Another alternative to the solid state reaction method to synthesize nanocrystalline YIG: Ammonium nitrate melt technique

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Abstract. The structural and magnetic properties of yttrium iron garnet particles, synthesized in an ammonium nitrate melt (ANM), were investigated by magnetization measurements, XRD analysis and SEM microscopy and compared with that of the samples prepared using a solid state reaction (SSR) route. The phase formation of YIG starts at lower temperatures with the ANM technique and then develops with increasing temperature and sintering time. An almost single-phase sample was obtained by annealing for 2 hours at 1300\textdegree C, after which the YIG fraction in the SSR sample was only 0.34. Similarly, saturation magnetization of the samples sintered in the same conditions is always higher in the samples sintered via the ANM technique. SEM micrographs were used to determine particle sizes of the ANM samples which vary from the sub-micron to the micron range depending on the sintering temperature. These samples have uniform structures, small grains, better magnetic properties and do not contain massive agglomerates. As a result, the synthesis of YIG via the ANM technique represents another alternative to the SSR route.

1. Introduction
Ytrrium iron garnet (YIG) is a ferrimagnetic material with unique features which make this material suitable for various device applications including circulators, oscillators, phase shifters for the microwave region, sensors and lasers. In addition, epitaxially grown YIG crystals on GGG (Gadolinium Gallium Garnet) substrates have been used in studies of the vortex dynamics in high-temperature superconductors for observation of magnetic field penetration [1-4].

Synthesis of this material with strict control of the composition, the homogeneity, the size and the particle shape is crucially important for both magnetic and structural properties of these garnets. The samples prepared by using a SSR route generally include YFeO\textsubscript{3} and Fe\textsubscript{2}O\textsubscript{3} as impurity phases and these remain in the sample unless heated to high temperatures [5]. Generally, the final product has a limited degree of homogeneity. The sol-gel, co-precipitation, and glycothermal synthesis have been developed for obtaining finer particles [6-10].
In this report, we introduce a combustion method to synthesize YIG as an alternative method to the SSR route, namely the ANM technique. The method has been successfully applied for sintering ceramic high-T$_c$ superconductors, like YBa$_2$Cu$_3$O$_{7-x}$ [11] and BSCCO [12]. The magnetic and structural properties of the samples were compared with those from materials synthesized via the SSR route.

2. Experimental
Appropriate amounts of high-purity Y$_2$O$_3$ and Fe$_2$O$_3$ were mixed at a 3:5 molar ratio and ground for 15 minutes in ethyl alcohol. The mixture was added to an ammonium nitrate melt, kept at 185°C, and a reddish liquid was formed. Next, the temperature of the mixture was gradually raised to 300°C over a period of 1 hour, and kept at this temperature for 24 hours to obtain the precursor. Milling was performed for 5 hours at 100 rpm with a ball-mixture weight ratio of 10:1. Finally, the powder obtained was sintered at different temperatures, starting from 800°C up to 1300°C, for varying durations, ranging from 1 to 12 hours.

The structural properties of the samples were investigated using an X-ray powder diffractometer (Rigaku Miniflex, Cu-K$_\alpha$ radiation). Quantitative analysis software was used to calculate the phase fractions. The surface morphology and microstructure of the samples were examined with a scanning electron microscope (JEOL 6335F Field Emission Gun). The magnetic characterization of the samples was performed at room temperature using a vibrating-sample magnetometer (LDJ Electronics, Inc. Model 9600) and an applied field of 2 kOe.

3. Results and Discussion
3.1. Structural Characterization
The X-Ray diffraction patterns of the YIG samples synthesized by both the ANM technique and the SSR route are shown in Fig.1. At 900°C the impurities, YFeO$_3$ (also known as YIP) and Fe$_2$O$_3$, are in the majority and the YIG does not appear, even as a minor phase. However, annealing at 1000°C for 1 hour revealed the conversion of the YIP into the YIG phase with a fraction of 0.35. When the sample was annealed for 2 hours or more at this temperature, the YIG became the major phase. As the sintering temperature and time were increased, the fraction of YIG was found to increase. For instance, at 1200 °C with 2 hours annealing, it was 0.95 with small traces of YIP retained. An almost pure YIG sample was sintered at 1300 °C with 2 hours annealing; it had a cubic structure with lattice parameter of 12.3585 ± 0.0015 Å. With the SSR method, on the other hand, YIG formation starts at 1200°C with a very small fraction of 0.08 and reaches 0.70 with 12 hours of annealing at 1300°C. Sintering at 1350°C for 12 hours did not result in a pure YIG phase.

The scanning electron microscopy (SEM) micrographs of the YIG samples synthesized with the ANM method show that sub-micron particles were formed at 1000°C with 6 hrs of annealing (Fig.2a). It seems that there is a homogeneous grain structure, i.e., there are no agglomerates or relatively big grains. The average particle size can be estimated as 0.3-0.4 μm. In a sample sintered at 1200°C, the particle size increased to approximately 1 μm and the particles were stuck to each other in a regular and homogeneous manner to form a network-like structure, see Fig.2b. Heat treatment at 1300°C for 2 hours resulted in an average particle size of 1.5 μm (Fig.2c). On the other hand, the samples sintered via the SSR route have grains with sizes that vary over a wide range (from 1 μm up to 10 μm), see Fig.2d-e.
Fig.1: XRD patterns of the samples sintered by ANM and SSR.
3.2. Magnetization Measurements

Fig. 2: SEM micrographs of the ANM samples sintered at a) 1000°C for 6 hours, b) 1200°C, c) 1300°C for 2 hours and SSR samples annealed at d) 1300°C, e) 1350°C for 2 hours.
Room-temperature magnetization curves of some selected YIG samples synthesized by the ANM technique and the SSR route are shown in Fig. 3a for a comparison. It is clear that the ANM sample sintered at 1200ºC for 2 hours has a higher $M_s$ value compared to the SSR samples sintered at higher temperatures for longer times. The saturation magnetization of the ANM samples starts with 9.39 emu/g for the sample annealed at 1000ºC for 1 hour and increases at higher sintering temperatures due to the increasing YIG fraction and the crystallinity of the particles, see Fig 3b. Then, it saturates at approximately 23 emu/g for the temperatures above 1200ºC.

4. Conclusion

YIG was synthesized using the ANM technique. The structural and magnetic properties appeared to be better than those of the SSR samples. It was observed that the phase formation starts at 1000ºC and increases with increasing annealing temperature and duration. $M_s$ first increases sharply and then saturates at approximately 23 emu/g for temperatures higher than 1100ºC. Meanwhile, $H_c$ decreases from 45 to 5 Oe due to the increasing particle size. This behavior of $H_c$ indicated that the average particle sizes of our garnets were greater than 200 nm, above which the particles have a multi-domain structure. However, the crystallite sizes of the samples determined using the Scherrer formula are between 50-60 nm. In contrast to the SSR samples, the ANM garnets have homogeneous structures, and no big agglomerates are observed in the SEM micrographs. This combustion technique appears to be another alternative to the SSR route, although further work is needed to decrease the average particle size, which will be subject of our next investigations.

5. References

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