Solid State Communications 241 (2016) 38–42

Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

Fabrication and characterization of TGG crystals containing paramagnetic rare-earth ions

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ARTICLE INFO

Article history:
Received 21 March 2016
Received in revised form
7 May 2016
Accepted 13 May 2016
By J. Fontcuberta
Available online 19 May 2016

Keywords:
A. Magnetic materials
A. Optical materials
C. Crystal growth
D. Magnetic properties

ABSTRACT

Highly transparent $Tb_{3-x}Re_xGa_5O_{12}$ (RE=Ce, Pr and Nd) single crystals were grown by the Czochralski (Cz) method. The optical and magneto-optical properties of $Tb_{3-x}Re_xGa_5O_{12}$ were analyzed in detailed. $Tb_{3-x}Re_xGa_5O_{12}$ exhibited very high transmittance in the visible-near infrared region (VIS–NIR). The absorption coefficient and Faraday rotation spectrum were investigated at VIS–NIR region at room temperature. The remarkable higher Verdet constants (V) and figure of merit showed superior characteristics of $Tb_{3-x}Re_xGa_5O_{12}$ compared to that of $Tb_3Ga_5O_{12}$ (TGG). We also investigated the thermal conductivity and laser induced damage threshold (LIDT) of the crystals. The superior performance of the materials indicate that $Tb_{3-x}Re_xGa_5O_{12}$ have great potential to meet the increasing demand for magneto-optical devices in the VIS–NIR region.

1. Introduction

Faraday isolators (FIs) are the important parts of currently used high-power-laser machinery and advanced optical communications, guarantying a unidirectional light propagation in the laser system [1,2]. Magneto-optical materials used in FIs are mainly crystals or ceramics with high Verdet constants (*V*), high thermal strength for high average power, low absorption coefficient, high damage threshold and size scalability [3,4]. For long distance communications, yttrium iron garnet (YIG) with high transparency in the infrared region is employed and it is characterized by a very large rotation angle of the polarization plane (about 220°/cm at 1300 nm [5,6]). However, the poor transparency of YIG below the 1100 nm leads to the implementation of TGG in FIs working at shorter wavelengths [7,8]. Although TGG is a material for Faraday devices for continuous high-average-power laser system, the low *V* (134 rad T^{-1} m^{-1} at 632.8 nm [9–12]) compared to $Tb_3Al_5O_{12}$ (TAG) means that a higher magnetic field intensity or larger size of the crystal can gain enough rotational angle to eliminate the back-reflection [13], increasing the instability of high power laser systems caused by decreasing of isolation ratio and the thermal birefringence effect.

TGG presents favorable growth characteristics in comparison with TAG, so the focus of attention was shifted to the rare-earth (Re) paramagnetic ions, mainly Ce, Pr, Nd and Ho doped TGG crystals or ceramics. The current investigation centers on producing larger Faraday effect based on TGG single crystal owing to its congruently nature. Some researchers have found that the quantum based super-exchange interaction between Tb^{3+} and other paramagnetic Re^{3+} ions can occur, greatly enhancing the Faraday effect. Ce^{3+} doped TAG ceramic has a *V* of 199.55 rad T^{-1} m^{-1} at 632.8 nm, 16% larger than that of TAG [14]. $\{Tb_3\}[Sc_{1.95}Lu_{0.05}](Al_3)O_{12}$ (TSLAG) single crystal having an increment of 20% of *V* compared to TGG dues to the doping of Sc^{3+}, Lu^{3+}, Al^{3+} ions [15,16]. Some fluoride single crystals with high concentration of efficient paramagnetic Re^{3+} ions in ultraviolet–visible region shows excellent magneto-optical properties [17,18]. The Ce^{3+}, Pr^{3+} and Nd^{3+}-doped TGG [19–21] possess 20–30% larger Verdet constant as compared to that of TGG in our previous study.

In searching for new FR materials, we basically fabricated the paramagnetic Re^{3+} ions doped TGG single crystal in this study and we hope to provide a garnet single crystal with large Faraday effect and high light transmission factor, finally we can potentially use this crystal for FIs in the VIS–NIR region.

2. Experimental details

High-purity Tb_4O_7, CeO_2, Nd_2O_3, Pr_6O_{11}, Ga_2O_3 (5N) chemicals were mixed according to the designed $Tb_{3-x}Re_xGa_5O_{12}$, then the mixture of powders (1–2% excess of Ga_2O_3) was pressed to sheet

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http://dx.doi.org/10.1016/j.ssc.2016.05.007

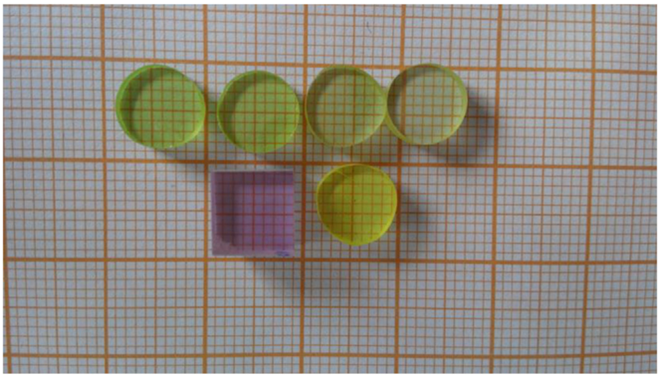

Fig. 1. (Color online) The picture of as-grown $Tb_{3-x}Re_xGa_5O_{12}$ crystals by the Cz method. The above are the 5, 3, 2, 1%Pr doping TGG and the bottom are 5%Nd, 1%Ce doping TGG crystals from the left to right.

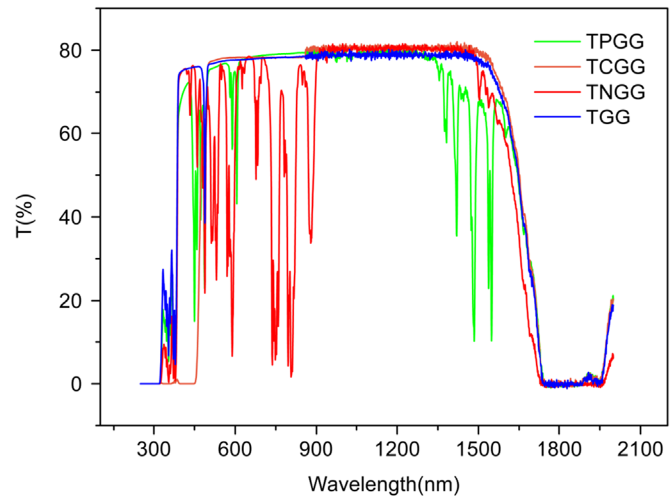

Fig. 2. (Color online) Transmittance of $Tb_{3-x}Re_xGa_5O_{12}$ single crystals. TPGG refers to the $Tb_{3-x}Pr_xGa_5O_{12}$, TCGG refers to the $Tb_{3-x}Ce_xGa_5O_{12}$ and TNGG refers to $Tb_{3-x}Nd_xGa_5O_{12}$.

and sintered for 12 h at 1200–1400 °C. Such formed materials were crushed, re-mixed and sintered again at 1200–1400 °C or 24 h. Finally, we obtained polycrystalline materials. The crystals were grown by the Cz method in an iridium crucible with radio frequency (RF) induction heating. After that the crystals growth was carried out under high purity N_2 (99.99%) atmosphere. They were grown in $<111>$ orientation at a pulling rate of 1.0 mm/h and a rotating rate of 10–15 rpm. Finally, $Tb_{3-x}Re_xGa_5O_{12}$ crystals were obtained.

Double-side polished specimens to the size of Φ8*5 mm^3, as shown in Fig. 1. All the samples were scattering free, indicating a high crystalline quality. The transmission spectra were measured using a Perkin-Elmer Lambda 900 UV–vis–NIR spectrophotometer (United States) in transmission mode over the wavelength range of 300 nm–2000 nm. The X-ray powder diffraction measurement was carried out by the Ultima IV (Rigaku, Japan). The Verdet constants of Re:TGG and TGG single crystals were measured under the same conditions at room temperature for several wavelengths using a magnetic system made of Nd–Fe–B magnets with maximum field of 1.2 T on the axis. The crystals were arranged inside the magnetic system that was placed between two crossed polarizers. By the angle of rotation of the second polarizer after the crystal, we measured the angle of Faraday rotation of the plane of polarization to an accuracy of ± 2 min. Knowing the magnetic field distribution in the system, crystal position and its length, we determined the Verdet constant at each of the considered wavelengths. Commercial TGG crystal (CASTECH, Φ8 mm × 10 mm, [111]) with best quality utilized for the calibration. All the measurements were performed at room temperature.

3. Results and discussion

3.1. Structural analysis

The as-grown single crystals were ground into powder and X-ray powder diffraction pattern was compared with the JCPDS standard card, the XRD of doped crystals agree well with the standard patterns of TGG crystal(JCPDS 88-0575) without any impurities peaks. The result indicates that the Re^{3+} ion did not influence the crystals structure and the unit-cell parameters were determined with the help of X Pert High Score Plus computer program. Since the Inductively Coupled Plasmas Atomic analysis (ICP-AES) determines the concentration of the whole face of the samples, it is given an average concentration of samples. Therefore, samples were cut from as-grown crystals along the top to the bottom. The formula of the segregation coefficient is as follows: $k_0 = C_s/C_l$, where C_s is the doped-ion concentration in the crystals and C_l is the doped-ion concentration in the melt. So the segregation coefficients of Pr^{3+}, Ce^{3+} and Nd^{3+} in $Tb_{3-x}Re_xGa_5O_{12}$ crystals were about 0.59, 0.41 and 0.45, respectively.

3.2. Transmittance spectrum

Transmittance of $Tb_{3-x}Re_xGa_5O_{12}$ crystals are shown in Fig. 2. TCGG exhibits extended transparency in the VIS–NIR region (500–1500 nm), the absorption band around 400–500 nm due to the Ce^{3+}:4f–5d$_1$ transition was so strong that the absorption of Tb^{3+}:$^7F_6$–$^5D_4$ was covered. TPGG are highly transparent in the 500–1350 nm region expect for some absorption bands below 600 nm.The optical transmittance of TNGG is beyond 80% in the 900–1500 nm region, even much higher than that of pure TGG. Therefore, the high transmittance indicates that the $Tb_{3-x}Re_xGa_5O_{12}$ single crystals in our work are suitable for application of Faraday rotator used in the important working wavelength around 850 nm, 1064 nm.

3.3. Magneto-optical characteristic

The FR of paramagnetic RE ions has been described by van Vleck–Hebb [22]. From quantum-mechanical considerations they deduced that the V constant dispersion is directly proportional to the magnetic susceptibility χ as follows:

$$V = \frac{4\pi^2\nu^2\chi}{g\mu_B ch}\sum ij\frac{Cij}{\nu^2 - \nu ij^2} \quad (1)$$

whereas ν is the frequency of the incident light, ν_{ij} is the transition frequency between electronic states, C_{ij} is the transition probability of the same, g is the Landé factor, μ_B is the Bohr magneton, c is the velocity of light, and h is the Planck constant.

The experimental data are described by a single electronic transition, and the Verdet constant dispersion is given as a function of the wavelength λ in simplified form as: $V = \frac{E}{\lambda^2 - \lambda_0^2}$, whereas E includes all the constant terms, and λ_0 is the transition wavelength, which is associated with the electronic transition of paramagnetic RE ions.

As is well known, Faraday rotation in a paramagnetic material is given by the equation $\theta = VHL$, where θ is the rotation angle, L is the length of the light path in a medium, H is the magnetic field applied along the light beam and V is the Verdet constant. Thus