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Room temperature fluorescence of $CsCdBr_3$:Re (Re=Pr, Nd, Dy, Ho, Er, Tm) in the 3–5-µm range

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Abstract

The room temperature mid-infrared fluorescence spectra of $CsCdBr_3$:Re (Re=Pr, Nd, Dy, Ho, Er, Tm) under various excitations have been investigated. Numerous lines have been observed in the 3–5-µm transparency window of the atmosphere. Fluorescence lifetimes have been measured for the most interesting transitions. © 1998 Elsevier Science S.A.

Keywords: $CsCdBr_3$; Rare earth; Mid-infrared; Fluorescence; Laser

1. Introduction

Compact and solid state laser sources emitting in the 3–5-µm transparency window of the atmosphere have both military and commercial applications for imaging and remote sensing. Low phonon host crystals are one the keys to achieve a rare earth room temperature laser in this range. Chloride- and bromide-based hosts fulfil this condition but are generally extremely moisture sensitive. Nevertheless, room temperature 7.2-µm laser action has been demonstrated in praseodymium-doped $LaCl_3$ [1]. From a number of chalcogenide and halide materials, we have chosen $CsCdBr_3$, which appears to be one of the most promising for this application. This host which belongs to the AMX_3 family has the hexagonal structure of $CsNiCl_3$. It exhibits a good transparency extending in the infrared as far as 20 µm (Figs. 1 and 2) and a phonon cut-off frequency around 160 cm^{-1} [2], which is a lower value than for $LaCl_3$ (210 cm^{-1}) or other related materials. Due to charge compensation, trivalent rare earths tend, in a large proportion, to associate in pairs around a vacancy [3]. In addition, this material could be exposed to ambient atmosphere for months without any visible degradation of the surface.

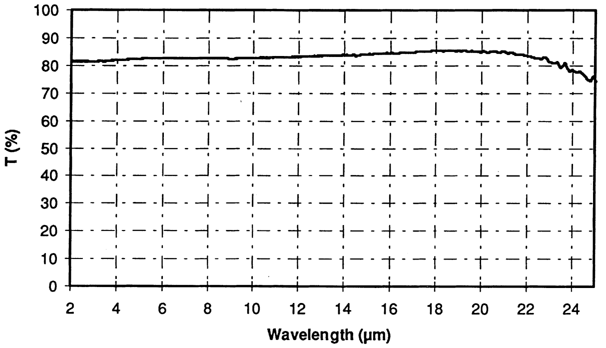

Fig. 1. Infrared transmission spectrum of a 2-cm thick slide of $CsCdBr_3$.

2. Experimental

Doped crystals were prepared from stoichiometric quantities of CsBr, $ReBr_3$ and $CdBr_2$ powders. Due to the lack of purity of commercially available products, $CdBr_2$ powders were prepared by solving metallic cadmium in HBr aqueous solution. After a drying process, powders were introduced in a modified Bridgman furnace which allows us to grow crystals under controlled atmosphere so

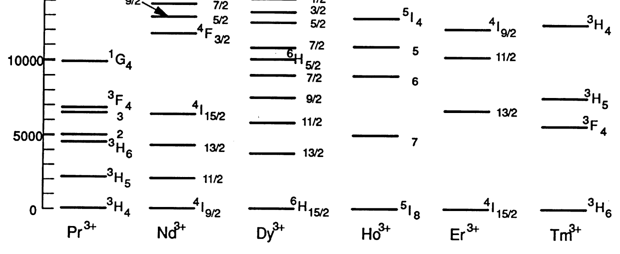

Fig. 2. Energy level diagram of trivalent rare earth.

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as to prevent the extremely sensitive purified starting materials from reacting with ambient water and oxygen. Grown crystals are about 8 cm long and 2.5 cm in diameter, but only two-thirds are of good optical quality. In addition, due to the high segregation coefficient of rare earth in this material, actual concentration in the crystal is likely to be less than 1%. The mid-infrared luminescence was excited either by a continuous wave sapphire–Ti^{3+} laser or a GWU OPO delivering 5-ns pulses at 10 Hz. Unfortunately the OPO's YAG pump generates a lot of noise which considerably decreases the signal/noise ratio and leads to very noisy spectra. Nevertheless, short pulses were very useful for lifetime measurements. The unpolarized spectra were recorded at room temperature with a Jobin Yvon HR320 monochromator having a 150-groove mm^{-1} grating. Mid-infrared light was detected with a liquid nitrogen-cooled InSb detector. Spectra were not corrected for the response of the whole detection system. Fluorescence lifetimes were also investigated using appropriate filters to isolate transients from each other.

3. Results

Fluorescence spectra are shown in Figs. 3–8. Results of lifetimes measurements are shown in Table 1. Numerous fluorescence lines have been observed at room temperature, most of them, to our knowledge, being reported here for the first time.

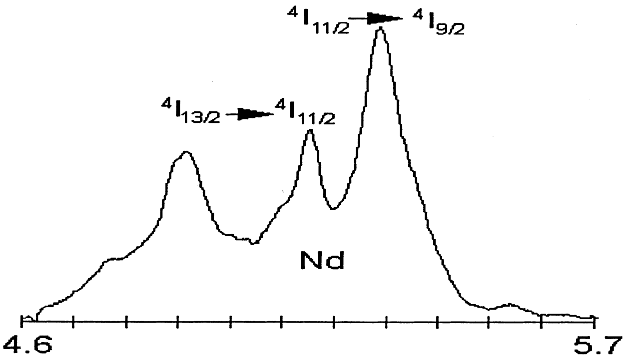

Fig. 4. Unpolarised room temperature fluorescence spectrum of $CsCdBr_3$:Nd under 812 nm excitation.

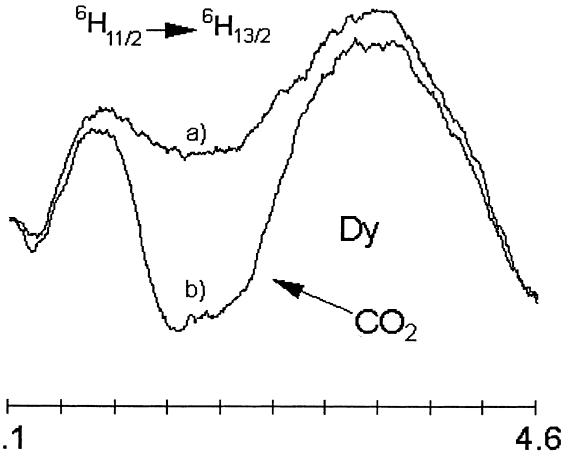

Fig. 5. Unpolarised room temperature fluorescence spectra of $CsCdBr_3$:Dy under 809 nm excitation. (a) The optical path is purged with N_2 gas. (b) Free atmosphere.

3.1. Praseodymium

As the $^3H_4 \rightarrow {}^1G_4$ transition of Pr^{3+} is forbidden, samples were codoped with 2% ytterbium to allow efficient pumping around 980 nm, as suggested by previous works [10]. The mid-infrared spectrum consists here in a broad band that should be compared with similar results obtained by direct pumping of the ($^3F_2$) level in $LaCl_3$ [11]. The main difference consists in a blue shift of the spectrum, and in a few lines around 3 and 3.5 μm, respectively attributed to $^1G_4 \rightarrow {}^3F_3$ and $^1G_4 \rightarrow {}^3F_4$ transi-

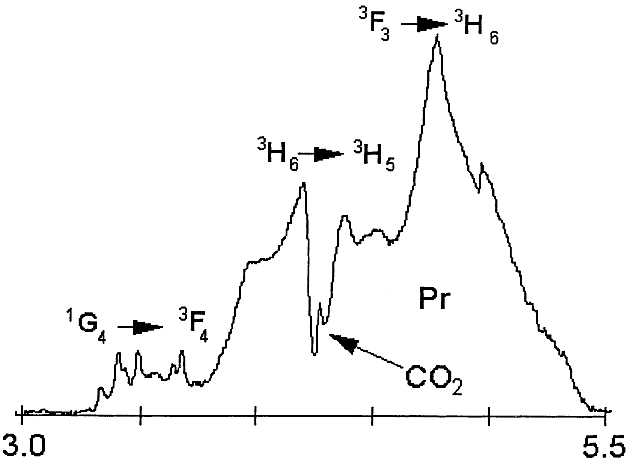

Fig. 3. Unpolarised room temperature fluorescence spectrum of $CsCdBr_3$:Pr–Yb under 943 nm excitation.

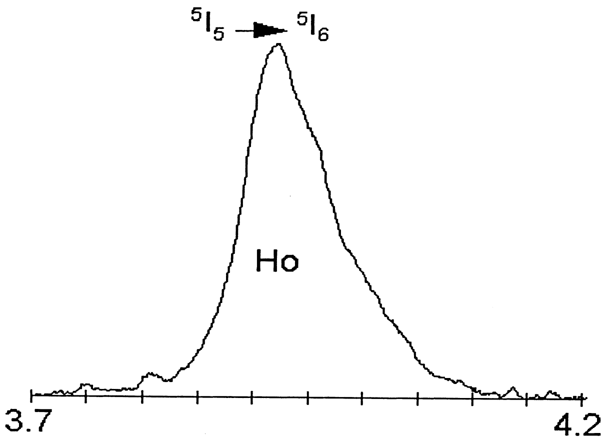

Fig. 6. Unpolarised room temperature fluorescence spectrum of $CsCdBr_3$:Ho under 894 nm excitation.

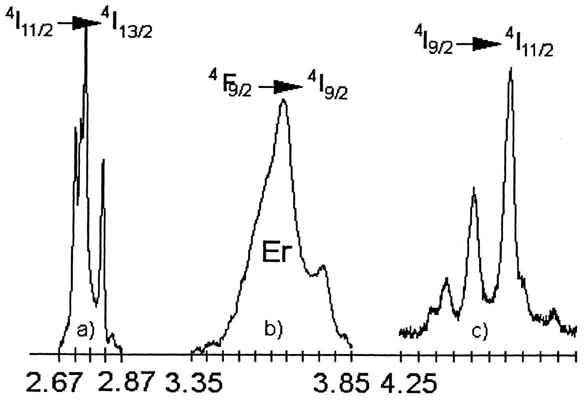

Fig. 7. Unpolarised room temperature fluorescence spectra of $CsCdBr_3$:Er under various excitation: (a) 980; (b) 660; (c) 804 nm.

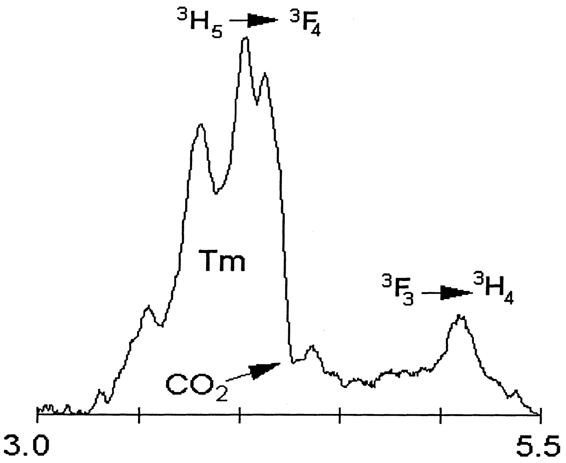

Fig. 8. Unpolarised room temperature fluorescence spectrum of $CsCdBr_3$:Tm under 800 nm excitation.

tion. Another interesting feature is the characteristic atmospheric CO_2 absorption around 4.3 μm due to the unpurged optical path.

3.2. Neodymium

Under 812 nm excitation, $CsCdBr_3$:Nd samples exhibit strong fluorescence from 4.6 to 5.6 μm which arise from $^4I_{15/2} \rightarrow {}^4I_{13/2}$, $^4I_{13/2} \rightarrow {}^4I_{11/2}$ and $^4I_{11/2} \rightarrow {}^4I_{9/2}$ transitions. Such a wide band is mainly due to the large splitting of the $^4I_{15/2}$ stark levels that are all significantly populated at room temperature. Another line attributed to a $^4I_{13/2} \rightarrow {}^4I_{9/2}$ transition is also reported at 2.6 μm.

Table 1
Room temperature fluorescence lifetimes in $CsCdBr_3$

	Er^{3+}			H^{o3+}		Dy^{3+}	Pr^{3+}	
	$^4F_{9/2}$	$^4I_{9/2}$	$^4I_{15/2}$	$^5I_5$	$^5I_6$	$^6H_{11/2}$	$^1G_4$	$^3F_3$
Lifetime (ms)	1.5	10.7	6.15	13	14	10	2.7	0.31

3.3. Dysprosium

Excitation of the $^6F_{5/2}$ level at 809 nm mainly gives 4.3 μm luminescence which is of great interest as it exactly overlaps the fundamental absorption of the atmospheric CO_2. In spite of a very short lifetime of 0.83 μs, the lasing action of this line has already been reported at room temperature in YLF [8]. Schweizer et al. measured a 540-μs lifetime in the lowest phonon sulphide glass Ga:La:S, and showed that it could dramatically increase the efficiency of this laser [9]. So, we expect that the 10-ms lifetime reported in $CsCdBr_3$ should lead to the same conclusions. Another 3-μm line attributed to the $^6H_{13/2} \rightarrow {}^6H_{15/2}$ transition was also observed.

3.4. Holmium

Pumping the $^5I_5$ level of Ho-doped crystal leads to 3.9 μm luminescence. This $^5I_5 \rightarrow {}^5I_6$ transition has already demonstrated laser action at liquid nitrogen temperature in fluorides fibers [7]. Here, again, the long $^5I_5$ lifetime could lead in $CsCdBr_3$ to a room temperature laser.

3.5. Erbium

The observed fluorescence lines were attributed to the following transitions: $^4F_{9/2} \rightarrow {}^4I_{9/2}$; $^4I_{9/2} \rightarrow {}^4I_{11/2}$; $^4I_{11/2} \rightarrow {}^4I_{13/2}$.

The first ones have already successfully lased at 3.5 μm in YLF and fluoride fibers at low temperature [4,5]. In these materials, the lifetime of the $^4F_{9/2}$ level is only a few μs. The longer lifetime (1.5 ms) observed in $CsCdBr_3$ could lead to an improved room temperature laser at this wavelength. The 4.55-μm transition has also been recently reported [6] in $LaCL_3$, but has in this material a shorter lifetime of only 2.5 ms. Finally, the $^4I_{11/2} \rightarrow {}^4I_{13/2}$ transition, which is already known in many materials to lead to a 3-μm laser could also give improved results, but would need to be pumped directly in the $^4I_{11/2}$ level, as efficient population through multiphonon relaxation from higher pumped level is not possible here.

3.6. Thulium

Tm^{3+}-doped samples also exhibit a broad band spectrum that arises from $^3H_5 \rightarrow {}^3F_4$ and $^3F_3 \rightarrow {}^3H_4$ transitions. We suppose the $^3F_3$ level to be populated by the following two conversion processes: (1) ($^3H_5$, $^3H_4$)→($^3F_4$, $^3F_2$) followed by fast relaxation to $^3F_3$; (2) ($^3H_5$, $^3H_4$)→($^3H_6$, $^1G_4$) followed by radiative desexcitation to $^3F_3$.

These mechanisms involve, respectively, a 230-cm^{-1} exothermic and 120-cm^{-1} endothermic energy mismatches that need only one or two phonons.

4. Discussion

The observation of new emission lines in the infrared spectral region for several lanthanides is possible due to the extremely low phonon cut-off frequency of the $CsCdBr_3$ host lattice (160 cm^{-1}). Due to this low phonon energy, multi-phonon relaxation processes are less competitive than in oxide or fluoride lattices. As a major consequence, the population mechanisms are therefore dominated by fluorescence decay, even for levels separated by energy gaps as small as 1500 cm^{-1}. As the multiphonon transition rate decreases exponentially with the number, N, of phonon needed to bridge the energy gap [12], it is easy to see that most of the reported transitions are very unlikely to be observed at room temperature in classical oxides or fluorides with higher phonon cut-off (YLF, 490 cm^{-1}; YAG, 700 cm^{-1}). Actually, radiative processes start to compete efficiently with multiphonon relaxation for $N \geq 5$ and become dominant for $N \geq 7$–8. The small value of the phonon frequencies, besides the reduction of the multiphonon relaxation efficiency, also reduces the efficiency of phonon-assisted energy transfers like up-conversion or quenching processes [13] that are, on the other hand, promoted by the pair structure of doping ions.

5. Conclusion

Numerous luminescent lines and fluorescence lifetimes are encouraging results in evaluating $CsCdBr_3$:Re as a suitable material for a 3–5-μm laser. These properties could be basically explained with simple considerations based on the energy gap law for multiphonon processes. Some of the reported transitions are particularly attractive, as they match the absorption wavelength of CO_2, H_2O or atmospheric contaminants. We are now in the process of depositing anti-reflective coatings in order to test laser action at various wavelengths.

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