

# Preparation and properties of yttrium iron garnet microcrystal in $P_2O_5$ –MgO glass

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## Abstract

The fabrication of phosphorus-based glasses containing  $Y_3Fe_5O_{12}$  crystals by the incorporation method was studied. From transmission electron microscopy observation, there is only one rod-like crystalline phase identified as  $Y_3Fe_5O_{12}$  existing in the glass matrix. When the content of YIG is 30 wt.%, the as-cast sample shows a Faraday rotation of  $85^\circ/cm$  and a magnetization of 0.4 emu/g in a field of 14 kOe. After heat treatment, the magnetic and optical properties of the glass ceramic changed owing to the thermal diffusion of iron ions into the glass matrix.

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## 1. Introduction

Yttrium iron garnet (YIG) has been studied owing to its various application potentials as components in microwave communication and optical devices [1–3]. For example, an optical isolator is used in optical communication to reduce the back-reflection noise. The isolator is constructed by using a Faraday rotator (FR). Since the single crystal of the YIG shows a significant magneto-optical effect, i.e. Faraday rotation, in both the visible light and the near infrared region, YIG becomes a suitable FR material. In practice, the garnets used in optical devices are often in single crystal form. Therefore, many efforts focused on single crystal growth of related garnets [4,5].

The most usual preparation methods of YIG single crystals are the floating zone method and flux growth. However, special attention has to be paid to precise control of growth conditions such as stability of growing temperature, atmo-

sphere, as well as the pulling rate in the former growth technique [6]. Pure, defect free and congruent single crystals are not easily achieved. Although, yttrium iron garnet has a large magneto-optical effect, it is also strongly light absorbent. To reduce light absorption of the garnet, several efforts had been made. One of them is the glass–ceramic method.

The glass–ceramic method was successfully developed in the crystallization of several kinds of ferrites from glasses [7–9]. When the glass–ceramic materials are used in optical applications, there are some factors that should be taken into consideration. Firstly, the matrix glasses exhibit excellent radiation transmittance in the visible to infrared regime. Secondly, the optical anisotropy and differences in the refractive index between the glasses and crystalline phases should be small [10]. The synthesis of YIG by crystallization in oxide glasses had been reported in the literature [11].

In this article, we attempted to fabricate phosphorus-based glass containing YIG crystals by the incorporation method. The effects of YIG content and annealing temperatures on microstructure, magnetic and magneto-optical properties of the glass ceramics were investigated.

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## 2. Experimental

$Y_3Fe_5O_{12}$  (yttrium iron garnet, YIG) phase was prepared by mixing metal oxides with a weight according to the molar ratio of 3:5. Powders were ball-milled with alcohol for 48 h, and calcined at 1200 °C for 2 h. The pre-fired powders were then ground till the average particle size was smaller than 0.45  $\mu\text{m}$ . The powders were then pressed into a disc ( $\varnothing = 12$  mm, 6 mm in thickness) followed by sintering at 1200 °C for 15 h and then slowly cooled to room temperature at a rate of 1 °C/min. Phosphorus-based glass was prepared from a melting mixture of reagent grade  $NH_4H_2PO_3$  and MgO (molar ratio 78:22) in a platinum crucible at 1200 °C for 30 min, then quenched in water.

Glass powder and YIG disc were pulverized, and these powders were well mixed. The amount of YIG crystals was in the range of 0–30 wt.%. The mixtures were remelted in a platinum crucible at 1200 °C for 3 min, then poured through a twin copper roller. The as-cast samples were then annealed at 300 to 600 °C for 5 h and slowly cooled down to room temperature.

The crystal structure of the samples was determined by X-ray diffraction analysis (XRD) using Cu  $K\alpha$  radiation at room temperature. The microstructure of the YIG phase incorporated in the glass matrix was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The compositions were examined by energy dispersive X-ray analysis (EDX). The magnetic properties were studied using a vibrating sample magnetometer (VSM) at room temperature with a maximum magnetic field of 14 kOe. The Faraday rotation of the samples was measured by using a polarized laser, 633 nm in wavelength, an electromagnet, an analyzer and a photodiode connected to a lock-in amplifier. We first applied a magnetic field of 14 kOe, and then put the sample into the measuring system.

## 3. Result and discussion

Fig. 1a shows the X-ray diffraction pattern of the conventionally sintered YIG disc. The diffraction pattern could be indexed based on a cubic garnet, which belongs to space group Ia3d. The X-ray results of the as-cast samples with various YIG contents are shown in Fig. 1b–d. The YIG contents were 10, 20, and 30 wt.%, respectively. When the YIG content was less than 10 wt.%, there was no crystalline phase in the as-cast sample. With higher addition, the peak indexed as (400) appeared and the intensity of the peak increased with YIG addition. From the pattern of the glass ceramic with the highest YIG content, the strong (400) and (800) peaks indicated that the garnet crystals preferred growing along (100), i.e. along the direction vertical to the glass–ceramic flakes. This crystallization feature was distinct from that of random YIG crystallization in glasses in previous reports [11].

Fig. 2a shows the microstructures of the incorporated YIG crystals in the  $P_2O_5$ –MgO glass. There was only one crys-

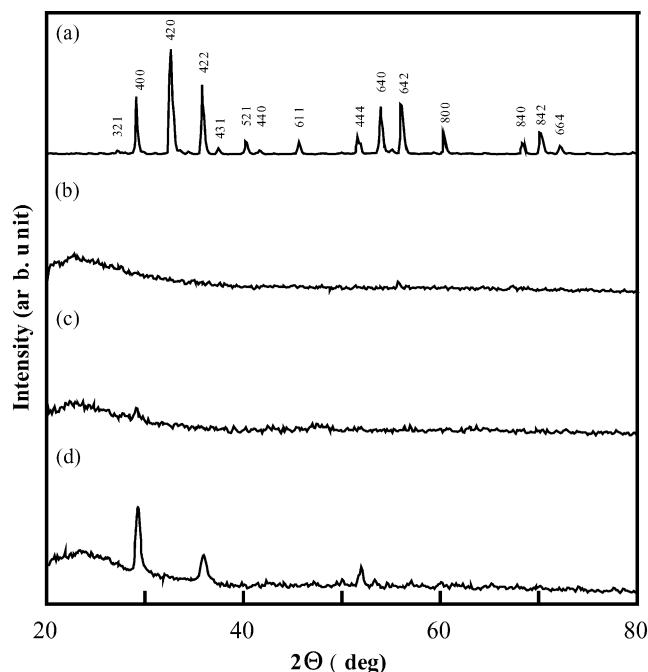


Fig. 1. X-ray diffraction patterns of: (a) the conventional sintered YIG disc and the as-cast samples with the YIG contents of: (b) 10 wt.%; (c) 20 wt.%; and (d) 30 wt.%.

talline phase existing in glass matrix. Rod-like crystals with an aspect ratio of 1–5 were observed. To clarify the crystalline phase, the selected area patterns with the electron beam along the two zone axes [100] and [111] of the crystal are shown in Fig. 2 b and c, respectively. By calculating the interplanar spacing of the diffraction spots in the patterns, the experimental  $d$  values found well fit those listed in the JCPDS card (43-507). The results confirmed that the crystalline phase was YIG. Since some of the  $Y_3Fe_5O_{12}$  particles have been dissolved into the glass matrix during annealing, the microstructural feature of the incorporated YIG crystal was quite different from that of sintered garnet crystals.

Fig. 3 shows the XRD patterns of the as-cast glass ceramic annealed at 300, 400, 500 and 600 °C. The intensity of YIG (400) peak was getting weaker with increasing annealing temperatures. There was no second phase observed after annealing. Besides, the position of (400) peak slightly shifted to lower diffraction angle with increasing temperature. It means the lattice parameter of YIG increased with increasing annealing temperature. Meanwhile, the average grain sizes were determined from the XRD pattern of the specimens according to the Scherrer equation:

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where  $D$  is the average grain size;  $k$  a constant equal to 0.89;  $\lambda$  the X-ray wavelength equal to 0.1542 nm and  $\beta$  the peak width at half of the (400) peak height. The average grain sizes were in the range of 0.4  $\mu\text{m}$  to about 2  $\mu\text{m}$ .

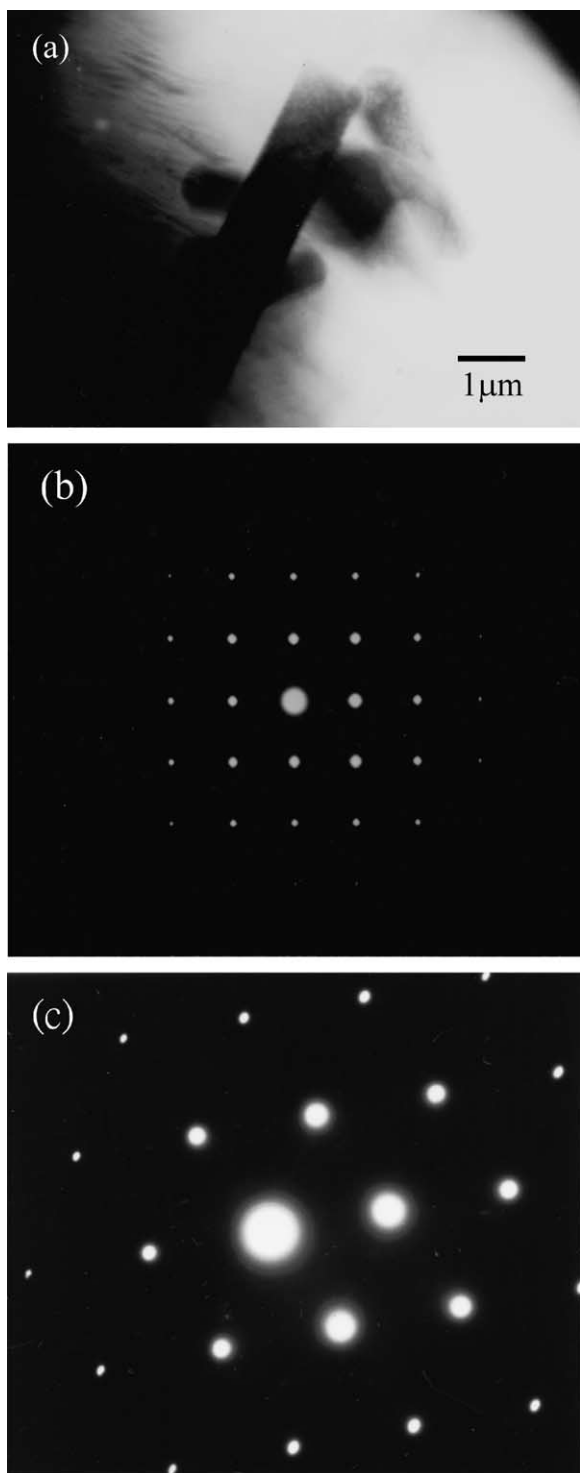


Fig. 2. TEM photographs of the as-cast glass ceramic with 30 wt.% YIG; (a) the bright field image; (b) and (c) are the selected area diffraction patterns along [1 1 0] and [1 1 1], respectively.

Fig. 4a–d shows the microstructures of the as-cast glass ceramic annealed at 300, 400, 500 and 600 °C, respectively. From SEM photographs in Fig. 4, the YIG rods with a width range of about 0.25–3 μm were observed. The volume fraction of the crystalline phase decreased with increasing the

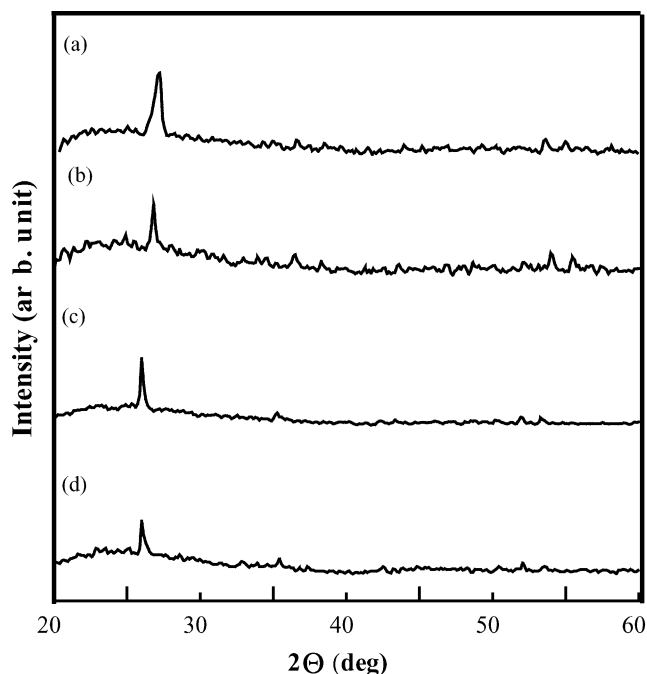


Fig. 3. X-ray diffraction patterns of the as-cast samples annealed at: (a) 300 °C; (b) 400 °C; (c) 500 °C; and (d) 600 °C.

annealing temperatures and the crystal size also reduced with temperature. Since the annealing was performed at 1200 °C for just 3 min, the sintered YIG particles were not fully dissolved in the annealing process. By analyzing the composition of the glass around the YIG particles, iron was also found to exist in the glass matrix, and its content increased with annealing temperature. The iron ions came from the reaction between YIG and phosphorus-based glass. Thus, the YIG crystal size became reduced during heat treatment. It is worthy to note that the degree of YIG crystal dispersion in the glass was not very good. Crystals seriously agglomerated at an annealing temperatures lower than 500 °C. Well dispersed YIG crystals were observed at the highest annealing temperature (600 °C) applied in the experiment.

Fig. 5 shows the YIG content and the annealing temperature dependent magnetization of the glass–ceramics. The measurements of magnetization of the samples were performed primarily perpendicular to the flakes at a maximum applied field of 14 kOe. Since the ferrimagnetic YIG and magnetic iron ions were dispersed in the glass matrix, not all of the samples were fully magnetized under the limited magnetic field. Hence, the magnetic properties correspond to a minor magnetization loop. The magnetization of the glass–ceramic samples decreased with annealing temperatures. The two main magnetic contributions in the glass ceramic came from the ferrimagnetic YIG and the diluted iron ions. As mentioned previously, some YIG particles dissolved into the glass matrix during annealing. The amount of YIG in the samples decreased with increasing annealing temperatures. According to the results of XRD and TEM observa-

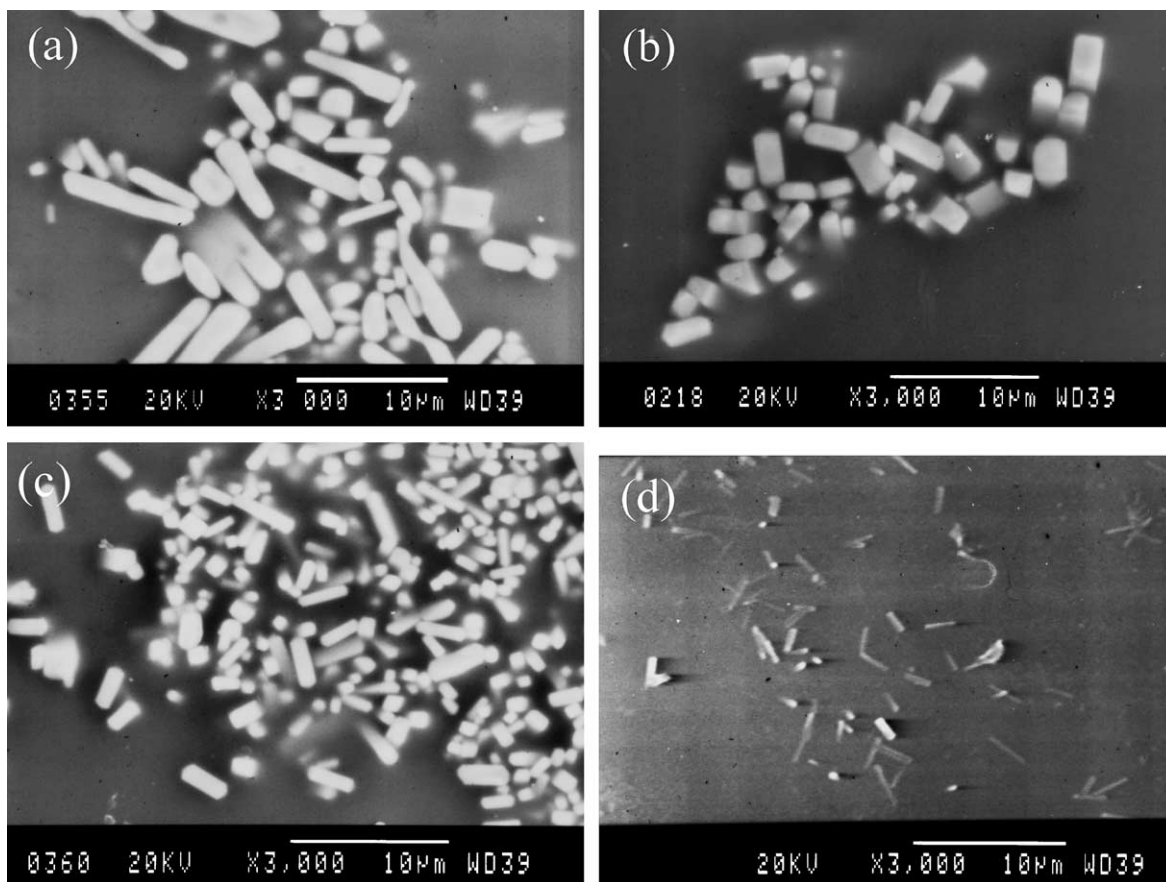


Fig. 4. SEM photographs of the as-cast samples annealed at: (a) 300 °C; (b) 400 °C; (c) 500 °C; and (d) 600 °C.

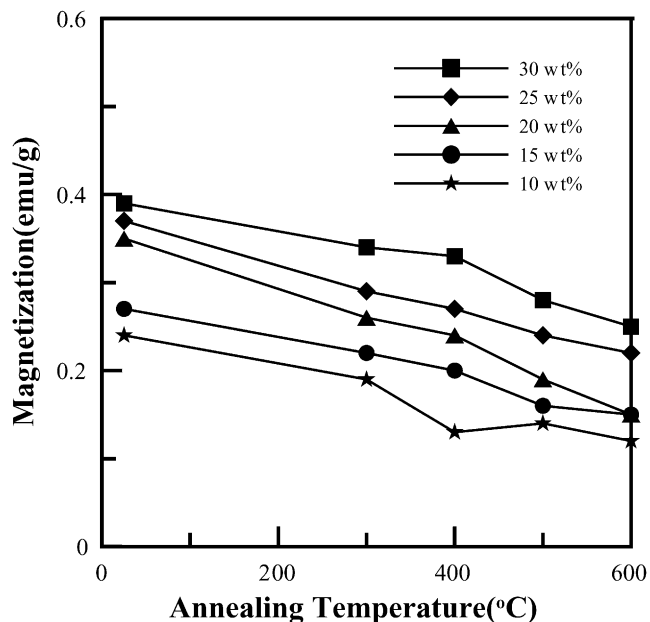


Fig. 5. YIG content and the annealing temperature dependent magnetization of the glass–ceramics.

tion, there was no other precipitated phase existing in the glass matrix except for YIG. Therefore, the content of iron ion also increased with annealing temperature. The  $\text{Fe}^{3+}$  ions in phosphate glass acted as a network former in octahedral or distorted octahedral coordination while the  $\text{Fe}^{2+}$  ions acted as a network modifier in octahedral coordination [12]. Since there is a large separation between the iron ions in the dilute glass matrix, extremely weak or no interaction between the ions was expected. The magnetization contribution from the iron ions was negligible at the measured magnetic field.  $\text{Y}^{3+}$  ions had no unpaired electron in the d-shell, they exhibited a diamagnetic behavior. So the magnetization of the sample merely depended on the content of YIG, i.e. decreasing with increasing annealing temperature and/or decreasing with the addition level of YIG.

Fig. 6 shows the IR transmittance spectra for the as-cast phosphate glass samples containing 0–30 wt.% YIG. The transmittance of the phosphate glass without incorporation was higher than 99% in the wavelength range of 2.5–2.8  $\mu\text{m}$ . At higher wavelength range, the transmittance of the sample decreases with increasing wavelength. A broadened absorption peak is located in the range 4.1–4.3  $\mu\text{m}$ . According to the handbook [13], there are two possible network structures of the phosphate glass, which are corresponding to the ab-

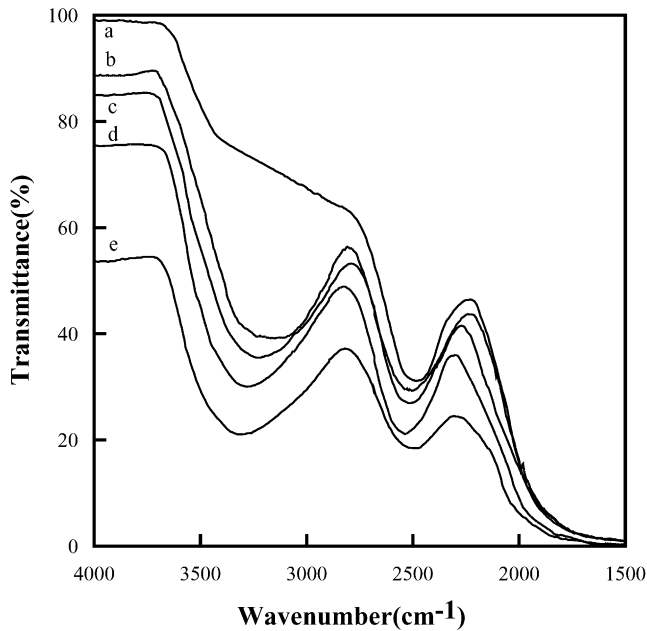
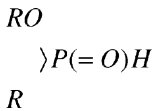


Fig. 6. IR transmittance spectra of the as-cast phosphate glass samples containing: (a) 0 wt.%; (b) 10 wt.%; (c) 15 wt.%; (d) 20 wt.%; and (e) 30 wt.% YIG.

sorptions, one is  $R_2P(=O)H$ , and the other is



where R is the alkaline-earth cation. The average transmittance ( $T_{ave}$ ) of the sample was calculated by dividing the area beneath the transmittance curve by the whole area in the wavelength range 2.5–5  $\mu m$  (i.e.  $T_{ave} = A_{sub}/A_{total}$ , where  $A_{sub}$  is the area beneath the transmittance curve and  $A_{total}$  the whole area). According to the equation, the average transmittance of the phosphate glass is 71.03%.

As for the incorporated samples, the average transmittance of the sample decreased with the increasing content of YIG. The values decreased from 65.32% to 33.23%, when the incorporation increased from 10 to 30 wt.%. The transmittance ( $T$ ) of light through material followed the Beer–Lambert law:

$$T = (1 - R)^2 \exp(-c\alpha x) \quad (2)$$

where  $\alpha$  is the absorption coefficient,  $c$  the concentration and  $x$  the sample thickness,  $R$  the fraction of light reflected at the particle/glass interface, which was estimated from Fresnel's law:

$$R = \left[ \frac{(n_p - n_g)}{(n_p + n_g)} \right]^2 \quad (3)$$

where  $n_p$  and  $n_g$  are the refractive indexes of particle and glass. Two possible reasons were considered to explain the tendency of the transmittance with the incorporation content. First, the light might be scattered by the interface between YIG particle and glass. To increase the amount of

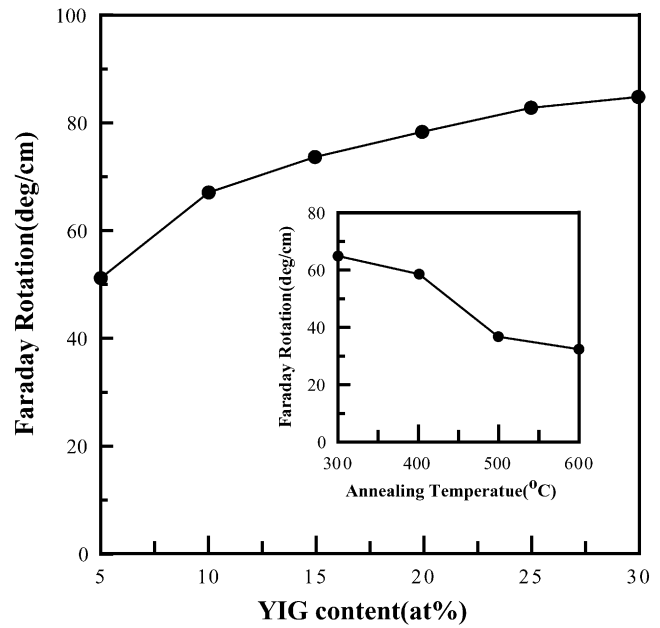


Fig. 7. YIG content and the annealing temperature dependent Faraday rotation angles of the glass–ceramics.

YIG is to increase the interfaces between particles and glass. The refractive indexes of glass and YIG crystal are 1.49 and 1.85, respectively. The fraction ( $R$ ) of light reflected at the particle/glass interface was estimated to be 1.16%. Second, the absorption coefficient of the phosphate glass might change with the composition. Although the remelting time was only 3 min, the remelting temperature was as high as 1200 °C. Iron ions might diffuse from YIG into glass during remelting. A similar tendency occurred in the annealed samples with higher annealing temperatures. The average transmittance of the annealed sample also became reduced with increasing temperatures (not shown here). From composition analysis, there is a large amount of iron ions in the glass matrix of the annealed samples, which came from the decomposition of the YIG particles.

Fig. 7 shows the Faraday rotation as a function of the YIG content in the as-incorporated samples after an applied field of 14 kOe. Since the Faraday rotation of the YIG crystal was quite large (220°/cm), the Faraday rotation of the as-incorporated sample depended on the YIG content. The Faraday rotation angle increased from 51.33 to 85°/cm while the incorporation content of YIG increased from 5 to 30 wt.%. The Faraday effect is described by the equation [14]:

$$\theta = V Hd \quad (4)$$

where  $\theta$  is the Faraday rotation on passage through a length,  $d$ , in a magnetic field ( $H$ ). The constant  $V$ , i.e. the Verdet constant, is a function of both the wavelength and the concentration of the active species. The Verdet constant of the glass ceramic increased with the YIG content from 0.22 to 0.35 min/(cm Oe). The annealing temperature dependent

Verdet constant of the annealed samples is shown in the inset of Fig. 7. As the annealing temperature increased, the Verdet constant decreased.

#### 4. Conclusions

The incorporation technique is shown to be suitable to obtain phosphate glass containing dispersive YIG microcrystals. Rod-like YIG crystals with an aspect ratio of 1–5 were observed in the as-incorporated glass. YIG particles dissolved into the phosphate glass during remelting and annealing process. The role of YIG microcrystals in the glass on the magnetic and magneto-optical properties is also discussed. The as-cast sample with 30 wt.% YIG showed a Faraday rotation of 85°/cm and a magnetization of 0.4 emu/g.

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