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Abstract: Laser results are summarized for the low-phonon hosts KPb_2Cl_5 and $CaGa_2S_4$. Radiative quantum efficiencies were determined in $KPb_2Cl_5:Dy^{3+}$ directly from emission spectra in order to accurately determine its long-wavelength potential. The results indicate that room-temperature laser action should be possible to near 9 μm in this host.
OCIS codes: (140.3380) Laser materials; (140.3580) Lasers, solid-state; (140.5680) Rare-earth and transition metal solid-state lasers

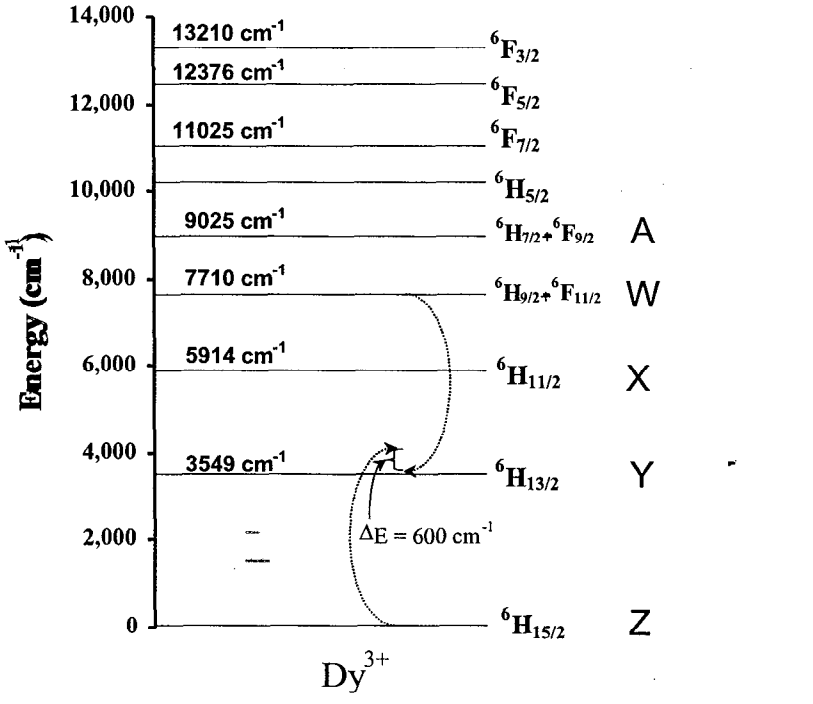
Introduction

We describe progress in demonstrating laser devices that directly generate laser light in the mid-infrared, based on employing rare earth ions in $CaGa_2S_4$ and KPb_2Cl_5.[1] These devices would be important for the development of compact, efficient mid-IR sources for remote-sensing and military countermeasures.

In order to operate rare-earth-based solid-state lasers further into the mid-infrared, say beyond 4 μm, it is potentially valuable to consider the use of low-phonon frequency crystals – especially chalcogenides and chlorides.[2,3] In particular, evaluation of the quantum efficiencies of these hosts is important in their evaluation as a mid-IR host material. In this paper we will summarize the quantum efficiency measurements made for $KPb_2Cl_5:Dy^{3+}$, and laser results obtained with this crystal and $CaGa_2S_4:Dy^{3+}$, and with $KPb_2Cl_5:Nd^{3+}$. Both of these hosts are able to incorporate rare earth ions, are stable in the laboratory ambient, and can be adequately polished to exhibit laser action. The maximum phonon frequency of $CaGa_2S_4$ is estimated to be 350 cm^{-1}, and that of KPb_2Cl_5 is 200 cm^{-1}.

Quantum efficiency measurements

With ground-state absorption at 2.9, 1.7, 1.3, 1.1, and 0.9 μm (see Figure 1), several low-lying energy levels in $KPb_2Cl_5:Dy^{3+}$ are accessible by direct laser excitation. Their quantum efficiencies can be deduced by exciting each level individually and analyzing the emission spectrum, which includes contributions from levels below the pumped level that can be populated by radiative, multiphonon, and cross-relaxation pathways.



in the W-level and an acceptor ion in the Z-level interacting to promote both ions into the Y-level.

Five samples of varying Dy^{3+} concentration (0.35, 0.40, 0.43, 0.54, 0.73 × 10^{20} cm^{-3}, respectively) were studied. Each of the two levels W and X was separately pumped with CW radiation and the emission spectra recorded. Rate equations were solved for quantum efficiencies and branching ratios which produced steady-state photon emission rates that matched the observed spectra. Intensity calibration constants were eliminated by taking ratios of the individual spectra. Further details on these measurements can be found in Ref. [4].

Results and analysis

Figure 2 shows emission spectra of a lower (0.35× 10^{20} cm^{-3}) and a higher (0.54× 10^{20} cm^{-3}) doped sample, normalized to conserve total photons emitted. Notice the 2.9-μm peak in Figure 2a is more prominent at higher doping, suggesting cross-relaxation. Indeed, self-consistent solutions were achieved only with the inclusion of the cross-relaxation pathway depicted in Figure 1. The data, which fit well with Burshtein's hopping mechanism of energy transfer,[5] show that the cross-relaxation mechanism accounts for a significant fraction of the total decay from the W level, thereby decreasing the radiative efficiency from that level. Figure 2b shows emission data obtained from pumping the X level. The quantum efficiency data for W, X and Y levels of Dy^{3+} are shown in Table 1.

A similar analysis was performed on the $KPb_2Cl_5:Nd^{3+}$ sample. The emission spectrum obtained by pumping the $^4F_{5/2}$ level in Nd^{3+} is shown in Figure 3. From this data we conclude the radiative

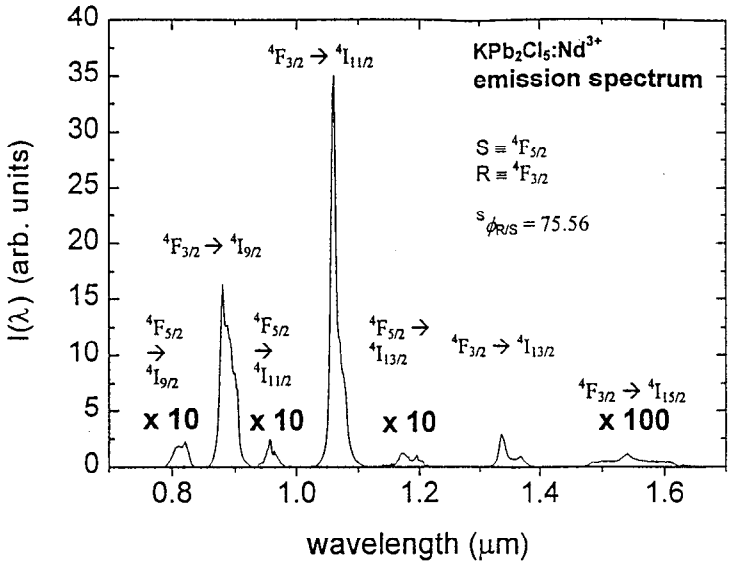


Fig. 3: Emission spectrum obtained by direct excitation of the $^4F_{5/2}$ level of $KPb_2Cl_5:Nd^{3+}$. Emission from both the $^4F_{3/2}$ and $^4F_{5/2}$ level is observed.

quantum efficiency of the $^4F_{5/2}$ level is 0.013. The measured lifetime of the $^4F_{5/2}$ level was found to be 3.4 μs. Using the measured lifetime data, the Nd^{3+} and Dy^{3+} quantum efficiency data can be combined to form a plot of multiphonon decay rate vs. energy gap. Such a plot is shown in Figure 4, indicating quantum efficiencies greater than 1% can be achieved to 1100 cm^{-1}, which suggests laser action could be possible to near 9 μm. We are currently working on systems to realize this potential.

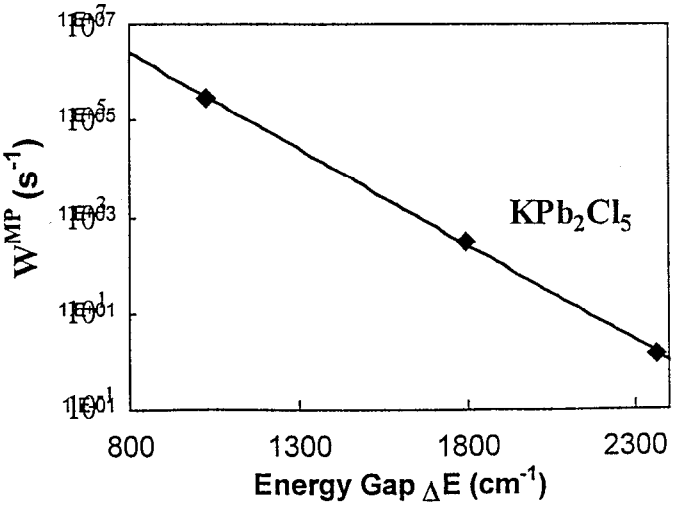


Fig. 4: Multiphonon emission rate W^{MP} vs. energy gap ΔE for KPb_2Cl_5.

Laser Demonstrations

Figure 5 includes plots of the laser transitions demonstrated thus far,[4,6] including the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ transition of $KPb_2Cl_5:Nd^{3+}$ at 1.06 μm, $^6H_{11/2} \rightarrow {}^6H_{13/2}$ of $CaGa_2S_4:Dy^{3+}$ at 4.3 μm, and the $(^6H_{9/2} + {}^6F_{11/2}) \rightarrow {}^6H_{13/2}$ of Dy^{3+} -doped $CaGa_2S_4$ and KPb_2Cl_5 at 2.4 μm. 4.3 μm laser action in $KPb_2Cl_5:Dy^{3+}$ was not attainable only due to lack of a proper pump source at 1.7 μm (to directly populate the upper laser level).

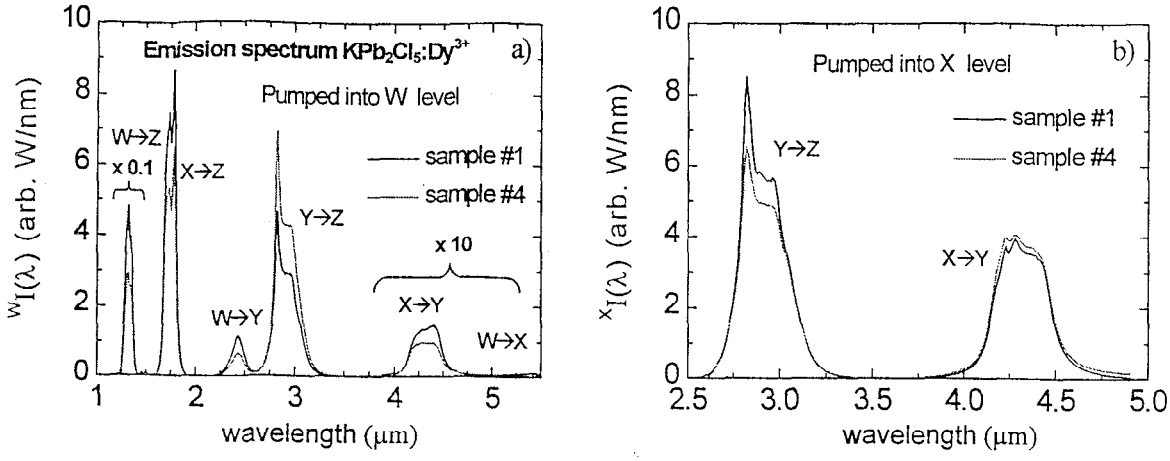


Fig. 2: (a) Emission spectrum ${}^{W}I(\lambda)$ obtained by direct excitation of the W level. (b) Emission spectrum ${}^{X}I(\lambda)$ obtained by direct excitation of the X level.

Table 1. Radiative, multiphonon, and cross-relaxation quantum efficiencies for $KPb_2Cl_5:Dy^{3+}$. rad = radiative, MP = multiphonon, c = concentration dependent cross-relaxation.

Level	Sample #	η^{rad}	η^{MP}	η^{c}	τ^{meas} (ms)	$\tau^{rad}=\tau^{meas}/\eta^{rad}$ (ms)
W	1	0.642 ± 0.022	0.216 ± 0.014	0.142[c] ± 0.007	0.717	1.12
	2	0.593 ± 0.020	0.210 ± 0.012	0.197[c] ± 0.010	0.671	1.13
	3	0.590 ± 0.019	0.208 ± 0.011	0.202[c] ± 0.010	0.667	1.13
	4	0.471 ± 0.020	0.184 ± 0.011	0.346[c] ± 0.017	0.547	1.16
	5	0.344 ± 0.021	0.216 ± 0.012	0.441[c] ± 0.022	0.467	1.36
	Ave.	**c.d.[e]**	**0.207 ± 0.005**	**c.d.[e]**	**c.d.[e]**	**1.18**
X	1	0.991 ± 0.049	0.009 ± 0.049	0.000[a]	5.964	6.02
	2	1.010 ± 0.047	0.000 ± 0.047	0.000[a]	6.394	6.39
	3	1.049 ± 0.048	0.000 ± 0.048	0.000[a]	6.493	6.49
	4	0.994 ± 0.059	0.006 ± 0.059	0.000[a]	6.939	6.98
	5	0.962 ± 0.100	0.038 ± 0.100	0.000[a]	6.565	6.83
	Ave.	**1.001 ± 0.027**	**0.011 ± 0.027**	**0.000**	**6.471**	**6.54**
Y	1	0.904 ± 0.073	0.000[a]	0.000[a]	14.62	16.2
	2	1.003 ± 0.082	0.000[a]	0.000[a]	15.46	15.5
	3	1.061 ± 0.084	0.000[a]	0.000[a]	15.31	15.3
	4	0.731[b] ± 0.071	0.000[a]	0.000[a]	16.16	22.1
	5	0.381[b] ± 0.047	0.000[a]	0.000[a]	11.40	29.9
	Ave.[d]	**0.989 ± 0.046**	**0.000**	**0.000**	**15.13**	**15.7**

a) assumed value
b) probably to be due to oxygen impurities in the host, rather than cross-relaxation
c) determined from measured lifetime data
d) samples #4 and #5 have been omitted from the average
e) concentration dependent

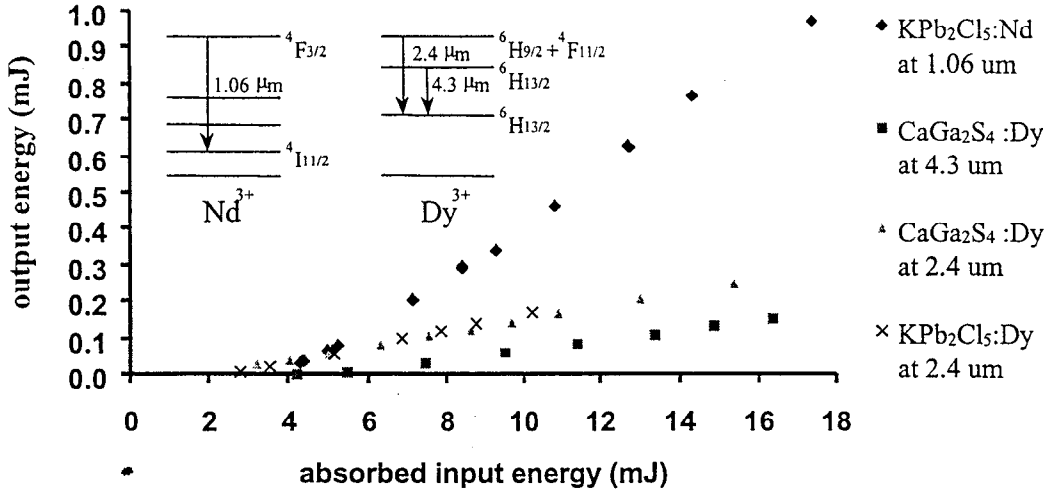


Fig. 5: Demonstrations of laser action using the $CaGa_2S_4$ and KPb_2Cl_5 host media. The Dy^{3+} doped samples were pumped at 1319 nm ($^6H_{9/2} + {}^6F_{11/2}$ level), while the Nd^{3+} doped sample was pumped at 882 nm ($^4F_{3/2}$ level).

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References

1. M.C. Nostrand, R.H. Page, S.A. Payne, W.F. Krupke, P.G. Schunemann, and L.I. Isaenko, in *ASSL TOPS*, M. Fejer, H. Injeyan, U. Keler, eds., Vol. **XXVI** of OSA Proceedings Series (Optical Society of America, Washington, D.C., 1999) , pp. 441-449.
2. T. Schweizer, B.N. Samson, J.R. Hector, W.S. Brocklesby, D.W. Hewak, and D.N. Payne, *J. Opt. Soc. Am. B* **16**, 308 (1999)
3. S.R. Bowman, L.B. Shaw, B.J. Feldman, and J. Ganem, *IEEE J. Quantum Electron.* **32**, 646 (1996)
4. M.C. Nostrand, R.H. Page, S.A. Payne, L.I. Isaenko, and A.P. Yelisseyev, *to be published*
5. A.I. Burshtein, *Sov. Phys. – JETP* **35**, 882 (1972)
6. M.C. Nostrand, R.H. Page, S.A. Payne, W.F. Krupke, and P.G. Schunemann, *Opt. Lett.* **24**, 1215 (1999)