Preparation and characterization of new magneto-optical crystals for optical communication

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Abstract

In optical fiber communication system, optical isolators are needed to eliminate the influence of reflected light. Faraday rotators made of magneto-optical (MO) garnet crystals can be used for optical isolators. The MO properties of the garnet crystals in the visible wavelength region have been heavily studied in the past decades. However, the research on the MO mechanism in the 1.55 \( \mu \text{m} \) band is not yet advanced enough to provide a material design for the MO crystal. Furthermore, the MO properties of rare-earth substituted ion garnets are not yet thoroughly studied in details in the optical communication band.

This thesis was to explore the contributions from the Ho\(^{3+}\), Yb\(^{3+}\), Tb\(^{3+}\), Bi\(^{3+}\) and Ce\(^{3+}\) in the garnet crystals to the Faraday rotation (FR), and FR’s stability against wavelength and temperature in the communication band. The theoretical calculation for FR in the 1.55 \( \mu \text{m} \) band was also to be established for the first time. The new materials relating to MO isolators like new substrate garnet (Ca\(_3\)(LiNbGa)\(_5\)O\(_{12}\) ), new MO crystals ( (TbBi)\(_3\)Fe\(_5\)O\(_{12}\), (HoBi)\(_3\)Fe\(_5\)O\(_{12}\), (YbBi)\(_3\)Fe\(_5\)O\(_{12}\), (HoYb)\(_3\)Fe\(_5\)O\(_{12}\), (TbHoYbBi)\(_3\)Fe\(_5\)O\(_{12}\), (CeHoYbBi)\(_3\)Fe\(_5\)O\(_{12}\) ) were prepared and their specific FR and FR’s stability against wavelength and temperature were characterized.

Ca\(_3\)(LiNbGa)\(_5\)O\(_{12}\) (CLNGG) crystal with 1 inch diameter was grown by CZ method as a promising garnet substrate for high Bi-containing iron garnet film deposition. The new MO crystals were grown by TSSG method. Results indicated that
all these garnet crystals showed a strong growth habits of {110} faces except CLNGG with {211} facets. The crystal growth conditions affected the values of the saturation field, although the specific FR and the saturation field were independent of the crystallographic direction.

The specific FR in $(\text{TbBi})_3\text{Fe}_5\text{O}_{12}$ (TbBiIG) crystals was as low as 300°/cm, but its saturation field was only 0.2 kG. Thick MO crystal is needed for the MO isolator if the specific FR is low, and magnet can be very small if MO element’s saturation field is small. The specific FR and the saturation field in the REBiIG (RE=Yb, Ho, Tb) crystals decreased with the increase of the radius of rare-earth ions ($r_{\text{Yb}^{3+}} < r_{\text{Ho}^{3+}} < r_{\text{Tb}^{3+}}$).

As a Faraday rotator in the optical isolator, the MO crystal must have good stability of FR against both wavelength and temperature. This target can be realized by doping more than one rare-earth element in the garnet crystals. Experimental results showed that the values of FR wavelength coefficient (FWC) and FR temperature coefficient (FTC) in HoYbBiIG crystal were between the values in HoBiIG crystal and YbBiIG crystal. Adding Tb$^{3+}$ ions into HoYbBiIG crystal effectively lowered the saturation field. CeHoYbBiIG crystal had lower saturation field (0.76 kG) and higher specific Faraday rotation (625 °/cm) than that in HoYbBiIG crystal (0.98 kG and 545 °/cm). However, the FWC and FTC in CeHoYbBiIG were a little bit worse than HoYbBiIG and the maximum doping amount of Ce$^{3+}$ in CeHoYbBiIG crystal were moderate.

The theoretical calculation of FR in bismuth- substituted rare- earth iron garnet in the optical communication band was established for the first time. The experimental results agreed with the theoretical calculation of FR in $(\text{HoBi})_3\text{Fe}_5\text{O}_{12}$, $(\text{YbBi})_3\text{Fe}_5\text{O}_{12}$, $(\text{YYBi})_3\text{Fe}_5\text{O}_{12}$, and $(\text{TbBi})_3\text{Fe}_5\text{O}_{12}$. The theoretical models can be
used to calculate the FR at different wavelength for the bismuth- substituted iron garnets with different Bi$^{3+}$ content.

For REBiIG crystals (RE=Yb, Ho, or Tb), they had almost the same cut-off edge at the short wavelength end, but the long wavelength end of the transparent region was shifted to longer wavelength side in the ascending atom radii sequence of Yb, Ho and Tb. The features of the transmittance spectrum of REBiIG crystals (RE=Yb, Ho, or Tb) were kept in the two- or three- rare-earth ions co-doped iron garnets, like (HoYbBi)$_3$Fe$_5$O$_{12}$ crystal, and (TbHoYbBi)$_3$Fe$_5$O$_{12}$ crystal.

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1. INTRODUCTION

In 1990, Bell labs researcher, Linn Mollenauet, transmitted a 2.6 Gb/s signal over 7,500 km without regeneration. His system used a soliton laser and an Erbium-doped fiber amplifier (EDFA) that allowed the light wave to maintain its shape and density.\(^1\) The optical signals were carried by glass (silica) fibers which had two “windows”, where attenuation was lower and bandwidth was bigger. One was around 1,320nm and the other was around 1,552.6 nm (generally simply termed 1,550 nm). The material choices in the fiber structure were designed so that the zero-dispersion wavelength with the minimum attenuation and greatest bandwidth was around 1,550nm.

The rare-earth doped fiber amplifiers are a key component in many new forms of optical sources and signal processing devices. The use of EDFA dramatically increases the channel capacities of fiber communication systems. A typical fiber amplifier configuration shown in Figure 1,\(^2\) consists of the doped fiber positioned between polarization-independent optical isolators. Pump light is input by a wavelength selective coupler which can be configured for forward, backward, or bi-directional pumping.

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**Figure 1** General erbium–doped fiber amplifier configuration, showing bi-directional pumping.
Isolators maintain unidirectional light propagation so that any reflected light from the next links cannot re-enter the amplifiers and cause gain quenching, noise enhancement, or possibly lasing. There is also a strong need to suppress the reflected signals appearing in fiber-optic connector and other functional optical devices. Therefore, there is a demand for optical isolators working at the 1550nm wavelength band in the optical communication industry.

1.1 Optical isolator

A schematic diagram of a magneto-optical (MO) isolator is presented in Figure 2. The magneto-optical element, which is enclosed inside a permanent magnet, is placed
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between the polarizer and the analyzer. When no field is applied, the MO element does not affect the light that is being transmitted, and the output intensity is described by the Malus Law:

$$I = I_0 \cos^2 \beta$$ \hspace{1cm} 1.1.1

Where $\beta$ is the angle between the transmission axes of the polarizer and the analyzer, and $I_0$ is the intensity of the incident radiation. If the MO element rotates the plane of polarization of the radiation by the angle $\Phi$, then:

$$I = I_0 \cos^2 (\beta - \Phi)$$ \hspace{1cm} 1.1.2

For the MO isolator, $\Phi = \beta = 45^\circ$, and $I = I_0$ for the forward propagating light signal. If there is any reflected light, the reflected light will be rotated by the angle, $\Phi' = -\Phi = -45^\circ$, and $I = 0$. It means the backward-propagating signal is blocked.

In practical optical isolator, the output intensity is affected by many other factors, like surface reflection, material absorption, etc.

$$I = I_0 (1-R)^2 \exp(-\alpha h)[1-R^2 \exp(-2\alpha h)]^{-1}$$ \hspace{1cm} 1.1.3

Where $R$ is the reflection coefficient, $\alpha$ is the absorption coefficient of the material, and $h$ is the sample thickness. The expression in the square brackets takes into account multiple reflections.

As real polarizers do not fully suppress the light in the crossing position, formula (1.1.2) should contain a coefficient $p$ which takes into account the finite transmission in the system. Then,

$$I = c I_0 \exp(-\alpha h)[(1-p)\cos^2(\beta - \Phi)+p]$$ \hspace{1cm} 1.1.4

Here the coefficient $c$ takes into account radiation losses in the system.

The MO element is magnetized by the magnet, and the plane of polarization of the light rotates due to the Faraday effect, by the angle:

$$\Phi = \Phi_F (M/M_0)h \cos \gamma$$ \hspace{1cm} 1.1.5
where $\Phi_F$ is the specific Faraday rotation of the MO element, $M$ and $M_s$ are the magnetic moment per unit volume and the saturation magnetization of the MO element, respectively, and $\gamma$ is the angle between the magnetization and the light propagation directions.

**Figure 3** Three types of nonreciprocal device configuration (a) Transverse, (b) longitudinal, and (c) waveguide.

**Figure 4** An octant of the garnet unit cell showing cations on octahedral, tetrahedral and dodecahedral sites.

In practical device, there are three types of nonreciprocal device configuration as shown in **Figure 3**. They are transverse, longitudinal and waveguide configurations. Magnetooptical transverse elements can process with light beams, but demand high saturation field. Longitudinal geometry utilizes lower saturation fields, but the film thickness must be more than 100 $\mu$m to provide an effective input of the laser radiation through the film edge. In the waveguide configuration epitaxial films with several
micrometer thickness are used. Devices of this kind require special radiation couplers to provide non-reciprocal light propagation, and a periodic variation of the material parameters of the film is necessary. The MO elements are indispensable in all the three configuration.

1.2 Objectives of the thesis

The objective of this thesis is to study new materials that can be used in optical isolator to realise the 45° polarised direction rotation at 1550 nm wavelength.

In order to achieve the objective, we conduct research on new substrate crystal and new Magneto-optical crystals. The new substrate crystal--CLNGG crystal is grown by CZ method, and its growth habits are studied. The new MO crystals \((\text{ReBi})_3\text{Fe}_5\text{O}_{12}\) (Re= Tb, Ho, Yb, or /and Ce) are grown by the TSSG method. Their growth habit and Faraday rotation characteristics at 1550 nm wavelength are studied.

Another objective of this thesis is to make theoretical study on the contribution of the different rare earth elements to the Faraday rotation.

This topic is important for the industry to develop the new product of isolators working at 1550 nm.

1.3 Literature review

During the last 20—30 years many kinds of magnetic materials have been studied. Existing magneto-optical materials can be divided into two groups. One group includes metals and alloys. They are partly transparent only at film thickness lower than 100 nm. Therefore, they are not suitable for the isolator. The other group includes the
The semi-magnetic materials, like Cd\(_{1-x}\)Mn\(_x\)Te, usually have a complicated Faraday rotation dispersion as a function of temperature when the sample composition is fixed. Furthermore, the preparation methods of the semi-magnetic semiconductors are usually complicated. The MO crystals of the most interesting are the magnetic dielectrics which are transparent media and easy to prepare. Only very few crystals among the magnetic dielectrics are promising candidates for the isolator devices, especially at wavelength of 1550 nm.

Magnetic dielectrics include orthoferrites, spinel ferrites and ferromagnetic garnets. The orthoferrites are orthorhombic crystals. Their magnetooptical behaviour is a combination of birefringence and Faraday rotation. In such a crystal, if the light propagates along the optical axis, the magnitude of Faraday rotation should be \(\Phi_F \cos(\alpha)\), where \(\alpha\) is the angle of the optical axis. The magnitude of the rotation is reduced by \(\cos(\alpha)\), since the magnetization is still constrained to lie along the crystalline c-axis. This kind of crystal is not suitable for the isolator device application because the isolator requires high Faraday rotation.

For the Co-containing spinel ferrites, strong magnetooptical transitions are found in CoFeRhO\(_4\), CeFeCrO\(_4\) and CoFeAlO\(_4\). These transitions are relatively narrow, and are centred at around 0.8 and 2.0 eV photon energy (1550 and 620 nm wavelength). This kind of crystals cannot meet the requirement for high Faraday rotation stability against wavelength as MO element in the isolator.

The ferromagnetic garnets are more useful for practical purpose in isolator. The MO effects in Rare- earth iron garnets (REIG) has been studied in considerable details. It has shown unambiguously that the Bi\(^{3+}\) and rare-earth ions (Ce\(^{3+}\)) enhance MO activity in REIG strongly at wavelength range of 0.6--2\(\mu\)m. For example, Bi-substituted iron garnets are widely used in developing different magnetooptical devices for optical signal
processing systems and optical communication systems (optical isolators and circulators, switches, time and spatial modulators, non-reciprocal devices, sensors, magnetooptical heads, and so on).\textsuperscript{3} The enhanced MO properties are strongly related to the crystal’s structure.

The most useful MO crystals for practical purpose are the ferromagnetic garnets. The unit cell of garnet is cubic with space group $O_h^{10}$ (Ia3d). The magnetic unit cell contains eight formula units of $\text{Re}_3\text{Fe}_5\text{O}_{12}$ with 24 Fe$^{3+}$ ions in the (d) (tetrahedral) sites, 16 Fe$^{3+}$ in the [a] (octahedral) sites, and 24 rare –earth ions Re$^{3+}$ in the \{c\} (dodecahedral) sites. The ions O$^{2-}$ form a close-packed structure, and the voids between the oxygen ions are filled by the rare –earth and iron ions. \{\} denotes dodecahedral sites, also know as c sites. [] denotes octahedral sites, also designated as a sites. () means tetrahedral sites or d sites. An octant of the garnet unit cell is shown in Figure 4.

There are three types of voids in the garnet structure—dodecahedral, octahedral and tetrahedral. In the dodecahedral position the rare earth ion is bonded to eight oxygen ions. In the octahedral positions the iron ion is bonded to six oxygen ions. In the tetrahedral position the iron ion is bonded to four oxygen ions. One formula unit of the garnet contains three dodecahedral, two octahedral, and three tetrahedral positions.

There is a wide range of cations available to substitute the ions in garnets. The first site to be considered for substituted ions will be the tetrahedral one which is the smallest and most restrictive in the number of possible substituted ions. The tetrahedral substituted ions are almost entirely of the spherically-symmetrical, closed-shell type.

The octahedral site is larger than the tetrahedral site in YIG with the distance to the surrounding oxygen ions being 2.01 Å vs 1.87 Å. There is a large variety of ions which have been observed to substitute for Fe$^{3+}$ on the octahedral site of YIG (like, Al$^{3+}$.
Ge$^{4+}$, Co$^{3+}$, Cr$^{3+}$, Ga$^{3+}$). Many but not all, of the ions which replace Fe$^{3+}$ in the tetrahedral site will also do so in the octahedral site.$^5$

The dodecahedral site is the largest of the three cation sites with the average distance to the oxygen ions being about 2.40 Å. Accordingly, a very large selection of ions, including all of the rare earths and alkaline earths, will occupy this site.

There will be site selectivity present not only with respect to site size and coordination but also with respect to the aspect presented by a given site in the growth face. The selectivity which arises purely with respect to the site size and symmetry was first reported by Gilleo and Geller.$^6$ In the case of rare earth–iron garnet crystals, the pair-ordering process which would be involved in the site selection by the rare earth ions during growth was first considered by LeCraw et al.$^7$ Nevertheless, there remains unambiguous evidence for site selectivity by rare earth ions as was shown by Wolfe et al.$^8$ in the case of Nd$^{3+}$- and Yb$^{3+}$-doped, flux-grown yttrium-aluminium garnet crystals by means of spin resonance measurements.

For one volume unit (cm$^3$) of the garnet there are 5.0 × 10$^{22}$ oxygen ions, 2.1 × 10$^{22}$ iron ions, and 1.3 × 10$^{22}$ rare–earth ions. The presence of the iron ions in the octahedral and tetrahedral positions gives rise to complicated optical and magnetooptical spectra as compared, for example, with those for the orthoferrites and other materials, containing iron ions only in the octahedral positions.

In the iron garnet the [Fe$^{3+}$] ions in [a] sites have the local point symmetry $\bar{3}$, and the (Fe$^{3+}$) ions in (d) sites have the local point symmetry $\bar{4}$, while the distance Fe$^{3+}$-O$^{2-}$ in oxygen polyhedral is constant, there is some distortion of the polyhedral. The Fe$^{3+}$ ions placed in the octahedral position form an octahedral magnetic sublattice, and the Fe$^{3+}$ ions placed in the tetrahedral position form a tetrahedral magnetic sublattice.
The main superexchange interaction is between the tetrahedral and octahedral iron ions. It is known that such an interaction gives rise to antiparallel ordering of the magnetic moments in the octahedral and tetrahedral iron sublattice. There are also superexchange interaction between the ions belonging the same sublattice, but such intra-sublattice interactions are only one tenth as strong as the inter-sublattice interactions.

When magnetic rare-earth ions are placed in dodecahedral positions they form a third magnetic sublattice—the dodecahedral magnetic sublattice. The superexchange interaction between the rare-earth and iron ions is the smallest among the inter-sublattice interactions. The main exchange interaction between the rare-earth and iron ions is the interaction between the dodecahedral rare-earth lattice and the tetrahedral iron lattice.

It can be said that the rare-earth ions are in the molecular field formed by the iron ions and the magnitude of such a field is of the order of 100—300 kOe at room temperature, depending on the kind of rare-earth ions involved. It should be noted that the effective magnetic field related to the superexchange between the octahedral and tetrahedral sublattice is nearly 2MOe.

Based on the results of the MO properties of Yttrium Iron Garnet crystal it is concluded that the bismuth increases strongly the MO activity of both octahedral (a) and tetrahedral (d) sublattices. The saturation magnetization Ms of a rare earth iron garnet can be expressed as the sum of the magnetizations of each individual sublattice: Ms=Ma + Md + Mc, where Ma, Md and Mc are the saturation magnetizations of the octahedral, tetrahedral, and dodecahedral sublattices, respectively. The Faraday rotation is strongly dependent on the saturation magnetization of the crystals.
There are a lot of substitutions in garnets. Besides the treatment of the substitutions on the basis of one ion from another, it is advantageous in many cases to consider the problem from the point of view of a solid solution of a garnet of one composition with another. The advantage of this approach is greatest when the end members of the solid-solution system exist. For example, in the solid solution systems of
Y₃Fe₂Fe₅O₁₂-Y₃Al₂Al₃O₁₂ and Y₃Fe₂Fe₅O₁₂-Y₃Ga₂Ga₃O₁₂, iron can be entirely replaced by Al³⁺ or Ga³⁺, respectively. In both cases the lattice constant decreases approximately linearly as the proportion of YIG decreases. However, for Y₃Fe₅₋ₓGaₓO₁₂ the lattice constant for 0<x<5 is always larger than that be calculated by a linear interpolation between the lattice constants of the end members (Figure 5). For Y₃Fe₅₋ₓAlₓO₁₂ the lattice constant again is greater than that given by linear interpolation, though for x≤2 the variations quite accurately linear (Figure 6)

Faraday Effect

When plane-polarized light passes through glass or crystal in a direction parallel to the applied field, the plane of polarization is rotated. It is called Faraday effect.

The angle of rotation of the plane of polarization, θ, is in the simplest case proportional to the magnitude of the magnetic field H and the distance L travelled by light in a medium along the direction of the field:

\[ \theta = V H L \]

The constant V, called the Verdet constant, is defined as the rotation per unit path, per unit field strength. The Verdet constant depends upon the properties of the medium, the frequency of light, and the temperature T.³

The sign of the angle θ depends on the sign of H. Therefore if the light travels twice through a field, first along the field direction, and then after normal reflection from a mirror in the opposite direction, the value of θ is doubled. This is a phenomenological distinction of the Faraday effect from the effect of natural optical activity. In the later case, when light returns, θ=0.

Faraday configuration in phenomenology
The magneto-optical effects can be described in terms of a complex rotation $\theta_F$ of the elliptically polarized transmitted light beam with respect to the incident linearly polarized beam. The Faraday rotation $\theta_F$ and the angle $\psi_F$ corresponding to the ellipticity $\varepsilon_F$ of the emerging light beam are related respectively to the real and imaginary parts of $\Phi_F$ and can be expressed as follows \cite{11,12}:

$$\theta_F = \text{Re} \left( \frac{\Phi_F}{t} \right) \quad 1.7.2$$

$$\psi_F = \text{Im} \left( \frac{\Phi_F}{t} \right) \quad 1.7.3$$

$$\varepsilon_F = \tanh(\psi_F t) \quad 1.7.4$$

where $\theta_F$ and $\psi_F$ are defined per unit length and $t$ represents the film thickness. The complex rotation is composed of magnetic dipole ($\Phi_F^{(m)}$) and electric dipole ($\Phi_F^{(e)}$) transition components given by

$$\Phi_F^{(m)} = \frac{2\pi n}{c} \sum \gamma_i M_i \quad 1.7.5$$

and

$$\Phi_F^{(e)} = -\frac{\omega}{2c} (N_+ - N_-) \quad 1.7.6$$

The sum extends over the magnetic sublattices ($M_1(T)$) and $\gamma_i$ is the complex gyromagnetic ratio of sublattice $i$. $N_+$ and $N_-$ denote the complex refractive indices for respectively right and left circularly polarized light.

$$N_\pm = n_\pm - ik_\pm \quad 1.7.7$$

$$\overline{n} = \frac{1}{2} (n_+ + n_-) \quad 1.7.8$$

$$\overline{k} = \frac{1}{2} (k_+ + k_-) \quad 1.7.9$$
The plane of polarization of the linearly polarized light therefore rotates through the angle

\[ \theta = \frac{\sigma}{2c} (n_r-n_l)L \]

where \( \sigma \) is the angular frequency, \( c \) is the velocity of light, and \( L \) is the path length of an optical beam in the medium. The magnetic-field-induced Larmor precession of electron orbits is the simplest mechanism for the Faraday effect. Instead of one eigenfrequency of the electron (\( \sigma \)), two (\( \sigma_+ \) and \( \sigma_- \)) arise, corresponding to the right-hand and the left-hand circular oscillations when there is a magnetic field in the medium.

Theory shows that

\[ \sigma \pm \sigma_0 = \sigma_0 \pm \frac{eH}{2mc} \]

where \( e \) and \( m \) are the electron charge and mass.

The appearance of two resonance frequencies (\( \sigma_+ \) and \( \sigma_- \)) in a medium placed in a magnetic field gives rise to the splitting of the absorption line. The difference between the resonance frequencies in the Zeeman doublet, \( \sigma_+ \) and \( \sigma_- \), results in a displacement of the curves \( n_\pm(\sigma) \) and \( n(\sigma) \) relative to each other on the frequency scale:

\[ n \pm (\sigma) \approx n(\sigma) \pm \frac{dn}{d\sigma} \frac{eH}{2mc} \]

where \( n(\sigma) \) is the refractive index in the absence of the field \( H \). Substituting (1.7.12) and (1.7.10) into (1.7.1) yields the well-known Becquerel formula

\[ V = \frac{e}{2mc^2} \lambda \frac{dn}{d\lambda} \]
Where $\lambda = 2\pi c/\sigma$ is the wavelength of light. Formula (1.7.13) is consistent with experimental data for diamagnetic media.

**Introduction of theory analysis on magneto-optical effects**

The substitution of diamagnetic ions in ferromagnetic garnets in general affects the magnetic and magneto-optical properties via the dilution of the respective sublattices. The ions $\text{Bi}^{3+}$, $\text{Pb}^{2+}$ and $\text{V}^{5+}$, however, are different in their behaviours, causing a significant increase in the magneto-optical effects. The magneto-optical effects can be understood qualitatively on the basis of transitions with either a strong oscillator strength or a high effective spin-orbit coupling of the excited $\text{Fe}^{3+}$ states.

The electric dipole consists of equal but opposite charges separated by a distance. The magnetic dipole comes from a current loop. The Faraday rotation of garnets originates from electric and magnetic dipole contributions of magnetic sublattices. Their magnetic properties are interpreted in terms of a ferromagnetic arrangement of the $\text{Fe}^{3+}$ ions on a (tetrahedral) and d (octahedral) sublattices giving a resultant magnetization which is aligned antiparallel to the moments of the rare earth ions on the c sublattice (dodecahedral). The magnetic (or electric) dipole contribution to the Faraday rotation from the sublattice is called magnetic (or electric) dipole transition. Electric-dipole transitions occur between ground state and excited states multiplets when magnetic dipole transitions are only within the ground state.

The specific Faraday rotation $\theta_F^{(e)}$ from the electric dipole transition for an isolated iron in the region away from absorption peaks can be expressed by

$$\theta_F^{(e)} = \frac{\pi N (n^2 + 2)^2}{9 \chi_{int}} f(\omega) \frac{\Delta \omega_{ge}}{\omega_{ge}}$$  \hspace{1cm} (1.7.14)
where some assumption concerning the energy level splitting have been made. \textsuperscript{14,15,16} \(N, c, \text{ and } t\) are the number of iron ions per cubic centimetre, the velocity of light and the film thickness respectively. \(f(\omega)\) describes the frequency dependence of the transitions and \(\hbar \omega_{ge}\) is the energy between the ground state and the excited states producing the rotation. \(\Delta \omega_{ge}\) denotes the difference between the transition frequencies for right and left circularly polarized light and thus is proportional to the splitting of the excited states depending on the magnitude of the effective spin-orbit coupling. Different mechanisms, \textsuperscript{17,18,19,20,21}, have been proposed to account for the observed transitions. These have to obey the parity and spin selection rules of the process of the double excitation of an exciton and a magnon. However, a quantitative agreement between theory and experiment has not yet been achieved. For yttrium iron garnet high magneto-optical effects are induced by transitions occurring in the range \(250 \text{ nm} \leq \lambda \leq 700 \text{ nm}\) where in particular the transitions at 250, 310, 440, 480 and 625 nm are involved. \textsuperscript{22,23,24} However, an interpretation of these spectra only in terms of isolated ions which applies to diamagnetic hosts gives rise to problems in the case of exchange-coupled Fe\textsuperscript{3+} ions. In this case iron pair transitions are more likely to account for the observed effects, which is strongly supported by the measured spectra of diamagnetically substituted iron garnets.\textsuperscript{25,26}.

The substitution of bismuth and lead leads to enhancements of the magneto-optical effects which are comparable in magnitude and are very similar with respect to their spectral dependence. Bi\textsuperscript{3+} and Pb\textsuperscript{2+} exhibit the same electronic configuration and are both characterized by a strong polarizability. This suggests the mixing of the 6p orbitals of these ions with the O 2p orbitals could be assumed. This increases the effective spin-orbit coupling responsible for the level splitting of the iron ions.\textsuperscript{27} This
appears to be the prime origin of the bismuth- and lead- enhanced magneto-optical transitions. For Bi$^{3+}$-substituted Y$_3$Fe$_5$O$_{12}$ strong transitions occur at 305 nm (4.1 eV), 375 nm (3.3 eV) and 440 nm (2.8 eV), while for Pb$^{2+}$-substituted Gd$_3$Fe$_5$O$_{12}$ a peak at 490 nm is observed. For shorter wavelengths the Pb$^{2+}$ spectrum has not been investigated.

Two basic types of transitions have been considered to describe the frequency dependence, i.e. transitions with a diamagnetic line shape and a paramagnetic line shape. In the first case the ground state is orbitally non-degenerate and the excited state is orbitally degenerate. In the paramagnetic case the situation is reversed. For low absorption and in the frequency range away from the transition the frequency dependence can be expressed in a simple form by

$$f_d(\omega) = \frac{\omega_0^2 \omega^2}{(\omega^2 - \omega_0^2)^2}$$

$$f_p(\omega) = \frac{\omega^2}{\omega^2 - \omega_0^2}$$

where $f_d(\omega)$ and $f_p(\omega)$ apply to the diamagnetic and the paramagnetic transitions respectively. $\omega_0 = c/\lambda_0$ denotes the frequency of the oscillator.

Wavelength dependence of Faraday rotation

The Faraday spectra of rare earth iron garnets at room temperature are displayed in Figure 7, and show a striking similarity to the absorption spectra in Figure 8. The typical shape of the $\theta_f$ versus $\lambda$ curve appears to be almost the same for all rare earth iron garnets owing to the similar environment of the Fe$^{3+}$ ions in the crystal and
thus their corresponding crystal field and charge transfer transitions. The incorporation of lead and bismuth gives rise to a strong increase in the rotation due to the strong enhancement of the iron transitions around 305, 375 and 440 nm. The influence of the lead on the wavelength dependence of $\theta_F$ for lead-substituted gadolinium iron garnet films at room temperature is displayed in Figure 9. For comparison the spectrum of a bismuth–containing sample is plotted (broken curves). The lead induces a positive rotation for $\lambda < 490$ nm and a negative rotation for large wavelengths. The spectral dependence of $\theta_F$ can be analyzed by assuming that the lead-enhanced iron transition is of the diamagnetic type (orbitally non-degenerate ground state and orbitally degenerate excited states). The wavelength dependence described by $f_d(\omega)$ in eqns. (1.7.15) can be rewritten as

$$f_d(\lambda) = \frac{\lambda_0^2 \lambda^2}{(\lambda^2 - \lambda_0^2)^2} \quad 1.7.16$$

where $\lambda_0 = c/\omega_0$. From a plot of $\lambda(\Delta\theta_F)^{1/2}$ versus $\lambda$ the location of the lead–enhanced transition is estimated to be at $\lambda_0 = 412$ nm where $\Delta\theta_F = \theta_F(x_{pb^2}) - \theta_F(0)$. For Gd$_3$$_x$Bi$_5$Fe$_5$O$_{12}$ films this peak is shifted by 40 nm towards shorter wavelengths, presumably because of a lower line width of the transition.
**Figure 7** Faraday rotation vs wavelength for rare earth iron garnets (Re$_3$Fe$_5$O$_{12}$)

**Figure 8** Optical absorption vs. wavelength at T= 295 K for Y$_3$Fe$_{5-x}$Ga$_x$O$_{12}$ film.
Figure 9 Faraday rotation spectra for $\text{Gd}_{3}\text{Pb}_x\text{Fe}_{5-y}M_y\text{O}_{12}$ ($M=\text{Pt, Ge, Sn}$) and $\text{Gd}_{3}\text{Bi}_x\text{Fe}_{4.7}\text{Ga}_{0.3}\text{O}_{12}$.

Figure 10 Faraday rotation spectra for $\text{Gd}_{3-x}\text{Bi}_x(\text{Fe,Al})_5\text{O}_{12}$ ($x=0.98$ for $\text{Gd}_{2.02}\text{Bi}_{0.98}(\text{Fe,Al})_5\text{O}_{12}$ prepared by r.f. sputtering, $x=1.1$ for an LPE film of composition $\text{Gd}_{1.9}\text{Bi}_{1.1}\text{Fe}_{4.1}(\text{Ga,Al})_{0.9}\text{O}_{12}$.)
The spectra of $\theta_F$ for $Y_{3-x}Bi_xFe_5O_{12}$ films, at room temperature are shown in Figure 10. In Figure 10, some results are got from gadolinium iron–based films prepared by r.f. sputtering or LPE deposition.

A linear plot of $\theta_F$ versus $\lambda$ (instead of the logarithmic plot given in Figure 10) reveals a contribution of the bismuth $\Delta \theta_F$ which is positive for $\lambda \leq 460$ nm and negative for $\lambda \geq 460$ nm. The spectrum appears to be very similar to that of the lead-containing garnets. The peaks in $\theta_F$ occurring at 375 nm (3.3 eV) and 440 nm (2.8 eV) increase linearly with the bismuth content and control the magneto-optical behaviour in the visible region. As to the lead-containing garnets from a plot of $\lambda(\Delta \theta_F)^{1/2}$ versus $\lambda^2$ the position of the corresponding oscillator is found to be around 420 nm in agreement with that obtained for other bismuth-substituted garnets.

In order to analyze the rare earth contribution to $\theta_F$, the contribution of Fe$^{3+}$ sublattices is assumed to be the same in all heavy rare earth garnets. This contribution is considered to have the same value as measured in YIG. The discussion of this hypothesis is given in ref. 43.

An ion garnet’s $\theta_F$ dependence on wavelength variation at a constant temperature can be expressed by the following:

$$\theta_F(\lambda) = \Theta_c(\lambda) + \Theta_a(\lambda) + \Theta_d(\lambda) \quad 1.7.17$$

where $\Theta_c(\lambda)$, $\Theta_a(\lambda)$ and $\Theta_d(\lambda)$ indicate contributions to the $\theta_F(\lambda)$ at sites c, a and d, respectively.

For example, $[Tb_{3-x}Bi_x]Fe_{5-y}Co_yO_{12}$:

$$\Theta_c(\lambda) = \Theta_y^{Tb}(\lambda) \times (3-x) + \Theta_x^{Bi}(\lambda) \times x \quad 1.7.18$$

$$\Theta_a(\lambda) + \Theta_d(\lambda) = \Theta_y^{YIG}(\lambda) \times \frac{5-y}{5} + \Theta_y^{Co}(\lambda) \times y \quad 1.7.19$$
where $\Theta_F^{\text{TB}}(\lambda)$, $\Theta_F^{\text{Bi}}(\lambda)$ and $\Theta_F^{\text{Co}}(\lambda)$ indicate the contributions of Tb, Bi and Co, to $\Theta_c(\lambda)$, $\Theta_a(\lambda)$ and $\Theta_d(\lambda)$ respectively, per formula unit.

### Temperature dependence of Faraday rotation

In the range of low losses which approximately applies to garnets in the wavelength range above 500 nm, the sublattice magnetization $M_1$ yields a linear dependence on temperature provided that the direction of the light propagation is parallel to the direction of $M_1$ \(^45\). Neglecting higher order terms, the Faraday rotation can be expressed by \(^46\),\(^47\)

$$
\theta_F(\lambda,T) = A(\lambda) M_a(T) + D(\lambda) M_d(T) + C(\lambda) M_c(T) \tag{1.7.20}
$$

where $A(\lambda)$, $D(\lambda)$ and $C(\lambda)$ are the magneto-optical coefficients of wavelength for octahedral, tetrahedral and dodecahedral sites respectively. $M_a(T)$, $M_d(T)$, $M_c(T)$ are the absolute values of the respective sublattice magnetizations. These magneto-optical coefficients depend on wavelength and the explicit form of this dependence is controlled by the special type of transition involved \(^48\),\(^49\). These coefficients are composed of electric and magnetic contributions. Therefore:

$$
A = A_e + A_m \quad D = D_e + D_m \quad C = C_e + C_m
$$

The theory predicts a temperature dependence of the magneto-optical properties which is controlled by the sublattice magnetizations as expressed by eqn. (1.7.20). A comparison between theory and experiment for rare earth iron garnets at $\lambda = 1152$ nm reveals an excellent agreements as demonstrated in Figure 11. The magneto-optical coefficients can be extracted from the fit of the calculated temperature dependence of $\theta_F$ to the measured data by assuming these coefficients to be temperature independent as predicted by the theory \(^50\). Some of the coefficients originating from the electric dipole transitions are listed in Table 1 \(^51\).
For diamagnetic substitutions the temperature behaviour of $\theta_F$ is affected by the dilution of the iron sublattices and the induced changes in the magneto-optical coefficients. For gallium – substituted iron garnet films it turned out that the temperature dependence for $\theta_F$ at $\lambda=633$ nm calculated from eqns. (1.7.20) accounts well for the measured data as shown in

Figure 11 Faraday rotation vs temperature at wavelength of 1152 nm for various rare earth ions.
As with these rare earth iron garnets the coefficients were assumed to be temperature independent. The sublattice magnetizations have been inferred from the fit of the molecular field theory to the measured saturation magnetization. In this case, however, the extracted coefficients plotted against the gallium content reveal an inconsistency at the compositional compensation point. The coefficients for $Y_3Fe_5O_{12}$ at $\lambda = 633$ nm are about an order of magnitude larger than at $\lambda = 1152$ nm (see Table 1). The rotation at $\lambda = 633$ nm thus can be expressed by

$$\theta_F = 484.3M_a(T) - 311.7M_d(T)$$  \hspace{1cm} 1.7.21

where $A_m = D_m = 9.57 \times 10^2$ deg m$^{-1}$ $\mu_B^{-1}$ and for example $M_a(0) = 20 \mu_B$ and $M_d(0) = 30 \mu_B$. The coefficients obtained for “pure” $Y_3Fe_5O_{12}$ films exhibit a considerable scatter owing to that of $\theta_F$ which is induced by the varying lead impurities coming from the flux.

The comparison of the calculated and measured temperature dependences of $\theta_F$ reveals small deviations which have been attributed to a temperature dependence of the magneto-optical coefficients. This has been interpreted in terms of the effect of the temperature dependence of the exchange field on the transition frequency $\omega_h$ (equ. 1.7.16). However, there are various other sources that may cause or simulate a temperature dependence of the coefficients such as the thermal expansion of the lattice or the temperature variation in $\bar{n}$. Furthermore, the expressions (1.7.20) represent only the linear term with respect to the sublattice magnetizations. Higher order terms may also contribute to $\theta_F$.

In this case of $Y_3Fe_5O_{12}$, a third-order term has been taken into account, leading to a significant improvement in the agreement between theory and experiment. Finally the lead impurities cause a change in the magnitude and the shape of
the temperature dependence of $\theta_F^{61}$, which is obvious from Figure 13. With increasing lead content a minimum in $\theta_F$ builds up around 120 K which also applies to Gd$_3$$_x$Pb$_y$Fe$_5$O$_{12}$ films $^{62,63}$. This change in the $\theta_F$ versus T curves gives rise to an increasing deviation between the calculated and measured data when temperature-independent magneto-optical coefficients are used $^{64,65}$.

The temperature variation in $\theta_F$ for bismuth –substituted yttrium iron garnet films is in Figure 14. For $x \geq 0.25$, $\theta_F$ decreases monotonically towards higher temperatures and these dependences can be well described with temperature-independent magneto-optical coefficients. For two compositions A and D given in Table 1, and their magnitudes compared with those for Y$_3$Fe$_5$O$_{12}$ reflect the strong enhancement of the magneto-optical transitions. The tetrahedral coefficient is raised much more than the octahedral coefficient, leading to a stronger dominance of the negative tetrahedral sublattice contribution. The sublattice magnetizations again have been inferred from the fit of the molecular field theory to the measured saturation magnetization.

From the coefficients of bismuth substituted films given in Table 1 it is expected that diamagnetic substitutions on tetrahedral sites reduce $\theta_F$ approximately according to the dilution of the tetrahedral sublattice. However, it turns out that the rotation for Y$_3$$_x$Bi$_y$Fe$_5$O$_{12}$ obeys the relation

$$\theta_F (x) = \theta_F (y) \left(1 - \frac{y_a}{2}\right) \left(1 - \frac{y_d}{2}\right)$$

1.7.22

where $y_a$ and $y_d$ are the concentrations of Al$^{3+}$ ions on octahedral and tetrahedral sites respectively ($y = y_a + y_d$). This dependence suggests that iron pair transitions are involved $^{66,67}$. The different concentration behaviour of bismuth substituted garnets in contrast with diamagnetically substituted Y$_3$Fe$_5$O$_{12}$ (eqn. 1.7.21) may be attributed to the
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The fact that $\theta_F$ in the visible region in the former case is caused by the transitions in the UV region while in the latter case it is due to crystal field transitions.

Table 1 Magneto-optical coefficients induced by the electric dipole transition for various garnet compositions

<table>
<thead>
<tr>
<th>Composition</th>
<th>$\lambda$ (nm)</th>
<th>$\theta_F$ ($\times 10^4$ deg m$^{-1}$)</th>
<th>$-A_e$ ($\times 10^2$ deg m$^{-1}$)</th>
<th>$-D_e$ ($\times 10^2$ deg m$^{-1}$)</th>
<th>$-C_e$ ($\mu_B^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_3Fe_5O_{12}$</td>
<td>1152</td>
<td>2.45</td>
<td>50 ± 3</td>
<td>29 ± 2</td>
<td>0</td>
</tr>
<tr>
<td>$Lu_3Fe_5O_{12}$</td>
<td>1152</td>
<td>2.02</td>
<td>55 ± 3</td>
<td>33 ± 2</td>
<td>0</td>
</tr>
<tr>
<td>$Gd_3Fe_5O_{12}$</td>
<td>1152</td>
<td>0.7</td>
<td>42.4 ± 1.8</td>
<td>27.1 ± 1.3</td>
<td>1 ± 0.2</td>
</tr>
<tr>
<td>$Tm_3Fe_5O_{12}$</td>
<td>1152</td>
<td>1.1</td>
<td>23 ± 7</td>
<td>12 ± 6</td>
<td>20 ± 4</td>
</tr>
<tr>
<td>$Tb_3Fe_5O_{12}$</td>
<td>1152</td>
<td>4.4</td>
<td>9 ± 15</td>
<td>10 ± 11</td>
<td>84.4 ± 2.5</td>
</tr>
<tr>
<td>$Y_3Fe_5O_{12}$</td>
<td>633</td>
<td>8.35</td>
<td>493.9</td>
<td>321.3</td>
<td>0</td>
</tr>
<tr>
<td>$Y_{3Fe_{10.5}Ga_{10.5}}O_{12}$</td>
<td>633</td>
<td>0</td>
<td>300.1</td>
<td>203.1</td>
<td>0</td>
</tr>
<tr>
<td>$Y_{2.35Bi_{0.65}}Fe_5O_{12}$</td>
<td>633</td>
<td>126</td>
<td>419.5</td>
<td>799.5</td>
<td>0</td>
</tr>
<tr>
<td>$Y_{1.97Bi_{1.03}}Fe_5O_{12}$</td>
<td>633</td>
<td>193</td>
<td>876.3</td>
<td>1394.1</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 12 Faraday rotation vs temperature at wavelength of 633 nm for $Y_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$.

Figure 13 Faraday rotation vs temperature at wavelength of 633 nm for $Y_{3-x}\text{Pb}_x\text{Fe}_5\text{O}_{12}$.

Figure 14 Faraday rotation vs temperature at wavelength of 633 nm for $Y_{3-x}\text{Bi}_x\text{Fe}_5\text{O}_{12}$. 
The dependence of $A_e$ and $D_e$ on the bismuth content turns out to be non-linear, which might be attributed to the influence of different transitions on $\theta_F$ at $\lambda = 633$ nm, especially for high bismuth contents. The accuracy of the extracted coefficients is strongly affected by the precision of $\theta_F$ and the sublattice magnetizations.

For the cerium-substituted garnet crystals, the circular magnetic birefringence is the result of the three sublattices contributions. For the dodecahedral sites which contain the Ce$^{3+}$ ions, this contribution is given by

$$\theta_F = (C_e + C_m)M_c$$

where $C_e$ and $C_m$ represent the electric and magnetic dipole transition coefficients respectively and $M_c$ represents the rare earth sublattice magnetizations. Due to the low of Ce$^{3+}$ contents, it is impossible to deduce $M_c$ from the magnetization measurements. Furthermore, the Lande’s factor of the Ce$^{3+}$ ion is unknown and $C_m$ cannot be calculated. Finally it appears that $C_e$ and $C_m$ cannot be separated as it is usually done in pure heavy rare earth garnets, so a mean magneto-optical coefficient $C^{MO} = C_e + C_m$ will be introduced.

When the temperature is higher than 77K, the behaviour of $M_c$ can be considered as purely paramagnetic in the molecular field created by the Fe$^{3+}$ sublattices. $M_c$ can be written as follows:

$$M_c = c \frac{n}{T} M_{VIG}$$

Where $c$ is the Curie constant and $n$ is a mean molecular field coefficient which is related to the classical coefficient by $n = 3n_{dc} - 2n_{ac}$.

Then one can obtain:

$$\theta_F = C^{MO} e \frac{n}{T} M_{VIG}$$
According to the idea of Neel \(^7^0\), \(n\) is a linear decreasing function of temperature: in a first order it has the form:

\[
n = n_0 (1 + \gamma T)
\]  \hspace{1cm} \text{(1.7.26)}

For the different heavy rare earth garnets, the electric dipole coefficient presents a linear temperature behaviour above 100K \(^7^1\). If we assume that this result can be extended to the Ce\(^{3+}\) case, \(C^{\text{MO}}\) is written:

\[
C^{\text{MO}}(T) = C^{\text{MO}}(0) (1 + \alpha T)
\]  \hspace{1cm} \text{(1.7.27)}

Finally it is obtained:

\[
\theta_F = \frac{M_{\text{YIG}} n_0 (1 + (\alpha + \gamma) T + \alpha \gamma T^2)}{T}
\]  \hspace{1cm} \text{(1.7.28)}

, where \(n_0\) is a constant determined by \(C^{\text{MO}}(0)\), \(n_0\) and \(c\).

For YIG, \(\alpha = 2.4 \times 10^{-2} \text{ K}^{-1}\), and \(\gamma = -1.3 \times 10^{-3}\). The temperature variation of \(\theta_F\) originates mainly from the evolution of the MO coefficient (it is reasonable to consider it is probably the electric dipole coefficient). Nevertheless above 200K the variation of the supercharge interaction with the temperature cannot be neglected.

**Compositional dependence of Faraday rotation**

The contribution of rare earth ions to the Faraday rotation of iron garnet is relatively small and their contributions are comparable in magnitude, except for Pr\(^{3+}\) ions which exhibit a rotation an order of magnitude higher \(^7^2, 7^3\). The magnitude of \(\theta_F\) for rare earth iron garnets is relatively small because the sublattice contributions \(\theta_F(a) = AM_a\) and \(\theta_F(d) = DM_d\) compensate each other to a large extent, e.g. the two sublattice rotations of \(Y_3\text{Fe}_5\text{O}_{12}\) at \(\lambda = 633\) nm and \(T = 295\) K are \(\theta_F(a) = 8.670 \times 10^5\) deg m\(^{-1}\) and \(\theta_F(d) = -7.835 \times 10^5\) deg m\(^{-1}\), while the total rotation amounts to \(0.835 \times 10^5\) deg m\(^{-1}\) \(^7^4\). The substitution of diamagnetic ions, therefore, may raise or reduce \(\theta_F\) depending on the substituted
sublattice, the substitution level and the wavelength. For a diamagnetically substituted garnet of composition $\mathrm{Y_3Fe_{2-x}U_xFe_{3-y}V_yO_{12}}$ the rotation at $\lambda=633$ nm and $T=295$K can be approximated by \(^{74}\)

$$\theta_F(x, y) = 8.670 \left(1 - \frac{x}{2}\right)^{-7.835} \left(1 - \frac{y}{3}\right)$$  \hspace{0.5cm} (1.7.29)

where $\theta_F$ is expressed in units of $10^5$ deg m\(^{-1}\). Equation (1.7.29) does not account for the influence of $x$ and $y$ on the magneto-optical coefficients. The substitution of small amounts of $\text{Ga}^{3+}$ ions thus leads to an increase in $\theta_F$ \(^{74}\) and that of $\text{Sc}^{3+}$ ions to a decrease in $\theta_F$ \(^{75}\). The influence of $\text{Al}^{3+}$ on $\theta_F$ at $\lambda=1152$ nm is reported in ref.\(^{76}\) For higher substitutional levels the decrease in the Curie temperature generally enforces a reduction in $\theta_F$.

The incorporation of $\text{Pb}^{2+}$ and $\text{Bi}^{3+}$ ions in the garnet crystal leads to much stronger effects owing to their influence on the super-exchange interaction and the effect on the spin-orbit coupling. In particular, the strong transitions at 440 nm (2.8 eV) and 380 nm (3.3 eV) cause the strong enhancement of $\theta_F$ in the visible and IR regions. The dependence of $\theta_F$ on the $\text{Bi}^{3+}$ content at $\lambda=633$ nm is shown in Figure \(15\) \(^{77,78,79}\). For comparison the variations in $\theta_F$ with the $\text{Ga}^{3+}$ \(^{80}\) and the $\text{Pr}^{3+}$ contents are also given, demonstrating the strong $\text{Bi}^{3+}$ effect which is comparable in magnitude for different garnet hosts. The contributions $\Lambda \theta_F/x$ for $\text{Y}_{3-x}\text{Bi}_x\text{Fe}_5\text{O}_{12}$ films at $\lambda=633$ nm are $-2.54 \times 10^6$ deg m\(^{-1}\) and $-2.06 \times 10^6$ deg m\(^{-1}\) for $T=4.2$K and $T=295$ K respectively. The highest rotation has been measured for a $\text{Bi}_{2.3}(\text{Y, Lu})_{0.7}\text{Fe}_5\text{O}_{12}$ film yielding $\theta_F=-4.8 \times 10^6$ deg m\(^{-1}\) at $\lambda=633$ nm and $T=295$ K \(^{81}\). The lead contribution to $\theta_F$ for $\text{Y}_{3-x}\text{Pb}_x\text{Fe}_5\text{O}_{12}$ films is comparable with that of bismuth as shown by the broken-dotted line which has been extrapolated from small lead concentrations and applies only to the amount of divalent
lead ions \(^{82}\). The contributions \( \Lambda \theta_F / x \) at \( \lambda = 633 \) nm are found to be \(-1.85 \times 10^6 \text{ deg m}^{-1}\) and \(-1.84 \times 10^6 \text{ deg m}^{-1}\) for \( T=4.2 \) K and \( T=295 \) K respectively. In gadolinium iron garnet the lead contribution turns out to be significantly lower \(^{83,84}\), which also applies to polycrystalline \( \text{Pb}^{2+}-\text{Ge}^{4+} \) substituted \( \text{Y}_3\text{Fe}_5\text{O}_{12} \) \(^{85}\).

The substitution of magnetic ions such as \( \text{Fe}^{2+}, \text{Co}^{2+} \) and \( \text{Co}^{3+} \) also affects \( \theta_F \) \(^{86,87}\). It should be mentioned that tetrahedral \( \text{Co}^{2+} \) induces pronounced magneto-optical effects around 700 and 1500 nm originating from crystal field transitions.

![Figure 15](image)

**Figure 15** Concentration dependence of the Faraday rotation at wavelength of 633 nm and \( T=295 \) K for various garnet films.

**Issues of some important rare-earth garnet crystals**

The iron garnets are highly transparent in the near infrared range 1.3-5.6 \( \mu \text{m} \) (Figure 16). Optical absorption coefficients as low as 0.03 cm\(^{-1}\) are attained. The increase of the optical absorption at wavelengths less than 1.6 \( \mu \text{m} \) is related to the intrinsic electron transition in octahedral [Fe\(^{3+}\)] ions, with the centre of the absorption band near 900 nm \(^{88}\).
Reduction in the absorption due to the iron dilution with Ga$^{3+}$ or Sc$^{3+}$

The iron garnet is widely used for developing non-reciprocal and other magnetooptical devices for wavelengths of 1.06, 1.15, 1.3, and 1.65 $\mu$m. Studies of the iron garnet compositions in which the iron sublattice has been diluted with either Ga$^{3+}$ or Sc$^{3+}$ have shown Figure 17 that there is, at all energies, a general trend of reduction in the absorption with iron dilution in either the tetrahedral or octahedral sublattices. In the former case the tetrahedral iron is removed, while in the latter case the octahedral iron is removed. When either tetrahedral or octahedral positions are diluted, the absorption coefficient changes according to $\alpha(y) = \alpha_0(1-y_a/2)(1-y_d/3)$ where $y_a$ and $y_d$ are the contents of dilution ions in the octahedral and tetrahedral positions, and $y=y_a+y_d$. As shown in Figure 17, the extent to the reduction in the absorption is very limited. 89, 90.

Faraday rotation due to the iron dilution with Ga

It is found that the Fe$^{3+}$ ions on different crystal sites (octahedral and tetrahedral) give different contributions, which are of opposite sign, to dispersive rotation, the octahedral ions giving the greater, positive, contribution.
Figure 16 The optical absorption of \( \text{Y}_3\text{Fe}_5\text{O}_{12} \) at low frequency due to lattice vibrations, and at high frequency due to octahedral \( \text{Fe}^{3+} \) crystal-field transitions (curve 1), and a detailed view of the absorption edge (curve 2).

Figure 17 Absorption spectra of \( \text{Y}_3\text{Fe}_5\text{O}_{12} \) (curve 1), (\( \text{YGdTm} \))\( \text{Fe}_{4.3}\text{Ga}_{0.7}\text{O}_{12} \) (curve 2), \( \text{Yb}_3\text{Fe}_{3.8}\text{Sc}_{1.2}\text{O}_{12} \) (curve 3).

The dependence of the Faraday rotation in \( \text{Y}_3\text{Fe}_{2-x}\text{U}_x\text{Fe}_{3-y}\text{V}_y\text{O}_{12} \) (at 633 nm and \( T=295 \text{ K} \)) on dilution of the iron sublattices, where \( U \) is the diluting ion in the octahedral
sublattice and \( x \) is the concentration, while \( V \) and \( y \) are the diluting ion and concentration for the tetrahedral sublattice, can be represented by the formula: \( \Phi_f(x,y) = 8670 \left(1-x/2\right)^{-7835} \left(1-y/3\right) \), where \( \Phi_f(x,y) \) is in deg cm\(^{-1}\) \(^91\).

When the tetrahedral sublattice is diluted, at first – while the dilution does not exceed 0.7 formula units (at room temperature) ---there is an increase in the Faraday rotation, because the negative contribution of the tetrahedral sublattice diminishes. When the dilution increases further, there is a decrease of Faraday rotation due to the diminishing of the exchange interaction.

Temperature dependencies of the Faraday rotation on the iron dilution with Ga

The introduction of diamagnetic and paramagnetic ions instead of iron ions in iron garnet, and changing one rare-earth ion to another leads to a change in the absolute value and temperature dependence of the Faraday rotation.

The temperature dependencies of the Faraday rotation of \( Y_3Fe_{5-x}Ga_xO_{12} \) at 633 nm for different values of \( x \) are shown in Figure 18 \(^91\).

The temperature dependence of the Faraday rotation at 633 nm in \( Y_3Fe_{5-x}Ga_xO_{12} \) can be represented by the formula: \( \Phi_f(T)=484M_a(T)-312M_d(T) \), where \( M_a \) and \( M_d \) are the sublattice magnetizations for the octahedral and tetrahedral sublattices, respectively.

In summary, in YIG crystal system, the dilution of the iron sublattices can increase the specific Faraday rotation, reduce the absorption, and improve the temperature dependence of the Faraday rotation. However the specific Faraday rotation of YIG at 1.6 \( \mu \)m wavelength is very small, 0.08 deg/\( \mu \) m, so that it is difficult to deposit YIG film with 500 \( \mu \)m thickness on the garnet substrate.
The optical properties of rare-earth iron garnets are mainly determined by the iron atoms, and therefore the spectral peculiarities are common to all iron garnets.

The presence of the rare-earth ions in the dodecahedral sublattice is exhibited in the following way: in the transparent band and in the background of bands of relatively low optical absorption there appear narrow peaks caused by transitions inside the partially filled 4f shells of the rare-earth ions. The intensities of the peaks are of the order of $\alpha \approx 100 \text{ cm}^{-1}$.

Among the trivalent rare-earth ions, only La$^{3+}$ and Lu$^{3+}$ ions have no characteristic transitions for the 4f electrons, because in the former the 4f electrons are absent and in the latter the 4f shell is full. Gd$^{3+}$ ions exhibit weak absorption bands near $\lambda \approx 0.33 \mu \text{m}$ that can be observed only for non-magnetic garnets.

Y$^{3+}$, Ca$^{2+}$, Si$^{4+}$, Ge$^{4+}$, Sc$^{3+}$, Ga$^{3+}$, and Al$^{3+}$ ions, which are often incorporated into various garnet sublattices, also do not produce absorption lines in the transparent region and in the visible spectral band.

The shift in position of the first transition $^6A_{1g}(^6S) \rightarrow ^6T_{1g}(^4G)$ of the octahedral Fe$^{3+}$ complex due to the rare-earth-induced change of the lattice parameter of the iron garnet is extremely important from the point of view of applied Magnetooptics. The shift

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**Figure 18** The temperature dependence of the Faraday rotation at 633 nm for Y$_3$Fe$_{5-x}$Ga$_x$O$_{12}$. 

![Graph showing the temperature dependence of the Faraday rotation at 633 nm for Y$_3$Fe$_{5-x}$Ga$_x$O$_{12}$](image-url)
is mainly caused by transformation of the crystalline field in which the Fe$^{3+}$ is located, due to the change in the distance between the iron and the oxygen ions. The change in the position of the transition leads to changes in the optical absorption at the wavelengths 1.06 and 1.15 $\mu$m, which are used in optical communication system.

For magneto-optical modulators and non-reciprocal elements that operate in these wavelength regions, it is advisable to use iron garnets with large unit-cell parameters. It should also be taken into account that the presence of small amounts of Fe$^{2+}$ and Fe$^{4+}$ significantly affects the optical absorption in this region. Therefore to minimize the optical absorption it is necessary to thoroughly control the charge compensation and growth parameters during the single-crystal growth and the film epitaxy.\(^92\)

The rare-earth iron garnets have magnetic compensation points, and all odd magneto-optical effects change their sign when crossing that point. The Faraday effect changes its sign because above the compensation point magnetization of the tetrahedral lattice orients along the direction of the external magnetic field, while below the compensation point the octahedral lattice orients along the field direction. As the rare-earth sublattice is antiferromagnetically bound to the tetrahedral sublattice, the direction of its magnetization also changes after crossing this point.

List of systems and their Faraday rotation spectra from the reference

- Tb$_3$Fe$_5$O$_{12}$
- Gd$_3$Fe$_5$O$_{12}$
- Eu$_3$Fe$_5$O$_{12}$
- Er$_3$Fe$_5$O$_{12}$
- Tm$_3$Fe$_5$O$_{12}$
- Sm$_3$Fe$_5$O$_{12}$
- Dy$_3$Fe$_5$O$_{12}$
- Lu$_3$Fe$_5$O$_{12}$
- Ho$_3$Fe$_5$O$_{12}$
- Yb$_3$Fe$_5$O$_{12}$
- (Ho$_{0.01}$Gd$_{0.99}$)$_3$Fe$_5$O$_{12}$
- Y$_3$(Ga$_1$Fe$_4$)$_{12}$
Introduction

Gd$_3$(YbGa)$_5$O$_{12}$
(NdLu)$_3$Fe$_5$O$_{12}$
(PrLu)$_3$Fe$_5$O$_{12}$
(YR1)$_3$(FeR2)$_5$O$_{12}$, R1=La, Bi, Lu, and/or Gd; R2=Ga, Al, In and/or Sc.
R$_3$(Ga$_{1-x}$Al$_x$)$_5$Fe$_y$O$_{12}$, R=Y, La, Gd, Nd, and Sm, x=0—1; 0<y<1.65.

![Figure 19](image_url)

Figure 19 (a) shows the spectral dependencies of the Faraday effect of the rare-earth iron garnets in the visible spectral band. In Table 2 the Faraday rotations for the rare-earth iron garnets RE$_3$Fe$_5$O$_{12}$ at $\lambda$ = 1.064 $\mu$m, T=300 K are summarized. The
temperature dependence of the Faraday rotation of some rare-earth garnets are presented in Figure 19(b).

The Faraday rotation spectra for a number of rare-earth iron garnets are shown in Figure 20. A characteristic feature of the spectra presented is the very low dispersion of the Faraday rotation in the long–wave length region of the transparent band.

Tb$_3$Fe$_5$O$_{12}$ has highest specific Faraday rotation and better temperature coefficient of Faraday rotation. It is very difficult to get the crystal. (Tm=1840 °C).

In iron garnets, Fe$^{2+}$ and Fe$^{4+}$ ions always exist simultaneously in low concentration. However, at equilibrium concentrations near 10$^{-4}$ formula units they do not affect the optical and magnetooptical properties in any observable way. When iron garnets are doped with non-trivalent ions, the concentrations of Fe$^{2+}$ and Fe$^{4+}$ ions can reach ~0.1 formula units, and in this case the optical and magnetooptical properties of the iron garnets can change drastically, in particular in the infra-red spectral region. For example, in yttrium iron garnet at the wavelength 1.3 $\mu$m, the absorption coefficient can be less than 0.1 cm$^{-1}$, provided that optimal growth conditions are maintained. However, in the samples doped with uncompensated Ca$^{2+}$ ions—which leads to the appearance of the Fe$^{4+}$ ions in the iron garnet—or with Ge$^{4+}$ ions—which leads to the appearance of the Fe$^{2+}$ ions in the iron garnet—at this wavelength the optical absorption coefficient can reach the level of 100 cm$^{-1}$ and even 10$^3$ cm$^{-1}$. 95

Doping of the iron garnets with doubly positive ions, e.g. Ca$^{2+}$ or Mg$^{2+}$, creates p-type conductivity; doping with the four-valent ions or five-valent ions, say Ge$^{4+}$, Si$^{4+}$, Zr$^{4+}$, or Nb$^{5+}$, leads to the appearance of conductivity of n type. It was also noted 96 that while the MCD spectra of Si$^{4+}$ and Ge$^{4+}$-doped iron garnets exhibit no magnetooptical peculiarities in the spectral region above 1.6 $\mu$m, in the samples doped with Sn$^{4+}$ and Zr$^{4+}$ ions the spectrum is far more complicated. It should be noted here that the Si$^{4+}$ and Ge$^{4+}$.
ions occupy tetrahedral sites, and the Sn^{4+} and Zr^{4+} ions occupy octahedral sites in the iron garnets.

Table 2 The Faraday rotation for rare-earth iron garnets, for $\lambda = 1.06 \ \mu m$ and $T=300 K$.[3]

<table>
<thead>
<tr>
<th>Garnet</th>
<th>$\Phi_F$ (deg cm$^{-1}$)</th>
<th>Garnet</th>
<th>$\Phi_F$ (deg cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y$_3$Fe$<em>5$O$</em>{12}$</td>
<td>+280</td>
<td>Ho$_3$Fe$<em>5$O$</em>{12}$</td>
<td>+135</td>
</tr>
<tr>
<td>Y$_2$Pr$_1$Fe$<em>5$O$</em>{12}$</td>
<td>-400</td>
<td>Er$_3$Fe$<em>5$O$</em>{12}$</td>
<td>-120</td>
</tr>
<tr>
<td>Sm$_3$Fe$<em>3$O$</em>{12}$</td>
<td>+15</td>
<td>Tm$_3$Fe$<em>5$O$</em>{12}$</td>
<td>+115</td>
</tr>
<tr>
<td>Eu$_3$Fe$<em>5$O$</em>{12}$</td>
<td>+167</td>
<td>Yb$_3$Fe$<em>5$O$</em>{12}$</td>
<td>+12</td>
</tr>
<tr>
<td>Gd$_3$Fe$<em>5$O$</em>{12}$</td>
<td>+65</td>
<td>[Lu$_3$Fe$<em>5$O$</em>{12}$]</td>
<td>+200</td>
</tr>
<tr>
<td>Tb$_3$Fe$<em>5$O$</em>{12}$</td>
<td>+535</td>
<td>[Nd$_3$Fe$<em>5$O$</em>{12}$]</td>
<td>-840</td>
</tr>
<tr>
<td>Dy$_3$Fe$<em>5$O$</em>{12}$</td>
<td>+310</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the brackets the hypothetical single crystal compositions are given.

![Figure 20](image)

Figure 20 The Faraday effect for Y$_3$Fe$_5$O$_{12}$ at T=77K (curve 1) and for Y$_3$Fe$_5$O$_{12}$ (curve 2), Er$_3$Fe$_5$O$_{12}$ (curve 3), and Ho$_3$Fe$_5$O$_{12}$ (curve 4) at T=290K, where H=2.4 KOe.

The most spectacular structures in the absorption spectra lie in the 0.9 $\mu m$ region for the Fe$^{2+}$ ion, and in the 0.95 $\mu m$ region for the Fe$^{4+}$ ion. Nassau $^9$ proposed the following empirical relationships between the absorption coefficient at the wavelength
\( \lambda = 1.2 \ \mu m \) and the concentration of \( Fe^{2+} \) and \( Fe^{4+} \) ions: \( \alpha_{12}^{Fe^{2+}} = 950[Fe^{2+}] \) and \( \alpha_{12}^{Fe^{4+}} = 6500[Fe^{4+}] \). For the iron garnets containing the substantial numbers of bivalent and tetravalent iron ions, a significant increase of the optical absorption is also observed in the visible spectral region. There is no unambiguous explanation of the mechanisms responsible for the observed growth of the absorption as yet.

From above analysis, ReIG is not perfect for working at 1.55 \( \mu \)m wavelength band as a Faraday rotator due to its low Faraday rotation effect and high absorption in this region.

Bismuth –substituted iron garnets and cerium – substituted iron garnets are the most important ferromagnetic garnets for the optical isolator applications. Extensive investigations on the magnetooptical properties of Bi-substituted iron garnets were conducted in the visible light band. The magnetooptic response changes linearly with the bismuth substitution.\(^98\) There are very little reports on the MO property of Bismuth – substituted iron garnets and cerium – substituted iron garnets in the 1550nm wavelength band. As the concentration of \( Bi^{3+} \) ion increases, the lattice parameter of the typical iron garnet \( Y_3Fe_5O_{12} \) (YIG) crystal increases linearly from 12.38\( \AA \) to 12.62 \( \AA \), which corresponds to the lattice parameter of \( Bi_3Fe_5O_{12} \).\(^99\) For \( (REBi)_3Fe_5O_{12} \) crystals (RE= rare earth elements), the rare earth elements with different atom sizes will cause the different lattice parameters which will contain different amount of Bi. The influences of the rare earth elements on the MO properties in the rare earth bismuth garnet crystals will be discussed in details in the thesis. The samples of Bismuth –substituted iron garnets and cerium – substituted iron garnets can be prepared by bulk crystal growth method.

The amount of literature on MO bulk crystal working at the 1550 nm band is moderate. T. Tamaki, et al\(^{100}\), reported that the Faraday rotation of \( (Tb_{2.75}Bi_{0.25})Fe_5O_{12} \) crystal was about \(-205^o/\text{cm} \) at \( \lambda = 1550 \text{nm} \) and was independent of the wavelength, and
that the specific Faraday rotation \( \theta_F(x) \) and Bi content \( x \) was given by \( \theta_F(x) = -1540x + 180 \) deg/cm. The bulk crystal of 2.2 mm thickness was needed for 45° Faraday rotators.

Min Huang et al.\(^{101} \) reported that the specific Faraday rotation of the crystal Ho\(_{3-x} \)\(_y\)Yb\(_x\)BiFe\(_5\)O\(_{12}\) (\( x=1.03, y=1.12 \)) was about \(-767^0/\)cm at 1550nm, and that their temperature and wavelength dependence of Faraday rotation were small.

The difficulty in bulk MO crystal growth is that the garnet crystals are incongruently melting compounds which decompose before melting. The flux is needed so that the garnet phase crystal can be crystallized from the melt at high temperature but lower than the decomposing temperature. The disadvantages of the flux crystal growth method are substitutional or interstitial incorporation of solvent ions into the crystal, microscopic or macroscopic inclusions of solvent or impurities, non-uniform doping, a slow growth rate. Large temperature fluctuations may facilitate inclusion formation or compositional variations and are likely to have an adverse effect on the crystal quality. The growing stability tends to decrease as the crystal increases in size. Therefore, it is difficult to get big size crystal samples.

For the Bi-containing garnet crystal, Bi\(_2\)O\(_3\) flux is an obvious choice. The addition of Bi\(_2\)O\(_3\) to the melt can increase the Bi content in the grown garnet crystal. Bi\(_2\)O\(_3\) is a nonvolatile flux and can be used with advantage for top seeded growth. However, the Bi\(_2\)O\(_3\) flux has high viscosity and corrosiveness, and causes inconvenience in growing bulk crystal from the melt.

However, the details about the growth habits of these crystals and the study on defects inside the bulk crystal are not reported yet. These data are very important if the bulk crystal is used as MO element in the isolator products. In this thesis, the growth
habits of (TbBi)$_3$Fe$_5$O$_{12}$ (abbr. TbBiIG) crystal will be discussed. The other garnet crystals have the similar habits due to the same structure.

If the cost of mass production is considered, the liquid phase epitaxy (LPE) growth method is preferred, compared to the bulk crystal growth method. LPE involves the deposition of epitaxial films on carefully prepared substrates of similar structure. The substrate materials should approximately match the material to be deposited in lattice parameter and in linear thermal expansion coefficient, otherwise strains are introduced into the film and dislocation or cracks occur if the mismatch is excessive. The thickness of the MO films deposited by LPE method depends on the specific Faraday rotation of the deposited films to meet the requirement of 45 degree rotation in the optical isolator.

The specific Faraday rotation of the MO films depends heavily on the concentration of Bi$^{3+}$ in the garnet structure. The radii of Bi$^{3+}$ is 0.96 Å, larger than Y$^{3+}$ (0.89 Å). The lattice parameter of the typical iron garnet Y$_3$Fe$_5$O$_{12}$ (YIG) is 12.38 Å, and the lattice parameter of Bi$_3$Fe$_5$O$_{12}$ is 12.62 Å. The larger the lattice constant of Bi containing garnet structure, the higher the concentration of the Bi$^{3+}$, the higher its specific Faraday rotation.

It is difficult to grow thick film, like several hundreds µm thick, by LPE method. In order to reduce the thickness of the MO films for optical isolator application deposited by LPE method, the garnet crystal with high Bi concentration is needed. Deposition of the high Bi concentration garnet crystal is possible only on the substrate with high lattice constant. Liquid phase epitaxy of oxide crystals requires the lattice parameter match and the thermal expansion match between the single crystal substrate and the epitaxial film. The tolerance of the lattice mismatch is controlled by the elastic deformation. The thermal expansion mismatch is governed by the fracture strength of the film. When the thermal stress exceeds a critical value, the film cracks. For the Bi-doped rare earth iron
garnets, the introduction of Bi into the garnet increases its thermal expansion.\textsuperscript{102} Besides, the thick film exert a substantial force on the substrate as well as vice versa. If grown in compression, a thick film (>100 µm) can fracture the substrate along the (211) crystalline planes while in the melt. On cooling to room temperature, the increased stress in the thicker film permits only a small room temperature tension mismatch before the film crack irregularly, break up, and peel off the substrates. Therefore, the requirement for the lattice match is stringent.

Gd$_3$Ga$_5$O$_{12}$ garnet (GGG) single crystal is at present used as substrate, its small lattice parameter (12.38 Å) will be a limiting factor for increasing of the Bi$^{3+}$ ion concentration in the epilayer.\textsuperscript{103} It is difficult to attain the thick film, e.g. 2.2 mm, by the LPE method.\textsuperscript{104} The new substrate with higher lattice constant than GGG is in demand.

Y.M. Yu et al,\textsuperscript{105} reported that Ca$_3$(Li$_{0.275}$Nb$_{1.775}$Ga$_{2.95}$)O$_{12}$ (CLNGG) crystal can be a promising candidate to replace GGG as a new substrate crystal due to its lower melting point (1450°C) and its larger lattice constant \textit{than} GGG crystal. However, large crack free CLNGG crystal is not yet obtained and commercialized. In this thesis, the growth of CLNGG bulk crystal will be studied.

Besides the preparation of the new substrate, the composition of the MO film and its growth conditions should be adjusted to the new substrate so that the good thick film garnets are achieved for the optical isolator application. Toshiyasu Suzuki, et al\textsuperscript{106}, grew the Co and Bi-substituted iron garnet films by LPE on (CaGd)$_3$(MgZrGa)$_5$O$_{12}$ substrate and found that the maximum stability of $\theta_F$ was achievable in the 1550 nm band, and that the film thickness of 560 µm was needed for 45° Faraday rotators. Min Huang et al \textsuperscript{101}, reported that the specific Faraday rotation of the crystal Ho$_{3-x}$Yb$_y$BiFe$_5$O$_{12}$ (x=1.03, y=1.12) was about -767°/cm at 1550nm, and that their temperature and wavelength
dependence of Faraday rotation were small. The films with 586 μm thickness were needed in order to realize the 45° Faraday rotation.

Faraday rotation of the Ce doped garnet crystal at room temperature was as large as 1.3 ×10^4 deg/cm per Ce ion at wavelengths of 1150nm. This rotation surpasses, by a factor of 6, that of the Bi doped garnet crystal. The Faraday rotation spectrum of CeY₂Fe₅O₁₂ crystal was only studied on the single layer film deposited by sputtering. Ken Tamanoi, et al, deposited the Y₂.₉₅Ce₀.₀₅Fe₅O₁₂ film of 0.88 μm from the MoO₃-K₂MoO₄-Y₂O₃ flux. Ce doping of less than 0.05 (at. /f. u.) was attained. The Faraday rotation characteristics of the grown films were observed in the range of wavelength 0.65 – 0.85 μm. Now we are interested in possible crystals working as the Faraday rotation elements in the 1550nm wavelength range.

It is not easy to grow such thick films with 560 μm and 586 μm thickness by the LPE method. Therefore, it is necessary to seek new composition MO crystals with high specific Faraday rotation. In this thesis, some efforts will be put on finding the new Ce or Bi- containing MO crystal compositions suitable for the optical isolator working at 1550 nm wavelength.
2. EXPERIMENTS

Bulk MO crystals were grown by the flux growth method. The new substrate (CLNGG) crystals, a candidate for MO film deposition on it, were grown by Czochalraski (CZ) method. The grown CLNGG boules were cut, oriented, ground, lapped, and polished. The Faraday rotation angle of the grown MO crystals was measured by our home-made Faraday Rotation Tester.

2.1 Flux growth

“Flux growth” is a method which allows the growth of single crystals of a wide range of materials. The components of the desired materials are dissolved in a solvent the so-called “flux”. In some papers the term “flux” is used for the high temperature solution.

The main advantage of this method is that the crystals are grown below the melting temperature. If the material melts incongruently, i.e. decomposes before melting, or exhibits a phase transition below the melting point, one has indeed to look for growth temperatures lower than these phase transitions.

The main disadvantage is the low growth rate. From the flux the growth rate of crystal is generally more than hundred times smaller than that in melt growth. Thus crystals from the flux are in general of small size. Since crystals grown from high temperature solution normally develop facets, the linear growth rate is difficult to determine and in most cases it is even not constant and might be different for each facet, which leads to in-homogeneities in the crystal.
A further disadvantage is the unavoidable presence of ions of the flux as impurities in the crystals, if the solvent contains additional elements. Frequently there are flux inclusions found in the crystal.

The following properties are desirable for the high temperature solution and the flux:

(1) The material to be grown as a single crystal must be the only stable solid phase under the growth conditions.

(2) The solubility of the crystal or its components in the flux should not be too low, in general between 5 and 50 wt %, and should decrease with temperature.

(3) The flux should have a low melting point.

(4) The flux or its components should have a very low solubility in the grown crystals.

(5) The flux should have a low vapor pressure.

(6) The viscosity of the solution should be low, in the range of 1 to 10 centipoise (cP).

(7) The solution should not attack the growth container.

(8) The solution should be easily prepared.

(9) The residual melt should be easily separated from the crystals.

The commonly used components of the flux are the basic oxides or fluorides: PbO, PbF₂, BaO, BaF, Bi₂O₃, Li₂O, Na₂O, K₂O, KF and the acidic oxides B₂O₃, SiO₂, P₂O₅, V₂O₅, MoO₃, in most cases a mixture consisting of two or three of them.

The selection of the optimum solvent for the growth of a given material is a difficult task frequently based on trial and error. Detailed investigations of the complex multi-component phase relations for the material to be grown are in most cases not possible.
Fundamental aspects of the flux for garnet growth are briefed as following. In mixtures the basic oxide loses oxygen ions and the acidic oxide adopts them (association). A classification of typical high temperature solvents for oxide materials is presented. The solute oxides can form both bare cations and complex anions depending on the basicity of the melts. As an example the melt of a mixture of Fe$_2$O$_3$, PbO and B$_2$O$_3$, the basic PbO will dissociate into Pb$^{2+}$ and O$^{2-}$, the acidic B$_2$O$_3$ associate three O$^{2-}$ forming two BO$_3^{3-}$ anions. The amphoteric Fe$_2$O$_3$ might associate oxygen ions forming FeO$_m^{3-3m}$ complexes. The free oxygen ions clearly influence the concentration and the coordination number of cation oxygen complexes. Hence the free oxygen ion concentration [O$^{2-}$] should be a key parameter for the species actually present in the melt and for the phase boundaries. For Y$_3$Fe$_5$O$_{12}$ in a flux of PbO, PbF$_2$ and B$_2$O$_3$, a dissociation into three Y$^{3+}$, two Fe$^{3+}$ and three FeO$_4^{5-}$ is suggested and further experimental studies are required to definitely determine the species actually present in the melt.

For a new material to be grown, the best way is to look in the literature to find a analogous compound. But sometimes even small changes make a big difference. For example, when Wolfgang Tolksdorf tried to grow Yb$_3$Fe$_5$O$_{12}$ instead of Y$_3$Fe$_5$O$_{12}$ (YIG) from the same flux, it was successful in small unstirred crucibles, but using five times larger melt volumes and forced convection no garnet crystals grew but crystals of an unknown compound were obtained instead. As in this example, such failures are mostly not published. The historical development of the flux for the incongruently melting ferromagnetic YIG might be of interest. Nielsen and Dearborn published some phase investigations of the pseudo-binary system Fe$_2$O$_3$ and Y$_2$O$_3$ with respect to YIG. They found that Y$_3$Fe$_5$O$_{12}$ melts incongruently and YFeO$_3$ congruently at temperatures above 1580 °C and 1720 °C, respectively. They knew that their colleague
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Remeika \(^{112}\) had grown single crystal rare earth orthoferrites, e.g. \(\text{YFeO}_3\) from molten lead oxide. So they selected lead oxide as a solvent for yttrium iron garnet (YIG). Now they had to look into the pseudo-ternary system with PbO and found that a higher iron to yttrium ration than that of garnet had to be used. In the melt composition Nielsen \(^{113}\) used, magneto-plumbite crystals grew together with garnets. He showed that YIG incorporated a substantial amount of bismuth, when \(\text{Bi}_2\text{O}_3\) was used instead of PbO. He published an improved flux in which a part of the PbO is replaced by PbF\(_2\) \(^{114}\). An important improvement of this flux was achieved by adding a small amount of \(\text{B}_2\text{O}_3\) as reported in ref. \(^{115}\).

Frequently excess of one component of the compound is used as a flux. In the case of YIG the growth temperature in air is between the eutectic (1469 °C) and the peritectic (1555 °C) temperature \(^{116}\). The iron-rich part of the simplified pseudo-binary phase diagram is shown in Figure 21. Abernethy et al. \(^{117}\) reported, rather soon after the proposed phase diagram for YIG, the growth of YIG single crystals using excess iron oxide and a traveling solvent zone. The concentration of the solute in a melt with excess of one component is mostly much higher than in other fluxes. Consequently the maximum growth rate can be higher too, reaching in some cases that of melt growth.

![Figure 21](image_url)  
**Figure 21** Simplified iron-rich part of the phase diagram of Fe\(_2\)O\(_3\) and Y\(_2\)O\(_3\).
In this thesis work, the MO crystals were grown from the flux solution using rotating seed on the top, the so called top seeded solution growth method. The melt was prepared from high purity raw materials. After weighting the raw chemicals, the mixture was thoroughly ground, mixed in the mortar with the pestle. The mixed powders were pressed into plates and then loaded into a Pt crucible. Crystals can be grown at the surface of the melt when the temperature near the surface is lower than that near the bottom. It is necessary, as in the melt growth using the Czochralski method (introduced in the next section), to have the coldest spot at the center of the surface. GGG was used as seed to be dipped into the melt after the melt was kept at high temperature for 14 hours (above the saturation temperature). Contrary to the situation in melt growth, the temperature gradient should be small and the growth temperature has to be continuously lowered by slow cooling of the melt. During growing, the seed rod was rotating at 50 rpm, the temperature was lowered at very low rate, e.g. 0.5°C/h. Convection plays an important role in avoiding nucleation elsewhere. When the growth was finished, the seed rod was raised and the grown crystal was pulled out of the melt. The furnace was cooled down to the room temperature at 50°C/h. A schematic drawing of a typical furnace is shown in Figure 22.

Figure 22 Schematic of a furnace for TSSG.
2.2 Czochralski growth of CLNGG crystals

Czochralski (CZ) growth technique is one of the crystal growth techniques. In its simplest form (Figure 23), the technique consists of a crucible which contains the charge material to be crystallized surrounded by a heater capable of melting the charge. A pull rod with a chuck attached to its lower end is mounted co-axially above the crucible. A seed crystal is attached to the chuck and the pull rod is lowered until the end of the seed crystal is dipped into the melt. The melt temperature is carefully adjusted until a meniscus is supported by the end of the seed. Once a thermal steady state has been achieved, the pull rod is slowly lifted and rotated and crystallization onto the end of the seed occurs. Lifting rates vary with the material. To increase the diameter of the crystal from that of the seed, small and careful heater power reduction is imposed either manually or under automatic control.

A typical procedure for operating might be as follows:

Load the charge material into the crucible. Fit an oriented seed crystal into the chuck.

Melt the charge, holding its temperature just a little above the melting point.

Lower the seed crystal to a position a little above the melt surface and allow it to come to thermal equilibrium; apply seed rotation. Then lower the end of the seed very slowly into the melt to minimize the thermal shock.

Make fine adjustments to the heater power until the seed stably supports a liquid meniscus. This is a crucial step. Too high a melt temperature and the seed is lost; too low a temperature and the introduction of the seed can nucleate a super-cooled melt which rapidly freezes over.
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Commence pulling and adjust the melt temperature and/or the pull rate so that a thin neck is grown onto the seed. This helps to prevent defects in the seed from propagating into the crystal.

Increase the crystal diameter slowly and smoothly by reducing the heater power until the crystal has grown out to the required diameter. Re-stabilize the process at this diameter by further adjustment of the heater power.

The linear rate of growth of a cylindrical crystal is roughly equal to the pulling speed plus the rate of fall of melt level in the crucible. However, this is achieved only by careful adjustment of the heat flow conditions such that the rate at which the latent heat of fusion is removed is exactly equal to its rate of generation so that a thermal quasi-steady state is obtained. In general it is this removal of latent heat which is the rate-controlling process. In fact CZ crystal growth is useful to the near-congruent compound growth.

Figure 23 Schematic representation of the elements of crystal pulling shown with rf induction heating of the crucible in CZ furnace.
Figure 24 The temperature profile along the growth direction in CZ furnace.

CLNGG single crystal is a congruent compound and is grown by the CZ method using RF induction heating. A Pt crucible with 60 mm diameter, 60 mm height and 1.5 mm thickness was applied under air atmosphere. The starting materials were 99.99% pure CaCO₃, Li₂CO₃, Nb₂O₅, and Ga₂O₃ powders. Thermogravimetry Analysis (TGA) analysis was conducted on these raw materials, respectively, to decide their loss amount. The corresponding loss at the growth temperature was compensated, and the raw materials were weighted and mixed based on the molar ratio of CaCO₃:Li₂CO₃:Nb₂O₅:Ga₂O₃ = 3:0.1375:0.8875:1.475. The mixture was pressed and melted at 1450 °C for 3h in air.

The initial growth was started on a Pt wire. The crystal with cracks was pulled up. The powder XRD analysis proved it was single crystal. The seed along <111> was cut from grown crystals. The crystal was grown from 600 g starting materials at first, and the later runs were carried out from the remaining melt by repeated re-crystallization. All crystals were pulled up at the rate of 1 mm/h, with the seed rotation rate of 20 rpm.
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To improve the temperature gradients during cooling in the furnace, the Al₂O₃ tubes around the crucible and Pt after-heater were used. The thermal stress during cooling can result in cracking of the crystals. A variety of shapes and sizes of the after-heater were tried and finally came to a better condition for CLNGG crystal growth. In order to measure the final thermal gradients, a thermal couple was bound on the seed rod to measure the temperature at different positions when the seed rod was lowered to the melt. The temperature profile along growth axial was shown in **Figure 24**.

### 2.3 Lapping and polishing

Lapping and polishing the grown MO crystals were done on the KENT 3 Automatic Lapping and Polishing Unit manufactured by Kemet International Ltd. Lapping operations on MO crystals were normally performed using 6, 3 and 1 micron Liquid Diamond. Finally the lapped MO crystal was polished using 0.5 micron Liquid Diamond on the polishing cloth. The polished sample was checked under optical microscope, and no cracks were found on it with magnification of 100.

### 2.4 Faraday rotation tester

**Figure 25** shows the experimental setup for measuring the Faraday rotation angles of the MO crystal. Light from a 1550nm LD was transmitted through a fiber collimator. An external magnetic field was applied in the horizontal direction using a coil. A polarizer and an analyzer were placed before and after the sample. The light passes through the polarizer, sample and analyzer, and was collected by another collimator with fiber connected to the spectrum analyzer. When there was no field, the
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Extinction position ($\theta_1$) was read out from the analyzer. When field was added, the extinction position ($\theta_2$) was read. The Faraday rotation angle under this field was ($\theta_2 - \theta_1$).

Figure 25 Setup for the measurement of Faraday rotation.
3. RESULTS AND DISCUSSION:
PREPARATION OF GARNET CRYSTALS

It is a well known fact that physical-chemical properties of Rare earth elements substituted garnet depends on the ratio of cations, method of preparation and experimental conditions. The properties for technical applications depend on the combination of the intrinsic properties and the microstructure. The intrinsic properties are in turn dependent almost wholly on chemical composition and the microstructure which are obviously related to the method of preparation. The objective of preparing specimens with specific properties can only be achieved by paying attention to the intrinsic properties and the method of preparation and the resulting structure\textsuperscript{118}.

In this thesis, flux growth method and melt growth method are used to grow the new garnet crystals. These garnet crystals can be new magneto-optical crystals or new substrate crystals for other magneto-optical crystal films to be deposited on.

The heavier rare-earth elements, e.g. Tb, Ho, and Yb, are selected (the reason behind the selection is discussed in the next chapter) and the new rare-earth iron garnet crystals based on these rare-earth elements were grown by the flux growth method. They are \((\text{TbBi})_3\text{Fe}_5\text{O}_{12}, (\text{YbBi})_3\text{Fe}_5\text{O}_{12}, (\text{HoBi})_3\text{Fe}_5\text{O}_{12}, (\text{HoYbBi})_3\text{Fe}_5\text{O}_{12}, (\text{HoYbTbBi})_3\text{Fe}_5\text{O}_{12}, \text{and (HoYbCeBi)}_3\text{Fe}_5\text{O}_{12}\).

The new substrate, \(\text{Ca}_3(\text{Li}_{0.275}\text{Nb}_{1.775}\text{Ga}_{2.95})\text{O}_{12}\), were also grown by the melt growth method---Czochralki method. The new garnet crystal is attractive due to its larger lattice constant than \(\text{Gd}_3\text{Ga}_5\text{O}_{12}\) garnet substrate at present used for MO film deposition.
3.1 Bulk crystal growth of \((\text{TbBi})_3\text{Fe}_5\text{O}_{12}\)

As a material suitable for an optical isolator used in a 1550nm band, a Bi-substitution type terbium –iron garnet single crystal, \(\text{Tb}_{3-x}\text{Bi}_x\text{Fe}_5\text{O}_{12}\) (TbBiIG), was reported in ref. [119]. However, the details about the crystal’s growth habits has not been reported.

The single crystal of TbBiIG was grown from the fluxed melt. The flux composition was 14.2 mol % \(\text{B}_2\text{O}_3\), 23.4 mol % \(\text{BaCO}_3\), and 62.4 mol % \(\text{Bi}_2\text{O}_3\). The solute was prepared according to the composition of \(\text{Tb}_{1.6}\text{Bi}_{1.4}\text{Fe}_5\text{O}_{12}\) crystal. The mixed raw materials were heated up to 1300\(^\circ\text{C}\) in a Pt crucible. After kept at high temperature for 15h, the fluxed melt was cooled down at 20\(^\circ\text{C}\)/h to a seeding temperature between 1050\(^\circ\text{C}\) and 1080\(^\circ\text{C}\). A small piece of GGG crystal was dipped into the melt as a seed. The seed rod was rotating at 60 rpm or 30 rpm when the crucible was cooled down to 1020\(^\circ\text{C}\) at 0.3-0.5 \(^\circ\text{C}\)/h, and at 1020\(^\circ\text{C}\) the seed rod was raised up from the melt to stop the crystal growing. Finally, the furnace was cooled down to room temperature at 50\(^\circ\text{C}\)/h.

**Figure 26** The grown bulk crystal of \((\text{TbBi})_3\text{Fe}_5\text{O}_{12}\).
Preparation of garnet crystals

Figure 27 XRD pattern of the grown TbBIG crystal performed on the flat face of \{110\}.

One of the as-grown TbBiIG crystal samples is shown in Figure 26. The garnet crystal belongs to cubic system and its space group is Ia3d \( (O^{10}_h) \). The grown crystal usually had a big square flat face. According to the morphology theory (BFDH law), the Morphological Importance (MI) of the faces is expected to be proportional to its thickness \( d_{ah,ak,al} \). With reference to the XRD data of \( Y_3Fe_5O_{12} \) garnet crystal, \{211\} faces are identified as the most important growth form. The second most important form is \{220\} face. In other words, the large flat facets should be \{211\} according to the BFDH law prediction. However, it is confirmed that the largest flat face was \{220\} faces for the TbBiIG crystal by the XRD analysis on the large flat facets, as shown in Figure 27. In Figure 27, the diffraction peaks at 20.34° and 41.22° correspond to (220) and (440), respectively. Therefore, the morphology of the grown TbBiIG crystal can be indexed according to the (110) stereographic projection, as shown in Figure 28.
3.2 Bulk crystal growth of (HoBi)$_3$Fe$_5$O$_{12}$

Single crystal of (HoBi)$_3$Fe$_5$O$_{12}$ was grown from the fluxed melt. The flux composition was B$_2$O$_3$ mol 14.2%+BaCO$_3$ mol 23.4%+ Bi$_2$O$_3$ mol 62.4%. The solute was prepared according to the composition of Ho$_{1.8}$Bi$_{1.4}$Fe$_5$O$_{12}$ crystal. The growing procedure is the same as the growth of (TbBi)$_3$Fe$_5$O$_{12}$ crystal, but the seeding temperature was tried through experiments until the crystal was grown on the seeding crystal. The grown (HoBi)$_3$Fe$_5$O$_{12}$ crystal has the growing habits as the (TbBi)$_3$Fe$_5$O$_{12}$ crystal, as shown in Figure 29. The bigger flat face was (110). Four (110) faces are distributed around <111> axis and forms the corner on the grown crystal.
3.3 Bulk crystal growth of (YbBi)$_3$Fe$_5$O$_{12}$

Single crystal of (YbBi)$_3$Fe$_5$O$_{12}$ was grown from the fluxed melt. The growing procedure is the same as the growth of (HoBi)$_3$Fe$_5$O$_{12}$ crystal with Yb$_2$O$_3$ replacing Ho$_2$O$_3$ in the composition. The flux composition was B$_2$O$_3$ mol 14.2%+BaCO$_3$ mol 23.4%+ Bi$_2$O$_3$ mol 62.4%. The solute was prepared according to the composition of Yb$_{1.6}$Bi$_{1.4}$Fe$_5$O$_{12}$ crystal. The grown (YbBi)$_3$Fe$_5$O$_{12}$ crystal has the growing habits as the (TbBi)$_3$Fe$_5$O$_{12}$ crystal, as shown in Figure 30.
3.4 Bulk crystal growth of (HoYbBi)$_3$Fe$_5$O$_{12}$

Single crystal of (HoYbBi)$_3$Fe$_5$O$_{12}$ was grown from the fluxed melt. The growing procedure is the same as the growth of (HoBi)$_3$Fe$_5$O$_{12}$ crystal with half amount of Ho$_2$O$_3$ replaced by Yb$_2$O$_3$ in the composition. The raw material composition is Ho$_2$O$_3$ 3mol% + Yb$_2$O$_3$ 3mol% + Fe$_2$O$_3$ 36mol% + Bi$_2$O$_3$ 58 mol%. The grown HoYbBiIG crystal is shown in Figure 31.

![Figure 31 The grown HoYbBiIG crystal.](image)

3.5 Bulk crystal growth of (TbHoYbBi)$_3$Fe$_5$O$_{12}$

Single crystal of (TbHoYbBi)$_3$Fe$_5$O$_{12}$ was grown from the flux. The growing procedure is the same as the growth of (HoYbBi)$_3$Fe$_5$O$_{12}$ crystal. The raw material composition for Tb$_{0.5}$HoYbBiIG crystal growth is Tb$_4$O$_7$ 0.5mol% + Ho$_2$O$_3$ 2.5mol% + Yb$_2$O$_3$ 2.5mol% + Fe$_2$O$_3$ 36mol% + Bi$_2$O$_3$ 58 mol%. The raw material composition for Tb$_{1.0}$HoYbBiIG crystal growth is Tb$_4$O$_7$ 1.0mol% + Ho$_2$O$_3$ 2.0mol% + Yb$_2$O$_3$
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2.0mol%+Fe₂O₃ 36mol%+ Bi₂O₃ 58 mol%. The grown HoYbBiIG crystal is shown in Figure 32.

The morphology of grown (TbHoYbBi)₃Fe₅O₁₂ crystal is a little bit different from that of previously discussed crystals. There are four types of cations competing for the dodecahedral sites in the growth process. Thus the crystal being grown may no longer exhibit nearly cubic symmetry, i.e. it may show uniaxial anisotropy.

Crystals growing from aqueous solutions often exhibit a change in the external appearance (growth forms) with a change in super-saturation and concentration of impurities. The growth habit can also be changed when two impurities are simultaneously used. Therefore, the different forms of (TbHoYbBi)₃Fe₅O₁₂ crystals are possibly caused by too many rare-earth ions in the melt.

Figure 32 The grown TbHoYbBiIG crystal.

3.6 Bulk crystal growth of (HoYbCeBi)₃Fe₅O₁₂

Single crystal of (HoYbCeBi)₃Fe₅O₁₂ was grown from the flux. The growing procedure is the same as the growth of (HoYbBi)₃Fe₅O₁₂ crystal. The raw material composition for HoYbCe₀.₅BiIG crystal growth is CeO₂ 2.0mol%+Ho₂O₃ 2.5mol% +
Preparation of garnet crystals

Yb$_2$O$_3$ 2.5mol%+Fe$_2$O$_3$ 36mol%+ Bi$_2$O$_3$ 58 mol%. The raw material composition for HoYbCe$_{1.0}$BiIG crystal growth is CeO$_2$ 4.0mol%+Ho$_2$O$_3$ 2.0mol%+ Yb$_2$O$_3$ 2.0mol%+Fe$_2$O$_3$ 36mol%+ Bi$_2$O$_3$ 58 mol%. The grown HoYbCe$_{0.5}$BiIG crystal is shown in Figure 33. It has similar forms to those of (TbHoYbBi)$_3$Fe$_5$O$_{12}$ crystal. The grown HoYbCe$_{1.0}$BiIG crystal does not show magneto-optical property. It means the grown crystal is not the garnet structure.

![Figure 33 The grown Ce$_{0.5}$HoYbBiIG crystal](image)

3.7 Bulk crystal growth of CLNGG

The high quality of epitaxy MO crystal films depends strongly on substrates. The rough fitting of the lattice parameters between substrates and films is accomplished by the growth of the garnet films in which the lattice parameter is controlled by the cations substitution, e.g. Bi, in the host lattice. The growth of films with a high bismuth content requires either substrates with a correspondingly large lattice constant or an additional
Preparation of garnet crystals

incorporation of ions with a small ionic radius. The Faraday rotation originates from the contribution of rare earth ions and bithmuth ion.

In this chapter, the crystal growth of CLNGG was studied by the CZ method. Its growth habits and lattice constant were studied.

3.7.1 Morphology of CLNGG crystal grown by CZ

Figure 34(a) shows the CLNGG boule with the size of Ø 20 mm × 80 mm grown along <111> direction. On the bottom of the boule, three facets are clearly seen as shown in Figure 34(b). The unequal areas of the three facets are caused by the little deviation of the actual growth direction from <111>. The angles between the normal directions of the facets and the growth direction <111> are around 20°. The result suggests that facets might be {211}. In order to prove it, the crystal was cut, parallel to one of the facets. XRD analysis was conducted on the cut plate. As shown in Figure 35, the peak of (211) with 2θ of 17.30° is observed.

The quality of the crystal is good. When a beam entering the crystal boule from the 5 mW He-Ne laser, no scattered light from the inclusions or bubbles is observed at the side of the crystal. The “gourd” shape is caused by the temperature of the melt decreasing too much at the end of the shouldering processing. This undershot temperature is due to the time lag between the end of the shouldering operation and the time when the constant temperature in the melt is achieved.

There are 12 growth ridges on the side part of the crystal. With the aid of stereographic projections, the orientations of growth ridges on the boule surface are found and illustrated in Figure 36. The ridges only appear on the side part of the crystal. On the conical tail part of the crystal, the ridges are not formed.
Figure 34  (a) Example of CZ- grown CLNGG crystal.  (b) Bottom of the CLNGG crystal shown in (a).
Figure 35 XRD pattern of one of the small facets on the bottom of CLNGG crystal.

Figure 36 Orientations of the growth ridges on the cylinder-like of the CLNGG crystal.
3.7.2 Lattice constant measurement of CLNGG crystal

The XRD analysis is conducted on the grown CLNGG crystal. The lattice constant is calculated from the observed d values for different $2\theta$ values along with their indices according to $2d \sin \theta = \lambda$ and $a = d_{(hkl)} \sqrt{h^2 + k^2 + l^2}$.

When a diffractometer is used to measure plane spacing, the most important source of systematic error in ‘d’ is the displacement of the specimen from the diffractometer axis. It causes an error in ‘d’ given by $\Delta d/d = (-D/R)(\cos^2 \theta / \sin \theta)$, where D is the specimen displacement parallel to the normal to the reflecting plane and R is the diffractometer radius. The precise ‘a’ value can be obtained by extrapolation of measured lattice parameters against $\cos^2 \theta / \sin \theta$.

The CLNGG samples for powder XRD analysis are cut from the boule grown by the first-run, the top part and bottom part of the boule by the 9th run. The XRD data of the first run grown CLNGG as shown in Figure 37, reveals that the lattice constant is $12.50512 \pm 0.006 Å$. From the XRD data of the top part and bottom part of the 9th run grown CLNGG crystal, their lattice constants are $12.50503 \pm 0.006 Å$ and $12.50683 \pm 0.006 Å$ respectively. The lattice constants from the three different sections are equal ($12.50512 \pm 0.006 Å$) in the error range. This result indicates that no composition segregation appears while growing the crystal from the $\text{Ca}_3(\text{Li}_{0.275}\text{Nb}_{1.775}\text{Ga}_{2.95})\text{O}_{12}$ melt, and that the above composition is the congruent composition of $\text{Ca}_3(\text{LiNbGa})_5\text{O}_{12}$ system.

Figure 38 shows the comparison of the lattice constants of GGG, CLNGG, YIG, BiIG crystal. If we assume the lattice constant varies linearly with the content of Bi in the MO crystal, the lattice constant of $(\text{Y}_{1.5}\text{Bi}_{1.5})\text{Fe}_5\text{O}_{12}$ crystal possibly matches with CLNGG substrates.
Preparation of garnet crystals

Figure 37 XRD analysis of the CLNGG crystal grown from first run: (a) XRD pattern; (b) the precise lattice constant derived by extrapolating the lattice constants calculated from the measured peaks.

Figure 38 The comparison of the lattice constants of GGG, CLNGG, YIG, BiIG crystal.
3.7.3 Feasibility study of CLNGG crystal as substrate for LPE growth.

Due to its larger lattice constant (12.54 Å), the sample easily grown of big size and high quality by Czochralski method as shown in previous chapter, \( \text{Ca}_3\text{Li}_{0.275}\text{Nb}_{1.775}\text{Ga}_{2.95}\text{O}_{12} \) (CLNGG) garnet single crystal is expected to be a candidate of substrates for MO garnet film by liquid phase epitaxy deposition.

Liquid phase epitaxy of oxide crystals requires a close lattice parameter match between the single crystal substrate and the epitaxial film. Furthermore, the thermal expansion mismatch between the substrate and the film should not be big enough to prevent the growth of films on the substrate. For these epitaxial garnets, there is no plastic deformation in these materials in tension, the maximum elastic deformation allowed negative mismatch is governed by the fracture strength of the film. When the thermal stress exceeds this value, the film cracks, either through the film alone or, once initiated, all the way through the substrate. As a result of the difference in thermal expansion, tension lattice mismatches are greatest at room temperature.\(^{125}\) Beyond a certain lattice mismatch (0.19Å), no film will form, and the substrate simply dissolves into the flux.\(^{126}\)

The growth of thick film bismuth doped rare-earth iron garnets has increased the problem of mismatch in two different ways. First, the introduction of Bi in to the garnet increases its thermal expansion even further.\(^ {127, 128}\) The difference in thermal expansion can be up to 2/3 greater with a substitution of 1.2 atoms of Bi per formula unit.\(^ {127}\) Second, as the total thickness of the film covers the substrate, the film begins to exert a substantial force on the substrate as well as vice versa. Even a thin film growth on one side of a substrate at a significant lattice mismatch can cause measurable bending of the substrate. A thick film (>100 \( \mu \text{m} \) per side) can, if grown in compression, actually fracture the substrate along the (211) crystalline planes while in the melt. On cooling to
Preparation of garnet crystals

room temperature, the increased stress in the thicker film permits only a small room
temperature tension mismatch before the film will crack irregularly, break up, and peel
off the substrate. These effects narrow the growth “window” in lattice mismatch.
Therefore, it will be very difficult to choose the composition and growth conditions to
allow the growth of good thick film garnets on the new substrate, CLNGG crystal. To our
knowledge, there is no any report on LPE film growth by using CLNGG crystal substrate
and Gd$_3$Ga$_5$O$_{12}$ (GGG) are currently used as substrate for LPE growth.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Lattice constant, Å</th>
<th>Thermal expansion coefficient, °C$^{-1}$</th>
<th>Size, mm$^3$</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>CLNGG</td>
<td>12.54</td>
<td>$9.2 \times 10^{-6}$</td>
<td>10×10×0.6</td>
<td>Grown by ourselves</td>
</tr>
<tr>
<td>GGG</td>
<td>12.38</td>
<td>$9 \times 10^{-6}$</td>
<td>10×10×0.5</td>
<td>Purchased</td>
</tr>
</tbody>
</table>

In this thesis, some primary experiments of LPE growth were done on CLNGG.
The thermal expansion coefficient of CLNGG crystal was measured, and compared with
GGG, as listed in Table 3.

As stated in Introduction chapter, there is no any theory to guide the selection of
fluxes. The successful deposition of MO by LPE method depends on experiments by trial
and error. Several kinds of flux have been used to grow MO garnet film on CLNGG
substrate. Table -2 summarized the flux systems and their corrosion effect on the
CLNGG substrate. Among them, MoO$_3$, PbO and Bi$_2$O$_3$ corrode CLNGG at high
temperature. However, BaO-B$_2$O$_3$ flux system does not corrode CLNGG obviously.
**Preparation of garnet crystals**

After one-hour dipped in BaO-B₂O₃ flux, no damage was observed on the CLNGG substrate.

<table>
<thead>
<tr>
<th>Flux</th>
<th>PbO-B₂O₃-Bi₂O₃</th>
<th>MoO₃-Li₂O</th>
<th>BaO-B₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>MO Garnet</td>
<td>HoYbBiIG</td>
<td>HoYbBiIG</td>
<td>Ce:YIG</td>
</tr>
<tr>
<td>Technique</td>
<td>LPE</td>
<td>LPE</td>
<td>LPE</td>
</tr>
<tr>
<td>Growth temp, °C</td>
<td>830</td>
<td>1150</td>
<td>1040</td>
</tr>
<tr>
<td>Growth dur, hr</td>
<td>0.25</td>
<td>N.A.  *</td>
<td>1</td>
</tr>
<tr>
<td>Corrosion</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
</tbody>
</table>

* The LPE growth failed due to heavy corrosion of the substrate.

**Figure 39** shows the corrosion results by PbO-Bi₂O₃-B₂O₃ flux system. The region exposed in flux vapor is damaged obviously. The main composition in the flux vapor is PbO. Another experiment was made by burying CLNGG substrate in pure Bi₂O₃ and holding at 950 °C for 1 hr (melt point of Bi₂O₃ is 817 °C). As a result, CLNGG substrate totally dissolved in melt Bi₂O₃.

One more experiment has been made to inspect the chemical interaction between MO garnet HoYbBiIG and non-magnetic garnet substrates CLNGG and GGG. Stoichiometric HoYbBiIG raw materials were pressed tightly on CLNGG and GGG substrates respectively, and then placed in furnaces for 10 hours at high temperature (1100 °C for CLNGG and 1200 °C for GGG, respectively). Inspected under microscope, irregular interface was observed between CLNGG substrate and HoYbBiIG system (see **Figure 40a**). However, even flat interface was obtained on GGG substrate.
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These results indicate that CLNGG are easily corroded by PbO or Bi containing flux. BaO-B₂O₃ flux did not corrode CLNGG but more works are needed to grow MO films on CLNGG substrate by LPE method.

Figure 39 Corrosion result of PbO -Bi₂O₃ -B₂O₃ flux systems on CLNGG substrate.

Figure 40 Interfaces between HoYbBiIG and CLNGG (a) and GGG (b) substrates.
4. RESULTS AND DISCUSSION: MO PROPERTIES OF NEW GARNET CRYSTALS

The MO crystal for the optical isolator is expected to have high Faraday rotation (FR) coefficient and low optical absorption coefficient in a wide range of wavelength band, e.g. 1-2 µm. The Faraday rotation coefficient increases proportionally with doping amount of Bi or Ce ions in YIG crystal in the near infrared region. The enhanced FR at room temperature is $0.6 \times 10^4$ deg/cm per Ce ion at a wavelength of 780nm, surpassing the enhancement by Bi ion by a factor of two. The optical absorption peak of Fe$^{3+}$ in an iron garnet crystal at the wavelength region of 1.06-1.15 µm can be shifted toward short wavelength if the lattice constant of the garnet crystal increases. The shift is mainly caused by transformation of the crystalline field in which the Fe$^{3+}$ is located, due to the change in the distance between the iron and the oxygen ions. Therefore, large lattice constant garnets are preferred to avoid the absorption in the working wavelength band.

Rare-earth garnet crystals usually have high lattice constants. For example, the lattice constants of (Re$_{0.9}$Y$_{0.1}$)$_3$Fe$_5$O$_{12}$ crystals can be empirically calculated as

$$ a = 7.02954 + 3.31277 r_c + 2.49398 r_a + 3.34124 r_d - 0.87758 r_c r_a - 1.38777 r_c r_d, \quad (1) $$

$$ r_c = 0.9 r_c(Y) + 0.1 r_c(R), \quad (2) $$

Here, $r_c$, $r_a$, and $r_d$ are the ionic radii occupied in dodecahedral (c), octahedral (a) and tetrahedral (d) sites, respectively. $r_a$ and $r_d$ are the ionic radii of Fe ions in octahedral and tetrahedral sites respectively, $r_c(Y)$ and $r_c(R)$ are the ionic radii of Y and rare-earth ions respectively.

Based on these, the heavier rare earth elements, Tb, Ho, and Yb, are selected to form rare earth iron garnet crystal ($\text{(REBi)}_3\text{Fe}_5\text{O}_{12}$, or $\text{(REBiCe)}_3\text{Fe}_5\text{O}_{12}$). Ionic radius of
**MO properties of new garnet crystals**

Yb, Ho, and Tb are 0.100nm, 0.105nm, and 0.11nm respectively. It will be interesting to compare the properties of (REBi)$_3$Fe$_5$O$_{12}$ (RE=Tb, Ho, or /and Yb) or (REBiCe)$_3$Fe$_5$O$_{12}$ crystals. Yb, Ho, and Tb are 3 rare-earth elements with different radii. Ce, and Bi are 2 elements that can enhance the Faraday rotation. Some common characterizations on MO properties are expected to be summarized after these crystals are investigated.

4.1 (TbBi)$_3$Fe$_5$O$_{12}$ crystal

As a material suitable for an optical isolator used in a 1550nm band, a Bi-substitution type terbium–iron garnet single crystal, Tb$_{3-x}$Bi$_x$Fe$_5$O$_{12}$ (TbBiIG), so far was the only potential candidate reported in J. Appl. Phys., 70(8), Oct. 15, 1991. However, TbBiIG crystal has a very small absolute value of a Faraday rotation coefficient, and needs a large thickness of about 1.5 mm to 2 mm to realize 45° rotation in the isolator. More information about properties of the crystal, e.g., the temperature and wavelength dependence of FR, and its optical property of the TbBIG crystals haven’t been reported yet.

4.1.1 Saturation field of (TbBi)$_3$Fe$_5$O$_{12}$

The saturation field is one of important parameters for the Faraday rotator in the optical isolator. It determines the size of the magnet in the optical isolator. The saturation field is measured by a Gauss meter when the maximum Faraday rotation is achieved. The tolerance of the measurement is 0.1 kG. **Figure 41** shows the Faraday rotation hysteresis of the TbBiIG crystal plates of (110) and (111) faces at $\lambda=1.55$ µm at room temperature. The two plates were cut
MO properties of new garnet crystals

from the same as-grown crystal. No hysteresis was observed in the two FR-H curves. The linear part follow:

\[
\text{Faraday rotation } \Phi_F = VHL \tag{3}
\]

\(V\)----Verdet constant, \(H\)----Applied field, \(L\)----MO film thickness).

Valiev et al have studied the Faraday effect of the rare –earth garnets over wide wavelength and temperature ranges. Verdet constant can be written as

\[
V = \frac{\omega^2}{\omega_{\text{eff}}^2 - \omega^2} \left[ \frac{2 \omega_{\text{eff}} A}{h(\omega_{\text{eff}}^2 - \omega^2)} + B + C \chi \right] + V_{gm} \tag{4}
\]

Where \(\chi\) is the paramagnetic susceptibility of a rare-earth subsystem, \(\omega_{\text{eff}}\) is the effective transition frequency, and \(V_{gm}\) is the gyromagnetic contribution to the Verdet constant. The diamagnetic contribution (the term involving \(A\)) is small for all of the garnets studied (except the gadolinium garnets). The Verdet constants of garnets containing Nd\(^{3+}\), Tb\(^{3+}\), Dy\(^{3+}\), Ho\(^{3+}\), Er\(^{3+}\), Tm\(^{3+}\), and Yb\(^{3+}\) are well described by (4). Here, the negative Verdet constant of TbBiIG crystal agree with Valiev’s results.\(^{132}\) When the light travels along the field direction, if the polarized direction is right-hand rotated, its Faraday Rotation is called positive, and if the polarized direction is right-hand rotated, its Faraday Rotation is called negative.\(^{133}\) For practical isolators, the left-hand or right-hand Faraday rotation does not affect the function of isolator. Following the convention of reference, the absolute value of Faraday rotation is considered in the thesis.

The saturated field is at \(H_s=0.4\text{kG}\), and the specific Faraday rotation is around 300°/cm. These two parameters keep the same values along different directions. Garnets are cubic crystals and their easy directions are usually \(\langle 100 \rangle\) or \(\langle 111 \rangle\) direction. However, in our experiments, the saturation forces along \(\langle 110 \rangle\), \(\langle 111 \rangle\) or \(\langle 100 \rangle\) are all equal in the FR measurements. It indicates that the anisotropy in REBiIG crystals is very low, which is in agreement with the results in the reference.\(^{134}\)
**MO properties of new garnet crystals**

**Figure 42** compares the Faraday rotation loops of two polished samples grown under different conditions. The saturation field of the TbBiIG grown at 30rpm is 0.2 kG, while that of the sample grown at 60 rpm is 0.4kG. The difference in the saturation field between these two samples can be explained from the crystal quality point of view. The sample grown at 30 rpm has fewer dark spots than the sample grown at 60 rpm as shown in **Figure 43**. The size of the inclusions in the former is much smaller than in the latter. The high speed rotating possibly causes the lack of solute in the backside of the grown crystal. Abrupt concentration gradients are formed at the crystal growth interface. The crystal growing happens at the interface with saturated concentration. The area which is lack of solute is surrounded by the area with saturated concentration. Then, the inclusions are easily formed in the grown crystal. The sample grown at 60 rpm with more inclusions requires higher field to achieve the saturated FR than the sample with fewer defects grown at 30 rpm.

![Figure 41](image)

**Figure 41** Faraday rotation hysteresis at 1.55 µm of the (111) and (110) plates of the TbBiIG crystal grown under same condition.
Figure 42 Comparison of the FR-H loops at 1.55 µm of two (111) samples grown at 60 rpm and 30 rpm, respectively.

The sample grown at 30 rpm of seed rotation has fewer and smaller inclusions than the sample grown at 60 rpm. The inclusion is generated due to lack of solute around the seed while crystal is grown. This means the inclusions will cause composition near the inclusion different from the composition in the area without inclusion. The spontaneous magnetization is usually a function of composition. The intensity of spontaneous magnetization will fluctuate from place to place. The divergence of the intensity of spontaneous magnetization will generate the free poles the sign of which is changed by the reversal of the direction of domain magnetization. Regions where there are high free pole densities should be divided into many domains so as to decrease the magnetostatic energy.

Besides this, the inclusions will also generate internal stress due to lattice mismatch between inclusions and bulk crystal. A local anisotropy will result by that, and its easy direction varies from place to place. In such a case, a single domain should again be changed into many small domains to minimize the total energy which is composed of
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the local anisotropy energy and the exchange energy stored in the regions where the magnetization changes direction.

![Image](a)

![Image](b)

**Figure 43** Comparison of two polished samples observed under the optical microscope with magnification of 500×: (a) grown at 30 rpm, (b) grown at 60 rpm.

Therefore, there are a lot of domains in the garnet crystal. The movement of domain walls around an inclusion was first predicted by Neel and first observed by Williams in Si-Fe crystal.\(^{136}\)

The bigger saturation field in the sample grown at 60 rpm rotation speed than that at 30 rpm can be explained from domain wall movement point of view. The coercive field can be defined as the largest field required to cause the irreversible wall motion of reverse domains that are already nucleated\(^{137}\). The magnetic field leading to domain wall displacements increases until all the domains with orientations opposite to the field have been substituted by domains with direction parallel to the field. There exists a threshold
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or critical field, $H_{cr}$, below which the wall is not displaced. This critical field, corresponding to the coercive field, depends on sample defects, including point defects, dislocations, other phases, porosity and even the sample’s external surface acting as pinning sites. Raul Valenzuela $^{138}$ explained the effect of defects from the point of an additional contribution to the magneto-static energy. A pore, for example, in Figure 44 (a), can give rise to free poles which will cause high magneto-static energy. The pore with free poles can not be stable until closed domains are formed around the pores, as shown in Figure 44 (b). The closed domains surrounding the pore reduce the magneto-static energy. However, closure domains hinder wall movement so that a higher critical field is needed to move the hindered walls. Besides this, the pore can attract the domain walls as shown in Figure 44 (c). Even if the wall is displaced, it is attracted around the pore again when the field is removed. In order to move the domain wall permanently, a larger field is also usually required. Therefore, it is easily understood that the sample grown at 60 rpm with more inclusions requires higher coercive field to achieve the saturated FR than the sample with fewer defects grown at 30 rpm.

![Figure 44](image)

**Figure 44** (a) A pore within a domain leads to free magnetic poles and therefore increases magneto-static energy. (b) Closure domains are created to reduce free poles. (c) A domain wall on the pore results in a further reduction of poles [6].
4.1.2 Wavelength dependence of the Faraday rotation in \((\text{TbBi})_3\text{Fe}_5\text{O}_{12}\)

Wideband optical isolator usually requires the FR crystal have good wavelength stability. Figure 45 shows the FR measurements of the same sample at wavelengths of 1310nm, 1470nm, 1510nm, 1550nm, and 1590nm, respectively. The specific FR of TbBiIG was reduced with the increase of the wavelength, as shown in Fig 4-1-3-2.

It is convenient to divide the dispersion effect into two contributions: gyroelectric and gyromagnetic. The contribution of gyroelectric is related to the light frequency. With the increase of wavelength, the frequency of the light is reduced. Therefore, the contribution of gyroelectric to the FR is reduced with the increase of wavelength. On the other hand, the gyromagnetic contribution to the FR in the IR spectral region is independent of the wavelength of the light. The combination of the two effects causes the characteristic feature of the spectrum of Faraday rotation. In Figure 46, very low dispersion of the Faraday rotation appears in the long wavelength end of the transparent band.

![Figure 45](image-url)

**Figure 45** Specific Faraday rotation measurements of the same sample (TbBiIG) at wavelengths of 1310nm, 1470nm, 1510nm, 1550nm, and 1590nm, respectively.
4.1.3 Temperature dependence of the Faraday rotation in (TbBi)_3Fe_5O_{12}

Good temperature stability of the Faraday rotation is required for the MO crystal so that the optical isolator can work at different environment temperature. The specific FR measurements were performed in the temperature range of 20—120°C. The obtained temperature dependence of the FR in the TbBiIG is shown in Figure 47. With increasing temperature, the value of the specific Faraday rotation of TbBiIG keeps constant. It is obvious that the TbBiIG is suitable for the isolator working in the temperature changing surroundings.

4.1.4 Optical property of (TbBi)_3Fe_5O_{12}

The interpretation of the optical transitions taking place in iron garnet is very difficult. However, if the crystal used as the Faraday rotator of the optical isolator has a optical absorption peak at a wavelength in the optical communication band, it will have a large optical absorption loss.
**MO properties of new garnet crystals**

Figure 48 shows the optical transmittance spectrum of the TbBiIG crystal. TbBiIG crystal has absorption peaks at wavelength of 1750 nm and 2250 nm. Its cut-off wavelength is at 1000 nm. TbBiIG is transparent in the optical communication band (1300—1600nm).

![Figure 47](image1.png)

**Figure 47** Temperature dependence of the Faraday rotation of TbBiIG.

![Figure 48](image2.png)

**Figure 48** The optical transmittance spectrum of the TbBiIG crystal.
4.1.5 Summary of results on (TbBi)$_3$Fe$_5$O$_{12}$

TbBiIG crystal was suitable for wide band optical isolator working at a wavelength region of 1.3 to 1.6 $\mu$m. Its specific Faraday rotation was as low as 300°/cm, and its saturation field was 0.2 kG. The two parameters were independent of the crystallographic direction of the sample. The saturation field was related to the defects, e.g. inclusions. The specific FR of TbBiIG was reduced with the increase of the wavelength, but very low dispersion of the Faraday rotation appears in the long wavelength end of the transparent band. In the wavelength region near 1.5 $\mu$m, TbBiIG crystal had good transparency and good stability of Faraday rotation against wavelength and temperature. The only disadvantage of TbBiIG as Faraday rotator in optical isolator was its low specific Faraday rotation.

4.2 (HoBi)$_3$Fe$_5$O$_{12}$ crystal

(HoBi)$_3$Fe$_5$O$_{12}$ crystal (abbr. HoBiIG) is a new garnet crystal. Upto now, there is no report on this crystal. It will be very interesting to investigate its MO properties as Ho$^{3+}$ ion is smaller than Tb$^{3+}$ ion. The change in the Bi$^{3+}$ amount in the grown crystal will be reflected in the changes in MO properties directly.

4.2.1 MO properties of (HoBi)$_3$Fe$_5$O$_{12}$

Figure 49 shows the specific Faraday rotation measurement of the grown (HoBi)IG crystal plates of (111) faces at $\lambda$=1550nm and room temperature. It demonstrates that the saturation field is at $H_c$=0.7kG, the specific Faraday rotation is
**MO properties of new garnet crystals**

around 548°/cm. The asymmetry phenomenon is caused by testing error. The accuracy of magnetic field is ± 0.1 kG.

**Figure 50** shows the FR measurements of the same sample at wavelengths of 1310nm, 1470nm, 1510nm, and 1590nm, respectively. Similar to the case of TbBiIG crystal, the specific FR of HoBiIG is reduced with the increase of the wavelength, as shown in **Figure 51**, and very low dispersion of the Faraday rotation appears in the long wavelength end of the transparent band.

![Figure 50](image)

**Figure 49** Specific Faraday rotation of HoBiIG crystal vs applied field.

![Figure 50](image)

**Figure 50** Specific Faraday rotation measurements of the same sample (HoBiIG) at wavelengths of 1310nm, 1470nm, 1510nm, and 1590nm, respectively.
**MO properties of new garnet crystals**

![Graph of wavelength vs. Faraday rotation](image1.png)

**Figure 51** The spectrum of specific Faraday rotation of HoBiIG in the wavelength region of 1310nm—1590nm.

![Graph of temperature vs. specific Faraday rotation](image2.png)

**Figure 52** Temperature dependence of the Faraday rotation of HoBiIG

The specific FR measurements were performed in the temperature range of 20—120°C. The obtained temperature dependence of the FR of the HoBiIG is shown in Figure 52. With increasing temperature, the value of the specific Faraday rotation of HoBiIG decreases. It demonstrates that the stability of FR against temperature for the HoBiIG crystal is worse than that for the TbBiIG crystal.
4.2.2 Optical property of $(\text{HoBi})_3\text{Fe}_5\text{O}_{12}$

Figure 53 shows the optical transmittance spectrum of the HoBiIG crystal. HoBiIG crystal has absorption peaks at wavelength of 1900 nm. Its cut-off wavelength is at 1000nm. At the end of short wavelength, there are two adjacent absorption peaks, sitting at 1206 nm and 1132 nm. However, HoBiIG is transparent in the optical communication band (1300—1600nm).

![Figure 53 The optical transmittance spectrum of the HoBiIG crystal.](image)

4.2.3 Summary of $(\text{HoBi})_3\text{Fe}_5\text{O}_{12}$

Ho, replacing Tb in the $(\text{REBi})_3\text{Fe}_5\text{O}_{12}$ crystal, enhances the Faraday rotation. The specific Faraday rotation of HoBiIG crystal is 548°/cm while the specific Faraday rotation of TbBiIG crystal is 378°/cm. The saturation field of HoBiIG is 0.98kG, higher than that of TbBiIG which is 0.2 kG. The specific FR of HoBiIG is reduced with the increase of the wavelength at almost linear rate. In the wavelength region near 1.5 μm, HoBiIG crystal has good transparency, but its stability of Faraday rotation against wavelength and temperature is not very good, compared to TbBiIG bulk crystal. Ho,
**MO properties of new garnet crystals**

Replacing Tb in rare earth garnet structure, enhance the specific Faraday rotation, but deteriorate the stability against wavelength and temperature.

### 4.3 \((\text{YbBi})_3\text{Fe}_5\text{O}_{12}\) CRYSTAL

In above section, when small ion Ho\(^{3+}\) replaces Tb\(^{3+}\) ion, some of the MO properties in the corresponding garnet crystal improves. In this chapter, Yb\(^{3+}\) ion which is smaller than Ho\(^{3+}\) is selected to form \((\text{YbBi})_3\text{Fe}_5\text{O}_{12}\) crystal (abbr. YbBiIG). The MO properties are expected to improve further.

![Figure 54](image.png)

**Figure 54** Specific Faraday rotation of YbBiIG crystal vs applied field.

### 4.3.1 MO properties of \((\text{YbBi})_3\text{Fe}_5\text{O}_{12}\)

**Figure 54** shows the specific Faraday rotation measurement of the grown (YbBi)IG crystal plates of (111) faces at \(\lambda=1550\)nm and room temperature. It demonstrates that the saturation field is at \(H_c=1.2\)kG, the specific Faraday rotation is around \(817^o/cm\).
**MO properties of new garnet crystals**

Figure 55 shows the FR measurements of the same sample at wavelengths of 1310nm, 1470nm, 1510nm, and 1590nm, respectively. Similar to the case of TbBiIG and HoBiIG crystals, the specific FR of YbBiIG is reduced with the increase of the wavelength, as shown in Figure 56, and very low dispersion of the Faraday rotation appears in the long wavelength end of the transparent band.

![Figure 55](image1.png)

**Figure 55** Specific Faraday rotation measurements of the same sample (YbBiIG) at wavelengths of 1310nm, 1470nm, 1510nm, and 1590nm, respectively.

![Figure 56](image2.png)

**Figure 56** The spectrum of specific Faraday rotation of YbBiIG in the wavelength region of 1310nm—1590nm.
The specific FR measurements were performed in the temperature range of 20—
120°C. The obtained temperature dependence of the FR in the YbBiIG is shown in
Figure 57. With increasing temperature, the value of the specific Faraday rotation of
YbBiIG keeps stable. It demonstrates that the stability of FR against temperature for the
YbBiIG crystal is good.

4.3.2 Optical property of (YbBi)$_3$Fe$_5$O$_{12}$

Figure 58 shows the optical transmittance spectrum of the YbBiIG crystal. Its
cut-off wavelength is at 1050nm. However, YbBiIG is transparent in the wavelength
region of 1050nm - 2000nm. It means that YbBiIG crystal has good transmittance in the
IR region.

4.3.3 Summary of (YbBi)$_3$Fe$_5$O$_{12}$

Yb, replacing Ho in the (REBi)$_3$Fe$_5$O$_{12}$ crystal, enhances the Faraday rotation.
The specific Faraday rotation of YbBiIG crystal is 817°/cm while the specific Faraday
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rotation of HoBiIG crystal is 548°/cm. The saturation field of YbBiIG is 1.2 kG, higher than that of HoBiIG which is 0.98 kG. The specific FR of HoBiIG is reduced with the increase of the wavelength. In the wavelength region greater than 1050 nm, YbBiIG crystal has good transparency, and good stability of Faraday rotation against temperature.

![Figure 58](image)

Figure 58 The optical transmittance spectrum of the YbBiIG crystal.

4.4 Comparison of MO properties of (REBi)$_3$Fe$_5$O$_{12}$ crystal
(RE=Tb, Ho, or Yb)

Section 4.1, 4.2, and 4.3 describe the properties in details of (TbBi)$_3$Fe$_5$O$_{12}$, (HoBi)$_3$Fe$_5$O$_{12}$, and (YbBi)$_3$Fe$_5$O$_{12}$ crystals. It is necessary to combine these results together and make comparisons in order to show the conclusion.

(REBi)$_3$Fe$_5$O$_{12}$ crystals (RE=Ho, Yb, or / and Tb) were grown under the same condition. They had similar morphology with strong habit faces of \{110\}. Figure 61 shows that the specific FR decreased with the increase of the radius of rare earth element in rare-earth garnet crystal. Here only the contributions from RE$^{3+}$ and Bi$^{3+}$ ions are concerned. The chemical compositions are listed in Table 5. Among (YbBi)$_3$Fe$_5$O$_{12}$,
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(HoBi)$_3$Fe$_5$O$_{12}$ and (TbBi)$_3$Fe$_5$O$_{12}$ crystals, the (YbBi)$_3$Fe$_5$O$_{12}$ crystal incorporated most Bi$^{3+}$ ions, whereas (TbBi)$_3$Fe$_5$O$_{12}$ contained fewest Bi$^{3+}$ ions, although the radius of Yb$^{3+}$ is smallest and the radius of Tb$^{3+}$ is the biggest. The Bi$^{3+}$ contribution to the specific FR is more than the RE$^{3+}$ contribution. Therefore, it is reasonable that the specific FR decreased with the increase of the radius of RE$^{3+}$ in the (REBi)$_3$Fe$_5$O$_{12}$ crystals.

Table 5 Chemical composition of the grown crystals.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Yb</th>
<th>Ho</th>
<th>Tb</th>
<th>Bi</th>
<th>Fe</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>(YbBi)$_3$Fe$<em>5$O$</em>{12}$</td>
<td>2.33</td>
<td>0</td>
<td>0</td>
<td>0.67</td>
<td>5</td>
<td>12</td>
</tr>
<tr>
<td>(HoBi)$_3$Fe$<em>5$O$</em>{12}$</td>
<td>0</td>
<td>2.587</td>
<td>0</td>
<td>0.413</td>
<td>5</td>
<td>12</td>
</tr>
<tr>
<td>(TbBi)$_3$Fe$<em>5$O$</em>{12}$</td>
<td>0</td>
<td>0</td>
<td>2.74</td>
<td>0.26</td>
<td>5</td>
<td>12</td>
</tr>
</tbody>
</table>

Table 6 Changes in anisotropy constants $K_1$ and unit cell parameters in RE$_3$Fe$_5$O$_{12}$ crystals, from those of Y$_3$Fe$_5$O$_{12}$ (YIG) by replacing Y$^{3+}$ with RE$^{3+}$. For YIG, $K_1$ (300 K)=-5.0x10$^3$ erg cm$^{-3}$, $K_1$(78 K)=-22.4x10$^3$ erg cm$^{-3}$, $K_1$(4 K)=-24.8x10$^3$ erg cm$^{-3}$.140

<table>
<thead>
<tr>
<th>Formula Unit</th>
<th>Temp. (K)</th>
<th>$K_1$ (10$^4$ erg cm$^{-3}$)</th>
<th>Unit Cell Parameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb$_3$Fe$<em>5$O$</em>{12}$</td>
<td>300</td>
<td>-5</td>
<td>12.436</td>
</tr>
<tr>
<td>Ho$_3$Fe$<em>5$O$</em>{12}$</td>
<td>300</td>
<td>-5</td>
<td>12.375</td>
</tr>
<tr>
<td>Yb$_3$Fe$<em>5$O$</em>{12}$</td>
<td>300</td>
<td>-7</td>
<td>12.302</td>
</tr>
</tbody>
</table>

Table 7 Changes in magnetization 4 $\pi$ $M_s$, $H_k$, and ($K_1/a$)$^{1/2}$ in RE$_3$Fe$_5$O$_{12}$, and the saturation field in their corresponding Bi-doping garnets

<table>
<thead>
<tr>
<th>Formula Unit</th>
<th>4 $\pi$ $M_s$ (Gauss)</th>
<th>$H_k$=(2$K_1/M_s$) (kG)</th>
<th>($K_1/a$)$^{1/2}$ (10$^3$ erg cm$^{-4}$)$^{1/2}$</th>
<th>Saturation field in (REBi)$_3$Fe$<em>5$O$</em>{12}$ (kG)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb$_3$Fe$<em>5$O$</em>{12}$</td>
<td>198</td>
<td>0.05</td>
<td>0.63</td>
<td>0.4</td>
</tr>
<tr>
<td>Ho$_3$Fe$<em>5$O$</em>{12}$</td>
<td>778</td>
<td>0.0129</td>
<td>0.64</td>
<td>0.8</td>
</tr>
<tr>
<td>Yb$_3$Fe$<em>5$O$</em>{12}$</td>
<td>1555</td>
<td>0.009</td>
<td>0.75</td>
<td>1.2</td>
</tr>
</tbody>
</table>
**MO properties of new garnet crystals**

Furthermore, the coercive force for (REBi)$_3$Fe$_5$O$_{12}$ crystals (RE=Ho, Yb, or Tb) also decreased when the rare earth ions became bigger, as shown in Figure 62. Coercive force can be defined as the largest field required to cause the irreversible wall motion of reverse domains that are already nucleated. All the spins within samples are collectively reoriented along the field direction. This occurs when the applied field exceeds the anisotropy field value, $H_k=2K_1/M_s$, where $K_1$ is the magneto-crystalline anisotropy constant, and $M_s$ is the saturation magnetization. Both parameters depend almost entirely on the material composition, and are considered as intrinsic. The anisotropy constants $K_1$ and $M_s$ of the RE$_3$Fe$_5$O$_{12}$ (RE=Ho, Yb, and Tb) are listed in Table 6 and Table 7. As listed in Table 5, the doping amount of Bi$^{3+}$ is very small, Bi$^{3+}$ will only enter the dodecahedral sites due to its ionic size. Therefore, the Bi$^{3+}$ effects in REBiIG crystals are neglectable. Table 7 shows that the change trend of saturation field in REBiIG crystals does not follow the $(2K_1/M_s)$ changes in REIG, especially very higher than the latter. Instead, the change of saturation field in REBiIG crystals follow the trend of $(K_1/a)^{1/2}$ which is main part of domain energy.

The difference between the experimental coercive field and the anisotropy field (as determined from the magneto-crystalline anisotropy constant) can be explained by the presence of domain walls. The domain wall energy and thickness for a $180^\circ$ wall, calculated from the minimum in exchange and anisotropy contributions, can be expressed respectively as:

$$\gamma_w = 2(A K_1)^{1/2} \quad 4.4.1$$

$$\delta_w = (A/ K_1)^{1/2} \quad 4.4.2$$

$$A = \pi J s^2 /a \quad 4.4.3$$

And

$$\gamma_w = 2(\pi J s^2 K_1/a)^{1/2} \quad 4.4.4$$
where $\gamma_w$ is the domain wall energy per area unit, $\delta_w$ the wall thickness, $K_1$ the anisotropy constant, $A$ the exchange constant, $J$ the exchange energy, $s$ the spin energy, and $a$ the unit cell parameter. From Table 7, $(K_1/a)^{1/2}$ increases when RE changes from Tb to Yb. Although $J$ and $s$ are unknown for the corresponding garnets, there is a trend from Eq (1) to (4) that the domain wall energy increases when rare-earth ion radius become smaller. In our work, the trend of the coercive force in $\text{(REBi)}_3\text{Fe}_5\text{O}_{12}$ crystals ($\text{RE}=\text{Ho, Yb, or Tb}$) accords with the trend of domain energy changes in $\text{RE}_3\text{Fe}_5\text{O}_{12}$ crystals. It seems to indicate rare-earth elements have effects on coercive force through the domain energy in the rare-earth garnet crystals. This explains why the coercive force in $\text{(REBi)}_3\text{Fe}_5\text{O}_{12}$ crystals decreases with the increase of radii of rare-earth ions, as shown in Figure 62.

![Figure 59](image.png)

**Figure 59** Relationship between the specific FR and rare-earth radii in $\text{(REBi)}_3\text{Fe}_5\text{O}_{12}$ crystals ($\text{RE}=\text{Yb, Ho, or Tb}$).

Furthermore, the saturation field for $\text{(REBi)}_3\text{Fe}_5\text{O}_{12}$ crystals ($\text{RE}=\text{Ho, Yb, or Tb}$) also decreased when the rare earth ions became bigger, as shown in Figure 62. This possibly related to the domain structures in the garnet crystals.
Figure 60 Coercive fields in REBiIG (RE=Yb, Ho or Tb) crystals decrease with the increase of their rare-earth ion radii.

Figure 61 Relationship between the specific FR and rare-earth radii in (REBi)$_3$Fe$_5$O$_{12}$ crystals (RE=Yb, Ho, or Tb).

As a FR element in optical isolator, the stability of FR against wavelength and temperature is also very important. The stability of FR in (REBi)$_3$Fe$_5$O$_{12}$ (RE=Ho, Yb, or Tb) crystals against wavelength is shown in Figure 61. In order to evaluate the stability
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of FR against wavelength, the FR wavelength coefficient (FWC) proposed by T. Tamali

was defined as following,

\[
\text{FWC} = (\Phi_{F, 1.55} - \Phi_{F, 1.57}) / \Phi_{F, 1.55} / 20 \times 100
\]

where \( \Phi_{F, 1.55} \) and \( \Phi_{F, 1.57} \) are FR values at the wavelength of 1.55 \( \mu \text{m} \) and 1.57 \( \mu \text{m} \) respectively. The values of FWC of \( (\text{REBi})_3\text{Fe}_5\text{O}_{12} \) (RE=Ho, Yb, or Tb) crystals are listed in Table 8. It is obvious that the FR stability in \( (\text{HoBi})_3\text{Fe}_5\text{O}_{12} \) crystal is best, \( (\text{TbBi})_3\text{Fe}_5\text{O}_{12} \) is worst among \( (\text{YbBi})_3\text{Fe}_5\text{O}_{12} \), \( (\text{HoBi})_3\text{Fe}_5\text{O}_{12} \), and \( (\text{TbBi})_3\text{Fe}_5\text{O}_{12} \) crystals.

![Figure 62](image)

**Figure 62** Saturation fields in REBiIG (RE=Yb,Ho or Tb) crystals decrease with the increase of their rare-earth ion radii.

<table>
<thead>
<tr>
<th>Table 8</th>
<th>Changes in FWC of ( (\text{REBi})_3\text{Fe}<em>5\text{O}</em>{12} ) (RE=Ho, Yb, or Tb) crystals.</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\text{HoBi})_3\text{Fe}<em>5\text{O}</em>{12})</td>
<td>((\text{YbBi})_3\text{Fe}<em>5\text{O}</em>{12})</td>
</tr>
<tr>
<td>FWC</td>
<td>0.05</td>
</tr>
</tbody>
</table>

The stability of FR against temperature in \( (\text{REBi})_3\text{Fe}_5\text{O}_{12} \) (RE=Ho, Yb, or Tb) crystals is shown in Figure 62. In order to evaluate the dependence of FR on temperature, the FR temperature coefficient (FTC) is suggested as below,
where $\Phi_{F25^\circ C}$ and $\Phi_{F100^\circ C}$ are FR values at 25$^\circ$C and 100$^\circ$C respectively. Table 9 shows the values of FTC of (REBi)$_3$Fe$_5$O$_{12}$ (RE=Ho, Yb, or Tb) crystals. Different from the case of the stability of FR against wavelength, the FR stability against temperature in (HoBi)$_3$Fe$_5$O$_{12}$ crystal is worst, and (TbBi)$_3$Fe$_5$O$_{12}$ best among (REBi)$_3$Fe$_5$O$_{12}$ (RE=Ho, Yb, or Tb) crystals.

![Figure 63](image_url) Comparison of the stability of Faraday rotation against wavelength between REBiIG crystals (RE=Yb, Ho, and Tb)

In brief, (HoBi)$_3$Fe$_5$O$_{12}$ crystal has best stability of FR against wavelength but worst stability against temperature, and (TbBi)$_3$Fe$_5$O$_{12}$ crystal has best stability against temperature but worst stability against wavelength among (REBi)$_3$Fe$_5$O$_{12}$ (RE=Ho, Yb, or Tb) crystals.

Figure 65 shows the comparison of transmittance spectrum of REBiIG crystals. Among the three crystals, they have almost the same cut-off edge at the short wavelength end, but the long wavelength end of the transparent region is shifting to longer wavelength side in the descending atom radii sequence of Tb, Ho, Yb. In the wavelength
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region of 1.06—1.15 µm, only HoBiIG crystal has two absorption peaks which are related to the first transition $^6A_{1g}(^6S) \rightarrow ^4T_{1g}(^4G)$ of the octahedral Fe$^{3+}$. The absorption peaks at the wavelength region of 1.7—2.0 µm are related to 4f transition for the rare-earth ions. They can also be shifted in position by the crystalline field of dodecahedral symmetry. \textsuperscript{143}

![Figure 64](image)

**Figure 64** Comparison of the stability of Faraday rotation against temperature between REBiIG crystals (RE=Yb, Ho, and Tb).

<table>
<thead>
<tr>
<th>Table 9</th>
<th>Changes in FTC of (REBi)$_3$Fe$<em>5$O$</em>{12}$ (RE=Ho, Yb, or (Ho+Yb)) crystals.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(HoBi)$_3$Fe$<em>5$O$</em>{12}$</td>
<td>(YbBi)$_3$Fe$<em>5$O$</em>{12}$</td>
</tr>
<tr>
<td>FTC</td>
<td>0.18</td>
</tr>
</tbody>
</table>
4.5 MO properties of (Re$_1$Re$_2$Bi)$_3$Fe$_5$O$_{12}$ crystal (Re$_1$=Ho, Re$_2$=Yb)

In section 4.4, it is concluded that HoBiIG crystal has best stability of FR against wavelength but worst stability against temperature, and that and YbBiIG crystal has worst stability of FR against wavelength but best stability against temperature. As a Faraday rotation element, the stability against both wavelength and temperature is prerequisite for practical optical isolator. If we combine the two kinds of crystals together, it is interesting to explore what will happen on the solid solution crystal of (HoYbBi)$_3$Fe$_5$O$_{12}$ (abbr. HoYbBiIG).

Figure 66 shows that the saturated specific Faraday rotation of HoYbBiIG (548°/cm) is almost equal to that of HoBiIG, but smaller than that of YbBiIG, and that the saturation field of HoYbBiIG (0.98kG) is in the middle position between the values of the saturation field of HoBiIG and YbBiIG crystals.
**Figure 66** Comparison of the specific Faraday rotation of \((\text{REBi})_3\text{Fe}_5\text{O}_{12}\) crystals as function of field. (\text{RE}=\text{Yb}, \text{Ho}, \text{or (Ho+Yb)}).

**Figure 67** Comparison of the specific Faraday rotation spectra of \((\text{REBi})_3\text{Fe}_5\text{O}_{12}\) crystals. (\text{RE}=\text{Yb}, \text{Ho}, \text{or (Ho+Yb)})

**Table 10** Changes in FWC of \((\text{REBi})_3\text{Fe}_5\text{O}_{12}\) (\text{RE}=\text{Ho, Yb, or (Ho+Yb)}) crystals.

<table>
<thead>
<tr>
<th></th>
<th>((\text{HoBi})_3\text{Fe}<em>5\text{O}</em>{12})</th>
<th>((\text{YbBi})_3\text{Fe}<em>5\text{O}</em>{12})</th>
<th>((\text{HoYbBi})_3\text{Fe}<em>5\text{O}</em>{12})</th>
</tr>
</thead>
<tbody>
<tr>
<td>FWC</td>
<td>0.05</td>
<td>0.26</td>
<td>0.11</td>
</tr>
</tbody>
</table>
**MO properties of new garnet crystals**

Figure 67 compares the specific Faraday rotation spectra among the three crystals. Their FWC are listed in Table 10. HoYbBiIG crystal shows improved stability of FR against wavelength, compared to YbBiIG crystal, but worse stability if compared to HoBiIG crystal.

Figure 68 demonstrates the comparison of the specific Faraday rotation stability against temperature among the three crystals. Their FTCs are listed in Table 11. HoYbBiIG crystal shows improved stability of FR against temperature, compared to HoBiIG crystal, but worse stability if compared to YbBiIG crystal.

### Table 11 Changes in FTC of (REBi)$_3$Fe$_5$O$_{12}$ (RE=Ho, Yb, or (Ho+Yb)) crystals.

<table>
<thead>
<tr>
<th></th>
<th>(HoBi)$_3$Fe$<em>5$O$</em>{12}$</th>
<th>(YbBi)$_3$Fe$<em>5$O$</em>{12}$</th>
<th>(HoYbBi)$_3$Fe$<em>5$O$</em>{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTC</td>
<td>0.18</td>
<td>-0.06</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Figure 68 Comparison of the specific Faraday rotation of (REBi)$_3$Fe$_5$O$_{12}$ crystals as a function of temperature. (RE=Yb, Ho, or (Ho+Yb))
The transmittance spectrum of HoYbBiIG crystal follows the pattern of that of HoBiIG crystal, as shown in Figure 69. The absorption peaks are related to the vibration of bonds between the anion and cation atoms. The spectrum of YbBiIG crystal is simple, and it is transparent in the wavelength region of longer than 1.1 µm. The spectrum of HoBiIG crystal in the same wavelength region is complicated, and it has two absorption peaks in the short wavelength end, and one in the long wavelength end. It is reasonable that the spectrum of HoYbBiIG crystal follows the pattern of HoBiIG crystal.

In summary, HoYbBiIG crystal, as the solid solution of HoBiIG crystal and YbBiIG crystal, shows the MO properties with their values between the HoBiIG crystal and YbBiIG crystal, such as saturation field, stability of FR against wavelength and temperature, apart from the saturated specific FR and transmittance spectrum following the behavior of HoBiIG. For practical purpose, as FR element in the optical isolator, the saturation field of HoYbBiIG (0.98 kG) is a little too high, and its specific FR (548°C/cm) is a little too low with consideration of the product cost.
4.6 MO properties of \((\text{Re}_1\text{Re}_2\text{Re}_3\text{Bi})_3\text{Fe}_5\text{O}_{12}\) crystal (\(\text{Re}_1=\text{Ho}, \text{Re}_2=\text{Yb}, \text{Re}_3=\text{Tb}\))

As discussed above, the determined factor for the saturation force is the rare-earth element doped in the garnet crystal, and TbBiIG crystal usually has low saturation field (0.2—0.4kG). In order to further reduce the saturation field of HoYbBiIG crystal, Tb is introduced into the solid solution, e.g. HoYbTbBiIG crystal.

![Figure 70](image-url) Comparison of the specific Faraday rotation of HoYbBiIG crystal and TbHoYbBiIG crystal as function of field.

Figure 70 demonstrates that the saturation field \(H_c(\text{TbBiIG}) < H_c(\text{Tb}_{1.0}\text{HoYbBiIG}) < H_c(\text{Tb}_{0.3}\text{HoYbBiIG}) < H_c(\text{HoYbBiIG})\). With more Tb amount introduced, the saturation field of the solid solution crystal is reduced further, but the specific Faraday rotation is also reduced, approaching the value of that of TbBiIG crystal. The specific Faraday rotation heavily depends on the content of Bi in the garnet structure. TbHoYbBiIG crystal is the solid solution of TbBiIG crystal and HoYbBiIG crystal. The amount of Bi in the TbBiIG crystal is lower than that in the HoYbBiIG crystal. It is reasonable that the higher amount of Tb in TbHoYbBiIG will cause the lower amount of
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Bi. It is obvious from Figure 70 that the addition of Tb to the crystal can lower the saturation field of the crystal, at least in the case of HoYbBiIG crystal.

Table 12 Changes in FWC of (REBi)_3Fe_5O_12 (RE=Ho, Yb, or (Ho+Yb)) crystals.

<table>
<thead>
<tr>
<th></th>
<th>TbBiIG</th>
<th>Tb_{1.0}HoYbBiIG</th>
<th>Tb_{0.5}HoYbBiIG</th>
<th>HoYbBiIG</th>
</tr>
</thead>
<tbody>
<tr>
<td>FWC</td>
<td>0.89</td>
<td>0.09</td>
<td>0.06</td>
<td>0.11</td>
</tr>
</tbody>
</table>

From Figure 71, it can be seen that the pattern of the stability of FR against wavelength of Tb_{0.5}HoYbBiIG crystal follows that of HoYbBiIG crystal while that of Tb_{1.0}HoYbBiIG crystal follows that of TbBiIG crystal. Furthermore, the stability of FR against wavelength (FWC) is improved at the wavelength of 1550nm after addition of Tb as listed in Table 12. As shown in Figure 69, the specific FR of TbHoYbBiIG is reduced with the increase of the wavelength and very lower dispersion of the Faraday rotation appears in the wavelength region of 1550nm-1560nm than HoYbBiIG crystal and TbBiIG crystal.

Figure 71 Comparison of the spectra of TbBiIG, Tb_{0.5}HoYbBiIG, Tb_{1.0}HoYbBiIG and HoYbBiIG crystal.
The features of transmittance spectra of HoYbBiIG crystal and TbBiIG crystal are all reflected in the spectra of TbHoBiIG crystals, as shown in Figure 72. The pattern of the spectra of Tb$_{0.5}$HoYbBiIG and Tb$_{1.0}$HoYbBiIG crystals are similar, and the transparent region is as narrow as that of TbBiIG crystal, and the absorption peaks are sitting at the same positions as that of HoYbBiIG crystal.

In summary, by adding the Tb into the HoYbBiIG crystal, the solid solution of TbHoYbBiIG crystal shows lower saturation field than that of HoYbBiIG crystal. Furthermore, the stability of FR against wavelength is improved in the 1550nm wavelength region, although the transparent region is narrowed due to the absorption features related to Tb.

4.7 MO properties of (Re$_1$Re$_2$Re$_3$Bi)$_3$Fe$_5$O$_{12}$ crystal (Re$_1$=Ho, Re$_2$=Yb, Re$_3$=Ce)

As discussed above, Tb can work as saturation force reducer in rare-earth garnet crystal. HoYbTbBiIG crystal usually has lower saturation field and specific Faraday
rotation than HoYbBiIG crystal. In order to further increase the specific Faraday rotation, Ce is introduced to the solid solution to form HoYbCeBiIG crystal.

![Graph showing comparison of Faraday rotation for HoYbBiIG and HoYbCe0.5BiIG crystals.](image)

**Figure 73** Comparison of the specific Faraday rotation of HoYbBiIG crystal and HoYbCe0.5BiIG crystal as function of field.

**Figure 73** demonstrates that addition of Ce to the HoYbBiIG crystal causes the reduction of the saturation field (0.76 kG) and the increases of the specific Faraday (625°/cm). The specific Faraday rotation heavily depends on the content of Bi and Ce in the garnet structure. Although the limit of the Ce concentration in the crystal is very small due to its large ion radii, the small amount of Ce enhances the Faraday rotation.

**Table 13** Changes in FWC of (REBi)₃Fe₅O₁₂ (RE=(Ce+Ho+ Yb), or (Ho+Yb)) crystals.

<table>
<thead>
<tr>
<th></th>
<th>(Ce₀.₅HoYbBi)₃Fe₅O₁₂</th>
<th>(HoYbBi)₃Fe₅O₁₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>FWC</td>
<td>0.156</td>
<td>0.11</td>
</tr>
</tbody>
</table>
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Figure 74 shows that the specific FR of Ce_{0.5}HoYbBiIG is reduced with the increase of the wavelength and very higher dispersion of the Faraday rotation appears at the long wavelength end than HoYbBiIG crystal. The addition of Ce deteriorates a little bit the stability of FR against wavelength, as shown in Table 13. As shown in Figure 75, and Table 14, the stability of Faraday rotation against temperature of Ce_{0.5}HoYbBiIG is also worse than that of HoYbBiIG crystal.

Figure 74 Comparison of the spectra of Ce_{0.5}HoYbBiIG and HoYbBiIG crystals.

Figure 75 Comparison of the stability of FR against temperature of Ce_{0.5}HoYbBiIG and HoYbBiIG crystals.
Table 14 Changes in FTC of \((\text{REBi})_3\text{Fe}_5\text{O}_{12}\) (\(\text{RE}=(\text{Ce}+\text{Ho}+\text{Yb}),\) or (\(\text{Ho}+\text{Yb}\)) crystals.

<table>
<thead>
<tr>
<th></th>
<th>((\text{Ce}_{0.5}\text{HoYbBi})_3\text{Fe}<em>5\text{O}</em>{12}))</th>
<th>((\text{HoYbBi})_3\text{Fe}<em>5\text{O}</em>{12}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>FTC</td>
<td>0.14</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Figure 76 Comparison of the transmittance spectra of Ce\(_{0.5}\)HoYbBiIG, and HoYbBiIG.

The features of transmittance spectra of HoYbBiIG crystal and CeHoYbBiIG crystal are similar as shown in Figure 76, and the absorption peaks are sitting at the same positions. The cut-off wavelength is shifted from 1015nm (HoYbBiIG crystal) to 1067nm (Ce\(_{0.5}\)HoYbBiIG) after addition of Ce.

In summary, by adding the Ce into the HoYbBiIG crystal, the solid solution of CeHoYbBiIG crystal shows lower saturation field (0.76 kG) and higher specific Faraday rotation (625 °/cm) than that of HoYbBiIG crystal (0.98kG, 545 °/cm). However, the stability of FR against wavelength and temperature is deteriorated, the cut-off wavelength at the short wavelength end is shifted to the longer wavelength after introducing Ce.
Both Ce$^{3+}$ and Bi$^{3+}$ ions doped in the garnet crystals can enhance their specific Faraday rotations. In order to compare their contributions, the chemical compositions of some of the grown crystals were analyzed by the SEM/EDX with an automated ZAF matrix correction, as listed in Table 15. The maximum amount of Ce substitution up to $x=0.164$ is in agreement with those obtained in the flux-grown$^{144,145}$ and LPE-grown$^{146}$ iron garnets. The co-substitution of Bi in two (HoYbCeBi)$_3$Fe$_5$O$_{12}$ samples was determined to be $y=0.665$ and $y=0.417$ in the crystals with $x=0.164$ and $x=0.135$, respectively. Their chemical formula should be (HoYb)$_{2.171}$Ce$_{0.164}$Bi$_{0.665}$Fe$_5$O$_{12}$, (HoYb)$_{2.501}$Bi$_{0.499}$Fe$_5$O$_{12}$, and (HoYb)$_{2.501}$Bi$_{0.499}$Fe$_5$O$_{12}$.

<table>
<thead>
<tr>
<th>Crystals</th>
<th>Ce(x)</th>
<th>Bi(y)</th>
<th>Ho</th>
<th>Yb</th>
</tr>
</thead>
<tbody>
<tr>
<td>(HoYb)$_{3-x-y}$Ce$_x$Bi$_y$Fe$<em>5$O$</em>{12}$-1</td>
<td>0.164</td>
<td>0.665</td>
<td>1.263</td>
<td>0.908</td>
</tr>
<tr>
<td>(HoYb)$_{3-x-y}$Ce$_x$Bi$_y$Fe$<em>5$O$</em>{12}$-2</td>
<td>0.135</td>
<td>0.417</td>
<td>1.475</td>
<td>0.973</td>
</tr>
<tr>
<td>(HoYb)$_{3-y}$Bi$_y$Fe$<em>5$O$</em>{12}$</td>
<td>0.499</td>
<td>1.537</td>
<td>0.964</td>
<td></td>
</tr>
</tbody>
</table>

Figure 77 presents the specific Faraday rotation spectra for (HoYb)$_{2.171}$Ce$_{0.164}$Bi$_{0.665}$Fe$_5$O$_{12}$ and (HoYb)$_{2.501}$Bi$_{0.499}$Fe$_5$O$_{12}$ in the wavelength range of 1520 to 1590 nm at room temperature.

The specific Faraday rotation linearly increased with an increase of Ce up to $x=2$ in Y$_{3-x}$Ce$_x$Fe$_5$O$_{12}$, giving an enhancement factor of $-1.3\times10^4$ deg/cm per Ce ion at 1150 nm. At 1550 nm, the specific Faraday rotation of Y$_3$Fe$_5$O$_{12}$ is about 180 deg/cm$^{148}$. The dependence of $\theta_F$ on Ce concentration at 1550 nm was studied by Higuchi et al.$^{149}$ in Y$_3$-xCe$_x$Fe$_5$O$_{12}$, from which the enhancement factor of $-4.7\times10^3$ deg/cm per Ce ion could be
extrapolated. This value was in agreement with \(-4.7 \times 10^3\) deg/cm and \(-5.0 \times 10^3\) deg/cm for Y$_2$Ce$_1$Fe$_5$O$_{12}$ prepared by RF sputtering $^{150,151}$. For Bi-substituted Tb$_{3-y}$Bi$_y$Fe$_5$O$_{12}$, in a wavelength region from 1500 to 1600 nm the enhancement factor per Bi$^{3+}$ ion was reported to be \(-1.54 \times 10^3\) deg/cm $^{152}$ that was much lower than that of Ce$^{3+}$.

![Figure 77](image)

**Figure 77** Wavelength dependence of the specific Faraday rotation for (HoYb)$_{2.171}$Ce$_{0.164}$Bi$_{0.665}$Fe$_5$O$_{12}$ and (HoYb)$_{2.501}$Bi$_{0.499}$Fe$_5$O$_{12}$ crystals around 1550 nm.

Since the substitution of Ho$^{3+}$, Yb$^{3+}$ or Tb$^{3+}$ ions in Y$_3$Fe$_5$O$_{12}$ resulted in a little variation in Faraday rotation at 1550 nm $^{153}$, it was reasonable to treat these ions here without difference in their contribution to the Faraday rotation. Hence by using the above-mentioned enhancement factors of Ce$^{3+}$ and Bi$^{3+}$, $\theta_F$ of (HoYb)$_{2.171}$Ce$_{0.164}$Bi$_{0.665}$Fe$_5$O$_{12}$ can be calculated to be about \(-1615\) deg/cm. It is noted that the estimated $\theta_F$ is much higher than the measured value of \(-1035\) deg/cm, which may be expected from the following two aspects. Firstly, it is possibly due to the coexistence of the Ce$^{4+}$ and Ce$^{3+}$ ions in (HoYb)$_{2.171}$Ce$_{0.164}$Bi$_{0.665}$Fe$_5$O$_{12}$, which results in a low Ce$^{3+}$ concentration in the iron garnets. Both Ce$^{3+}$ and Ce$^{4+}$ ions were reported to be present in Ce-substituted iron garnets $^{154}$. However, the Ce$^{3+}$ ions significantly
contributed to the MO effect rather than Ce\(^{4+}\). Many attempts have been made to determine the valence of Ce in (HoYb\(_2\)\(_{1.71}\)Ce\(_{0.164}\)Bi\(_{0.665}\)Fe\(_5\)O\(_{12}\) by using X-ray photo spectroscopy (XPS). However, it is difficult to identify the ratio of Ce\(^{4+}/Ce^{3+}\) since the concentration of Ce in the crystal is very low. To verify this hypothesis, further annealing experiments should be performed on the as-grown (HoYb\(_2\)\(_{1.71}\)Ce\(_{0.164}\)Bi\(_{0.665}\)Fe\(_5\)O\(_{12}\) crystal in a reduction atmosphere and a higher value of \(\theta_F\) is expected. Secondly, a charge transfer transition from Ce\(^{3+}\) (4f) to Fe\(^{3+}\) (tetrahedral)\(^{147}\) was proposed to elucidate the Faraday rotation enhancement of Ce. For the Bi-substituted iron garnets, the Faraday rotation enhancement resulted from the increase of the spin-orbit interaction caused by the formation of the molecular orbit between 3d orbit of Fe\(^{3+}\), 2p orbit of O\(^{2-}\) and 6p orbit of Bi\(^{3+}\)\(^{156,157}\). Since both Ce- and Bi-substituted iron garnets have involved the interaction with Fe\(^{3+}\), it is possible that Ce\(^{3+}\) in (HoYb)\(_{3-x-y}\)Ce\(_{x}\)Bi\(_{y}\)Fe\(_5\)O\(_{12}\) might affect the Faraday rotation component contributed by Bi\(^{3+}\) and vice versa. However, further studies are needed to interpret whether the two transitions are correlated and how they affect each other.

### 4.9 Feasibility of application in 1550 nm wideband optical isolators

Table 16 Optical and MO properties of (HoYb)\(_{2.171}\)Ce\(_{0.164}\)Bi\(_{0.665}\)Fe\(_5\)O\(_{12}\) and (HoYb)\(_{2.501}\)Bi\(_{0.499}\)Fe\(_5\)O\(_{12}\) crystals at 1550 nm.

<table>
<thead>
<tr>
<th>Crystals</th>
<th>(\theta_F) (deg/cm)</th>
<th>(\alpha) (cm(^{-1}))</th>
<th>FWC(^*) (deg/nm)</th>
<th>FTC(^*) (deg/°C)</th>
<th>Figure of merit (deg/dB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(HoYb)(<em>{2.501})Bi(</em>{0.499})Fe(<em>5)O(</em>{12})</td>
<td>–588</td>
<td>1.84</td>
<td>0.044</td>
<td>0.046</td>
<td>74</td>
</tr>
<tr>
<td>(HoYb)(<em>{2.171})Ce(</em>{0.164})Bi(_{0.665})Fe(<em>5)O(</em>{12})</td>
<td>–1035</td>
<td>2.18</td>
<td>0.057</td>
<td>0.085</td>
<td>109</td>
</tr>
<tr>
<td>(HoYb)(<em>{1.87})Bi(</em>{1.13})Fe(<em>5)O(</em>{12}) [13]</td>
<td>–767</td>
<td>3.93</td>
<td>0.022</td>
<td>0.021</td>
<td>45</td>
</tr>
</tbody>
</table>

\(^*\) For Faraday rotation angle of 45\(^°\)
**MO properties of new garnet crystals**

As a key part of optical isolators, the Faraday rotator should satisfy the following requirements: large $\theta_F$, low $\alpha$, small wavelength and temperature coefficients of $\theta_F$, and low saturation magnetic field. For a Faraday rotation angle of 45°, the Faraday rotation wavelength coefficient ($FWC$) at 1550 nm for $(\text{HoYb})_{2.17}\text{Ce}_{0.164}\text{Bi}_{0.665}\text{Fe}_5\text{O}_{12}$ was obtained to be 0.057 deg/nm, which was higher than 0.044 deg/nm for $(\text{HoYb})_{2.501}\text{Bi}_{0.499}\text{Fe}_5\text{O}_{12}$. **Figure 78** shows the dependence of $\theta_F$ on temperature for both $(\text{HoYb})_{2.17}\text{Ce}_{0.164}\text{Bi}_{0.665}\text{Fe}_5\text{O}_{12}$ and $(\text{HoYb})_{2.501}\text{Bi}_{0.499}\text{Fe}_5\text{O}_{12}$ in the temperature range from 19 to 80 °C. For a Faraday rotation angle of 45°, the Faraday rotation temperature coefficient ($FTC$) at 1550 nm was determined to be 0.085 deg/°C for $(\text{HoYb})_{2.17}\text{Ce}_{0.164}\text{Bi}_{0.665}\text{Fe}_5\text{O}_{12}$ and 0.046 deg/°C for $(\text{HoYb})_{2.501}\text{Bi}_{0.499}\text{Fe}_5\text{O}_{12}$. Higher values of $FWC$ and $FTC$ for $(\text{HoYb})_{2.17}\text{Ce}_{0.164}\text{Bi}_{0.665}\text{Fe}_5\text{O}_{12}$ are probably due to the incorporation of Ce in the iron garnets $^{158,159,160}$. **Table 16** summarizes the optical and MO properties of $(\text{HoYb})_{2.17}\text{Ce}_{0.164}\text{Bi}_{0.665}\text{Fe}_5\text{O}_{12}$ and $(\text{HoYb})_{2.501}\text{Bi}_{0.499}\text{Fe}_5\text{O}_{12}$ at 1550 nm. The results reported by Huang and Zhang $^{161}$ are also listed for comparison. It is noted that further studies should be carried out to reduce the values of $FWC$ and $FTC$. However, the large specific Faraday rotation, low absorption and high figure of merit make $(\text{HoYb})_{3-x-y}\text{Ce}_x\text{Bi}_y\text{Fe}_5\text{O}_{12}$ feasible and promising for the application in 1550 nm optical isolators.

![Figure 78](image)

**Figure 78** Temperature dependence of the specific Faraday rotation for $(\text{HoYb})_{2.17}\text{Ce}_{0.164}\text{Bi}_{0.665}\text{Fe}_5\text{O}_{12}$ and $(\text{HoYb})_{2.501}\text{Bi}_{0.499}\text{Fe}_5\text{O}_{12}$ crystals at 1550 nm.
**MO properties of new garnet crystals**

![Graph showing absorption spectra](image)

**Figure 79** Absorption spectra of (HoYb)_{2.171}Ce_{0.164}Bi_{0.665}Fe_{5}O_{12} and (HoYb)_{2.501}Bi_{0.499}Fe_{5}O_{12} crystals at 1550nm.

### 4.10 Summary of the properties of new garnet crystals

For (REBi)$_3$Fe$_5$O$_{12}$ crystals (RE=Ho, Yb, or Tb), the specific FR decreased with the increase of the radius of rare earth elements. (HoBi)$_3$Fe$_5$O$_{12}$ crystal has best stability of FR against wavelength but worst stability against temperature, and (TbBi)$_3$Fe$_5$O$_{12}$ crystal has best stability against temperature but worst stability against wavelength.

HoYbBiIG crystal, as the solid solution of HoBiIG crystal and YbBiIG crystal, showed the MO properties with their values between the HoBiIG crystal and YbBiIG crystal. This trade-off between MO properties can be realized further by doping more RE ions into the garnet crystal, like TbHoYBBiIG crystal lowering the saturation field of HoYbBiIG crystal, Ce$_{0.5}$HoYbBiIG improving the Specific Faraday Rotation of HoYbBiIG crystal. As the result of doping effect, the (HoYb)$_{3-x-y}$Ce$_x$Bi$_y$Fe$_5$O$_{12}$ crystal become feasible and promising for the application in 1550 nm optical isolators.
5. RESULTS AND DISCUSSION: THEORETICAL CALCULATION OF FARADAY ROTATION

It is necessary to understand the microscopical mechanism on the magneto-optical (MO) effects in order to explain the experimental results of new MO crystals. The understanding of the microscopical mechanisms of MO effects is based on the knowledge of the electronic structure and electron wave functions in the crystals. Of particular importance are the selection rules for light-induced quantum transitions. It is known that right or left circularly polarized photons excite electron transitions, which, in accordance with the law of angular momentum conservation, change the appropriate projection of the system’s angular momentum by $\Delta m = \pm 1$. The different transitions are reflected by the non-zero off-diagonal elements of the polarizability tensors in the electric dipole approximation. The Faraday effects are defined by the difference between the contributions of the ‘right’ and ‘left’ processes (i.e., the transitions with $\Delta m = +1$ and with $\Delta m = -1$). In non-magnetic materials at $H=0$, these processes have become equalized. Therefore, no odd magneto-optical effects take place. In a magnetic field and in magnetically ordered materials the balance between the total contribution of the ‘right’ and ‘left’ processes to the permittivity is broken. This results in a rotation of the plane of polarization of light or a difference between the absorption coefficients of the light with different polarizations.\textsuperscript{130}

The implementation of this simple idea in particular cases strongly depends on the character of the wave functions and the electron energy spectrum in the magnetic medium. There are two approaches to the enhanced MO activity by Bi doping in garnet
Theoretical calculation of Faraday rotation

crystals. One is that the enhanced MO effects originate from covalent interactions between Bi$^{3+}$ and Fe$^{3+}$ ions. The other approach is the enhanced MO effect that is due to that Bismuth puts influence on the dodecahedral Re$^{3+}$ electric dipole that contributes to the MO activity. Here we just present some models from the practical point of view.

5.1 Helseth’s model on FR from electron dipole transitions

The understanding of the magnetooptical spectra in garnets is based on the knowledge of the spin orbit interaction in these materials. The spin orbit interaction generally causes a splitting of both the ground and excited states. However, in many cases it is possible to assume splitting of one of the states. Then only two situations are possible: (I) a paramagnetic transition, which is due to an orbital degenerate ground state with a singlet excited state, (II) a diamagnetic transition, which is due to an orbital singlet ground state with a spin orbit split excited state. L.E. Helseth, used second approach and their analysis of the Faraday rotation spectra is based on the molecular –orbital energy –level diagram of Dionne and Allen, as shown in Figure 80.

![Figure 80](image-url)

**Figure 80** The basic molecular-orbital energy –level diagram. (+1) and (-1) represents right and left –hand circular polarization, respectively. Note that there are two transitions that influence the Faraday rotation. One is associated with the tetrahedral site, the other with the octahedral site. The transitions are assumed to follow the selection rules for electric dipole transitions.
Theoretical calculation of Faraday rotation

In order to calculate the magneto-optic response, an expression which links the microscopic parameters to the Faraday rotation is needed. In Magnetoptics, this is usually expressed through the complex permittivity tensor. The Bi substituted garnet has the form of permittivity tensor, like:

\[
\varepsilon = \begin{pmatrix}
\varepsilon_0 & \varepsilon_1 & 0 \\
-\varepsilon_1 & \varepsilon_0 & 0 \\
0 & 0 & \varepsilon_0
\end{pmatrix}
\]

where \( \varepsilon_1 = \varepsilon_1^\prime + j\varepsilon_1^\prime\prime \) represents the magneto-optical response and \( \varepsilon_0 \) the nonmagneto-optical part. In the visible region, the Faraday rotation can be written:

\[
\theta_F = \frac{\sigma}{2nc}\varepsilon_1^\prime
\]

where \( \sigma \) is the frequency, or equivalently the energy of the light, \( c \) is the speed of light in vacuum, and \( n \) is the refractive index. Independent measurements show that it is reasonable to set \( n=2.5 \) in the visible range.

Assuming that the transitions are of electric dipole nature, the off-diagonal elements derived from first order time-dependent perturbation theory are given by

\[
\varepsilon_1 = \frac{2\pi Ne^2}{m} \sum_{i=a,d} \sum_{\pm} (\pm) f_{ix} \\
\times \frac{\sigma(\sigma_i^2 - \sigma^2 - \Gamma_i^2) + j\Gamma_i(\sigma_i^2 + \sigma^2 + \Gamma_i^2)}{\sigma_i^2(\sigma_i^2 - \sigma^2 + \Gamma_i^2)^2 + 4\sigma^2 \sigma_i^2 \Gamma_i^2}
\]

The inner sum is over the right – and left – hand circular polarized light, whereas the outer is over the optical transitions in the tetrahedral and octahedral sublattices. The
Theoretical calculation of Faraday rotation

prefactor (±) denotes a subtraction. The \( \sigma_+ \) and \( \sigma_- \) represent the resonance energy for right and left-hand circular polarized light, respectively. Similarly, \( f_+ \) and \( f_- \) are the respective oscillator strengths, while \( \Gamma_i \) is the half-linewidth of the transition.

Furthermore, \( e \) and \( m \) are the electron charge and mass, respectively, whereas \( N \) is the active ion density.

To first order, it is reasonable to assume that \( N \) is directly proportional to the bismuth content \( x \). This assumption has also been confirmed by experiments.\(^{166}\) Furthermore, it is known that the strong enhancement of Faraday rotation is caused by iron-pair transitions, involving both octahedral and tetrahedral transitions simultaneously. Therefore, iron dilution of either sublattice results in a reduction of the active ion density. For these reasons it is proposed that the active ion density be written as

\[
N = N_0(1-u_d/3)(1-u_a/2)x \quad \text{5.1.4}
\]

\( N_0 \) is a constant, and may be expected to be 1/3 of the density of rare-earth ions on the dodecahedral site, i.e., \( 1.3 \times 10^{22} \text{ cm}^{-3}/3 \). When \( x=3 \), this implies that the dodecahedral site is fully occupied by bismuth.

The oscillator strength for right- and left-hand circular polarized light is given by

\[
f_{iz} = \frac{m\sigma_{iz}}{2\hbar}\left|\langle g_i | X | e_{iz} \rangle \right|^2, \quad \text{5.1.5}
\]

where \( h \) is Planck’s constant, \( X \) is the electric dipole operator, and \( |g_i>, |e_{iz}>, \) are the wave function of the ground state and excited state, respectively. For the present case where \( \sigma_{iz} = \sigma_i \pm \Delta_i \), we obtain from Eq. (5),

\[
f_{iz} = \frac{f_i}{2\sigma_i}(\sigma_i \pm \Delta_i), \quad \text{5.1.6}
\]

where \( f_i \) is an effective oscillator strength. This expression is based on neglecting the difference between \( |e_{iz}>, \) and \( |e_i> \).
Theoretical calculation of Faraday rotation

In order to fully predict the Faraday spectra, one needs detailed knowledge about the quantum mechanical oscillator strengths. However, this is not easily accessible with so many ions involved, and they will be instead treated as adjustable parameters in comparison with experimental data. With Eq. (5.1.6) inserted in Eqs. (5.1.2) and (5.1.3), one obtains

\[
\Theta_F = \frac{\pi e^2 \sigma^2}{nmc} \sum_{i=a,d} N f_i \left\{ \frac{(\sigma_i + \Delta_i)^2 - \sigma^2 - \Gamma_i^2}{[(\sigma_i + \Delta_i)^2 - \sigma^2 + \Gamma_i^2]^2 + 4\sigma^2\Gamma_i^2} - \frac{(\sigma_i - \Delta_i)^2 - \sigma^2 - \Gamma_i^2}{[(\sigma_i - \Delta_i)^2 - \sigma^2 + \Gamma_i^2]^2 + 4\sigma^2\Gamma_i^2} \right\},
\]

which represents L.E. Helseth, et al’s model for the Faraday rotation \(^{164}\). The expression is the base of the interpretation of the Faraday rotation spectra.

5.2 Calculation of FR of ReBiIG crystal in the 1550 nm band

The principal source of the MO effect in Y\(_{3-x}\)Bi\(_x\)Fe\(_5\)O\(_{12}\) is the large splittings of the upper states of selected optical transitions. The optical transitions can be electric dipole transitions or magnetic dipole transitions. Two strong lines with opposite sign from Fe\(^{3+}\) in tetrahedral (d) and octahedral (a) sublattices are determined to be responsible for most of the MO enhancements in the wavelength range of 0.25 to 0.62 \(\mu\)m.\(^{165}\) These lines are associated with two spin orbits in Fe\(^{3+}\). These two spin orbits in Fe\(^{3+}\) are split by interaction with Bi\(^{3+}\) or rare-earth ions. In Helseth’s model to calculate the FR in the visible region, the contribution to the spin orbit splitting from bismuth substitution was considered, whereas the contributions from the rare-earth ions were ignored.\(^{164}\)
In the infrared region, it is convenient to divide the effect into two contributions, i.e., electric dipole transition contribution and magnetic dipole transition contribution. If the magnetic dipole contribution is dominated, the FR is independent of the wavelength. Early investigations showed that the FR was independent of wavelength at wavelength greater than 6 \( \mu \text{m} \) in \( \text{Tb}_3\text{Fe}_5\text{O}_{12} \), and greater than 4 \( \mu \text{m} \) in \( \text{Bi}_{0.24}\text{Ca}_{2.76}\text{Fe}_{3.62}\text{V}_{1.38}\text{O}_{12} \). Therefore it is reasonable to assume that the FR in the wavelength range of 1.3-1.6 \( \mu \text{m} \) is dominated by the electric dipole transitions. Helseth’s theoretical model will possibly be valid to interpret the behavior of the FR spectra of REBIG crystals near the wavelength of 1.55 \( \mu \text{m} \).

Helseth et al presented a simple model to interpret the measured FR spectra in the visible wavelength region. As discussed in previous section, the analysis was based on the molecular–orbital energy level diagram of iron ions in the tetrahedral and octahedral sites. The transitions associated with the two sites were assumed to follow the selection rules for electric dipole transitions. In order to calculate the MO response, they linked the FR with the microscopic parameters through the complex permittivity tensor, which had the form of Eq (5.1.1). Finally the FR expression of Eq. (5.1.7) was obtained:

In Eq. (5.1.7), the \( \sigma_i \) was the resonance energy for polarized light, \( f_i \) was the effective oscillator strengths, \( (2\Delta_i) \) was the energy difference between the two spin orbit splitting levels, and \( \Gamma_i \) was the half-line width of the transition. Furthermore, \( e \) and \( m \) were the electron charge and mass, respectively, whereas \( N \) was the active ion density.

The compositions of the grown \( (\text{HoBi})_3\text{Fe}_5\text{O}_{12} \) and \( (\text{YbBi})_3\text{Fe}_5\text{O}_{12} \) crystals were listed in Table 17. The Faraday rotations of these two crystals were measured at different wavelengths. Their specific FR loops at 1550 nm are shown in Figure 81 and Figure 82, respectively.
Theoretical calculation of Faraday rotation

Table 17 Chemical composition of the grown crystals.

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Yb</th>
<th>Ho</th>
<th>Bi</th>
<th>Fe</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>(YbBi)$_3$Fe$<em>5$O$</em>{12}$</td>
<td>2.33</td>
<td>0</td>
<td>0.67</td>
<td>5</td>
<td>12</td>
</tr>
<tr>
<td>(HoBi)$_3$Fe$<em>5$O$</em>{12}$</td>
<td>0</td>
<td>2.587</td>
<td>0.413</td>
<td>5</td>
<td>12</td>
</tr>
</tbody>
</table>

Taking into account the influence of the bismuth, the refractive index was calculated using the empirical relation:

\[ n = 2.174 + 0.0593\lambda^{-2} + (0.103 + 0.0371\lambda^{-2})x, \]

where \( x \) was the bismuth content in \( \text{RE}_3\text{Bi}_x\text{Fe}_5\text{O}_{12} \), \( \lambda \) was the wavelength in \( \mu \text{m} \).

Table 18 Parameters used in Eq. (5.1.7). \( \text{Nf}/\text{x} \) is calculated in \( \text{[cm}^{-3}\text{]} \), whereas \( \Delta_i, \Sigma_i, \) and \( \Gamma_i \) are sample-independent and given in \( \text{[eV]} \).

<table>
<thead>
<tr>
<th>Site</th>
<th>( \Delta_i )</th>
<th>( \Sigma_i )</th>
<th>( \Gamma_i )</th>
<th>( \text{Nf}/\text{x} ) ( (\text{YbBi})_3\text{Fe}<em>5\text{O}</em>{12} )</th>
<th>( \text{Nf}/\text{x} ) ( (\text{HoBi})_3\text{Fe}<em>5\text{O}</em>{12} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.27</td>
<td>3.15</td>
<td>0.47</td>
<td>4.8805\times10^{21}</td>
<td>-4.8199\times10^{23}</td>
</tr>
<tr>
<td>d</td>
<td>0.11</td>
<td>2.51</td>
<td>0.38</td>
<td>-1.2682\times10^{23}</td>
<td>3.1353\times10^{23}</td>
</tr>
</tbody>
</table>

Figure 81 Specific FR loop of \( (\text{YbBi})_3\text{Fe}_5\text{O}_{12} \) at 1550 nm with a saturated FR=81.7°/mm.
In order to calculate the FR spectra, eight variables in Eq. (5.1.7) are needed, i.e. $\Delta_i, \sigma_i, \Gamma_i$, and $N_f$ ( $i = a, d$). In the model presented by Helseth et al, the spin orbit splitting ($2\Delta_i$) are associated with the tetrahedral (d) and octahedral (a) sites. $N = N_o x$ is the density of transition centers, depends on the bismuth content ($x$), and $N_o$ is constant for the Re$_{3-x}$Bi$_x$Fe$_5$O$_{12}$ crystals. The product ($N_f/x$) is adjusted to any substitutions and transitions. All these parameters are not easy to access and are adjustable in Helseth’s model. Finally, Helseth et al chose the parameters $\Delta_i, \sigma_i$, and $\Gamma_i$ as sample-independent, and ($N_f/x$) as free parameters. We used the values for $\Delta_i, \sigma_i$, and $\Gamma_i$ suggested by Helseth et al. The ($N_f/x$) parameters were calculated by using the specific Faraday rotations at two different wavelengths and taken as constant for calculation of FR in samples at other wavelengths or with different bismuth content. These parameters are listed in Table 18. In Table 17, there is a big difference in the ($N_f/x$) value between (HoBi)$_3$Fe$_5$O$_{12}$ and (YbBi)$_3$Fe$_5$O$_{12}$ crystals. This is possibly relevant to the different contribution to FR from Ho and Yb. Although the contributions from rare-earth ions are not included in Helseth’s model, ($N_f/x$) parameters are determined from the
Theoretical calculation of Faraday rotation

Experimental specific Faraday rotations at two different wavelengths and possibly include the contributions from rare-earth ions to some extent.

There are two approaches to solve the contribution to the Faraday rotation (FR) from rare-earth ions and bismuth ions. One is to compare the FR in different rare-earth garnets using the hypothesis where the contribution from Fe$^{3+}$ sub-lattices is the same in all heavy rare-earth garnets and this contribution is considered to have the same value as measured in Y$_3$Fe$_5$O$_{12}$ (YIG). Using this approach, the contribution to FR from rare-earth ions and bismuth ions at a definite wavelength can be calculated by comparing the values of FR in REIG or REBIG and YIG crystals. However, it is difficult to predict the FR at different wavelengths. The other approach is to attribute the large increase of the FR in rare-earth ions substituted Y$_3$Fe$_5$O$_{12}$ to the substituted ions’ influence on the Fe(a)-Fe(d) super-exchange coupling and spin-orbit interaction. The intense electric dipole transitions between 4f and 5d levels of the rare-earth ions, and the charge-transfer transitions from oxygen to rare-earth ions, which both correspond to the ultra-violet spectral band, substantially affect the MO properties of a number of rare-earth iron garnets in both the infrared and the visible regions. The influence of Bi$^{3+}$ ions on the MO properties in the visible band was included in the effects of two spin orbits splitting in Fe$^{3+}$ by interaction with Bi$^{3+}$ ions, as described in Helseth’s model, and the contributions from the rare-earth ions were ignored.

The contributions from Ho and Yb can be estimated by the first approach. For example, at 1.06 µm, FR(Ho$_3$Fe$_5$O$_{12}$)=13.5°/mm, FR(Y$_3$Fe$_5$O$_{12}$) = 28°/mm, FR(Yb$_3$Fe$_5$O$_{12}$) = 1.2°/mm, FR(Ho) = [FR(Ho$_3$Fe$_5$O$_{12}$) - FR(Y$_3$Fe$_5$O$_{12}$)]/3 = -4.8°/mm, FR(Yb) = [FR(Yb$_3$Fe$_5$O$_{12}$) -FR(Y$_3$Fe$_5$O$_{12}$)]/3= -8.9°/mm. It is quite possible that the big difference in FR(Ho) and FR(Yb) causes the big difference in the (Nf/x) value between (HoBi)$_3$Fe$_5$O$_{12}$ and (YbBi)$_3$Fe$_5$O$_{12}$ crystals.
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Based on the parameters listed in Table 17, the FR spectra were calculated by Eq. (5.2.3) and Eq. (5.2.4). Figure 83 and Figure 84 show the comparison of the experimental values and the theoretical values of the FR in the (HoBi)\textsubscript{3}Fe\textsubscript{5}O\textsubscript{12} and (YbBi)\textsubscript{3}Fe\textsubscript{5}O\textsubscript{12} crystals, respectively. In these two figures, solid lines represent the theoretical calculation according to Eq.(5.2.3). The scattered points are the experimental data, the dashed and dotted lines represent the contribution from the tetrahedral and octahedral transitions, respectively. The net FR comes from the difference between the contributions from the tetrahedral and octahedral transitions. For these two samples, their specific FR decreased with the wavelength. The predicted FR accored with those measured. These results suggest that the assumption is correct that the FR in the wavelength region of 1.3-1.6 \(\mu\)m originates mainly from the electric dipole transitions.

Figure 83 Specific FR spectra for (YbBi)\textsubscript{3}Fe\textsubscript{5}O\textsubscript{12} crystal. The solid line represents the theoretical calculation data based on specific FRs at 1.47 \(\mu\)m and 1.59 \(\mu\)m.
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Figure 84 Specific FR spectra for (HoBi)$_3$Fe$_5$O$_{12}$ crystal. The solid line represents the theoretical calculation data based on specific FRs at 1.51 $\mu$m and 1.59 $\mu$m.

Figure 85 Specific FR spectra for (YybBi)$_3$Fe$_5$O$_{12}$ crystal. The solid line represents the theoretical calculation data. The scattered points represent the experimental data from ref. [171].
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In order to further confirm Helseth’s model in the 1.55 μm band, the FR spectra in Y_{2.289}Yb_{0.246}Bi_{0.465}Fe_{5}O_{12} crystal was also calculated. Two points, (θ_\text{F}=252.1^\circ/cm, at 1.0052 μm) and (θ_\text{F}=583.59^\circ/cm, at 1.4081 μm), were taken from reference 171 to calculate the (Nf/x). The values of FR at other wavelengths in Y_{2.289}Yb_{0.246}Bi_{0.465}Fe_{5}O_{12} crystal were calculated using Eq. (5.2.3). The calculated FR at different wavelengths also agreed with the experimental data in reference [171] as shown in Figure 85.

According to Eq. (5.2.3), there is a linear relationship between FR and x. In order to prove the linear relationship, garnet crystal with different Bi content (x) are needed. In reference 172, Tb_{3-x}Bi_{x}Fe_{5}O_{12} crystals (x=0, 0.15, 0.29, 0.35, 0.51, 0.84, 1.3) were reported. The sample with x=0.84 was selected and two points, (θ_\text{F}=-1239.1^\circ/cm, at

![Figure 86 Specific FR of (TbBi)_3Fe_5O_{12} crystal as a function of bismuth content x at 1.55 μm. The solid line represents the calculation results. The scattered points represent the experimental results in reference 172.](image)
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1.4083 µm) and (θF = -1043.5°/cm, at 1.5132 µm), were obtained to calculate the values of (Nfi/x). The linear relationship between θF and x in Tb3-xBixFe5O12 crystals was also calculated using Eq. (5.2.3). As shown in Figure 86, the calculated results agree with the experimental data. These results suggest that Eq. (5.2.3) can be used to predict the FR in a crystal at different wavelengths or with different Bi content only if two values of FR at two wavelengths are given.

In summary, in order to interpret the FR spectra of (HoBi)3Fe5O12, (YbBi)3Fe5O12, (YyBbBi)3Fe5O12, and (TbBi)3Fe5O12 crystals, Helseth’s model was used that was based on molecular-orbital levels of Fe3+ in tetrahedral and octahedral sites. It was assumed that the Faraday rotation (FR) in the wavelength range of 1.3-1.6 µm was still dominated by the electric dipole transitions. To some extent, the contributions from rare-earth and bismuth ions were included in spin orbit splittings in Fe3+. The experimental results agreed with the theoretical calculation results in the above-mentioned wavelength range. The FR in (HoBi)3Fe5O12, (YbBi)3Fe5O12, and (YyBbBi)3Fe5O12 crystals decreased with the wavelength. The linear relationship between the specific FR(θF) and Bi content (x) was calculated and confirmed by the experimental data in Tb3-xBixFe5O12 crystals.
6. CONCLUSION

With the development of optical communication technique, much interest is attracted onto the new magneto-optical (MO) crystals as Faraday rotators in isolators working in the 1550 nm wavelength band. In this study, the specific FR, saturation field, the stability of FR against wavelength and temperature, optical transmittance spectrum were investigated in REBiIG crystals (RE=Yb, Ho, Tb, (Ho+Yb), (Ce+Ho+Yb)). REBiIG crystals were grown by TSSG method. The new garnet substrate CLNGG crystal for MO film deposition by LPE method with 1 inch diameter was grown by CZ method. The morphology of these garnet crystals were studied. CLNGG crystal followed the morphology BFDH theory and the most important growth form of {211} appeared as growth facets on the bottom of the CLNGG boule. In contrast, the large flat facets of the grown REBiIG crystals were the second important growth form of {220} according to the XRD analysis. The growth parameters had influence on the MO properties of the grown crystals.

The specific FR and the saturation field in the REBiIG crystals decreased with the increases of the radius of rare-earth ions. The bigger rare-earth ions in the garnet structure cause fewer Bi$^{3+}$ incorporated and reduce the domain wall’s energy and thickness in the crystal. Bismuth addition enhances strongly the FR in REBiIG crystal. The difference between the experimental saturation field and the anisotropy field depends on the domain wall’s energy and thickness. Therefore, TbBiIG crystal had the lowest specific FR (300 o/cm) and saturation field (0.2 kG) due to largest radius of Tb$^{3+}$ among TbBiIG, HoBiIG, and YbBiIG crystals.
The specific FR, its stability against both wavelength and temperature, and the saturation field can be improved by doping more than one rare-earth element. The specific FR in HoYbBiIG crystal was higher than that in HoBiIG crystal but lower than that in YbBiIG crystal. The FR wavelength coefficient (FWC) of HoYbBiIG crystals was better than that of YbBiIG crystal but worse than that of HoBiIG crystals whereas the FR temperature coefficient of HoYbBiIG crystal was better than HoBiIG crystal but worse than that of YbBiIG crystal. HoYbBiIG crystal is a trade-off between HoBiIG crystal and YbBiIG crystal in MO properties. The possible explanation is that HoYbBiIG crystal is the solid solution of HoBiIG crystal and YbBiIG crystal, and that the MO properties of HoYbBiIG crystals is the combination of MO activities in both HoBiIG and YbBiIG crystals. This explanation is also supported by the experimental results from TbHoYbBiIG crystal. TbBiIG crystal had as low saturation field as 0.2kG. HoYbBiIG crystal had saturation field of 0.98 kG. After Tb was added, the TbHoYbBiIG crystal had lower saturation field than HoYbBiIG but higher than TbBiIG crystal. The assumption that solid solution demonstrates the combination of MO properties of two individual garnet crystals can also explain: FWC (HoYbBiIG) < FWC (TbHoYbBiIG) < FWC (TbBiIG).

Besides Bi\(^{3+}\) ions that enhance the MO properties in garnet crystals, Ce\(^{3+}\) ions in CeHoYbBiIG crystal brought in lower saturation field (0.76 kG) and higher specific FR (625°/cm) than HoYbBiIG (0.98 kG and 545°/cm). However, the stability of FR against both wavelength and temperature in CeHoYbBiIG was a little bit worse than HoYbBiIG. The mechanism behind this is unknown yet.

For Bi-substituted iron garnet crystal, Helseth’s model in the visible wavelength band was applied to interpret the FR spectra in the 1.55 \(\mu\)m band. It was assumed that FR in the wavelength range of 1.3-1.6 \(\mu\)m was still dominated by the electric dipole
transitions. To some extent, the contributions from rare-earth and bismuth ions were included in spin orbit splitting in Fe$^{3+}$. The variation of FR with wavelength for (HoBi)$_3$Fe$_5$O$_{12}$, (YbBi)$_3$Fe$_5$O$_{12}$ and (YYbBi)$_3$Fe$_5$O$_{12}$ crystals agreed with the theoretical calculation results. The linear relationship between the specific FR and Bi content was also calculated and confirmed by the experimental data in Tb$_{3-x}$Bi$_{x}$Fe$_5$O$_{12}$ crystals.

The transmittance spectrum of REBiIG crystals (RE=Yb, Ho, Tb, or/and Ce) were measured and compared. The absorption peaks in the 1.55 $\mu$m band are related to 4f transition for the rare-earth ions and shifted in positions by the crystalline field of dodecahedral symmetry. The transmittance spectrum of more than one rare-earth element doped garnet crystals contain all the features in the spectrum of single rare-earth element doped garnet crystals.
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