Effect of temperature on electrical properties of auto combustion derived nano calcium ferrite

P. Shankar¹, Bhavyashri², R.S. Raveendra³, A. Jayasheelan⁴, C.S. Prakash⁵, B. Daruka Prasad⁶, K.G.Rewathkar⁷, B.M. Nagabhushana⁸

¹Department of Physics, Sai Vidya Institute of Technology, Bengaluru - 560 064, India
²Visveswaraya Technological University, Belagavi - 590 014, India
³Department of Physics, A.C.S. College of Engineering, Bengaluru -560 074, India
⁴Department of Chemistry, Sai Vidya Institute of Technology, Bengaluru - 560 064, India
⁵Department of Physics, Maharani’s science college for women Bengaluru - 560 001, India
⁶Department of Physics, SJC Institute of Technology, Chikkaballapura - 562 101, India
⁷Department of Physics, B.M.S. Institute of Technology, Bengaluru - 560 064, India
⁸Department of Physics, Dr. Ambedkar College, Pune - 440 010, India

ABSTRACT

In the present research work, calcium nano ferrite was synthesized using wet chemical technique, namely solution combustion method. The powder sample thus obtained was calcinated at 900 °C for 1 hour and characterized by PXRD, FTIR, SEM and TEM. The powder X-ray analysis showed that, the sample was found to exist in orthorhombic phase structure. The electrical properties such as, conductance, dielectric constant and dielectric loss were analyzed using impedance precision analyzer (Wayn kerr 6500 B) at a constant frequency of 100 Hz for temperatures ranging from 373- 623 °K. The conductance and dielectric constant are found to increase with temperature. Also tan δ has small value and indicates a peak around 475 °K at a frequency of 100Hz.

Key words: Wet chemical method, conductivity, dielectric loss, CaFe₂O₄, orthorhombic

INTRODUCTION

For the past few decades, With the advances in the field of magnetic nanoparticles, spinel nano ferrites have emerged as one of the well-known soft magnetic materials due to their high resistivity, low eddy current, and hysteresis losses (West and Blankenship 1967; Argentina and Baba 1974). Due to their extremely small sizes they may possess novel and improved properties in comparison to the properties of bulk materials. A great technological importance is given to nano sized ferrites which forms a group of semiconducting materials. The interest in the nano ferrites is because of their important physical and chemical properties for various applications. They were used in many fields such as making micro-wave devices [1], catalysts [2], antenna materials high frequency transformer core, and magnetically-guided drug delivery devices [3–5]. The high resistivity of ferrites makes them suitable for applications in the growth of microwave
and millimeter wave-based communication technologies, the invention of dielectric resonators has emerged as one of the most quick growth areas in electroceramic manufacturing [6-8]. Doping, substitutions and Preparation methods [9, 10] play a very important role in controlling the properties of ferrites. Among these magnetic materials, spinal-type ferrite nano particles, MFe$_2$O$_4$ (M=Ca, Mn, Co, Ni, Zn, Mg, Fe, etc.), have gained great interest because of their good electromagnetic performance and wide range of applications.

The CaFe$_2$O$_4$-type structure includes edge- and corner sharing BO$_6$ octahedral, constituting a very unique network similar to perovskite-related compounds. This structural network leads to interesting physical properties of CaFe$_2$O$_4$-type compounds, where the B-site atoms are transition-metal magnetic elements, such as high-critical temperature superconductivity in cuprates [11], quantum magnetic characters in ruthenates [12], strongly correlated features in manganates [13], etc. In particular, unique quantum behavior characteristic of low dimensional systems may occur in the CaFe$_2$O$_4$-type compounds. In comparison with other ferrites such as MnFe$_2$O$_4$, NiFe$_2$O$_4$, ZnFe$_2$O$_4$, CoFe$_2$O$_4$ and CuFe$_2$O$_4$, calcium ferrite has a significant advantage; it is biocompatible and eco-friendly due to the presence of Ca$^{2+}$ instead of heavy metals [14]. In the present study, the variation of ac conducting properties for different temperature for the calcium nano ferrite were determined for as formed and calcined samples.

MATERIALS AND METHODS

Commercially pure ferric nitrate (Fe(NO$_3$)$_3$, AR 99 % Nice), Calcium nitrate hexa hydrate (Ca(NO$_3$)$_2$ 6H$_2$O AR 99 % Aldrich), Glycine (C$_2$H$_5$NO$_2$) AR 99 % Merck), were used as such without any further purification. Electrical properties are measured as function of temperature in the range 373- 623 K at a constant frequency of 100 Hz were carried out using impedance precision analyzer (Wayn kerr 6500 B) .The dielectric constant ,dielectric loss and conductivity were calculated by using suitable formulae.

EXPERIMENTAL PROCEDURE
SYNTHESIS OF NANO CALCIUM FERRITES

Nano calcium ferrite was prepared by facile solution combustion method was used [15-17]. In this method, the reaction mixture was calculated based on the total oxidizing and reducing valances of the oxidizer and fuel required to release the maximum energy for the reaction. The stoichiometric quantities of Fe(NO$_3$)$_3$ and Ca(NO$_3$)$_2$ 6 H$_2$O were dissolved double distilled water and stirred well using a magnetic stirrer for about 30 min. The crystalline dish containing the above solution was introduced into preheated muffle furnace maintained at 500 ± 10 °C. The solution was boiled and resulted in a highly viscous liquid. This viscous liquid catches fire and auto ignited with smoldering type of burning on the surface, which rapidly proceeded throughout the entire volume forming a brownish powdered product. Then it was calcinated to 900 °C for 1 hour. The overall reaction can be written as

18 Fe(NO$_3$)$_3$ + 9 Ca(NO$_3$)$_2$ + 40 C$_2$H$_5$NO$_2$ → 9 CaFe$_2$O$_4$ + 56 N$_2$ + 80 CO$_2$ + 100 H$_2$O …… (1)

CHARACTERIZATION TECHNIQUES

Solution combustion derived nano calcium ferrite was characterized by PXRD. Powder X-ray diffraction patterns were collected on a Shimadzu XRD-700 X-ray diffractometer with CuKα radiation with diffraction angle range 2θ = 20–80°, operating at 40 kV and 30 mA.
Product was morphologically characterized by SEM performed on a JSM-6490 scanning electron microscope with a voltage of 5 kV. The FT-IR studies have been performed on a Perkin Elmer Spectrometer (Spectrum 1000) with KBr pellet technique in the range of 400–4000 cm⁻¹.

RESULT AND DISCUSSIONS
PXRD

The phase formation of nano calcium ferrite was confirmed by PXRD measurements. The PXRD of sample calcinated at 900 °C confirms well-defined and broader diffraction peaks (Figure. 1). These peaks indicate the nano crystalline nature of the sample with orthorhombic phase (matched with JCPDS card number 72-1199). The diffraction peaks can be indexed to (2 2 0), (3 2 0), (0 4 0), (1 3 1) (3 1 1), (3 3 1), (4 0 1), (5 2 0), (2 6 0), (6 0 0), (1 7 0), (0 2 2), and (0 4 2) reflections. The broadening of the reflections clearly indicates the inherent nature of nano crystals. Figure-1 shows the powder X-ray diffraction patterns of sample calcined at 900 °C. The crystallite size is calculated from the full width at half maximum (FWHM (β)) of the diffraction peaks using Debye- Scherer’s method [18] using the following equation.

\[ d = \frac{k\lambda}{\beta \cos \theta} \]

Figure-1

Where ‘d’ is the average crystalline dimension perpendicular to the reflecting phases, ‘λ’ is the X-ray wavelength, ‘k’ is Scherer’s constant (0.92), ‘β’ is the full width at half maximum (FWHM) intensity of a Bragg reflection excluding instrumental broadening and ‘θ’ is the Bragg’s angle. The calculated average crystallite size of the sample is found to be 16 -20 nm. The lattice and the structural parameters of the nano calcium ferrite are summarized in Table-1.
FT-IR SPECTROSCOPIC STUDIES

Figure- 2 represents FT-IR spectrum of the nano calcium ferrite recorded to define the vibrational frequency of metal–oxygen and other bonds related to impurities present. It can be seen that no impurity peaks were observed. The frequency band at 468 cm\(^{-1}\) can be attributed to the stretching vibration of Fe\(^{3+}\) in the octahedral site of structure [19].

![FT-IR Spectrum](image)

**Figure-2**

MORPHOLOGICAL ANALYSIS

The morphology of ferrite powders were investigated using SEM analysis. Figure- 3 (a-b) shows SEM micrographs of nano calcium ferrite. Micrographs reveal a fluffy and sponge like morphology with porous structure for the sample. The porous structure has a large specific area that implies a much more active surface required for many applications. SEM micrographs also reveals that the particles are spherically agglomerated having uniform size and distribution. Agglomeration may be due to the magnetic dipole interaction between ferrite particles [20, 21]. The proof for the crystallinity of the calcium nanoferrite was obtained by TEM analysis. TEM image of CaFe\(_2\)O\(_4\) (Fig- 4) shows that the particles obtained are in nano range and have highly crystalline in nature and having average particle size ~ 20 nm.

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>orthorhombic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>Pnam (62)</td>
</tr>
<tr>
<td>JCPDS no</td>
<td>72-1199</td>
</tr>
<tr>
<td>Particle size</td>
<td>20 nm</td>
</tr>
<tr>
<td>Unit cell lattice parameters</td>
<td>(a = 9.23000 \text{ Å}), (b= 10.70500 \text{ Å}), (c= 3.02400 \text{ Å})</td>
</tr>
</tbody>
</table>
ELECTRICAL PROPERTIES

The variations in dielectric constant of the real part ($\varepsilon'$), imaginary part ($\varepsilon''$), and dielectric loss (tan $\delta$) with temperature for nano calcium ferrite at 100 Hz were as shown in Figure-5. The dielectric constant is calculated using the formula (3).

$$\varepsilon' = \frac{Cd}{A\varepsilon_0}$$  

Where ‘C’ is the capacitance, ‘d’ is the thickness of the pellet ‘A’ is the area of the pellet. It is observed that, the dielectric constant increases with increase in temperature from 373 to 623 °K for both as formed and calcined samples. The value of $\varepsilon'$ is 11 at 373 °K and increased to 11223 at 623 °K for as formed sample, where as for calcined sample varied from 133 to 12224 respectively. The sharp increase in $\varepsilon'$ is may be due to space charge polarization [22]. It is observed from the graph that, the value of $\varepsilon'$ is almost independent of temperature between 373 to 450 °K. This constancy in $\varepsilon'$ up to 450 °K may be due to localization of impurities at low temperature [23]. It is also observed from the figure-5 that, beyond 450 °K there is a considerable increase in $\varepsilon'$ with temperature, which may be attributed to the free movement of impurities causing polarization.
It is observed from the study that, $\tan \delta$ has small values and indicates a peak around 475 K at a frequency of 100Hz. as shown in the fig-6. The dielectric loss in calcined sample is slightly higher than that of the as formed samples. The presence of a maximum (peak) in $\tan \delta$ could be explained by using Koops's model [24]. This model considers the solid to be composed of grains and grain boundaries. The peak due to the as formed and the calcined samples have different parameters where the grains have low resistivity and large thickness while the grain boundaries have high resistivity and small thickness. Also it was assumed that each of the grains and grain boundaries has its characteristic peak [25]. The dielectric loss both in as formed and calcined samples were nearly independent of temperature from 550 to 625 K. The peaks observed in $\tan \delta$ may be attributed to the contribution from the grain boundaries, where the impurities reside, which take part in the conduction at low temperatures. The grains also play a major at higher temperatures [26]. The dielectric loss is calculated using the formula (4).

$$\tan \delta = \frac{\varepsilon''}{\varepsilon}$$

Figure-6
The variation of conductivity for various temperatures at 100 Hz is shown in Fig-(7). The conductivity increases with increase in temperature this could be related thermal activation localized electronic charge carriers [27]. The conductivity is calculated using the formula (5). It is also concluded that the conductivity is more for the calcined sample compared to the as formed sample.

\[ \sigma = \frac{Gd}{A} \] .............................. (5)

Where ‘G’ is the conductance, ‘d’ is the thickness of the pellet ‘A’ is the area of the pellet.

The variation of the imaginary part of the dielectric constant is as shown in the Fig-8.

\[ \varepsilon'' \]

CONCLUSION

CaFe$_2$O$_4$ nanoparticles prepared by the simple solution combustion method using ferric nitrate and calcium nitrate as oxidizer and glycine as fuel. Synthesized product is well matched with ICDD card number 72-1199 and having orthorhombic structure. The study of the electrical properties such as conductance, dielectric constant and dielectric loss were studied by varying the temperature at a constant frequency of 100Hz. The increase in \( \varepsilon' \) may be due to space charge
polarization. The conductivity is found to increase with temperatures this could be related thermal activation of localized electronic charge carriers.

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REFERENCES

[21] Yuping W, Liangcho L, Jing J, Hui L, HaiZhen Q, Feng X, Conductivity and magnetic properties of Zn$_{0.6}$Cu$_{0.4}$Cr$_{0.5}$La$_{0.04}$Fe$_{1.46}$O$_4$/PPy composites prepared by in situ inverse microemulsion polymerization, React. Funct. Polym., 2008, 68, 1587-1593.
[22] Dielectric, AC-impedance, modulus studies on 0.5 BaTiO$_3$ _ 0.5CaCu$_3$Ti$_4$O$_{12}$ nanocomposite ceramics synthesized by one-pot, glycine-assisted nitrate-gel route Laxman Singha, UmaShankerRaib, KamdeoMandalc, ByungCheolSina, Sang-Ick Leed, YoungilLeea,n Ceramics International science direct 40 (2014) 10073–10083.