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Effect of precursory solution anion and non-stoichiometry on the properties of yttrium gadolinium iron garnet

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Experimental data for the $Y_{2.01}Gd_{0.99}Fe_5O_{12}$ system indicates that addition of sulphate anion to the $Fe(NO_3)_3$ solutions increases sintered density of the garnet made by spray drying precursory solutions followed by rotary calcining. A smaller particle size and a higher green density of calcined powders obtained from solutions with sulphate added, provide a higher sinterability compared to the powders obtained from nitrate solutions. Conventional ball-milling of calcined powders is eliminated. Sintered density of more than 99% theoretical can be obtained. Data for the $Y_{2.01(1-x)}Gd_{0.99(1-x)}Fe_{5(1-y)}O_{12}$ system indicates that a second phase of (Y, Gd)FeO_3 decreases the sintered density of iron deficient garnet. A second phase of (Y, Gd)FeO_3 also accounts for lower dielectric loss tangent for these compositions.

1. Introduction

Garnet ferrites have been used in many microwave systems. Compositions based on $Y_{3-x}Gd_xFe_5O_{12}$ were considered to be a good candidate material for microwave applications where very low dielectric loss tangent and medium magnetization are critical [1]. Controls of density, chemical homogeneity, grain-size uniformity and compositions are greatly demanded. Spray drying offers a significant improvement in these properties compared to conventional ceramic preparation techniques. NiZn–ferrite [2], MgMn–ferrite and $Y_3Fe_5O_{12}$ [3], and $LiFe_5O_8$ and $LiFe_{4.7}Mn_{0.3}O_8$ [4] have been prepared by spray drying. Gallagher *et al.* found α–Fe_2O_3 powders derived from iron sulphate have smaller aggregrate size than powders from iron nitrate [5]. He also found that materials derived from sulphate gave better sintered density than from nitrate. Poorer sintering behaviour has also been observed in materials prepared from nitrates than from sulphates by O'Bryan *et al.* [6]. In this study, spray drying and rotary calcining were used to form $Y_{2.01(1-x)}Gd_{0.99(1-x)}Fe_{5(1-y)}O_{12}$ powders. The principle objective of the study was to investigate the effect of sulphate anion addition and non-stoichiometry on the sintered density and properties of these garnets.

2. Experimental procedures

2.1. Sample preparation

2.1.1. Solutions

Raw materials employed for this study are 99.9% or better in purity and listed in Table I.

TABLE I Raw materials

Material	Purity (%)	Supplier
Gd_2O_3	99.99	Molycorp
Y_2O_3	99.99	Molycorp
Fe wire	99.90	J.T. Baker
Reagent grade HNO_3 and H_2SO_4		Fisher

2.1.1.1. Solutions for anion addition study. $Y_{2.01}Gd_{0.99}Fe_5O_{12}$ was chosen for anion addition study. Iron solutions of $Fe(NO_3)_3$ calculated to contain 25% by weight of nitrate.salt were prepared by dissolving reagent garde iron wire in 4 M nitric acid. Various amounts of 18 M sulphuric acid were then added to these iron nitrate solutions. Addition of sulphuric acid was 1.3, 2.8 and 8.2 wt% of nitric acid used. Rare earth solutions of $Y(NO_3)_3$

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and $Gd(NO_3)_3$ containing 25% by weight of nitrate salts were obtained by dissolving Y_2O_3 and Gd_2O_3 in 4 M nitric acid. The quantities of oxides are chosen to match the batch of iron so that after the rate earth and iron solutions were prepared, they were mixed directly to give the spray dryer feed solution. Quantitative dissolution was desired to avoid the need for chemical analysis on the solutions.

2.1.1.2. Solutions for non-stoichiometry study. $Y_{2.01(1-x)}Gd_{0.99(1-x)}Fe_{5(1-y)}O_{12}$, for $x = 0$, 0.005 and 0.01 when $y = 0$, and also $y = 0.005$, 0.01, 0.015, 0.02, 0.025 and 0.03 when $x = 0$, were studied. Rare earth and iron solutions were prepared as same as the solutions for acid addition study, except, iron solutions were added with a 8.2 wt % sulphuric acid.

2.1.2. Spray drying, rotary calcining and sintering

The mixed solutions were spray dried in a concurrent flow Bowen laboratory size spray drier. Spray dried powders were calcined by passing them through a rotating-tube furnace at 1150° C. Compacts formed by isostatic pressing the as-calcined powders to 20 000 psi were sintered to 1400° C for 4 h in an oxygen atmosphere.

2.2. Measurement

Sintered densities were measured by using a mercury immersion technique. Dielectric loss tangent was determined by a cavity perturbation technique at approximately 9.3 GHz as outlined in ASTM Document C523-63T. The measured sample was 0.040 in. diameter and 0.625 in long. Cell dimensions were obtained by a standard X-ray technique. α-quartz was used as a internal standard. Microstructures were characterized using an optical or a scanning electron microscope. Spray dried and rotary calcined powders were characterized by using a scanning electron microscope, and in some cases, a Quantimet 720 was used in conjunction with the SEM.

3. Results and discussion

3.1. Sulphate anion addition

Fig. 1 shows that sintered density of $Y_{2.01}Gd_{0.99}Fe_5O_{12}$ was influenced by the amount of addition of sulphate anion to $Fe(NO_3)_3$ solutions. Addition of sulphate anion to $Fe(NO_3)_3$ solutions increased the sintered density of the garnet. Sintered density reached to 99% of theoretical at 8.2 wt % of sulphate addition. Theoretical density is 5.576 g cm^{-3}. A single phase of $Y_{2.01}Gd_{0.99}Fe_5O_{12}$ was obtained after the spray drying powders were rotary calcined at 1150° C in an air atmosphere.

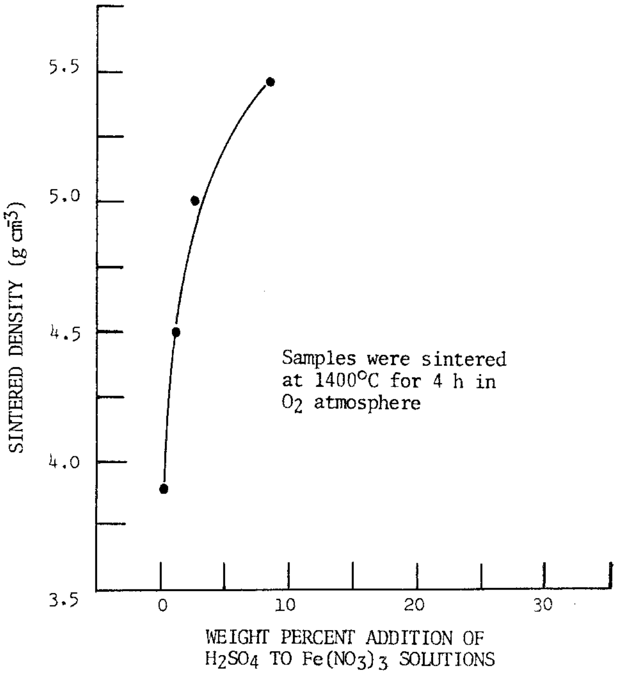

Figure 1 Effect of sulphate anion addition on the sintered density of $Y_{2.01}Gd_{0.99}Fe_5O_{12}$.

TABLE II Effect of sulphate anion on aggregate particle size and green density of rotary calcining $Y_{2.01}Gd_{0.99}Fe_5O_{12}$

Type of Fe solution	Particle size (μm)	Green density (g cm^{-3})
$Fe(NO_3)_3$	2–10	2.80
$Fe(NO_3)_3$ + 8.2 wt% H_2SO_4	0.4–6	2.95

Particle size of rotary calcined powders and green density of compacted power are shown in Table II. It can be seen that garnet powders prepared from $Fe(NO_3)_3$ + 8.2 wt% H_2SO_4 solutions has smaller particle size and larger green density compared to the garnet powders prepared from $Fe(NO_3)_3$ solutions. It shows that smaller particle size of the calcined powders and larger green density of compacts provide higher sintering reactivity.

3.2. Non-stoichiometry

Fig. 2 shows the effect of rare earth and iron deficiencies on green and sintered densities of $Y_{2.01(1-x)}Gd_{0.99(1-x)}Fe_{5(1-y)}O_{12}$. The green and sintered densities were decreased as the amount of iron deficiency increases. X-ray diffraction analysis indicated that the garnet lines do not shift as the amount of iron deficiency increases, but shift to a higher angle as the amount of rare earth deficiency increases in accordance with Vegard's Law. Cell dimensions as a function of rare earth and iron deficiencies are plotted in Fig. 3. It can be seen that the lattice constant does not change for iron deficient samples and decreases as amount of rare earth deficiency increases. What is observed is that for iron deficient samples, $Y_{2.01}Gd_{0.99}Fe_5O_{12}$ and a second phase of (Y, Gd)FeO_3 appear. For the rare earth deficient samples, only a single phase of $Y_{2.01}Gd_{0.99}Fe_5O_{12}$ was detected. Optical micrographs show that many pores appear inside the grains of acid-etched iron deficient samples. Discontinuous grain growth was seen. Grain-shaped pull-outs were also observed. This tendensy toward pull-out is probably a result of a second phase. No pull-outs were found in rare earth deficient

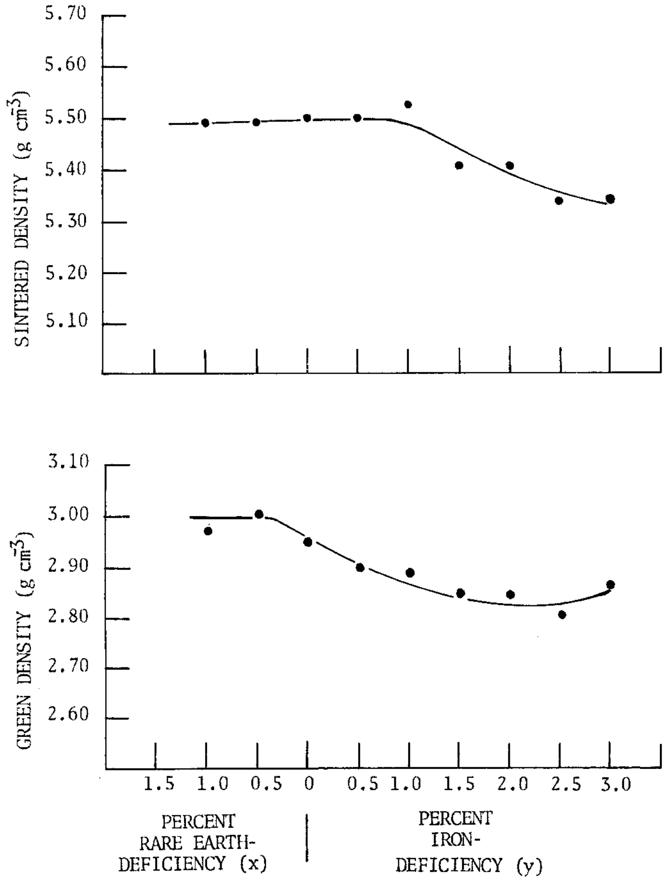

Figure 2 Effect of rare earth and iron deficiencies on the green and sintered densities of $Y_{2.01(1-x)}Gd_{0.99(1-x)}Fe_{5(1-y)}O_{12}$.

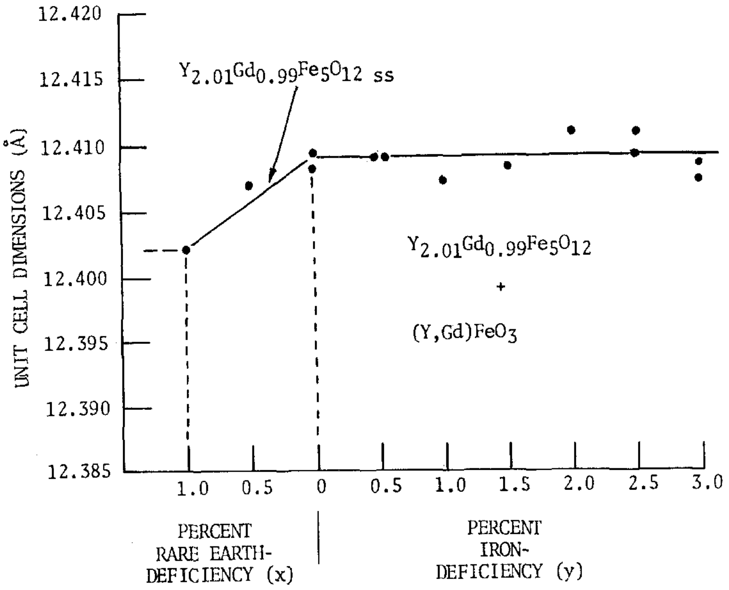

Figure 3 Unit cell dimensions versus rare earth and iron deficiencies of $Y_{2.01(1-x)}Gd_{0.99(1-x)}Fe_{5(1-y)}O_{12}$.

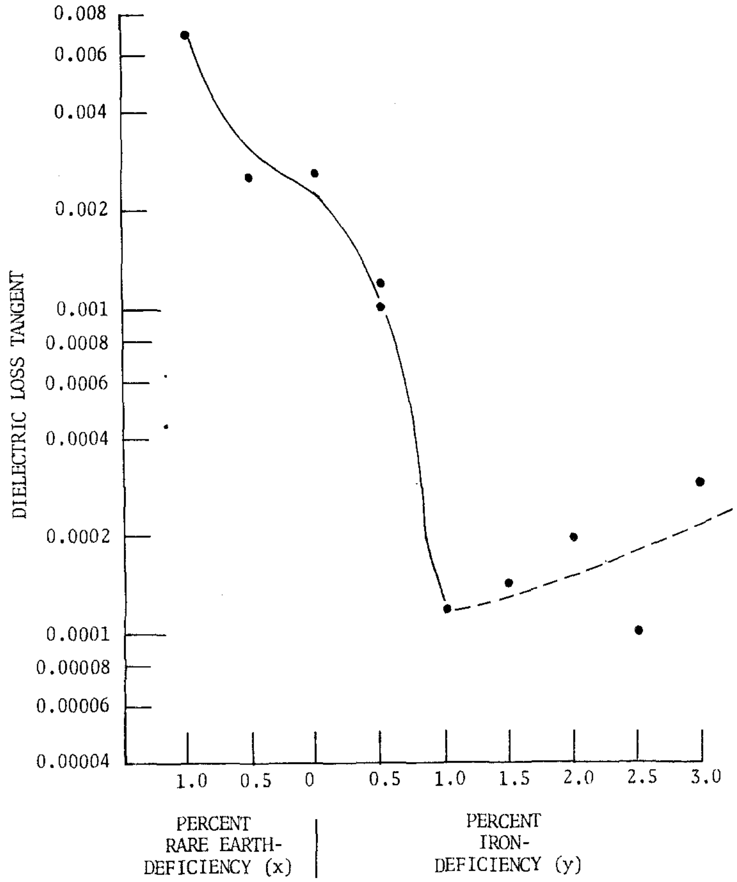

Figure 4 Effect of rare earth and iron-deficiencies on the dielectric loss tangent of $Y_{2.01(1-x)}Gd_{0.99(1-x)}Fe_{5(1-y)}O_{12}$.

samples. It appears that a second phase of (Y, Gd) FeO_3 promotes the discontinuous grain growth and hinders the densification of iron deficient samples. A solid solution of $Y_{2.01}Gd_{0.99}Fe_5O_{12}$ was formed as the amount of rare earth deficiency increases. This agrees with Van Hook who found the same narrow range of solid solution in the system Fe_2O_3–Y_2O_3 [7]. That complete solid solutions of $(Y, Gd)_3Fe_5O_{12}$ and $(Y, Gd)FeO_3$ can be formed has been shown by Keith and Roy [8] and Geller [9]. Fig. 4 shows the effect of rare earth and iron deficiencies on dielectric loss tangent. A low dielectric loss tangent was obtained as the amount of iron deficiency was increased. This agrees with Seiden *et. al.* [10] and Hermosin [11] who obtained low dielectric loss tangent data for iron deficient $Y_3Fe_{5(1-y)}O_{12}$ garnet. A similar effect of the second phase of $YFeO_3$ on the dielectric loss tangent of $Y_3Fe_5O_{12}$ was found by Seiden *et al.* [10]. The effect of $(Y, Gd)FeO_3$ on the dielectric loss tangent of $Y_{2.01}Gd_{0.99}Fe_5O_{12}$ was found in this study. However, the behaviour of abrupt change in dielectric loss tangent at approximately 1% iron deficiency of yttrium gadolinium iron garnet is not understood.

4. Conclusions

It has been shown that addition of sulphate anion to the $Fe(NO_3)_3$ solutions increases the sinterability of $Y_{2.01}Gd_{0.99}Fe_5O_{12}$ powders obtained by spray drying precursory solutions followed by rotary calcining.

It has also been shown that a second phase of $(Y, Gd)FeO_3$ decreases the sintered density and dielectric loss tangent of iron deficient garnet of $Y_{2.01}Gd_{0.99}Fe_{5(1-y)}O_{12}$.

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