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Efficient tunable laser operation of diode-pumped Yb,Tm:KY(WO₄)₂ around 1.9 μm

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ABSTRACT A new laser medium – Yb,Tm:KY(WO₄)₂ – for diode pumped solid state laser applications operating around 1.9 to 2.0 μm has been investigated and the main laser characteristics are presented. Diode pumping at 981 nm and around 805 nm was realised. For 981-nm pumping, the excitation occurs into Yb³⁺ ions followed by an energy transfer to Tm³⁺ ions. A slope efficiency of 19% was realised. For pumping around 805 nm, the excitation occurs directly into the Tm³⁺ ions. Here a maximum slope efficiency of 52%, an optical efficiency of 40%, and output powers of more than 1 W were realised. Using a birefringent quartz plate as an intracavity tuning element, the tunability of the Yb,Tm:KY(WO₄)₂ laser in the spectral range of 1.85–2.0 μm has been demonstrated. The possibility of laser operation in a microchip cavity configuration for this material has also been shown.

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1 Introduction

Diode-pumped solid-state lasers (DPSSLs) operating in the eye-safe spectral region near 2 μm and based on Tm³⁺-doped solid-state media have a number of applications, first of all medical, because of the strong water absorption in this wavelength region. Surgical tissue treatment using such systems can be performed with minimal local thermal damage, which is especially important in ophthalmologic surgery. Due to water-vapour transparency and the presence of absorption lines of a number of chemical compounds in the 1.9–2.0-μm spectral region, two-micron tunable lasers offer the possibility to be used for such applications as a coherent source for laser radar, atmospheric sensing, and also for laser photoacoustic spectrometry where free-running multi-mode operation can be successfully used.

The performance of the Tm³⁺ ions in a number of solid-state hosts has been studied and laser operation under diode pumping has been successfully realised [1–7]. Among them Tm:YAG showed the best laser performance. For this crystal

a slope efficiency of 56% has been reported at 2.02 μm with 785-nm diode-laser pumping [1]. Unfortunately in all known Tm³⁺-doped crystals a convenient pump absorption band (around 780 to 800 nm) is shorter with respect to the wavelengths of commercially available high-power laser diodes, which are normally used for pumping neodymium-doped laser media. From this point of view Tm:GdVO₄ seems to be better because of a stronger and broader (770–820 nm) absorption band in comparison to Tm:YAG. However, the efficiency of laser operation of this crystal is not very high. Under Ti:sapphire laser pumping Tm:GdVO₄ showed a slope efficiency of 21% relative to the absorbed pump power [8].

Another way to avoid inconvenient pump wavelengths is to apply an Yb-Tm co-doped system where ytterbium plays a role of a sensitiser. Recently an Yb co-doped Tm:YLiF₄ system was proposed for continuous-wave (cw), quasi-cw, and Q-switched laser operation at 1.5 and 2.3 μm [9]. In this system the pump light is absorbed by Yb³⁺ ions and then the energy is transferred from Yb³⁺ to Tm³⁺. In comparison with solely Tm³⁺-doped media, Yb-Tm co-doped crystals possess a broad absorption band convenient for pumping within the 960- to 980-nm wavelength range. However, under these pumping conditions, the efficient cross-relaxation process between Tm³⁺ ions is bypassed, leading to lower overall laser efficiencies.

Our paper presents results on the investigation of laser properties of a new medium, which can be a perspective material for DPSSL applications – Yb-Tm co-doped potassium yttrium tungstate (Yb³⁺,Tm³⁺:KY(WO₄)₂ or Yb,Tm:KYW). Potassium yttrium and potassium gadolinium tungstates are known as reproducible and easy-to-grow host materials for efficient neodymium- and ytterbium-doped laser media which are used in miniature lasers, including diode-pumped solid-state Raman lasers with self-frequency conversion [10–13]. Recently, high-efficiency laser operation with a slope efficiency of 45% has been demonstrated for solely doped Tm:KYW under Ti:sapphire laser pumping at 800 nm [14, 15].

In our previous studies it has been shown that Yb,Tm:KYW possesses two strong and broad absorption bands convenient for diode pumping. The absorption band between 770 and 815 nm with a maximum at 802 nm ($\alpha_{\text{peak}} \approx$

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21 cm^{-1} for 6 at% of Tm^{3+} , $\mathbf{E} \perp \mathbf{c}$ axis) is associated with the ${}^3\text{H}_6 \rightarrow {}^3\text{H}_4$ transition of Tm^{3+} . Another absorption band between 900 and 1000 nm with a maximum at 981 nm ($\alpha_{\text{peak}} \approx 17 \text{ cm}^{-1}$ for 5 at% of Yb^{3+} , $\mathbf{E} \perp \mathbf{c}$ axis) is associated with the ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$ transition of Yb^{3+} . For this material the values of peak emission cross section and lifetime for the ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ transition are estimated to be $\sigma_{\text{em}} \sim 2.8 \times 10^{-20} \text{ cm}^2$ ($\mathbf{E} \perp \mathbf{c}$ axis) and 1.25 ms, respectively [16]. Thus the value $\sigma_{\text{em}} \times \tau$ is about $3.5 \times 10^{-23} \text{ cm}^2 \text{ s}$ and therefore comparable with the one for Tm:YAG ($\sigma_{\text{em}} \times \tau = 3.6 \times 10^{-23} \text{ cm}^2 \text{ s}$). Another estimation of peak emission cross-section value ($\sigma_{\text{em}} \sim 2.0 \times 10^{-20} \text{ cm}^2$) has been done in [14, 15].

In this communication we present the laser properties of diode-pumped Yb:Tm:KYW crystals with different concentrations of Yb^{3+} and Tm^{3+} pumped at 980 nm and around 805 nm, i.e. at wavelengths where powerful and commercial laser diodes are very reliable and easily available.

2 Experimental

2.1 Laser-element samples

$\text{KY}(\text{WO}_4)_2$ crystals are monoclinic with space group $C_{2h}^6 - C2/c$. The parameters of the crystal unit cell are $a = 8.05 \text{ \AA}$, $b = 10.35 \text{ \AA}$, $c = 7.54 \text{ \AA}$, and $\beta = 94^\circ$; the material density is 6.5 g/cm^3 [17]. Yb:Tm:KYW crystals were grown by the modified Czochralski technique from solution in $\text{K}_2\text{W}_2\text{O}_7$ melt. For our experiments two concentration sets of samples have been grown. For the first set – named ‘Tm-set’ – the concentration of Tm ions was varied (3, 6, and 12 at%), while the percentage of Yb ions remained the same (5 at%) for all crystals. The second set – named ‘Yb-set’ – contained the samples with constant Tm concentration (12 at%), while the percentage of Yb ions was varied (5, 10, and 15 at%). The samples were parallel-sided polished plates cut along the b axes with thickness of 1.64 mm for the Tm-set and 0.83 mm for the Yb-set.

2.2 Pump wavelengths

As mentioned above, Yb,Tm:KYW possesses two absorption bands convenient for diode pumping with maxima of the absorption cross section at 981 nm ($\sigma_a \approx 5.4 \times 10^{-20} \text{ cm}^2$) and 802 nm ($\sigma_a \approx 5.3 \times 10^{-20} \text{ cm}^2$) where coherent pumping is most efficient.

In the case of pumping the ${}^2\text{F}_{7/2} \rightarrow {}^2\text{F}_{5/2}$ transition of Yb^{3+} , a laser diode emitting at 981 nm, i.e. in the maximum of the Yb absorption band, was used. For directly pumping the ${}^3\text{H}_6 \rightarrow {}^3\text{H}_4$ transition of Tm^{3+} , the pump wavelength was chosen to be equal to 803 nm or 805 nm. Thus it was possible to use commercially available laser diodes commonly used for pumping of Nd-doped laser media. The emission wavelength of this diode laser (808 nm at 25°C) can be easily tuned to 803 nm and 805 nm by decreasing the thermo-electric cooler (TEC) temperature to the appropriate value. On the other hand, the bending of the shoulder in the Yb,Tm:KYW absorption spectrum around 805 nm seems to be attractive for relatively stable pumping in the case of uncontrollable temperature wavelength shift of the laser diode emission, because the value of the absorption cross section remains constant and quite high at $\sim 2.7 \times 10^{-20} \text{ cm}^2$ (see Fig. 1).

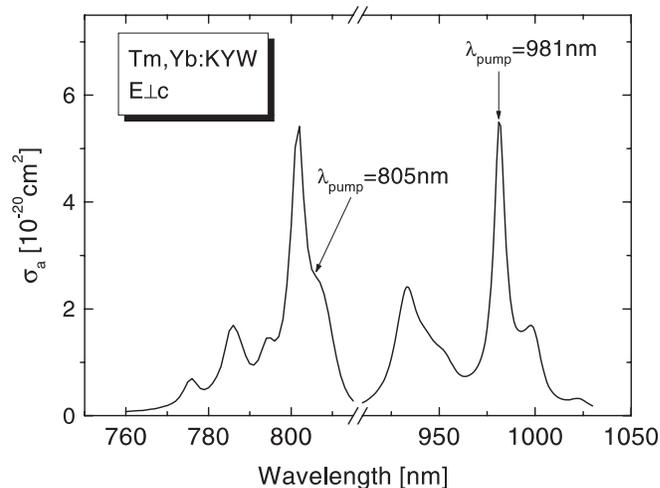


FIGURE 1 Absorption cross-section spectrum of Yb,Tm:KYW for $\mathbf{E} \perp \mathbf{c}$. The pump wavelengths used in the laser experiments are also indicated

2.3 Experimental setup

A simple configuration of a hemispherical resonator for end pumping was used in our experiments. The pump sources were multimode (FWHM $\sim 7 \text{ nm}$) continuous-wave diode lasers with an output power of 1 W at 980 and 808 nm mounted on a TEC for temperature and thus wavelength control. The optical system for focusing the pump beam into the laser crystal consisted of a triplet collimator (NA = 0.5), $\times 4.5$ cylindrical telescope, and a focusing lens ($f = 10 \text{ mm}$) with an overall transmission of $\sim 75\%$. For both laser diodes the pump spot size formed by this optical system was $\sim 80 \mu\text{m}$.

Polished surfaces of active-element plates were coated to be highly transmitting between 1800 and 2000 nm. The resonator was formed by a flat input mirror and a spherical output mirror of 30-mm radius of curvature. The total cavity length was about 29.5 mm. The input mirror had a transmission of $\sim 88\%$ at 981 and 805 nm, and a reflectivity of $R > 99.9\%$ for the 1800–2000-nm range. The output coupler transmitted $\sim 5\%$ at 1800–2000 nm. A plate of Yb,Tm:KYW was attached directly to the input mirror; no other special arrangements were made to promote heat removal from the active element. Some preliminary experiments with active cooling of the laser element were performed using a copper holder on a thermo-electric cooler. In these experiments the copper holder was cooled to 15°C . The output power in these cases increased by less than 10%.

For the high-power laser experiments we used a fibre-coupled laser diode at a centre wavelength of 803 nm. The fibre had a numerical aperture of 0.22 and a diameter of $150 \mu\text{m}$. The laser diode output beam was collimated and focussed by two achromatic lenses with focal lengths of 50 (or 30) mm and 50 mm, respectively. Two different resonator setups were used: the first resonator was formed to a hemispherical cavity of $\sim 4.9\text{-cm}$ length by a plane high-reflective mirror and a curved mirror of 50-mm radius of curvature and a transmission of $\sim 1.8\%$ at the laser wavelength. Secondly, we used a plane parallel resonator of approximately $\sim 5\text{-mm}$ length, whereby the output coupler transmit-

ted $\sim 1.2\%$ at the laser wavelength. In both resonator setups, the end-pumped Yb (5 at%), Tm (6 at%):KYW crystal plate was mounted on a water-cooled aluminium heat sink, which was closely placed to the plane mirror.

3 Results and discussion

3.1 Pumping at 981 nm

Tm-set. We have not achieved laser operation for the samples with $C_{\text{Tm}} = 1$ at% and $C_{\text{Tm}} = 3$ at%, most probably due to the low transfer efficiency for these low Tm concentrations [16]. The output characteristics obtained for cw operation for the samples with $C_{\text{Tm}} = 6$ at% and $C_{\text{Tm}} = 12$ at% are shown in Fig. 2. Maximum cw output power achieved in our experiments was 56 mW for ~ 451 mW of absorbed pump power with a slope efficiency of $\sim 19\%$. The best laser performance was observed for Yb (5 at%), Tm (6 at%):KYW, which is in good agreement with our previous spectroscopic investigations [16]. The threshold pump power for this sample was measured to be as low as 61 mW.

The spectra of the Yb:Tm:KYW laser are shown in Fig. 3. With an increase of the Tm³⁺ concentration the emission wavelength shifts towards longer wavelength, which can be attributed to the rise of the reabsorption losses. The beam

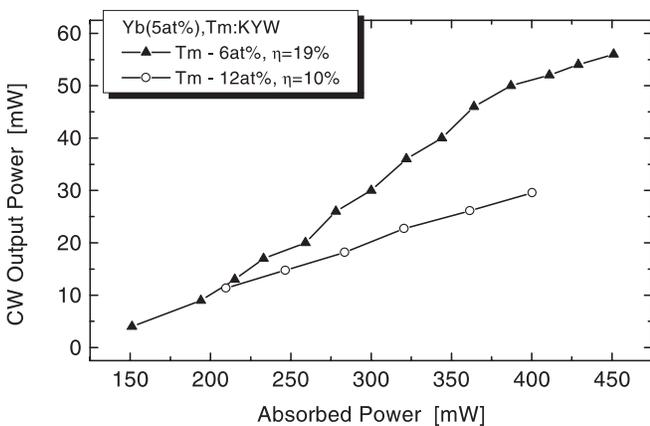


FIGURE 2 Input-output characteristics of the Yb,Tm:KYW laser pumped at 981 nm

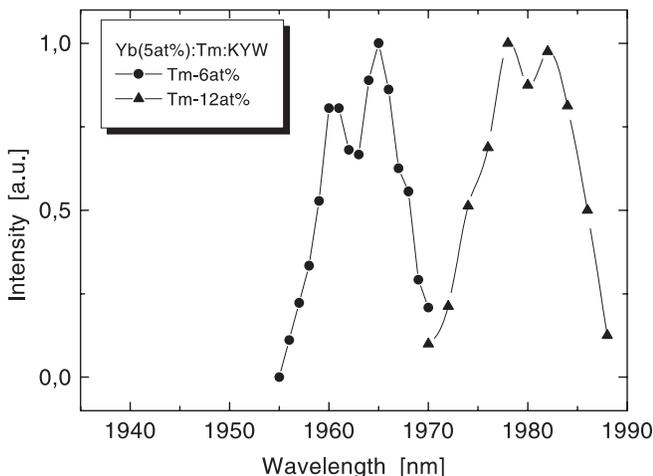


FIGURE 3 Free-running Yb,Tm:KYW laser spectra pumped at 981 nm

profile observed behind the output coupler is in good approximation described by a Gaussian function. The kinetics of the output intensity in the quasi-cw regime of pumping (pulse duration: 1 ms, pulse period: 2 ms, duty cycle: 1 : 1) exhibits a transient process with a spike structure at the beginning of the pulse with a half-width of the spikes of ~ 10 μs. After 200 to 300 μs a steady-state regime is observed with an intensity fluctuation less than 10%. At the same time, the kinetics in a narrow spectral range was observed to be appreciably unstable during the whole output pulse, which is most likely caused by the competition of several spectral modes.

Yb-set. Laser operation achieved for Yb (5, 10, 15 at%), Tm (12 at%) was essentially unstable, most likely due to thermal stresses and deformations of thin uncooled plates. Two of the tested samples were cracked during our experiments with pumping at 981 nm.

3.2 Pumping at 805 nm

Tm-set. In general, the laser results obtained for pumping at 805 nm are much better than those for 981-nm pumping. The input-output characteristics obtained in cw operation for the Tm (3, 6, 12 at%), Yb (5 at%):KYW samples are shown in Fig. 4a. The maximum output power was

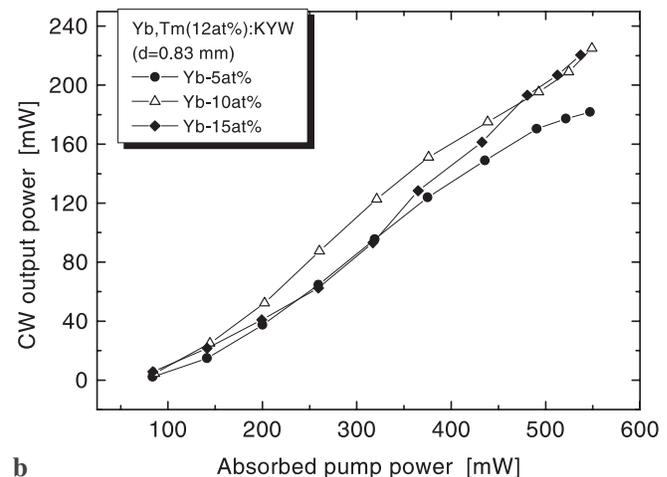
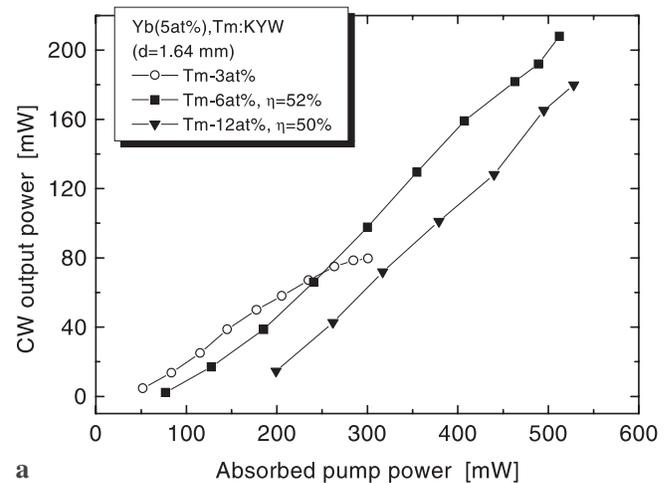


FIGURE 4 Input-output curves of Yb,Tm:KYW laser pumped at 805 nm. **a** Tm-set samples, **b** Yb-set samples

207 mW for ~ 512 mW of absorbed pump power with a slope efficiency of $\sim 52\%$. The best laser performance was observed for the Yb (5 at%):Tm (6 at%):KYW sample, as it was for pumping at 980 nm. The free-running laser spectrum was centred at 1921, 1939, and 1946 nm for $C_{\text{Tm}} = 3$ at%, 6 at%, and 12 at%, respectively, with a total bandwidth (at the 0.1 level) of ~ 10 nm for all samples.

In our previous paper [16] we have estimated that under pumping into the Yb^{3+} absorption band at 981 nm the energy-transfer efficiency η_t between the Yb^{3+} and Tm^{3+} ions for the Yb (5 at%),Tm (6 at%):KYW sample is about 0.76. In a simple approximation we can suppose that the output power of the laser pumped at 981 nm is proportional to the value of η_t . Then, by taking into account that the pump efficiency for a laser pumped at 805 nm should be ~ 2 due to the efficient cross-relaxation process (${}^3\text{H}_6, {}^3\text{H}_4 \rightarrow ({}^3\text{F}_4, {}^3\text{F}_4)$) [9, 14, 16], the output power for the laser pumped at 805 nm can be estimated with the help of the simple formula $P_{\text{out}}^{\lambda_{\text{pump}}=805 \text{ nm}} = \frac{2}{\eta_t} P_{\text{out}}^{\lambda_{\text{pump}}=981 \text{ nm}}$. Using this formula we found that the laser output power data for the Yb (5 at%),Tm (6 at%):KYW sample pumped at 805 and 981 nm are in good agreement over the whole input–output curve with a maximum error of $\sim 20\%$.

Yb-set. The main aim of experiments with Yb-set samples pumped at 805 nm was to investigate the influence of ytterbium ions on laser performance when excitation is realised directly in the ${}^3\text{H}_4$ level of the Tm^{3+} ion, in other words to estimate possible back-energy transfer between Tm^{3+} and Yb^{3+} ions under a 980-nm pump condition. As seen in Fig. 4b, the efficiency for all samples with different Yb concentrations remains almost the same, which can be an evidence that the $\text{Tm}^{3+} \rightarrow \text{Yb}^{3+}$ energy-transfer process very weakly influences the laser operation of the ${}^3\text{F}_4 \rightarrow {}^3\text{H}_6$ laser channel.

3.3 Tuning experiments

The tuning performance of the laser was investigated for the Yb (5 at%),Tm (6 at%):KYW crystal at a pump wavelength of 805 nm, where it demonstrated the best efficiency. In order to achieve a wider tuning range an output coupler with a lower transmission ($T_{\text{oc}} \sim 1\%–2\%$) in the 1.8–2.0- μm wavelength range was used. A quartz plate, inserted into the cavity at Brewster's angle, serves as the tuning element. The laser was tuned by rotating the birefringent plate. The quartz plate of 1.67-mm thickness placed the centre wavelength of the seventh order of the birefringent filter at 1.986 μm for a plate-axis orientation of 45° . Figure 7 shows the room-temperature tuning curve of the Yb,Tm:KYW laser in the wavelength range of 1850–2004 nm. A total bandwidth of the laser emission bandwidth becomes narrower at least by a factor of four when the birefringent plate was inserted into the cavity. The tuning curve was smooth in the wavelength range of 1850–2004 nm. In comparison with the output power of 85 mW for an empty cavity, the maximum output power of the laser with the birefringent plate was 49 mW. From this point of view further improvement of the laser efficiency could be the optimisation of the cavity elements, including the transmission of the output coupler and the thickness of the birefringent quartz plate.

3.4 High-power laser experiments

Figure 5 shows the input–output characteristics for the high-power laser experiments with the Yb (5 at%), Tm (6 at%):KYW sample pumped at 803 nm in a hemispherical resonator cavity. Using a collimating lens of 30-mm focal length and a focussing lens of 50-mm focal length, the pump spot size had a diameter of 250 μm . Under these conditions, a maximum output power of 1.8 W and a slope efficiency of 44% with respect to the absorbed pump power were obtained. The laser threshold was 398 mW of absorbed pump power. Reducing the pump spot size to 150 μm in diameter, a slope efficiency of 50% with a maximum output power of 1.3 W was achieved. The laser threshold was in this case 205 mW of absorbed pump power. Higher pump powers were not used in order to prevent crystal damage. The free-running laser spectral range covers wavelengths between 1956 nm and 1976 nm. For the plane parallel resonator (see Fig. 6) the pump spot had a size of 150 μm in diameter. A maximum output power of nearly 1.0 W and a slope efficiency of 44% with respect to the

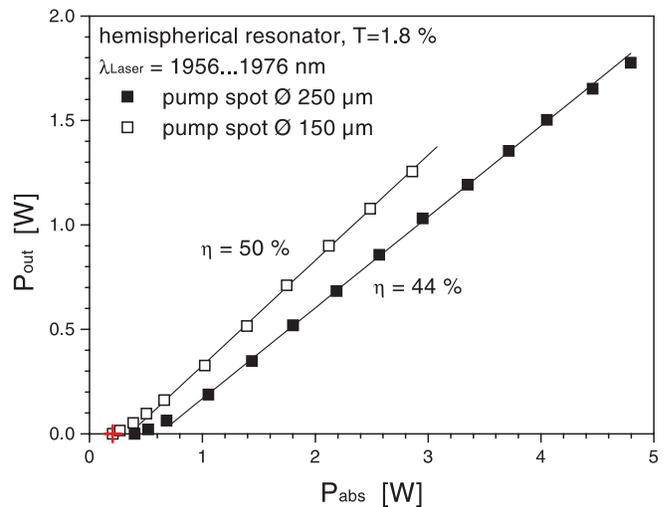


FIGURE 5 High-power input–output characteristics with the Yb(5 at%), Tm(6 at%):KYW sample pumped at 803 nm in the hemispherical resonator

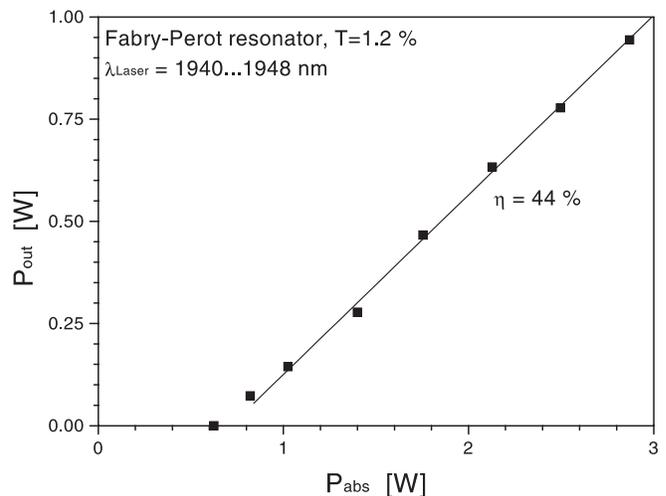


FIGURE 6 High power input–output characteristics for the Yb(5 at%), Tm(6 at%):KYW sample in the plane parallel resonator

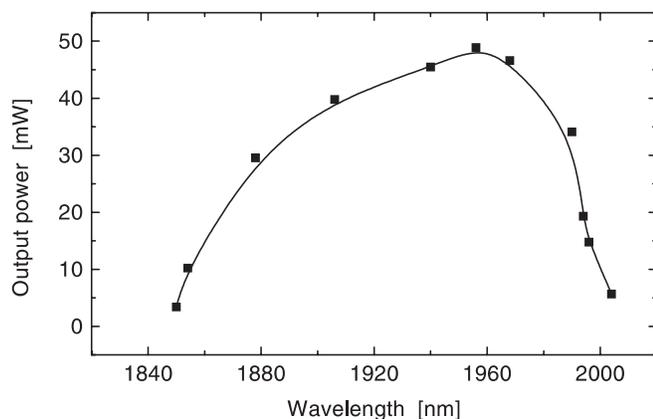


FIGURE 7 Tuning curve of the Yb(5 at%), Tm(6 at%):KYW sample ($\lambda_{\text{pump}} = 805$ nm, $P_{\text{abs}} = 512$ mW, $T_{\text{oc}} = 1\% - 2\%$)

absorbed pump power were achieved. The free-running laser spectral range was from 1940 nm to 1948 nm. For the best output power results the resonator length was reduced as far as possible down to ~ 5 mm. The output power beam had in this case a beam quality factor of $M^2 = \sim 1.1$.

3.5 Microchip-laser performance

Microchip lasers are extremely compact, simple to fabricate, and robust and therefore find wide application in different laser systems. In order to test the Yb,Tm:KYW laser medium as a potential material for microchip application, we changed the hemispherical laser resonator used in low-pump power experiments to a plano–plano configuration. In this configuration the Yb(5 at%),Tm(6 at%) crystal was clamped between the plane input mirror described above and a plane output coupler with a transmission of 5%. The maximum output power which we have obtained for such a microchip laser was 18 mW for a maximum absorbed pump power of 520 mW with a slope efficiency of 6%. The threshold of the microchip-laser operation was estimated to be ~ 220 mW. The emission spectrum of the microchip laser was shifted up to 100 nm to shorter wavelengths in comparison with the spectrum of a laser with the usual hemispherical resonator, and centred near 1838 nm. This effect of spectral line shift takes place due to increasing intracavity losses when the hemispherical resonator is replaced by a plano–plano configuration.

4 Summary

We have investigated the cw laser performance under diode pumping of Yb,Tm:KYW crystals with different concentrations of Yb³⁺ and Tm³⁺ at different pump wavelengths, i.e. at 980 nm and around 805 nm. The latter case, which does not coincide with the absorption peak of these crystals, was chosen in order to have a possibility to use commercially available laser diodes commonly used for pumping

Nd-doped laser media. The results of the investigation showed an efficient and broadly tunable laser operation of this material around 1.9 μm. The best laser performance was demonstrated with the sample with Yb(5 at%)-Tm(6 at%) dopant concentration for both pump wavelengths. A 52% slope efficiency and a 40% optical efficiency have been achieved for this crystal pumped at 805 nm. This result is very close to that of a diode pumped Tm:YAG laser [2], the most efficient among the two-micron thulium lasers. Using a birefringent plate as an intracavity tuning element, a tunability of the Yb,Tm:KYW laser in the range of 1.85–2.0 μm has been realised, which could be useful for further application in remote sensing and photoacoustic spectrometry. The possibility of laser operation in a microchip cavity configuration for this material has been also demonstrated.

By pumping the Yb(5 at%)-Tm(6 at%):KYW crystal with a high-power laser diode at a central wavelength of 803 nm, a maximum output power of 1.8 W and a maximum slope efficiency of 50% were obtained. High-power laser operation has also been demonstrated using a plane parallel resonator, where a maximum output power of nearly 1 W and a slope efficiency of 44% were achieved. The beam quality was in this setup nearly diffraction-limited ($M^2 = 1.1$).

REFERENCES

- G.J. Kintz, R. Allen, L. Esterowitz: In Dig. CLEO (OSA, Washington, DC 1988) FB2
- R.C. Stoneman, L. Esterowitz: Opt. Lett. **15**, 486 (1990)
- J.J. Zayehowski, J. Harrison, C. Dill III, J. Ochoa: Appl. Opt. **34**, 435 (1995)
- R.J. Beach, S.B. Sutton, E.C. Honea: OSA TOPS Adv. Solid-State Lasers **1**, 213 (1996)
- I.F. Elder, M.J.P. Payne: OSA TOPS Adv. Solid-State Lasers **1**, 319 (1996)
- V. Sudesh, J.A. Piper, D.S. Knowles, R.S. Seimour: Tech. Dig. Adv. Solid-State Lasers **FC17-3**, 339 (1996)
- G. Rustad, K. Stenersen: IEEE J. Quantum Electron. **QE-32**, 1645 (1996)
- C.P. Wyss, W. Luethy, H.P. Weber, V.I. Vlasov, Y.D. Zavartsev, P.A. Studenikin, A.I. Zagumennyi, I.A. Shcherbakov: Opt. Commun. **153**, 63 (1998)
- A. Diening, P.E.-A. Moebert, G. Huber: J. Appl. Phys. **84**, 5900 (1998)
- T. Graf, J.E. Balmer: Opt. Eng. **34**, 2349 (1995)
- N.V. Kuleshov, A.A. Lagatsky, A.V. Podlipensky, V.P. Mikhailov, G. Huber: Opt. Lett. **22**, 1317 (1997)
- A.A. Demidovich, A.P. Shkadarevich, M.V. Danailov, P. Apai, T. Gasmii, V.P. Gribkovskii, A.N. Kuzmin, G.I. Ryabtsev, L.E. Batay: Appl. Phys. B **67**, 11 (1998)
- A.S. Grabtchikov, A.N. Kuzmin, V.A. Lisinetskii, V.A. Orlovich, G.I. Ryabtsev, A.A. Demidovich: Appl. Phys. Lett. **75**, 3742 (1999)
- S.N. Bagayev, S.M. Vatnik, A.P. Majorov, A.A. Pavlyuk, D.V. Plakushchev: Quantum Electron. **30**, 310 (2000)
- S.N. Bagayev, S.M. Vatnik, A.P. Majorov, A.A. Pavlyuk: In Tech. Dig. CLEO/Europe-2000, CTuA7, p. 53
- A.A. Demidovich, A.N. Kuzmin, N.K. Nikeenko, A.N. Titov, M. Mond, S. Küick: J. Alloys Compd. **341**, 124 (2002)
- A.A. Kaminskii, P.V. Klevtsov, L. Li, A.A. Pavluk: Sov. Non-org. Mater. **8**, 2153 (1972)