

Optical cooling in $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$

Nicholas J. Condon,^{1,*} Steven R. Bowman,¹ Shawn P. O'Connor,¹ Richard S. Quimby,²
Carl E. Mungan³

¹Optical Sciences Division, U.S. Naval Research Laboratory, 4555 Overlook Avenue, Washington, DC 20375, USA

²Department of Physics, Worcester Polytechnic Institute, Worcester, MA 01609, USA

³Department of Physics, United States Naval Academy, Mailstop 9c, 572C Holloway Rd, Annapolis MD 21402, USA

*Corresponding author: nicholas.condon@nrl.navy.mil

Abstract: For the first time, optical cooling has been observed in the $^4\text{I}_{13/2}$ excited state of erbium(III), using the low phonon energy host material, potassium lead chloride (KPb_2Cl_5). Cooling was observed when samples were pumped at wavelengths longer than 1557 nm, 17 nm longer than the mean fluorescence wavelength of 1540 nm, which implies a nonradiative heat load of 1.1% for the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition. When pumped at 1568 nm, the total cooling efficiency was 0.38% of the absorbed power. These results highlight the potential of $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$ as a material for lasers operating in an eye safe spectral region.

©2009 Optical Society of America

OCIS Codes: (160.3380) Laser materials; (160.5690) Rare-earth-doped materials; (140.3500) Lasers, erbium; (140.3320) Laser cooling

References and links

1. P. Pringsheim, "Zwei Bemerkungen über den Unterschied von Lumineszenz- und Temperaturstrahlung," *Z. Phys.* **57**, 739-746 (1929).
2. N. Djeu and W. T. Whitney, "Laser cooling by spontaneous anti-Stokes scattering," *Phys. Rev. Lett.* **46**, 236-239 (1981).
3. R. I. Epstein, M. I. Buchwald, B. C. Edwards, T. R. Gosnell, and C. E. Mungan, "Observation of laser-induced fluorescent cooling of a solid," *Nature* **377**, 500-503 (1995).
4. C. W. Hoyt, M. Sheik-Bahae, R. I. Epstein, B. C. Edwards, and J. E. Anderson, "Observation of Anti-Stokes Fluorescence Cooling in Thulium-Doped Glass," *Phys. Rev. Lett.* **85**, 3600-3603 (2000).
5. S. R. Bowman and C. E. Mungan, "New materials for optical cooling," *Appl. Phys. B* **71**, 807-811 (2000).
6. R. I. Epstein, J. J. Brown, B. C. Edwards, and A. Gibbs, "Measurements of optical refrigeration in ytterbium-doped crystals," *J. Appl. Phys.* **90**, 4815-4819 (2001).
7. C. E. Mungan, M. I. Buchwald, and G. L. Mills, "All-Solid-State Optical Coolers: History, Status, and Potential," in *Cryocoolers 14*, S.D. Miller and R.G. Ross, Jr, eds. (International Cryocooler Conference, Inc., 2007) 539-548.
8. S. R. Bowman, "Lasers Without Internal Heat Generation," *IEEE J. Quantum Electron.* **35**, 115-122 (1999).
9. S. R. Bowman, S. P. O'Connor, and S. Biswal, "Ytterbium Laser With Reduced Thermal Loading," *IEEE J. Quantum Electron.* **41**, 1510-1517 (2005).
10. D. Garbuzov, I. Kudryashov, and M. Dubinskii, "110 W (0.9 J) pulsed power from resonantly diode-laser-pumped 1.6- μm Er:YAG laser," *Appl. Phys. Lett.* **87**, 121101 (2005).
11. D. Y. Shen, J. K. Sahu, and W. A. Clarkson, "Highly efficient in-band pumped Er:YAG laser with 60 W of output at 1645 nm," *Opt. Lett.* **31**, 754-756 (2006).
12. K. Spariosu, V. Levya, R. A. Reeder, and M. J. Klotz, "Efficient Er:YAG Laser Operating at 1645 and 1617 nm," *IEEE J. Quantum Electron.* **42**, 182-186 (2006).
13. J. O. White, M. Dubinskii, L. D. Merkle, I. Kudryashov, and D. Garbuzov, "Resonant pumping and upconversion in 1.6 μm Er^{3+} lasers," *J. Opt. Soc. Am. B* **24**, 2454-2460 (2007).
14. N. J. Condon, S. O'Connor, and S. R. Bowman, "Growth and characterization of single-crystal $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$ as a mid-infrared laser material," *J. Cryst. Growth* **291**, 472-478 (2006).
15. S. R. Bowman, S. K. Searles, N. W. Jenkins, S. B. Qadri, E. F. Skelton, and J. Ganem, "New mid-IR laser based on an erbium activated low phonon energy crystal," presented at the Conference on Lasers and Electro-Optics, Baltimore, MD, 11 May 2001.
16. J. Fernandez, A. J. Garcia-Adeva, and R. Balda, "Anti-Stokes Laser Cooling in Bulk Erbium-Doped Materials," *Phys. Rev. Lett.* **97**, 033001 (2006).
17. R. S. Quimby, N. J. Condon, S. P. O'Connor, S. Biswal, and S. R. Bowman, "Upconversion and excited-state absorption in the lower levels of $\text{Er}:\text{KPb}_2\text{Cl}_5$," *Opt. Mater.* **30**, 827-834 (2008).

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 2009		2. REPORT TYPE		3. DATES COVERED 00-00-2009 to 00-00-2009	
4. TITLE AND SUBTITLE Optical cooling in Er3+:KPb2Cl5				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Optical Sciences Division,U.S. Naval Research Laboratory,4555 Overlook Avenue,Washington,DC,20375				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 7	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

18. O. L. Antipov, D. V. Bredikhin, O. N. Eremykin, A. P. Savikin, E. V. Ivankin, and A. V. Sukhadolau, "Electronic mechanism for refractive-index changes in intensively pumped Yb:YAG laser crystals," *Opt. Lett.* **31**, 763-765 (2006).
19. S. Biswal, S. P. O'Connor, and S. R. Bowman, "Nonradiative losses in Yb:KGd(WO₄)₂ and Yb:Y₃Al₅O₁₂," *App. Phys. Lett.* **89**, 091911 (2006).
20. N. W. Jenkins, S. R. Bowman, S. O'Connor, S. K. Searles, and J. Ganem, "Spectroscopic characterization of Er-doped KPb₂Cl₅ laser crystals," *Optical Materials* **22**, 311-320 (2003).
21. C. E. Mungan and T. R. Gosnell, "Laser cooling of solids," *Adv. At. Mol. Opt. Phys.* **40**, 161-228 (1999).

1. Introduction

Over the last decade or so, there has been a great deal of interest in the optical cooling of materials by anti-Stokes fluorescence. If a chromophore absorbs a photon whose energy is below its average emitted photon's energy, then the energy difference is extracted from the system and cooling can occur. This effect was first described in 1929 [1], but it was not observed experimentally until experiments on gaseous CO₂ were reported in 1981 [2]. The first observation of anti-Stokes cooling in a solid, Yb³⁺:ZBLANP glass, was reported in 1995 [3], followed by observations of cooling in Tm³⁺:ZBLANP [4] and in the crystalline materials Yb³⁺:KGd(WO₄)₂ [5] and Yb³⁺:YAG [6]. Typical reported cooling efficiencies are small, with cooling powers of < 3% for the ytterbium-doped materials.

While much of the work in optical cooling of solids has focused on its potential applications in cryocooling [7], other work has shown the utility of anti-Stokes fluorescence cooling in removing heat from laser media [8, 9]. This work so far has focused on ytterbium-doped materials lasing near 1 μ m. It would be desirable, however, to make similar high-power sources in the "eye safe" spectral region beyond 1.4 μ m. An obvious ion for such a source is erbium (III), whose ⁴I_{13/2} $\rightarrow$ ⁴I_{15/2} transition emits light at $\sim$ 1.5 μ m and has served as the basis for many lasers. There has been a substantial amount of recent work on resonant or near-resonant pumping of this transition in Er:YAG [10-13] in order to reduce heat loading due to the quantum defect and increase power. In most hosts, however, there is a tendency for excitations into this state to upconvert to the ⁴I_{9/2} state, which, when it nonradiatively relaxes to the ⁴I_{11/2} state, generates heat. Potassium lead chloride (KPb₂Cl₅) has the potential to overcome the upconversion problems. Er:KPb₂Cl₅ can be grown with high optical quality [14], and lasing has been demonstrated in it [15]. There has also been one report of optical cooling in this system from the ⁴I_{9/2} state [16]. Its low phonon energy and uniquely low upconversion rates [17] promise to strongly mitigate heating from upconversion and nonradiative relaxation.

Previous measurements of optical cooling have typically been made using photothermal deflection spectroscopy or observation with a thermal camera. The latter method is inappropriate for KPb₂Cl₅, because the material is completely transparent in most of the mid-infrared and is therefore invisible to the thermal camera. Photothermal deflection is also problematic for several reasons. It requires laser sources and sample material of very high optical quality, and changes in the index of refraction of the sample due to excited-state population changes can confound the result and lead to false cooling signatures [18, 19]. It is also inherently limited to probing one small region of a sample, defined by the probe laser, at a time, so there is no guarantee that the probed region is representative of the sample as a whole. To avoid these problems, the data presented here employ direct measurement of a well-insulated sample in an evacuated chamber using a fine wire thermocouple. This allows for the direct and unambiguous measurement of the temperature of the entire sample.

2. Experimental

Samples of single-crystal, laser-grade Er:KPb₂Cl₅ were grown using a modified Bridgman method similar to that described previously [14]. To improve optical quality, zone-refined KPb₂Cl₅ was used in the initial charge and an extended cooldown routine was employed. The

resulting boule, with an Er^{3+} concentration of $3.6 \times 10^{19} \text{ cm}^{-3}$ (as determined by comparison of the absorption strength with the known cross sections) was cut and turned to produce a rod 3 mm in diameter and 13.6 mm long with a polished barrel and end faces. The rod was aligned such that its axis was parallel to the $[1\ 0\ 0]$ lattice pole, and all data were collected with the pump laser polarization oriented parallel to $[0\ 1\ 0]$. The specific heat of the material was measured to be $0.3 \text{ J g}^{-1} \text{ K}^{-1}$ using direct calorimetry by immersion of heated sample in n-heptane. Fig. 1 shows the previously-published absorption spectrum [20] of the sample polarized parallel to $[0\ 1\ 0]$ and emission spectrum [17] averaged over all orientations; the average emission spectrum is shown since the fluorescence will be radiated in all orientations for any orientation of pump. The mark at 1539.8 nm denotes the fluorescence line center.

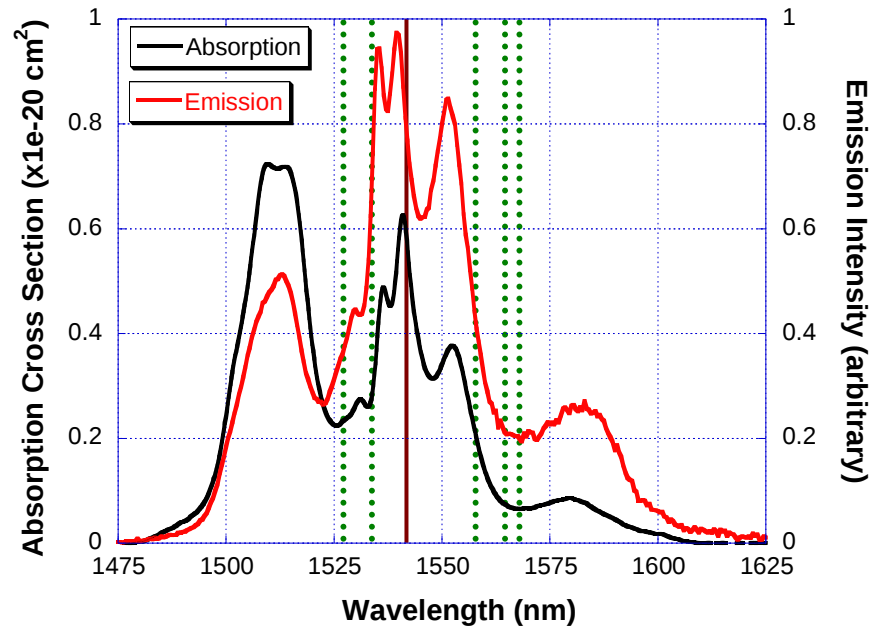


Fig. 1. Absorption (parallel to $[0\ 1\ 0]$) and emission (averaged over all orientations) spectra of $\text{Er:KPb}_2\text{Cl}_5$. The five dotted vertical lines denote the five pump diode center wavelengths used in the experiment, while solid vertical line denotes the fluorescence line center, $\lambda_F = 1539.8 \text{ nm}$.

Three diode lasers (nLight NL-C-1.0) with different nominal wavelengths were used as pump sources. Two of the diodes were run at two different temperatures (15°C and 29°C) while the third was operated only at 29°C , to provide a total of five measured wavelengths. The spectra of each diode at the appropriate operating temperatures were recorded with an optical spectrum analyzer (ANDO 6317B); spectral linewidths were 4-7 nm. The center wavelengths of these diodes are shown in Fig. 1 overlaid on the absorption and emission spectra. For each measurement, the laser in use was collimated with a cylindrical and a spherical lens, focused through a 1 mm pinhole to improve the beam quality, then refocused onto the sample with a beam diameter of 1 mm.



Fig. 2. The vacuum chamber with the sample and sample mount. The chamber itself is aluminum, with calcium fluoride windows on all four sides. The sample mount is made from two pairs of crossed glass cover slips mounted on a polycarbonate block to provide minimal thermal contact with the sample. The pump beam enters from the left and exits to the right.

The sample mount consisted of two pairs of crossed soda-lime glass cover slides attached to a polycarbonate post set inside an evacuated sample chamber (approximately 70 mm on a side) with 50 mm diameter by 6.5 mm thick CaF_2 windows on four sides; a photograph of this chamber is shown in Fig. 2. A power meter (Scientech AC2500) was placed on the other side of the chamber to measure the transmitted laser power. The absorbed power was calculated from the transmitted power (corrected for reflection losses) using the absorption spectrum of the sample and the emission spectra of the laser diodes. A fine wire (0.001" diameter) T-type (copper/constantan) thermocouple was positioned to contact the sample near its center, and its complementary junction was held in an isothermal block to prevent room temperature drifts from affecting the signal. The use of a fine wire thermocouple prevents heat transfer through it and improves its response time. In order to measure changes in the apparent temperature of the sample's surroundings, a second T-type thermocouple (with its complementary junction in the isothermal block) was placed in the chamber near the sample, but not in contact with it. The thermocouple voltages were measured with a picovoltmeter (Hewlett-Packard 34420A), and the signal from the analog output of the picovoltmeter was recorded using the high-resolution mode of a digital oscilloscope (Tektronix TDS744A).

For each measurement, the sample was exposed to the laser for ~6 minutes, or until thermal equilibrium was reached. A very small amount of visible (green) upconversion could be observed while the laser was illuminating the sample, although no attempts were made to measure it. The laser was then shut off and the temperature was recorded at 0.2 s intervals for 200 s. This measurement was performed five times at each measured wavelength and the resulting traces were averaged. Collection of the data as the sample relaxes back to equilibrium with the environment, rather than collection while the sample is illuminated, eliminates potential problems due to short-term drifts of the pump laser or errors due to illumination of the measurement thermocouples by fluorescence and stray pump light.

3. Results and discussion

The measured thermal transients were analyzed with a simple model, based on a previous one developed for analyzing photothermal deflection results [5,21]. As the crystal was in a vacuum chamber and in very weak conductive contact with its mount, the heat transfer is assumed to be completely radiative and the data were fit to a single exponential:

$$\Delta T(t) = \Delta T_{eq} \exp\left(\frac{-t}{\tau}\right) \quad (1)$$

where t is the time since the laser turnoff, $\Delta T(t)$ is the change in temperature from ambient, ΔT_{eq} is the equilibrium ($t = \infty$) change in temperature, and τ is the thermal time constant of the sample. The fraction of the absorbed power that is converted into heat by the sample, ξ , can then be calculated:

$$\xi = \frac{mc_p \Delta T_{eq}}{\tau P_{abs}} \quad (2)$$

where m is the mass of the sample, c_p is its specific heat, and P_{abs} is the amount of power absorbed by the sample. This equation assumes that the temperature of the crystal is spatially uniform, a valid assumption given the small size of the sample and the small fraction (<15%) of pump power absorbed by the sample. As a function of pump wavelength, λ_p , the fractional heat load is given by:

$$\xi(\lambda_p) = \xi_{QD}(\lambda_p) + \xi_{NR}(\lambda_p) \quad (3)$$

where ξ_{NR} is the heat load due to nonradiative losses and ξ_{QD} is the heat load due to the quantum defect. ξ_{NR} is simply the (pump wavelength independent) complement of the radiative quantum efficiency, η :

$$\xi_{NR} = 1 - \eta \quad (4)$$

ξ_{QD} is given, in terms of the mean fluorescence wavelength, λ_F , by:

$$\xi_{QD}(\lambda_p) = \frac{\eta E(\lambda_p) - \eta E(\lambda_F)}{E(\lambda_p)} = \eta \left(1 - \frac{\lambda_p}{\lambda_F}\right) \quad (5)$$

We may define the crossover wavelength, λ_0 , as the wavelength where, as λ_p is tuned from blue to red, the sample switches from net heating to net cooling:

$$\xi(\lambda_0) = 0 \Rightarrow \lambda_0 = \frac{\lambda_F}{\eta} \quad (6)$$

Substituting Eq. (4), Eq. (5), and Eq. (6) into Eq. (3) gives:

$$\xi(\lambda_p) = 1 - \frac{\lambda_p}{\lambda_0} \quad (7)$$

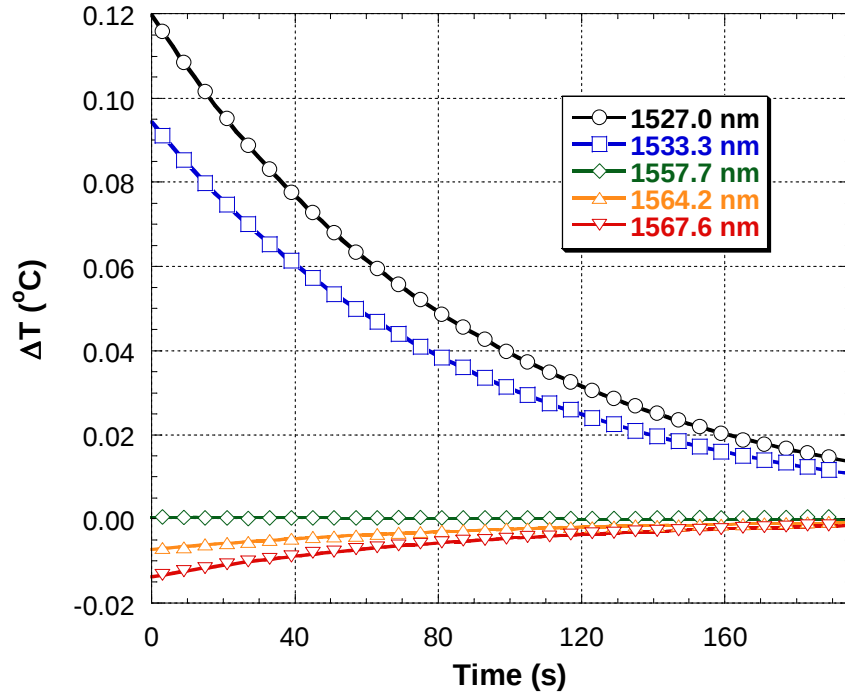


Fig. 3. Temperature transients, corrected for chamber temperature drift, following shutoff of the pump lasers. Every thirtieth data point is plotted, and each transient is fit to an exponential. The two shorter-wavelength curves show evidence of heating, while the two longer-wavelength curves show cooling.

Table 1. Temperature transient fitting results and the resulting calculated heat loads.

λ_{laser} (nm)	P_{abs} (mW)	ΔT_{eq} (C)	Heat Load
1527.0	20.3	0.1205	0.90%
1533.3	21.8	0.0943	0.66%
1557.7	18.9	0.0000	0.00%
1564.2	7.4	-0.0072	-0.15%
1567.6	5.3	-0.0136	-0.38%

Figure 3 shows the averaged temperature transients recorded after the pump laser was shut off at the five measured pump wavelengths. Measurements of the chamber temperature (using a non-contacted thermocouple inside the chamber) showed a drift with time after shutoff of the pump lasers that was consistently linear, but inconsistent in value from run to run. Given this, each temperature transient was fit to the sum of a linear term (to account for the behavior of the chamber) and an exponential term of the form given in Eq. (1). For the sake of clarity, the data shown in Fig. 3 were corrected for the sample drift term, and only the exponential part is shown. Based on the results from fitting the strongest signals, the time constant, τ , was set to 90 s for all fits.

Table 1 summarizes the results of the fits, all of which were of very high quality ($R^2 > 0.997$). From the fit value for ΔT_{eq} at each wavelength, the fractional heat load was calculated using Eq. (2). The data from the two shorter wavelengths, 1527.0 nm and 1533.3 nm, show that heating occurred, with 0.90% and 0.66%, respectively, of the absorbed pump energy transferred to heating. The middle wavelength, 1557.7 nm, produced a nearly linear transient,

suggesting that this diode is near the crossover wavelength. The two longest wavelengths, 1564.2 nm and 1567.6 nm, both showed cooling, with cooling efficiencies of 0.15% and 0.38%, respectively. No attempt was made to account for radiation trapping; given the low optical density of these samples ($\alpha < 0.15 \text{ cm}^{-1}$) and their narrow radius (1.5 mm), the effect of trapping should be negligible.

Figure 4 shows the measured fractional heat load of the sample plotted as a function of wavelength. The data fit well ($R^2 = 0.99$) to a line with a slope of $2.97 \times 10^{-4} \text{ nm}^{-1}$ and a crossover wavelength of 1557 nm. The mean fluorescence wavelength for the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition was calculated to be 1539.8 nm. From (7), assuming 100% quantum efficiency, this would imply a slope of $6.49 \times 10^{-4} \text{ nm}^{-1}$, significantly greater than the observed value. This result suggests that excited states other than $^4I_{13/2}$ are important to the observed heat load, and that further study is required to pin down the mechanisms of heating and cooling in this material. The crossover wavelength of 1557 nm implies a nonradiative fractional heat load of 1.1%.

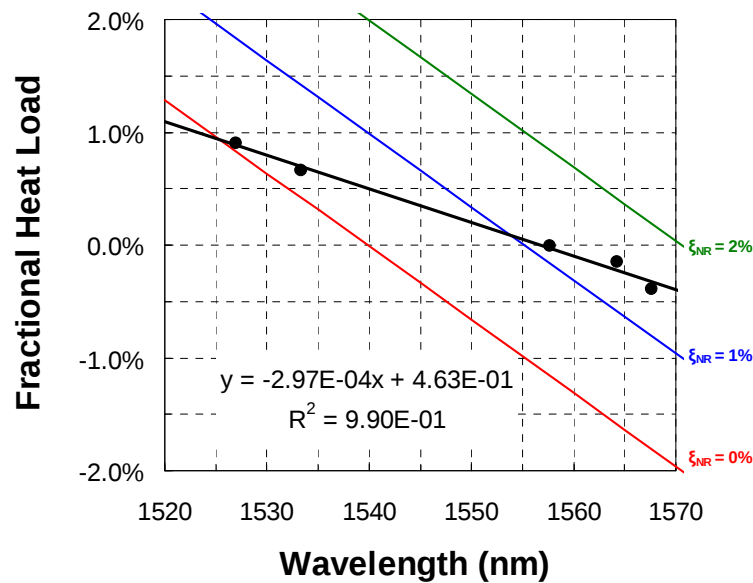


Fig. 4. Fractional heat load as a function of pump diode wavelength. The three diagonal lines are the expected lines for nonradiative contributions, ξ_{NR} , of 0%, 1%, and 2%.

4. Conclusions

Optical cooling has been observed for the first time from the $^4I_{13/2}$ state of erbium (III) in $\text{Er}^{3+}:\text{KPb}_2\text{Cl}_5$. The maximum observed cooling efficiency was 0.38% at 1567.6 nm. The nonradiative fractional heat load for pumping into this state was found to be 1.1%, but the wavelength dependence of the overall heat load suggests the importance of other excited states. The low heat loads at all wavelengths suggest the possible use of this material system in resonantly-pumped eyesafe lasers.

Acknowledgment

This work was supported by the Office of Naval Research.