	0.65
$\text{CaFe}_2\text{O}_4/\text{CaTiO}_3$	80 KHz	103	1.44

Furthermore, similar behavior of dielectric loss with frequency can be shown by all samples as shown in Fig.4 (b). The dissipation factor value decreases with increase in frequency and become constant at higher frequency and reaches a constant value of 0.65 and 1.44 for  $\text{CaTiO}_3$ , and  $\text{CaFe}_2\text{O}_4/\text{CaTiO}_3$ , respectively. This lower value obtained for the specimens reflects that these materials are less lossy and can be used in sensors, memory devices, recording tapes, microprocessors, etc.

## Conclusion

In conclusion, the Co-precipitation and solid state method has been employed to prepare CFO and CTO/CFO (1:1) successfully. The absorption edges have been found to be in UV-B (280–320 nm) range and UV-C (100–279 nm) range. The gap between energy levels has

been calculated in range 4.95 eV to 5.70 eV. The band gap increases with incorporation of CFO. The transmittance of UV-Vis rays has been estimated around 40% and 20% for CTO and CFO/CTO, respectively. The CTO and CFO/CTO exhibited a high relative permittivity of 74 and 103, respectively and dissipation factor have been decreased with increase in frequency and become constant at higher frequency due to interfacial polarization.

## References

- [1] M. Khan, M. Kumari, H. Pawar, U. K. Dwivedi, R. Kurchania, D. Rathore, *Applied Physics A: Materials Science and Processing*, 127(2021) 654.
- [2] Y. Wong, J. Hassan, M. Hashim, *Journal of Alloys and Compound*, 571(2013) 138.
- [2] L. S. Oliveria, D. X. Gouveia, M. A. S. Silva, A. S. B. Sombra, *Microwave & Optical Technology Letters*, 57(2015) 4.
- [4] S. Yin, Y. Zeng, T. Cai, C. Li, Chen X, & Cao L, *International Journal of Hydrogen Energy*, 39(2014) 6295.
- [5] F. Yang, X. Zhao, & P. Xiao, *Solid State Ionics*, 181(2010) 783.
- [6] H. Pawar, M. Khan, C. Mitharwal, U. K. Dwivedi, S. Mitra, D. Rathore, *RSC Advance*, 10(2020) 35265.
- [7] K. Hkiri, M. Ben Salem, A. Othmani, M. Zouaoui, *Ionics (Kiel)*. 26(2020) 5099.
- [8] S. Cherdchom, T. Rattanaphan, & T. Chanadee, *Advances in Materials Science and Engineering*, 2019(2019) 9.
- [9] K. Dhabekar, K. M. Kant, *Physica B: Physics of Condensed Matter*, 603(2021) 412752.
- [10] U. K. Dwivedi, M. Kumari, M. Khan, H. Pawar, R. Singhal, D. Rathore, *Applied Physics A: Materials Science and Processing*, 127(2021) 431.
- [11] M. Khan, H. Pawar, M. Kumari, C. Patra, G. Patel, U. K. Dwivedi, D. Rathore, *Journal of Alloys and Compound*, 840(2020) 155596.
- [12] D. Rathore, R. Kurchania, R. K. Pandey, *International Journal Minerals, Metallurgy and Materials*, 21(2014) 408.