Bridgman growth and magneto-optical properties of CeF$_3$ crystal as Faraday Rotator

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A B S T R A C T
In this work, CeF$_3$ crystal with maximum diameter of 35 mm was successfully grown with the Bridgman-Stockbarger (BS) method. The crystal diffraction peaks match well with the standard pattern of CeF$_3$ (PDF#01-099-0967), which proofs that obtained samples are of high purity. The transmittance of CeF$_3$ crystal is relatively high in the UV-NIR region and reach 92% in comparison with TGG crystal. The UV cut-off absorption edge of CeF$_3$ crystal is located at 270 nm contrary to 400 nm for TGG. The Verdet constant of CeF$_3$ crystal is largest at 450 nm wavelength and reach 247 rad/T m. The results show that CeF$_3$ possess better optical and magneto-optical properties than TGG. CeF$_3$ can be a potential candidate for Faraday Rotators used in the field of high-power lasers.

1. Introduction

In recent years, diode pumped solid state lasers (DPSSL) play an important role in military, processing, medical and scientific research applications [1–3]. Faraday Rotators (FR) as a key component of DPSSL can protect laser devices and laser amplifiers from backfire [4–6]. A traditional FR material, TGG crystal gained much attention in commercial applications due to its high Verdet constant, especially in the visible wavelength region (>395 nm) [7,8]. However, there are several disadvantages of TGG crystal that restricts its further utilization. The examples are: complex synthesis process, high cost, increasing absorption losses in the visible (VIS) range and a possession of absorption edge at 400 nm. TGG can neither be used at wavelengths beneath 400 nm nor at around 490 nm. Therefore, it is urgent to find a material that can replace TGG in aforementioned wavelength ranges.

It is well known that among the rare earths, ions such as, Ce$^{3+}$, Pr$^{3+}$, Dy$^{3+}$ and Tb$^{3+}$ have been pointed to possess the excellent MO properties [9,10] due to their 4f-5d transitions [11]. Ce$^{3+}$ is characterized by a full transparency in the VIS region compared to other mentioned RE$^{3+}$ [12], and has the highest concentration among RE$^{3+}$-fluorides [13]. A proven production technology is a significant advantage of the CeF$_3$ crystal over other novel magnetically activated media, since this material has long been used in scintillation detectors [14,15]. Compared with the TGG crystal, the CeF$_3$ has similar Verdet constant, lower absorption coefficient and wider transmission wavelength range [16]. Due to afore-mentioned advantages, CeF$_3$ could substitute TGG in Faraday Rotators.

The theory of the Faraday effect has been distinguished and calculated by Serber, including the effects of the components of magnetic moment [17]. It was the first time shown by Faraday Rotation that optical activity in material is induced by a magnetic field and revealed the nature of magnetic optical properties especially in regions of absorption [18]. The Verdet constant of CeF$_3$ crystal in the 450–1550 nm had been also measured in the previous works [19], but not for Faraday Rotation angle. At the same time, the optical Faraday Rotation has been investigated in the temperature range 8–300 K at 632.8 nm wavelength [20–22], missing the data over 800 nm, whereas the majority of the available high-power lasers process in this range.

In this work, the Bridgman growth of CeF$_3$ crystal was investigated. The dependence of the Faraday Rotation angle on visible to near-infrared whole wavelengths were systematically studied by using

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continuously changing magnetic field. Meanwhile, a huge potential for utilization of CeF$_3$ was predicted as a NIR high-power laser FR for a broad variety of wavelengths.

2. Experimental procedure

2.1. Processing of raw materials

The growth of high-quality CeF$_3$ crystal by the Bridgman method is reported using CeF$_3$ (99.999%) and PbF$_2$ (99.999%) powders as raw materials. Commercial CeF$_3$ raw material cannot be used directly for the growth due to the presence of moisture and oxides. To get rid of oxygen and water, CeF$_3$ raw material underwent an effective fluoridation treatment. At the same time, PbF$_2$ is used as an oxygen scavenger to eliminate residual oxygen during crystal growth. CeF$_3$ and PbF$_2$ powders were weighted on the basis of the certain proportion.

2.2. Preparation of precursor

A total of 400–500g of materials were charged in a columnar-shaped crucible, which was put into a quartz glass tube in a resistive heating furnace. A gaseous HF of high purity (4 N) was used as the gas source in the process. The starting materials were heated at 200–230 °C in dry HF gas flow for 6–7 h to eliminate the moisture absorbed. By this way, the moisture in the raw materials was thoroughly removed. As the fluoridation process was terminated, the HF gas flow was ceased and the furnace was cooled. Then the vacuum was used for driving away residual HF gas and the exhaust gas was absorbed by Na$_2$CO$_3$ solution.

2.3. Crystal growth

The feed materials for crystal growth were prepared of CeF$_3$ and PbF$_2$ powders. They were mixed and loaded into the graphite crucible located vertically in the furnace. To avoid the oxidation of the melt, the assembled crucible was sealed immediately. By means of sealing the graphite crucible firmly, it was possible to grow the fluoride crystal in a nonvacuum atmosphere. Whereas, in normal atmosphere, there was always a volume of air that remained in the crucible when it was sealed. When the growth process finished, the furnace was cooled down slowly to a room temperature and then as-grown crystal was moved to the annealing furnace.

2.4. Characterisations

The X-ray diffraction analysis of the grown crystal was performed with the Ultima IV (Rigaku, Japan). The powder diffraction measurements of CeF$_3$ grounded crystal as well as a-axis and c-axis samples were done using Bruker D8 diffractometer with Cu Kα radiation (λ = 1.54056 Å) at a scan step of 0.02°. The optical transmission spectra of the CeF$_3$ crystal partII and partIII were measured by VARIAN CARY 5000 UV-VIS-NIR Spectrometer at room temperature. We measured the dependence of the Verdet constant on wavelength in the 450–1310 nm range using different wavelengths (450 nm, 532 nm, 633 nm, 810 nm, 980 nm, 1075 nm, 1310 nm) at room temperature. The Faraday Rotation angle in function of magnetic field strength was measured using homemade system provided by University of Electronic Science and Technology of China.

3. Results and discussion

As shown in Fig. 1(a), it is observed that the crystal consist three parts, the polycrystalline part I resulted from its weak bending force, the transparent part II and nontransparent part III caused by the oxygen impurities. According to the cleavage plane of cerium fluoride crystal perpendicular to the optical axis, the (001)-oriented sample with 20*20*20 mm dimensions was cut out from the part II, and both sides were further polished as shown in Fig. 1 (b). Similarly, the (100)-oriented and (001)-oriented crystals can be obtained by the above processing.

The phases present in the ingot were analyzed using X-ray diffraction. The cuboid sample was collected from the part II of the ingot and
Fig. 3. Transmission spectra of CeF₃ crystals in different positions in comparison with the reference crystal TGG.

Fine powders from grounding of the ingot. Fig. 2 shows the obtained XRD patterns. The lattice constants of the sample (from the part II) were determined to be a = b = 7.112 Å, c = 7.279 Å using Jade software. XRD patterns of (100) and (001)-orientated samples match well with the standard pattern (PDF#01-089-0967), confirming the sample is a single-phase hexagonal system with a space group P3(−)c1 and six molecules per unit cell [23].

In order to evaluate the quality for different parts of the ingot and to compare the corresponding performance with TGG, the parts II and III (the two parts cut from CeF₃ ingot) and a TGG sample were selected for characterization. Fig. 3 shows the corresponding transmission spectra in the UV-NIR region. It can be observed that two CeF₃ samples are completely transparent in the UV-NIR region and possess short-wave absorption cut-off edges at 270 nm. The part II has a higher transmittance than part III for wavelengths higher than 336 nm. An average transmission, ranging between 86% and 92%, may be attributed to the presence of scattering centers in the bulk of the CeF₃ crystal and the quality of the surface polishing.

The average transmittance of the part III above 350 nm equals 80% without any absorption band. This may be caused by segregation of impurities during the growth process. Such segregation is the main reason of the transmittance gradient along different parts of the crystal. The impurities were gradually accumulated as crystallization front traversed the crucible during growth. This is the reason why the transmittance of part III is worse than part II. For TGG crystal, a strong absorption peak related to (⁷F₆→⁵D₄ transition of Tb³⁺ ions) can be observed at 488 nm, which severely restricts the application of TGG as FRs in the visible region. In this sense, CeF₃ is a good replacement for TGG in application as FR.

To evaluate the rotation efficiency of CeF₃ crystal, the magneto-optical properties of CeF₃ and TGG crystal were characterized. The crystal structures of CeF₃ and NdF₃ has been proved to be a hexagonal tisonite-type structure (space group P-3c1, Z = 6), whose third-order optical axis coincides with the crystallographic c-axis. All the investigations were performed for the samples cut perpendicular to the optical axis because only on this account the influence of the natural birefringence on the Faraday Rotation measurement results [10] can be excluded. Fig. 4a and b shows the magnetic field strength dependences of Faraday Rotation angle in the external magnetic field for the CeF₃ crystal oriented along c-axis and the TGG one, respectively. It can be observed that for a given wavelength, the plots of Faraday Rotation angle vs the magnetic field of both CeF₃ crystal and TGG crystals have a

Table 1

<table>
<thead>
<tr>
<th>λ(nm)</th>
<th>450</th>
<th>532</th>
<th>633</th>
<th>810</th>
<th>980</th>
<th>1075</th>
<th>1310</th>
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<tr>
<td>V(Ω⁻¹cm⁻¹)</td>
<td>247</td>
<td>180</td>
<td>129</td>
<td>63</td>
<td>44</td>
<td>33</td>
<td>10</td>
</tr>
<tr>
<td>V(Ω⁻¹cm⁻¹)</td>
<td>408</td>
<td>205</td>
<td>137</td>
<td>75</td>
<td>47</td>
<td>35</td>
<td>14</td>
</tr>
</tbody>
</table>

Fig. 5. Figure of Verdet Constant Dispersion as a function of the wavelength for CeF₃ in comparison with TGG.

Fig. 4. Faraday Rotation angle as a function of the magnetic field strength for (a)CeF₃ and (b) TGG.
symmetry center with point (0, 0). The absolute values of Faraday Rotation angle increase with increase of magnetic field, according to the Faraday equation $\beta = VBL$, where $V$ is Verdet constant, $B$ represents the magnetic field strength and $L$ stands for the crystal length. The slope of the fitted curve for both CeF$_3$ and TGG sample increase with decrease of a wavelength.(as shown in Table 1) This behavior is consistent with the previous data [13]. For CeF$_3$ Verdet constant value at 450 nm, equals 247 rad/T/m. The value of TGG Verdet constant at 450 nm is 408 rad/T m.

The measured values are used to find the dependence of the Verdet constant of the CeF$_3$ crystal on the radiation wavelength. The Verdet constant fitting values as a function of wavelength are depicted in Fig. 5. In the approximation of the single-oscillator model of the permitted electronic $4f \rightarrow 5d$ transition in the Ce$^{3+}$ ions, the spectral $V$ dependence can be described by the spectral one of “paramagnetic” $\epsilon$-term of FR [24, 25].

$$V = C\alpha^2/\omega_0^2 - \alpha^2 = A/\lambda^2 - \lambda_0^2$$

where $\lambda_0$ is relevant to the $4f \rightarrow 5d$ transition wavelength of the Re$^{3+}$ ions, and the factor $E$ is in direct proportion to the concentration of magnetic ions per volume, the Lande splitting factor, and the transition probability. The parameters $A$ and $\lambda_0$ of CeF$_3$ and TGG crystals were found by the least squares method to be $A = 4.4\times10^7$ rad nm$^2$/m(T m) and $\lambda_0 = 159$ nm, $A = 5.1\times10^7$ rad nm$^2$/m(T m) and $\lambda_0 = 283$ nm, respectively.

4. Conclusions

The CeF$_3$ crystal was grown successfully by the Vertical Bridgman process. Commercial CeF$_3$ raw materials were treated in an electric resistive furnace to remove moisture and residual oxides. The CeF$_3$ single crystal exhibit transmittance as high as 92% without any absorption band compared to the traditional FR material TGG. In addition, the CeF$_3$ single crystal can complement the falling magneto-optical properties at 450 nm, and its Verdet constant can reach 247 rad/T m at 450 nm. The results show that CeF$_3$ crystal is a promising magneto-optical material in the VIS-NIR range. Further experiments are needed to prove its usability as the optical isolator for the strong laser field.

Declaration of competing interest

The authors declare that they have no known competing interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Huifang Li: Conceptualization, Methodology, Investigation, Data curation, Writing - original draft, Writing - review & editing. Jingya Wang: Conceptualization, Methodology, Formal analysis. Junfeng Chen: Resources, Investigation. Yun Dai: Investigation. Liangbi Su: Supervision, Project administration. Xiang Li: Conceptualization, Writing - review & editing. A.M. Kalashnikova: Supervision. Anhua Wu: Conceptualization, Methodology, Supervision, Funding acquisition, Writing - review & editing, Project administration.

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