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Effect of Gd^{3+} on dielectric and magnetic properties of $Y_3Fe_5O_{12}$

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ABSTRACT

The Gd^{3+} doped $Y_{3-x}Gd_xFe_5O_{12}$ (x=0.0, 0.05, 0.15, and 0.25) nanopowders were prepared using modified sol–gel route. The structural characterizations such as X-ray diffraction, transmission electron microscopy has been carried out. The nanopowders were sintered at 700 °C/3 h. The lattice parameters and density of the samples were increased with an increase of Gd^{3+} concentration. The microstructure was analyzed using atomic force microscopy. The room temperature dielectric (ε' and ε'') and magnetic (μ' and μ'') properties were measured in the frequency range 5–50 GHz. with Gd^{3+} the dielectric properties were enhanced, but there is a decrease in the magnetic properties. The room temperature magnetization studies were carried out up to 1.5 T. the saturation and remnant magnetization were decreased with an increase of gadolinium concentration. These garnets have low permeability, low losses and a broad distribution of FMR line width which makes them a promising material for microwave devices can be used in the high frequency range i.e. up to 50 GHz.

1. Introduction

$RE_3M_5O_{12}$ garnets (where RE=rare-earth, M=transition metal) present unique magnetic and magneto-optical properties such as ferromagnetic ordering at room temperature, with constant magnetization over a large temperature range, ferromagnetic resonance and Faraday rotation among others. These features make this system one of the most promising materials for application in the technology of passive not-reciprocal and magneto-optical recording devices [1,2]. YIG was employed for its narrow line width in magnetic resonance and controllable saturation magnetization in magnetic microwave devices [3]. Superparamagnetic YIG nanoparticles have been studied for biomedical applications, such as magnetic field induced localized hyperthermia for the treatment of cancer [4,5]. Generally garnets crystallize in the cubic structure (space group *Ia3d*) and can be synthesized with partial substitutions in the different cationic sites, e.g., with the ideal formula $(RE'\ RE'')_3(M'\ M'')_5O_{12}$.

In industry level the YIG powders are prepared by reacting Y_2O_3 and Fe_2O_3 oxides at a high temperature (1100–1200 °C) [6]. Using this method, we cannot avoid the formation of $YFeO_3$ which is an intermediate phase and the existence of starting materials Fe_2O_3, which remain as impurities unless heated to high temperature. Further, to meet the sintering requirements, powders prepared by this method needed prolonged grinding which will reduce the purity of the material, and the obtained product contains larger grain of several micrometers and a limited degree of homogeneity. So to get pure YIG phase high sintering temperatures (> 1450 °C) and long soaking time (> 10 h) are required with a density of 97% for device applications [7]

It is well-known that the sizes and the shapes of these particles largely determine the overall properties especially magnetic properties. Therefore, it is important to produce garnets with strict control of the composition, the homogeneity, the size and the particle shape. In recent years, several approaches such as sol–gel, co-precipitation, citrate–nitrate gel combustion, and mechano-chemical synthesis have been employed to synthesize finer and more homogeneous YIG powder in order to prepare the ceramics at low sintering temperatures [8–11].

Praveena et al. [12] made an attempt to synthesize the YIG nanopowders using the chemical co-precipitation method and were successful in getting the pure YIG phase sintered at 800 °C/5 h using the conventional sintering method. Here we tried to reduce the crystallization temperature further so as to avoid grain growth and we are able to do that with the modified sol–gel process. As sol–gel reactions with a variety of gelling agents [13–17] were frequently used for the synthesis of YIG. An intimate mixing of Y^{3+}, Gd^{3+} and Fe^{3+} ions causes a decrease in the crystallization temperature down to about 700 °C. Sol–gel reactions allow also more to control over the crystallite size by changing gelating conditions and thermal treatment.

It is well known that their properties can change significantly depending on the nature and amount of ion substitution and the synthesis conditions route. In this paper we investigated the novel synthesis route followed by their structural characterization, morphology and the effect of Gd^{3+} on dielectric and magnetic properties.

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We believe that after rigorous literature survey only very few researchers reported the synthesis, characterization of YIG and GdIG for some device applications, but nobody has reported the systematic synthesis of $Y_{3-x}Gd_xFe_5O_{12}$ (x=0.0, 0.05, 0.15 and 0.25) and their properties for microwave frequencies.

2. Experimental

The $Y_{3-x}Gd_xFe_5O_{12}$ (x=0.0, 0.05, 0.15 and 0.25) nanoparticles were synthesized using yttrium nitrate [$Y(NO_3)_3 \cdot 6H_2O$], gadolinium nitrate [$Gd(NO_3)_3 \cdot 6H_2O$] and ferric nitrate [$Fe(NO_3)_3 \cdot 9H_2O$] as the starting precursors taken in 3:5 ratio and was gelated by using mono-hydrated citric acid solution, it was taken in such a way so that the molar ratio of the total nitrate to citric acid becomes unity. With constant stirring at 60 °C/1 h, the pH of the solution was adjusted to about 7 with ammonia solution. All these mixtures were kept for constant stirring at 60–70 °C to avoid precipitation so as to obtain a homogeneous mixture. The brown color citrate mixture obtained was a clear solution with no precipitation. After that ethylene glycol was added to the solution in proportionate to citric acid/ethylene glycol ratio of 60:40. The gel initially started to swell and filled the beaker, producing foam like precursor consisting of very light and homogeneous particles of nanosize. The resultant gel was dried at 100 °C in hot air oven for 12 h. The obtained powders were calcined at 400 °C, leached in diluted HNO_3, grounded and pressed into pellets and sintered at 700 °C/3 h. Leaching was done to get a single phase nanopowder [18]. As we know the synthesis method plays a major role on the phase formation to get the pure YIG at low temperatures from literature (synthesized by hydrothermal method) we found that at 200 °C, it is amorphous phase, if we heat treat at 225 °C only $Y_3Fe_5O_{12}$ phase will exist. At the intermediate temperature of 215 °C, orthoferrite $YFeO_3$ was observed as a main phase with peak traces of Fe_2O_3. From these studies it is clear that to get the pure YIG phase as-prepared (400 °C) and sintered (700 °C) is sufficient. [19–21], though the synthesis conditions may vary. If we sinter the samples above 700 °C in which the garnet phase synthesized from the oxide source of *Y* and Fe under hydrothermal conditions began to decompose abruptly into orthoferrite and magnetite above 725 °C, resulting in a narrow stable temperature range for hydrothermal synthesis of garnets. In order to avoid all these we have synthesized using the modified sol–gel method.

The phase identification of powders was performed using X-ray diffraction (XRD) with Cu K_α (CuK_α=1.54056 Å) radiation. The particle size and morphology of the samples was analyzed using transmission electron microscope (TEM), high resolution transmission electron microscope (HRTEM) JEOL, Japan, and atomic force microscopy (AFM). Quantasorb equipment (Quantachrome Corporation) was used to determine the specific surface area by the Brunauer–Emmett–Teller (BET) technique. Accurate density measurements are an important part of characterizing the physical properties of ferrites. Archimedes' method was used to determine the density of the samples. The bulk density of the sample was calculated from precise measurements of the dry, saturated, and suspended weight. The weight loss of the sample in the water was measured using a digital balance with an accuracy of 0.001 mg. The bulk density of the samples was calculated using the below formula:

$$d_{\text{bulk}} = \frac{M_{\text{air}}}{M_{\text{air}} - M_{\text{xylene}}}\, g/cm^3$$

Table 1
Comparison of crystallite size from Scherer and TEM of Gd^{3+} doped YIG.

Composition, x	Crystallite size Scherer (420) (nm)	Crystallite size (TEM) (nm)
0	22	21
0.05	26	25
0.15	30	29
0.25	32	33

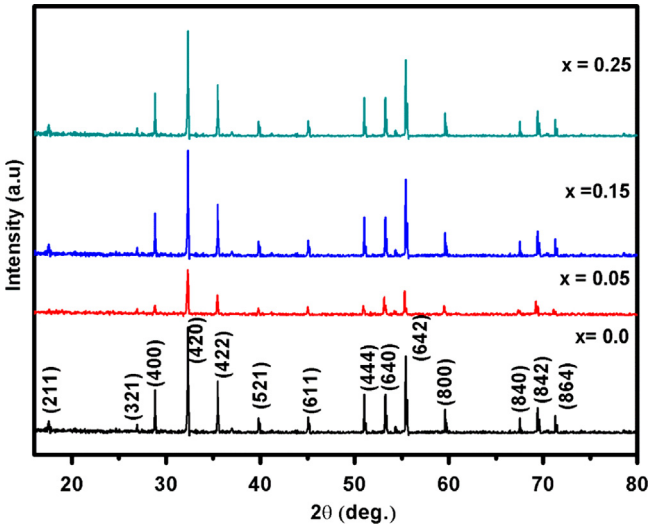

Fig. 2. XRD patterns of sintered Gd^{3+} YIG at 700 °C/3 h.

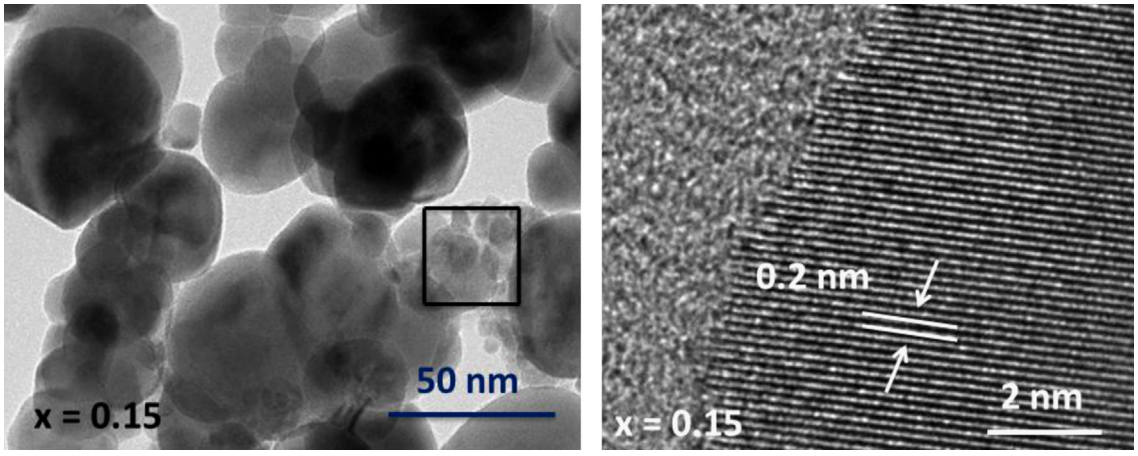

Fig. 1. TEM and HR-TEM of $Y_{3-x}Gd_xFe_5O_{12}$ at x=0.15.