Synthesis and dielectric properties of Zn doped GdFeO$_3$ ceramics

C Sai Vandana, J Guravamma and B Hemalatha Rudramadevi

Department of Physics, Sri Venkateswara University, Tirupati-517 502, Chittoor, Andhra Pradesh, India

Email: drbhrd@gmail.com

Abstract. GdFeO$_3$ and GdZn$_{0.3}$Fe$_{0.7}$O$_3$ ceramics were prepared by standard Solid State Reaction method at 1200°C. The structural changes and crystallite sizes of the undoped and Zn doped ceramics were studied using the XRD data. Microstructural features and elemental composition of GdFeO$_3$ and GdZn$_{0.3}$Fe$_{0.7}$O$_3$ ceramics were determined from SEM and EDS analysis. Room temperature dielectric measurements such as dielectric constant ($\varepsilon'$), tangent loss (tan$\delta$) and AC conductivity ($\sigma_{ac}$) were carried out in the frequency range (100Hz to 1MHz). Improved dielectric properties of GdZn$_{0.3}$Fe$_{0.7}$O$_3$ over GdFeO$_3$ ceramics with low values of dielectric loss render them as potential materials in the areas of microwave communication systems, information storage, spintronics, sensors, etc.

1. Introduction

Microwave communication systems have strongly driven the development of dielectric ceramics for their application to be used for dielectric resonators, and filters at microwave frequencies. Perovskite oxides give good opportunities for designing materials owing to the possibility of controlling their properties by varying their chemical composition [1],[2]. In the processing of GdFeO$_3$, the valence fluctuations of iron ions leads to large leakage and impurities masks the intrinsic properties of GdFeO$_3$. It was also found that doping of transition metal ions will facilitate the enhancement of electrical properties of the GdFeO$_3$ ceramics. Therefore, it is expected that the resistivity of GdFeO$_3$ can be controlled by donor doping and thus also the dielectric properties of the prepared ceramics [3].

In the present work, Gd based orthoferrite (GdFeO$_3$) has been undertaken to study its structural and dielectric properties. It is well known that the intrinsic properties of the materials depend on the chemical composition and preparative methods [4]. In our present work Zn doped GdFeO$_3$ is prepared by the standard Solid State Reaction method. Zn is selected as one of the dopant materials for GdFeO$_3$ because it causes structural changes like lattice parameter, density etc., in the host matrix resulting in a linear increase in the conductivity [5]. To understand the nature of conduction and defects centers which are present in the crystalline materials, the knowledge of AC conductivity and dielectric properties of semiconductors is very important [6] Therefore, the effect of Zn concentration on structural and electrical properties of GdFeO$_3$ has been investigated in our present paper.

2. Experimental methods

GdFeO$_3$ and GdZn$_{0.3}$Fe$_{0.7}$O$_3$ ceramics were synthesized by standard solid-state reaction method. The precursors Gd$_2$O$_3$ and Fe$_2$O$_3$ of analytical grade, taken in stoichiometric ratio were well mixed in an agate mortar for 1 h with a suitable amount of acetone for homogenous mixing and then sintered at 1200°C for 5 h in an electrical muffle furnace. Then the powder obtained was made into a pellet by adding KBr as binding agent and it was finally sintered at 1000°C for 2 hrs. The powders obtained were made into pellets for dielectric measurements. The final product thus obtained was used for further characterizations. X-ray diffraction pattern of GdFeO$_3$ was collected using a Philips diffractometer with Cu K$_\alpha$ radiation. The microstructure and morphology of the ceramics were observed by using Carl Zeiss scanning electron microscope (SEM) operated at 20 kV.

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI.

Published under licence by IOP Publishing Ltd
measurements were made using PSM 1700 LCR METER in the frequency range 100Hz – 1MHz. All the measurements were performed at room temperature.

3. Results and Discussion

3.1. XRD

The XRD patterns of GdFeO$_3$ and GdZn$_{0.3}$Fe$_{0.7}$O$_3$ ceramics were shown in figure 1. GdFeO$_3$ crystallizes into orthorhombic structure in Pbnm space group. All the peaks were well matched and are in accordance with JCPDS card number 074-1476 [7]. The additional peaks marked with * in the given XRD pattern are due to the presence of small amounts of cubic Gadolinium Oxide Gd$_2$O$_3$ (JCPDS 43-1014) and Garnet Gd$_3$Fe$_5$O$_{12}$ (JCPDS 48-0077) phases along with the GdFeO$_3$ structure. The successful incorporation of Zn into the lattice of GdFeO$_3$ is confirmed from the peaks obtained at around 35.4° and 42.25° in the XRD pattern of Zn doped GdFeO$_3$.

![Figure 1: XRD Patterns of GdFeO$_3$ and GdZn$_{0.3}$Fe$_{0.7}$O$_3$ ceramics.](image)

The average crystallite size was calculated by the Scherrer’s formula expressed in equation (1) using the full width at half maximum (FWHM) of the most intense peak (1 1 2). The Scherrer’s formula is described as

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

where $D$ is the average crystallite size or particle size, $\lambda$ is the X-ray wavelength (0.1540593 nm), $\theta$ is the Bragg angle and $B$ is the FWHM [8]. The crystallite sizes of GdFeO$_3$ and GdZn$_{0.3}$Fe$_{0.7}$O$_3$ ceramics were found to be 120.21 nm and 367.5 nm respectively. The increase in crystallite size is due to incorporation larger ionic radii Zn atoms ($r = 0.74\text{Å}$) into some of the sites of Fe atoms ($r = 0.64\text{Å}$).

3.2. SEM and EDS analysis

Figures 2 & 3 show the SEM and EDS analysis of GdFeO$_3$ and GdZn$_{0.3}$Fe$_{0.7}$O$_3$ ceramics respectively. The microstructural features of these ceramics are mostly similar apart from slightly different grain sizes. The particles are found to be agglomerated on doping with Zn into the matrix of GdFeO$_3$. EDS elemental analysis confirmed the presence of the Gadolinium(Gd), Iron(Fe), Zinc(Zn) and Oxygen(O) in the lattice of the prepared ceramics. The weight percentage and atomic percentage of the constituent elements are tabulated below.
3.3. Dielectric Measurements

The dielectric properties of GdFeO$_3$ and GdZn$_{0.3}$Fe$_{0.7}$O$_3$ ceramics were studied by using the Phase Sensitive Multimeter with applied frequency range from 100 Hz to 1 MHz at room temperature. Based on the recorded data of the sample we have calculated the dielectric constant by using the parallel plate capacitance formula as given in equation (2),

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A}$$  \hspace{1cm} (2)

Where C is the capacitance, d is the distance of separation between the plates, A is the area of the parallel plates. The room temperature behaviour of dielectric constant $\varepsilon'$ (real part) of GdFeO$_3$ and GdZn$_{0.3}$Fe$_{0.7}$O$_3$ ceramics with frequency is shown in figure 4 [[9],[10]].
The dielectric constant values were decreased rapidly in lower frequency region because of the rapid polarization occurring in GdZn$_{0.3}$Fe$_{0.7}$O$_3$ ceramics. The electric dipoles do not comply with the applied external field and they lag behind the applied field. Hence the dielectric constant decreases with the increase of frequency and shows almost frequency independent behaviour at higher frequencies [6]. The dielectric constant and dielectric loss both are inversely proportional to the frequency. The normal behavior dielectric is that both dielectric and dielectric loss decrease with increasing the frequency. As frequency increases, a point will be reached where the space charge cannot sustain and the values of dielectric loss gets diminished with external field. From the previously done work it was found that the average grain size also played crucial role on dielectric constant. When average grain size increases, the number of grains per unit volume decreases. So, the number of electric dipoles per unit volume in the dielectric medium also decreases which in turn decreases the dielectric constant of the material. The frequency dependence of tan δ for GdFeO$_3$ and GdZn$_{0.3}$Fe$_{0.7}$O$_3$ ceramics at room temperature is shown in figure 5. It is represented as dissipated energy in a dielectric system. GdZn$_{0.3}$Fe$_{0.7}$O$_3$ sample has higher loss at lower frequencies and lower loss at higher frequencies which exhibit dispersion behaviour similar to the dielectric constant. At higher frequency, domain wall rotation predominate their motion resulting in low dielectric losses. The low dielectric constant and dielectric loss of GdZn$_{0.3}$Fe$_{0.7}$O$_3$ ceramics at high frequency region make it to be a suitable material for high frequency applications [[11],[12]].

![Figure 5: Dielectric loss in GdFeO$_3$ and GdZn$_{0.3}$Fe$_{0.7}$O$_3$ ceramics with frequency change at room temperature.](image1)

![Figure 6: AC Conductivity profiles of GdFeO$_3$ and GdZn$_{0.3}$Fe$_{0.7}$O$_3$ ceramics at room temperature.](image2)

The AC conductivity of the sample ($\sigma_{ac}$) is determined from the dielectric data using the equation 3:

$$\sigma_{ac} = \omega\varepsilon_0\varepsilon'\tan\delta$$ (3)

where $\varepsilon'$ is the real or measured permittivity, tan$\delta$ is the tangent loss, $\omega = 2\pi f$ is angular frequency and $\sigma_{ac}$ is the AC conductivity [[13],[14]]. The profiles of the ac conductivity ($\sigma_{ac}$) as a function of frequency (logf) at room temperature are shown in figure 6. Contrary to $\varepsilon'$, AC conductivity ($\sigma_{ac}$) is almost constant up to a log frequency of 4Hz and later it increases rapidly up to 6Hz. We have observed an increase in conductivity of the ceramics with an increase in frequency. At lower frequency, conductivity has a constant value because of the inertia of molecules or ions. The AC conductivity values at room temperature for GdFeO$_3$ and GdZn$_{0.3}$Fe$_{0.7}$O$_3$ ceramics from the graph are $1.01 \times 10^{-5}$ Scm$^{-1}$ and $1.29 \times 10^{-5}$ Scm$^{-1}$ respectively. At higher frequencies the increased conductivity is due to the increased mobility of ions with the change in the applied frequency [15].
4. Conclusions
Polycrystalline GdFeO$_3$ and GdZn$_{0.3}$Fe$_{0.7}$O$_3$ ceramics were synthesized by conventional solid state reaction method at 1200$^\circ$C. XRD pattern confirmed the orthorhombic structure of the prepared ceramics and successful incorporation of Zn into the GdFeO$_3$ lattice. The crystallite size of the prepared ceramics was calculated using Scherrer formula and it is observed to be 120.21 nm and 367.5 nm respectively. SEM with EDS analysis revealed the different grain sizes and the presence of constituent elements without impurities in the prepared sample. The behaviour of dielectric parameters such as dielectric constant ($\varepsilon'$), tangent loss (tan$\delta$) and AC conductivity ($\sigma_{ac}$) were studied in the frequency range (100 Hz to 1MHz) at room temperature. We have observed an increase in the AC conductivity of the Zn doped GdFeO$_3$ ceramics and it is found to be $1.01 \times 10^{-5}$ S cm$^{-1}$ and $1.29 \times 10^{-5}$ S cm$^{-1}$ for the undoped and Zn doped ceramics respectively. The dielectric behaviour studied as a function of frequency reveals the application of prepared GdFeO$_3$ ceramic material in the field of information storage devices, sensors and spintronic applications.

5. References
[1] Das N, Nath M A, Thakur G S, Thirumal M and Ganguli A K 2015 J. Solid State Chem. 229 97-102
[2] R.J. Cava, 2001 J. Mater. Chem. 11 54–62
[3] Sen K, Singh K, Gautam A and Singh M 2012 Ceram. Int. 38 243-49
[4] Murugesan C and Chandrasekaran G 2015 RSC Adv. 5 73714-25
[5] Grigoryan R A and Grigoryan L A 2004 Inorg. Mater. 40 295-99
[6] Ashokkumar M and Muthukumaran S 2015 J. Lumin. 162 97-103
[7] Bashir A, Ikram M and Kumar R 2011 Mod. Phys. Lett. B 25 1787-94
[8] Bedekar V, Jayakumar O D, Manjanna J and Tyagi A K 2008 Mater. Lett. 62 3793-95
[9] Jaya Prakash B, Rudramadevi B H and Buddhudu S 2014 Ferroelectr. Lett. 41 110-22
[10] Shibeshi P and Veeraiah V 2014 J. Phys. Chem. Solids 75 1075-79
[11] Elissalde C and Ravez J 2001 J. Mater. Chem. 11 1957-67
[12] Dygas J R 2005 Solid State Ionics 176 2065 – 2078
[13] Sultan k, Ikram M, Asokan K, 2014 Vacuum 99 251-258
[14] Durga Rao T, Asmitha kumari, Niranjan M K and Saket A 2014 Physica B 448 267-72
[15] Izquierdo J, Bolanos G, Zapata V H and Moran O 2014 Curr. Appl. Phys. 14 1492-97