氏　　　名	LI ENHAO
学位（専攻分野）	博士（学術）
学 位 記 番 号	総研大甲第 2444 号
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学 位 論 文 題 目	Development of high-performance mid-infrared laser sources for isotope detection applications
論 文 審 査 委 員	主　査　　後藤　基志 核融合科学コース　准教授 安原　亮 核融合科学コース　教授 村上　泉 核融合科学コース　教授 時田　茂樹 京都大学　化学研究所　教授 戸倉川　正樹 電気通信大学 レーザー新世代研究センター　准教授

Summary of Doctoral Thesis

Name in Full : LI ENHAO

Title : Development of high-performance mid-infrared laser sources for isotope detection applications

Isotope detection plays a vital role in the development of advanced diagnostics and monitoring systems for nuclear fusion reactors, providing real-time feedback on plasma parameters, isotopic changes, and potential anomalies, which could help to ensure safe and efficient operation. Particularly for a D-T fusion reactor, monitoring the tritium fuel cycle is essential because the tritium is naturally scarce and often exists as tritiated water (HTO) in the cooling system due to unpredictable permeation. Therefore, from the perspective of recycling valuable fusion fuel and managing radioactive contaminants, it is indispensable to continuously monitor the water isotopes in nuclear fusion environments to ensure a safe and steady operation.

Two commonly used methods for isotope detection are mass spectrometry (MS) and liquid scintillation counter (LSC). Both of these techniques can determine the isotopic composition of samples with high sensitivity and accuracy. However, typical MS or LSC facilities are huge, complex, and costly. Additionally, they usually necessitate complicated sample preparation processes and are difficult to measure gaseous samples directly, thus making them unavailable for continuous, real-time, and in-situ measurements.

The optical method using laser absorption spectroscopy (LAS) is an alternative approach for isotope detection that enables real-time, in-situ measurements while also providing high detection sensitivity. In comparison, an LAS device can be designed to be portable and compact at a lower cost. This portability makes them advantageous for on-site applications. An optical measurement system generally comprises a laser source, a sample chamber, and a detector, in which the laser source is the core component that determines the detection sensitivity of the entire system. Regarding laser wavelength, the 3–5 μm mid-infrared band is the most desired spectral region for water isotope detection because it covers the strongest stretching vibrational absorption peaks of water isotope molecules. The stretching vibrational absorption spectrum typically consists of multiple peaks with fine absorption lines, and the presence of isotopes in a molecule can cause shifts in the positions of absorption peaks, such that each isotope has its distinctive absorption spectrum. These characteristics require the laser source to be widely tunable with a narrow spectral linewidth. Additionally, in scenarios where weakly absorbing molecules or trace-level samples need to be measured with high detection sensitivity, high laser power is required to increase the signal intensity, hence

achieving sufficient signal-to-noise ratios. Therefore, the general requirements for the laser source to realize high-sensitivity detection of water isotopes should be high output power, narrow spectral linewidth, and widely tunable in the 3–5 μm spectral region. The main objective of my Ph.D. project is to develop such high-performance mid-infrared laser sources to advance the development of optical isotope detection systems.

This thesis presents several state-of-the-art mid-infrared lasers developed in our lab. We focus on the exploration of experimental techniques to develop laser systems capable of combining high power, narrow linewidth, and widely tunable abilities in one, which is rather difficult to achieve for conventional lasers. The details of my research are summarized as follows:

1. 3-μm laser development based on Er:YAP crystal

3-μm lasers are ideally suited for water isotope detection because the 3-μm band exactly corresponds to the strongest stretching vibrational absorption peaks of the hydroxyl group. However, obtaining a high-power 3-μm laser is not easy due to the inherently large quantum defect. Our previous work has identified the Er:YAP crystal as a potential medium to break the power limit of the current 3-μm laser. Our previous study demonstrated 7-W output power from a very simple and compact Er:YAP laser design. However, further power scaling was limited by the severe thermal effects in the Er:YAP crystal, including thermal lensing and thermally induced fracture. This indicates that improving thermal management is essential to break the power bottleneck.

Cryogenically cooling the gain medium is the most straightforward and effective means of improving thermal management, as the thermal conductivity of the material increases while the thermal expansion coefficient decreases significantly at low temperatures. However, the laser performance of Er:YAP under cryogenic cooling conditions is not yet known. In this work, I aim to study the spectroscopic and laser properties of a 5at.% Er:YAP crystal at cooling temperatures ranging from 77–290 K.

The spectroscopic property, especially the fluorescence lifetime, of the Er:YAP crystal was first investigated at different cooling temperatures. The crystal was excited by a quasi-CW modulated 976-nm LD with a 100 μs pulse width, and two high-speed photodetectors working at 1.5 μm and 3 μm were used to detect the fluorescence decay signals. It was found that the fluorescence lifetime of the upper laser level gradually increased from 0.94 ms to 1.34 ms, whereas the lifetime of the lower laser level decreased from 6.27 ms to 4.61 ms when cooling the crystal from 290 K to 77 K. These results indicate that low operating temperature is beneficial for population inversion and hence 3-μm laser transition.

Laser experiments on the cryogenic Er:YAP crystal were conducted using the setup shown in Fig. 1(a). The best laser performance was achieved when the output coupling transmission T = 2.5% (see Fig. 1(b)). The laser slope efficiency increased by 1.4 times, from 14% to 20%, as the crystal was cooled from 290 K to 77 K. At 7.3-W absorbed pump power, a maximum output power of 1.2 W was achieved without thermal rollover, indicating that further scaling of the output power to multi-watt levels is possible. These results proved that cryogenically cooling the Er:YAP can significantly improve its laser performance and is a promising approach to breaking the current power record of 3-μm lasers. More importantly, the measured laser wavelengths showed a red shift with increasing laser power, which can be explained by the reabsorption effect from the lower laser level. Compared with the room-temperature operation (2920 nm), the cryogenic Er:YAP emitted at a much shorter wavelength (2798 nm), and the laser spectra remained narrow linewidths of < 2 nm. These results indicate that the Er:YAP laser is discretely tunable by controlling the cooling temperature or the laser power.

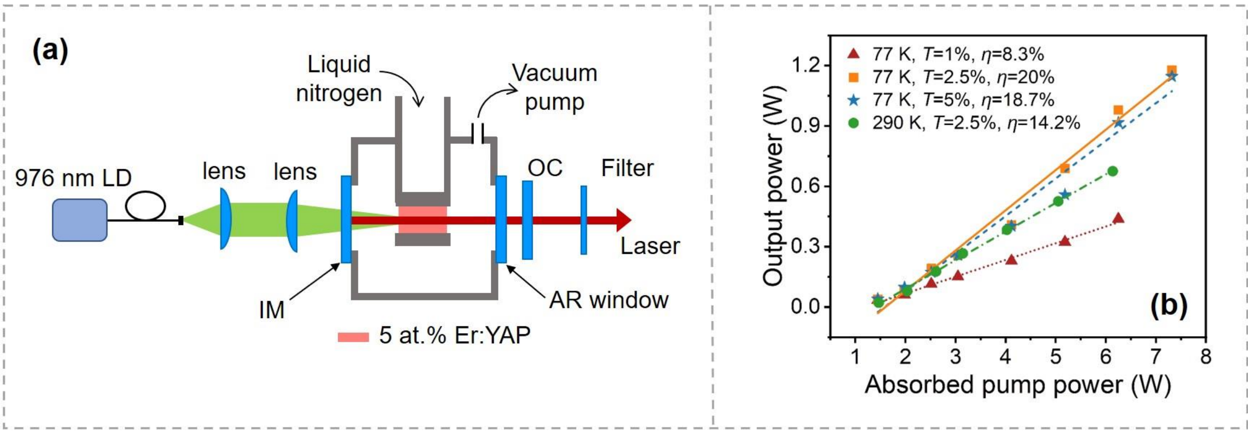

Fig. 1. (a) Schematic diagram of the cryogenic Er:YAP laser. (b) Er:YAP laser output power as a function of the absorbed pump power. [2]

In conclusion, I have demonstrated the spectroscopic properties and laser performance of a cryogenically cooled Er:YAP for the first time to my knowledge. Laser experiments showed a 1.4-times increase in laser slope efficiency by cooling the crystal from room temperature to 77 K. The possibility for further power scaling and the ability to achieve narrow-linewidth, spectrally controllable laser output indicate that the Er:YAP laser is an ideal source for water isotope detection.

2. 4-μm Fe:ZnSe laser oscillator end pumped by an Er:YAP laser

Lasers operating in the 4-μm band, especially the 4.4 μm, are ideally suited for measuring HTO because the absorption peaks of HTO are exactly located around the 4-μm band. Iron-doped zinc selenide (Fe:ZnSe), as one of the transition metal-doped II-VI chalcogenides, is a promising candidate for direct generation of 4-μm lasers. Due to the broad absorption and emission bands as well as large cross-section values, Fe:ZnSe is capable of producing tunable lasers and ultrafast lasers with high power and high efficiency. However, the development of Fe:ZnSe lasers has remained limited due to the lack of reliable 3-μm pump sources with high output power and good beam quality.

Our self-developed Er:YAP laser, which could produce a high-power, high-efficiency 3-μm laser with low requirements for thermal management, is a potential pump source for Fe:ZnSe to generate high-efficiency 4-μm lasers. In this work, I present the novel development of a CW Fe:ZnSe laser end pumped by a self-built Er:YAP laser and demonstrates its output power, spectral and beam quality in detail.

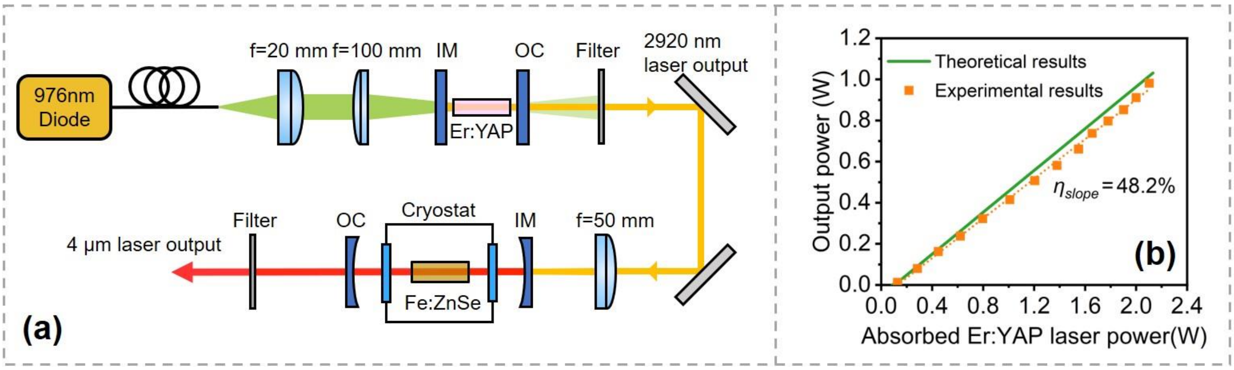

Fig. 2. (a) Schematic diagram of the Fe:ZnSe laser end pumped by an Er:YAP laser. (b) Fe:ZnSe laser output power as a function of the absorbed Er:YAP pump power. [1]

An Er:YAP laser based on a compact plane-plane cavity design was built as the pump source, which could deliver a maximum output power of 3.6W with a high beam quality of $M^2 < 2$. The Fe:ZnSe laser oscillator (see Fig. 2(a)) was constructed based on a concave-concave cavity to ensure good mode matching. The laser performance was mainly optimized using three output couplers with T=2.5%, 10%, and 20%. A larger output coupling transmission of 20% was preferred for higher lasing efficiency and output power owing to the high gain of Fe:ZnSe. A maximum output power of ~1 W was obtained at the maximum absorbed pump power of 2.1 W, as shown in Fig. 2(b). It is worth noting that the overall conversion efficiency, from the 976-nm diode laser to the 4-μm Fe:ZnSe laser, was 8.8%, which represents the highest conversion efficiency for the Fe:ZnSe laser reported thus far.

In conclusion, I have demonstrated a high-efficiency Fe:ZnSe laser operating at 4 μm, end pumped by an Er:YAP laser, which produced watt-level output power with the highest optical efficiency to date and a high beam quality. These results indicate that the Er:YAP laser can be a reliable pump source for Fe:ZnSe to obtain high-efficiency 4-μm lasers with a simple, low-cost design.

3. Hybrid Fe:ZnSe amplifier for high-power, narrow-linewidth, and widely tunable MIR laser

Despite the impressive laser performance of Fe:ZnSe, as presented in the previous section, the Fe:ZnSe oscillator still has a big problem of difficulty in precise spectral control. A free-running Fe:ZnSe laser generally emits multiple spectral peaks with a broad wavelength spanning range, typically ~100 nm, due to the inhomogeneous broadening property of the Fe^{2+} doped in ZnSe. Such broad-spectrum characteristic precludes its use in high-precision spectroscopy applications.

To achieve spectral control in Fe:ZnSe, I proposed a novel laser design based on a hybrid Fe:ZnSe amplifier scheme, in which the Fe:ZnSe serves only as a power amplifier and is injection-seed by a narrow-linewidth quantum cascade laser (QCL). Currently, the QCLs can easily obtain narrow-linewidth laser operation through a distributed-feedback QCL (DFB-QCL) or an external cavity QCL (EC-QCL) architecture. The laser wavelength is entirely determined by the QCL, and the Fe:ZnSe just amplifies the laser power while keeping the spectrum unchanged. In this work, I present a record high-power, pure single-frequency laser operating at 4.3 μm and a high-power, narrow-linewidth, and widely tunable laser with a tuning range of 630 nm by using the hybrid Fe:ZnSe amplifier designs.

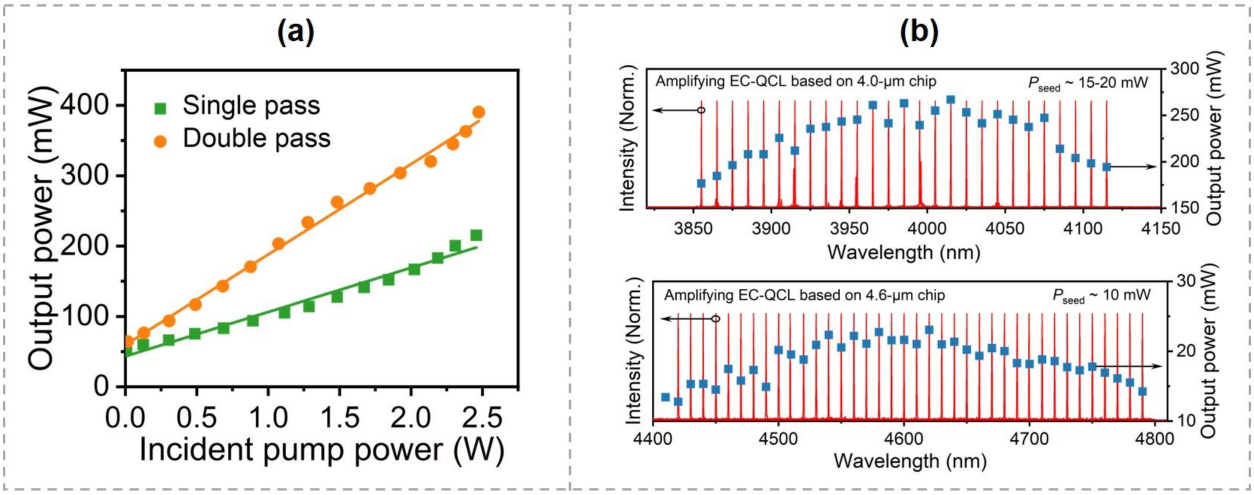

Fig. 3. (a) Laser performance of the DFB-QCL/Fe:ZnSe hybrid amplifier. (b) Tuning behavior of the EC-QCL/Fe:ZnSe amplifier.

The single-frequency laser amplification was achieved using a DFB-QCL seeded Fe:ZnSe amplifier. The DFB-QCL seed provided a 55-mW input signal, and the Fe:ZnSe was pumped by the same Er:YAP laser described above. At the maximum absorbed pump power of 2.5 W, the Fe:ZnSe amplifier produced a maximum output power of 390 mW (see Fig. 3(a)), which is the largest value reported to date for a single-frequency 4.3-μm laser. The laser output was confirmed to be single-frequency with an FWHM spectral linewidth of 29.6 MHz and a tuning range of 12 nm. To further broaden the tuning ability of the amplifier system, an EC-QCL based on a Littman-Metcalf configuration was constructed as the input signal. Figure 3(b) summarizes the tuning behavior of the EC-QCL/Fe:ZnSe amplifiers. After amplification, the laser output power was more than 177 mW over a tuning range of 260 nm from 3850 to 4110 nm and was more than 13 mW for a tuning range of 4420 to 4790 nm. The spectral linewidth was confirmed to be less than 0.3 nm over the entire tuning range. These results indicate that the QCL/Fe:ZnSe hybrid amplifier is an ideal solution for obtaining a high power, narrow linewidth, and widely tuned mid-infrared laser.

In conclusion, I have explored a new path to achieve a high-power, spectra-controlled mid-infrared laser based on a hybrid Fe:ZnSe amplifier scheme. A mode-hop-free, pure single-frequency 4.3-μm laser with a record-high output power and a widely tunable laser with a tuning range of 630 nm were successfully constructed. These laser systems can meet the requirements of high-sensitivity spectroscopy applications and are well-suited for real-time, in-situ detection of HTO isotopes in nuclear fusion reactors.

4. Preliminary study on water isotope detection using mid-infrared laser

In addition to laser developments, I conducted a preliminary study on water isotope detection using mid-infrared DFB-QCLs operating at 6.3 μm and 7.4 μm. The reason for choosing a 6-7 μm laser as the detection light source instead of our self-developed 3-5 μm lasers is because the 6-7 μm band can avoid the atmospheric CO_2 absorption and corresponds to the second strongest absorption peak of the water isotope. In the preliminary experiments, we did not deploy a pure gas circulator to exclude the influence of atmospheric CO_2 and water vapor, such that using a 6-7 μm laser is a simpler and more practical choice for the measurements.

A detection setup based on a conventional "light source→sample→detector" scheme was constructed. The wavelength of the laser source was precisely tuned by controlling the driving current in conjunction with the operating temperature of the QCL chips. The gas sample (H_2O, HDO, and $H_2{}^{18}O$) was sealed in a 10-cm long gas cell with a pressure of approximately 5 Torr. The transmittance of the gas sample can be calculated by the ratio of the power measured in the presence of the gas sample to the power measured with a vacuum cell. Figure 4 shows typical transmission spectra measured using the 7.4-μm QCL. The absorption peaks of all three water isotopes were successfully calibrated. Based on the transmission spectra, interference-free detection of individual samples can be performed by tuning the laser to a distinguishable wavelength, which enables accurate calculation of the gas concentration.

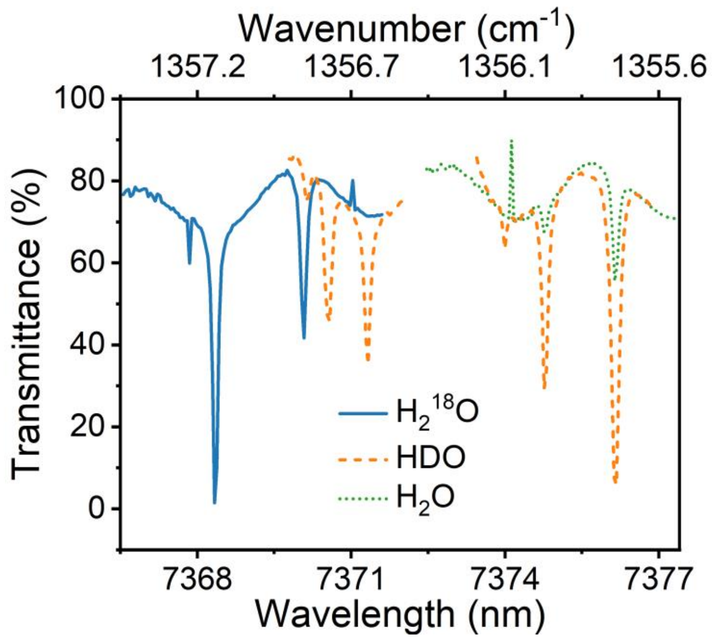

Fig. 4. Typical transmittance spectra of water isotopes measured using the 7.4-μm QCL.

In conclusion, I have constructed a laser spectroscopy system for water isotope detection and verified its usability. This compact and portable detection system can be used for real-time, in-situ measurement applications. In future studies, ultra-high sensitivity water isotope detection can be expected by using absorption enhancement techniques in combination with our self-built high-performance mid-infrared laser sources, thus guaranteeing the safe and stable operation of nuclear fusion reactors.

Related publications:

[1]. **Enhao Li**, Hiyori Uehara, Weichao Yao, Shigeki Tokita, Fedor Potemkin, and Ryo Yasuhara, "High-efficiency, continuous-wave Fe:ZnSe mid-IR laser end pumped by an Er:YAP laser," Optics Express 29(26), 44118-44128 (2021)

[2]. **Enhao Li**, Weichao Yao, Hiyori Uehara, and Ryo Yasuhara, "Cryogenically cooled 2.8 µm Er:YAP laser with watt-level output power," Applied Physics Express 15(9), 092003 (2022)

[3]. **Enhao Li**, Hiyori Uehara, Shigeki Tokita, Weichao Yao, and Ryo Yasuhara, "A hybrid quantum cascade laser/Fe:ZnSe amplifier system for power scaling of CW lasers at 4.0–4.6 µm," Optics and Laser Technology 157, 108783 (2023)

（別紙１ Separate Sheet 1）

Results of the doctoral thesis defense

博士論文審査結果

Name in Full
氏　　名　李　恩昊（Li Enhao）

Title
論文題目 Development of high-performance mid-infrared laser sources for isotope detection applications

OH 基、OD 基、OT 基を含む水は、波長 2.7μm から 7μmの中赤外域に、伸縮振動モードに起因する大きな吸収ピークがある。また炭素同位体についても、4μm帯に ^{12}C および ^{14}C が波長の異なる固有の吸収ピークを持ち、分光的な手法による分別が期待される。出願者は、分光計測において課題の一つであるプローブレーザーの高出力化手法について実験的研究を行った。OH 基に大きな吸収を持つ 3μm帯では、これまでに Er 添加 YAP 結晶を用いたレーザー光源が非常に有効であることが示されている。しかしながらレーザー媒質内に反転分布を形成するために投じる光励起パワーの一部は熱となり高出力化を阻害することが課題であった。出願者は、レーザー媒質を液体窒素温度まで低温化することで、材料の熱伝導率が向上し、光-光変換過程で生じる発熱による制限を克服できることを明らかにした。低温時のレーザー発振波長及び高出力化へ向けたスケーリングの議論などと共に結果を論文にまとめ、Applied Physics Express 誌から発表した。

4μm 帯、特に 4.4μm で動作するレーザーは、HTO の吸収ピークがちょうど 4μm 帯の周辺に位置するため、HTO の測定に理想的である。鉄ドープセレン化亜鉛（Fe:ZnSe）は、遷移金属ドープ II-VI カルコゲナイドの一つとして、4μm レーザーの直接発生に有望な候補とされている。出願者は、上記で特性を明らかにした Er：YAP レーザーを励起源として、Fe:ZnSe をレーザー媒質とした 4μmレーザーの開発に成功した。これまで、非線形光学効果を用いた比較的複雑な手法、あるいは半導体技術によって得られる低出力レーザー光源が一般的であった 4μm帯において、高出力化が可能な光源の実現は有意義である。得られた光源の分光特性や出力特性を理論モデルと比較し考察した結果を論文にまとめ、Optics Express 誌から発表した。さらに申請者は、4μm帯のレーザー吸収分光においてより精密に波長制御を行うために、量子カスケードレーザーを種光にして、Fe:ZnSe レーザーを増幅として用いたレーザー増幅構成の実証を行った。これによって量子カスケードレーザーから出力された狭帯域レーザー発振波長、波長可変性を維持したまま、平均出力１ワット級まで高出力化することに成功している。本成果については、Optics and Laser Technology 誌から論文を発表した。これらの光源開発結果に加えて、中赤外レーザーを用いた水素同位体検出に関する模擬実験を、大気中の二酸化炭素の影響の少ない 7μm 帯で行った。出願者の博士論文では、光源研究とレーザー吸収計測の模擬実験結果から中赤外レーザーを用いた同位体検出の将来展開がまとめられている。

出願者は、主著者として３編の査読付き論文を出版し、加えて１編が投稿中である。また、国際会議での３ 回のポスター発表、１回の口頭発表、国内会議での７回の口頭発表を行っている。これらの研究成果に対して多くの賞が与えられ客観的にも高い評価を受けて

いる。論文構成も堅固で、実験結果の表現法、検討は十分である。以上より本論文の内容は博士（学術）の授与に値すると結論した。