

Influence of the particle size distribution on magneto-optical property of Bi-YIG particulate film

C. S. Kuroda, T. Taniyama*, Y. Kitamoto*, Y. Yamazaki*, K. Uchida, and F. Ikazaki

Institute of Materials and Chemical Process, National Institute of Advanced Science and Technology, AIST Tsukuba
Central 5, 1-1, Higashi 1-chome, Tsukuba-shi, Ibaraki 305-8565 JAPAN
Fax: 81-29-861-4454, e-mail: Ikazaki-fumikazu@aist.go.jp

Department of Innovative and Engineered Materials, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku,
Yokohama-shi Kanagawa 226-8502, JAPAN
Fax: 81-45-924-5433, e-mail: kitamoto@iem.titech.ac.jp

Nano-composite film was prepared consisting of bismuth substituted yttrium iron garnet (Bi-YIG) nano-sized particles homogeneously dispersed in transparent epoxy matrix. The Bi-YIG particles were prepared by addition of acid aqueous solution of cations into the ammonia solution set and controlled at pH 12.5 by simultaneous addition of NaOH solution. The precipitate was heat-treated at 540°C for 4 hours. The particles were mixed with transparent epoxy matrix and disaggregated in planetary milling machine for 30, and 100 hours. The film was prepared by coating the mixture on glass substrate followed by drying. The morphology and crystallization of the Bi-YIG particles were investigated by Transmission Electron Microscopy (TEM) images and show garnet crystallization with a primary size around 20nm and a distribution of 5-44nm. The TEM images of the sample milled for 30 and 100 hours confirm that the particles are aggregates of the crystallites. The nano-composite film shows Faraday rotation spectrum similar to the Bi-YIG bulk material and without any influence of the other components materials. The Faraday rotation exhibits a dependence of the inter-particles interaction and diminishes by increasing of the milling time. The absorption coefficient exhibits a reduction as a function of wavelength by increasing of the milling time at the wavelength shorter than 560nm.

Key words: Particulate film, Coprecipitation, Bi-YIG particles, Small particles, and Faraday rotation

1. INTRODUCTION

Optically functional nano-composite materials have been expanding its application from optical switches for future use in optical computing to hard transparent coating as protective or barrier layers [1]. Among them, Bi-YIG particles dispersed in transparent plastic binder (particulate film) is a promising candidate to use as magneto-optical (MO) nano-composite films. However its MO performance factor (ratio between Faraday rotation and absorption coefficient, θ_F/α) is not enough to substitute the garnet single-crystal film in MO device.

The increase of the MO performance in Bi-YIG nano-composite film is expected as a result of the reduction of the particles size into the composite. It is well known that the optical scattering extrinsically increases the value α of the film, decreasing the MO performance of the nano-composite film [2]. The optical scattering of larger particles in composites arises from the difference between refractive index of matrix and particles. However, for very small particles (typically < 25nm) the scattering is avoid because the light propagates in this system as a continuous media due to the extension of particles be much smaller than the wavelength [1]. To avoid the large Bi-YIG particles, controls in the nucleation of the precursor during the preparation of the particles is required. The large particle

normally is a result of the inter-aggregate growth of particles at heat treatment process. In the case of coprecipitation process, the inter-aggregate growth is caused by an unbalanced distribution of the cations [3] into the precursor particle. Previously we reported [4] preparation of Bi-YIG particles by coprecipitation in which the cations solution is added drop by drop in ammonia solution controlled in pH 12.5 by simultaneous addition of the NaOH solution from a pH control apparatus. The nano-composite film of this particle exhibits an improvement of the MO performance from 2.56 to 4.80deg at 520nm (300K).

The objective of our work is to study the relation between the particles size and MO response of nano-composite film.

2. EXPERIMENTAL

The Bismuth (III) Nitrate Pentahydrate 99.9% (Wako Chemical - 0.08mol/l), Yttrium (III) Nitrate Hexahydrate 4N (Kanto Chemical - 0.08mol/l), and Iron (III) Nitrate Enneahydrate 99.0% (Wako Chemical - 0.27mol/l) were dissolved in nitric acid of 0.48mol/l. The solution of the cations was added drop by drop on NH₄OH solution (6.0%) that pH was adjusted and controlled during coprecipitation process at pH

12.5 by simultaneous addition of the NaOH (8.0mol/l) using pH controller apparatus (TOA, AUT-501). Then, the coprecipitated was washed, dried at 100°C for 4 hours and heat treated at 540°C for 4 hours.

Crystallographic properties of the particles were examined by X-ray diffraction (XRD) Cu-K α (RINT2100V). The crystallite size and its distribution were measured from Dark-field image of Transmission electron microscopy (TEM, Hitachi H-8100 (200kV)).

The Bi-YIG particulate film was prepared by milling the mixture consisting of the 1g of the Bi-YIG powder, 2.681g Epoxy (Epoxytechnology, Epo-tek 396), 18g of Cyclohexanone (Wako chemical), and 0.2g of dispersoid Hypermer MT-1 (ICI-Japan) dissolved in toluene (Wako Chemical) at 50% of weight. The mixture was milled in a planetary milling machine (Pulveritte 7, Fritsch Co) at 600rpm for 30, and 100 hours to form inks. The inks were coated on glass substrate (Corning # 7059) using wire bar coater (# 36) and dried at 60°C for 4 hours. A Bi-YIG particulate film of the 40% in volume exhibits a thickness of the 1.5 to 2.0 μ m after the dry process.

The MO property was measured using the polarization modulation method by MO-250 (JASCO) and absorption coefficient by using V-560 (JASCO). The magnetic property was measured using Mössbauer spectroscopy (^{57}Co , 1.85GBq). The thickness of the film was measured using surface step analyzer (DEKTAK 3030, Sloan). The morphology of the particles dispersed in the epoxy film and the crystallite size of the particles were analyzed using

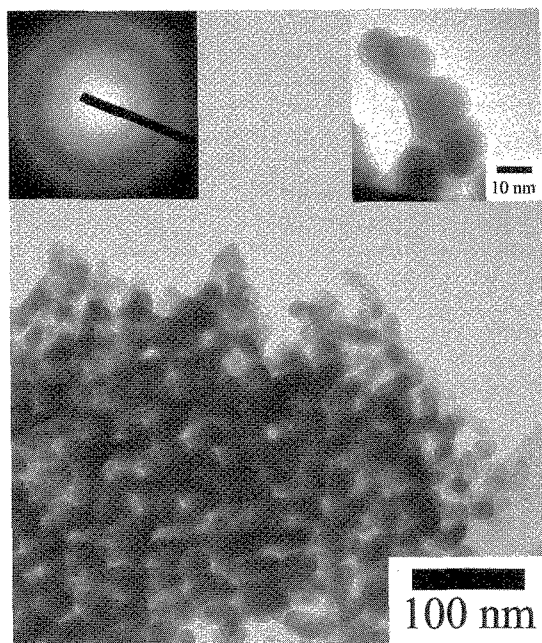


Fig.1 TEM image of Bi-YIG particles heated at 540°C for 4 hours. The insets exhibit electron diffraction patterns and enlarged TEM image of the small particles.

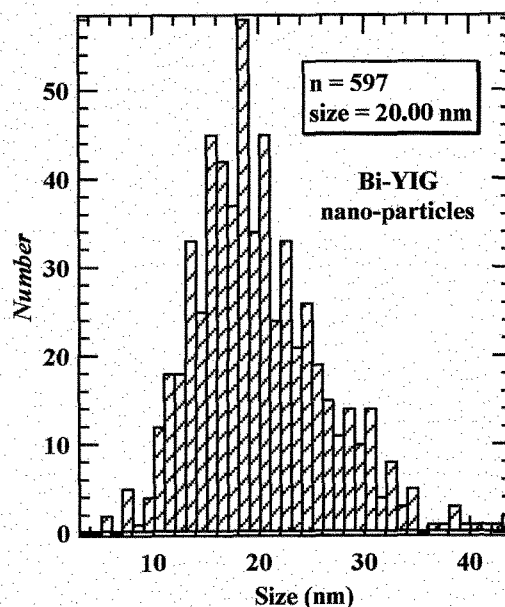


Fig.2 Crystallite size distribution measured from dark field TEM images of Bi-YIG particles heated at 540°C for 4 hours.

Transmission electron microscopy H-8100 (Hitachi).

3. RESULTS AND DISCUSSIONS

3.1 Bi-YIG particles

The XRD of the particles shows broad and well-resolved peaks pattern of single-phase Bi-YIG garnet crystal.

Fig. 1 shows the TEM images of the particles heated at 540°C for 4 hours. The image exhibits aggregates of nano-particles smaller than 50nm. The garnet phase is also confirmed by the electron diffraction patterns shown in the inset. Spots of garnet structure and ring of nano-crystal

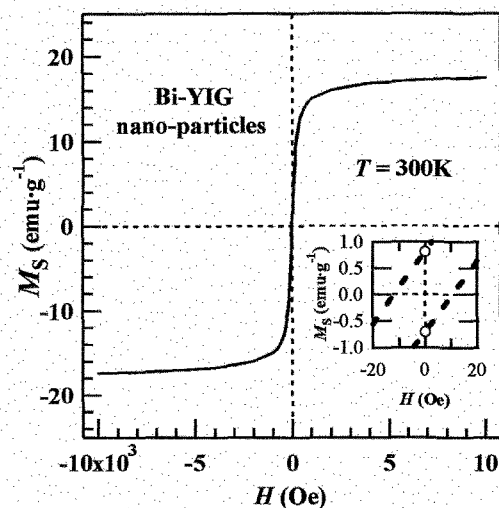


Fig.3 Hysteresis loop of Bi-YIG particles heated at 540°C for 4 hours. Inset shows the enlargement of central region of this hysteresis loop.

are observed. The enlarged image of the Bi-YIG smaller particles suggests that the particles magnetically interact with each other by inter-crystallite dipolar interaction.

The crystallite size distribution measured from dark field TEM images is shown in Fig. 2 that exhibits an average size of 20nm and a size distribution range between 5 to 44nm. The Bi-YIG nano-particles smaller than 10nm are observed in the histogram of Fig. 2, which explains the presence of nano-crystal in the electron diffraction pattern of Fig. 1.

Fig. 3 shows the field dependence of the magnetization measured at 300K. Fig. 3 and its inset show coercive force (H_C) of the 10Oe and

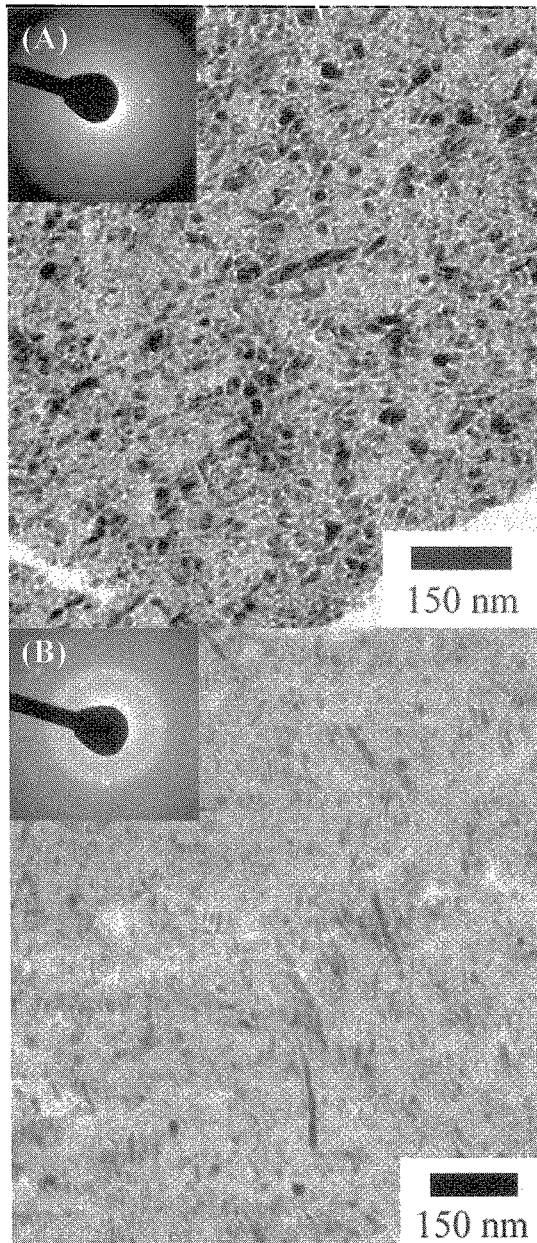


Fig.4 (A) and (B) show the cross-section TEM images of nano-composite films of Bi-YIG particles milled for 30 and 100 hours respectively with correspondent electron diffraction patterns.

saturation magnetization (M_S) of the 17.4emu/g. The M_S is smaller than that observed in bulk samples (26.2emu/g) [5]. It is known that the size to Bi-YIG particles become superparamagnetic is around 35nm [6]. The Bi-YIG particles with crystallite size distribution shown in Fig. 2 normally should exhibit superparamagnetic behavior in the isolated state of the particles. However a soft ferromagnetic behavior with M_S around 17.4emu/g at 10kOe is observed. This can be attributed to the inter-crystallite magnetic dipolar interaction of the particles in powder state closely packed as shown in Fig. 1.

3.2 Bi-YIG nano-composite film

Fig. 4 shows the cross-section TEM images (A) and (B) of the Bi-YIG nano-composites of particles nano-sized in planetary milling process for 30 and 100 hours respectively. The insets show their electron diffraction patterns. The TEM image (A) exhibits particles larger than image (B), indicating that the planetary milling process disaggregate the crystallites as a function of the milling time. Note that large particles and/or aggregates remain into the nano-composite film milled for 30 hours. At this condition, light is more scattered in the film milled for 30 hours than in 100.

Both electron diffraction patterns of the Bi-YIG nano-composite film show identical spot of the garnet structure and ring of nano-crystal similar to the pattern observed for powder in Fig. 1. This confirms that the crystallites do not change their size but only the particles are disaggregate during the planetary milling process.

Fig. 5 shows the Faraday rotation (θ_F) on 3kOe and absorption coefficient (α) of the Bi-YIG nano-composite as a function of the wavelength measured at 300K. The

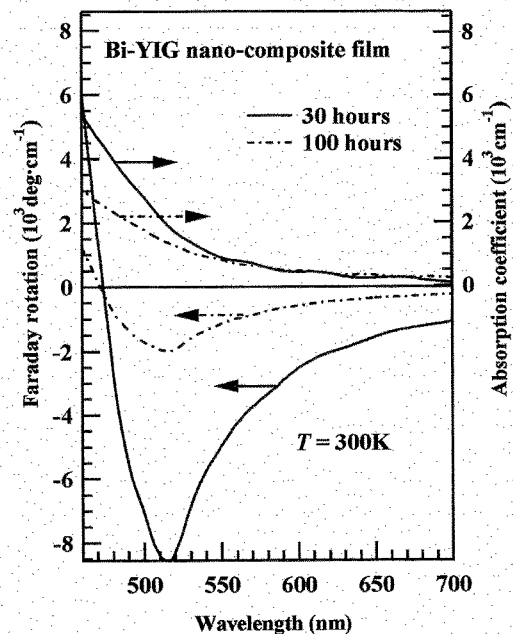


Fig.5 Faraday rotation (3kOe) and absorption coefficient as a function of the wavelength of Bi-YIG nano-composite film milled for 30 and 100 hours.

θ_F and α spectra show similar dependence of the Bi-YIG bulk film with wavelength and exhibit a figure of merit (θ_F/α) at 520nm of the 4.80deg. The θ_F angle of the sample milled for 100 hours is lower than that of the sample milled for 30 hours. It is known that the θ_F angle of the polarized light is originated from the asymmetry between the polarizabilities of the quantum system in the fields of right and left circularly polarized waves [7] that appear in a magnetic field and/or in magnetic ordered materials. By planetary milling process of the Bi-YIG particles, the crystallites smaller than the critical size to show superparamagnetism are isolated in the nano-composite film and the inter-crystallite magnetic dipolar interaction diminishes, reducing the θ_F of the nano-composite film.

The α of the sample milled for 100 hours is smaller than sample milled for 30 hours up to 560nm. Two causes may be attributed to this behavior. The first might be induced by the scattering effect of light caused by larger particles that is more sensible in the short wavelength. It was mentioned before that to neglect the scattering effect, the dispersed particles and matrix should have refracted index mismatch very smaller (<0.01) or dispersed particles smaller than 25nm in the matrix [1]. The other cause should be due to the intrinsic absorption of the Bi-YIG structure by higher inter-crystallites magnetic dipolar interaction into the particles of sample milled for 30 hours. It is known that not only the electron transition responsible by θ_F but other transition of the Fe^{3+} is influenced by the magnetic interaction at this wavelength region [8].

4. CONCLUSIONS

Bi-YIG particles were prepared by reverse addition of the cations solution into the ammonia solution assisted by pH control apparatus that controls the pH at 12.5 by simultaneous addition of the NaOH solution. The nano-composite film was prepared by mixing this particle with transparent epoxy binder by planetary milling process followed by a coating and drying processes.

The Bi-YIG particles exhibit an average crystallite size of 20nm and a size distribution of the 5 to 44nm. The particles show soft ferromagnetic property compared to the bulk and indicate that the magnetism may arise from inter-crystallite magnetic dipolar interaction.

The TEM images and MO property of Bi-YIG nano-composite film indicate that the planetary milling process only disaggregate the particles, maintains the structure of crystallites, and confirms the dependence of inter-crystallite magnetic dipolar interaction on the magnetic property. It is showed that the θ_F is sensible to the magnetic interaction of each particle dispersed into the matrix. On the other hand, the α of the nano-composite milled for 100 hours shows a gradual reduction as a function of wavelength up to 560nm in relation to the sample milled 30 hours, suggesting dependence between particles size and wavelength and/or increase of the intrinsic absorption of the Bi-YIG particles due to the higher inter-crystallite dipolar

magnetic interaction in the particle.

The detailed dependence between particle size and MO property of this work gave important information about particle dimension and morphology required to improve the MO properties of Bi-YIG nano-composite films.

Our research on the improvement of the MO performance of particulate film will continue, mainly focusing on the preparation method to obtain nano-sized Bi-YIG with narrow particle size distribution using reverse micelle process.

5. ACKNOWLEDGEMENT

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