The UV fluorescence and absorption spectra of some rare earth bromides

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The UV fluorescence spectra of polycrystalline power $LaBr_3(Pr^{3+})$, $LaBr_3(Pr^{3+}, Ce^{3+})$, $LaBr_3(Nd^{3+})$, $LaBr_3(Eu^{2+}, Ce^{3+})$, $LaBr_3(Dy^{3+})$, $HoBr_3$, $LuBr_3$ and $ErBr_3$ were measured, through which some of the energy level information and relative intensity of different emission peaks of the cations in the crystals can be identified. The phenomenon that the relative intensity of fluorescence peaks changes can be attributed to fluorescence trapping effect in different Pr^{3+} concentration of $LaBr_3(Pr^{3+})$. The excitation spectra of polycrystalline power $LaBr_3(Pr^{3+})$ were measured. The absorption spectrum of single crystal $LaBr_3(Pr^{3+})$ was measured, from which the phenomenological intensity parameters of Pr^{3+} in $LaBr_3(Pr^{3+})$ can be calculated.

1. Introduction

The energy levels of lanthanide ions have been ascertained[1]. But the energy levels of cations in different crystal fields are a little different. What's more, the relative fluorescence intensity of different emission peaks can't be acquired intuitively just from the energy level information. So the fluorescence spectra of $LaBr_3(0.25\%Pr^{3+})$, $LaBr_3(0.5\%Pr^{3+})$, $LaBr_3(1\%Pr^{3+})$, $LaBr_3(2\%Pr^{3+})$, $LaBr_3(4\%Pr^{3+}, 2.6\%Ce^{3+})$, $LaBr_3(8\%Pr^{3+}, 2.6\%Ce^{3+})$, $LaBr_3(16\%Pr^{3+}, 0.15\%Ce^{3+})$, $LaBr_3(31\%Dy^{3+})$, $LaBr_3(14.2\%Nd^{3+})$, $LaBr_3(22\%Eu^{2+}, 0.89\%Ce^{3+})$, $HoBr_3$, $LuBr_3$, $ErBr_3$ were measured, most of which were polycrystalline power, and some were single crystals. The absorption and excitation spectra of some bromides were also measured, all of which haven't been reported before.

2. Experimental procedures

The Hitachi F-4500 FL Spectrophotometer and Hitachi U-2010 Spectrophotometer were used to get the fluorescence and absorption spectra. When the fluorescence spectra were measured, the photomultiplier (PMT) voltage was 700 V, and the response time was 0.1 s. When the absorption spectra were measured, the starting and ending wavelength was 1100 and 190 nm, respectively, and the scan speed was 800 nm/min. The slit width was 2 nm and the light changed from WI lamp to Deuterium lamp at 325.0 nm.

The UV light was used to excite the cations. In order to get the emission peaks of rare earth cations, several wavelengths were used to excite the compounds, for the rare earth cations may have many emission peaks, if just one single wavelength was used, the secondary or tertiary scattering peak may cover some of the emission peaks. In spite of this, we also can't conclude that all of the emission peaks can be observed through the experiment. In fact, just a few of them can be found according to the abundant energy levels of rare earth cations[1]. Maybe using X-ray is a better way to get the whole fluorescence information which can avoid secondary or tertiary scattering peak.

3. Results and discussion

307 nm wavelength was used to excite $LaBr_3(x\% Pr^{3+}, y\% Ce^{3+})$ (Fig. 1). The broad band peaking at 440 nm disappear due to high concentration of Ce^{3+}[3]. In fact, slight displacement of peak position can be observed near 355 and 385 nm between different concentration of Pr^{3+}, which can just be attributed to the crystal field effect.

454 nm wavelength was used to excite $LaBr_3(x\% Pr^{3+}, y\% Ce^{3+})$ to get the fluorescence information of Pr^{3+} (Fig. 2).
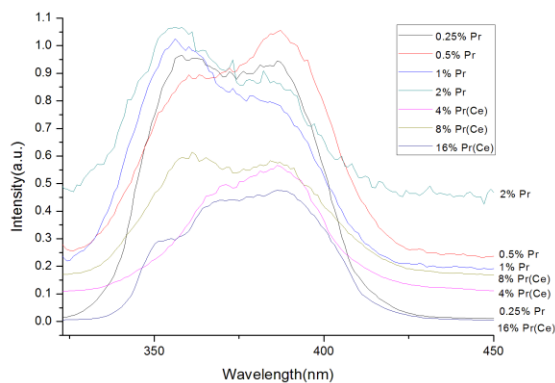
Fig. 1. The emission spectrum of polycrystalline power LaBr₃(x% Pr³⁺, y% Ce³⁺) (x=0.25, y=0; x=0.5, y=0; x=1, y=0; x=2, y=0; x=4, y=2.6; x=8, y=2.6; x=16, y=0.15). The excitation wavelength is 307 nm.

Fig. 2. The emission spectrum of polycrystalline power LaBr₃(x% Pr³⁺, y% Ce³⁺)(x=0.25, y=0; x=0.5, y=0; x=1, y=0; x=2, y=0; x=4, y=2.6; x=8, y=2.6; x=16, y=0.15). The excitation wavelength is 454 nm.
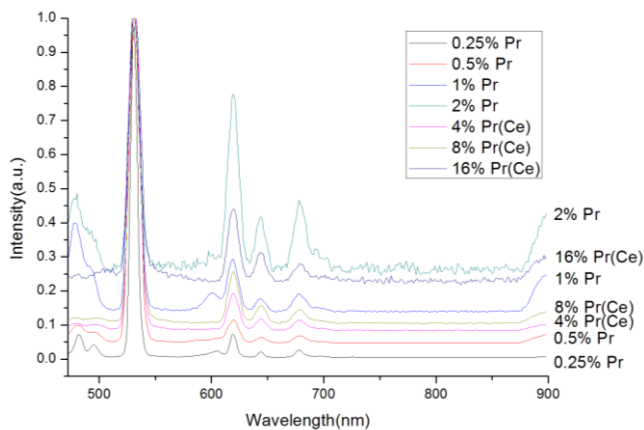
From Fig. 2, eight fluorescence peaks due to Pr^{3+} emission are found. The assignment of Pr^{3+} emission lines is summarized by Ref. 4 in Table 1. The main fluorescence process of Pr^{3+} comes from the transition of the metastable energy level $^3P_0$ to ^3H_J and ^3F_J [1]. All of the eight emission peaks were acquired, though the 703 nm emission peak was the weakest of all and can just be found in LaBr₃(0.25% Pr³⁺). The 531 nm peak ($^3P_1{\rightarrow}^3H_5$) is the strongest of all the eight emission peaks.

Table 1.   Emission wavelengths, wave numbers, and assignments of Pr^{3+} $4f_2$–$4f_2$ emission lines in LaBr₃ [4].

λ(nm)	ν(cm⁻¹)	Transition
479	20900	$^3P_1{\rightarrow}^3H_4$
491	20400	$^3P_0{\rightarrow}^3H_4$
532	18800	$^3P_1{\rightarrow}^3H_5$
600	16700	$^3P_1{\rightarrow}^3H_6$
621	16100	$^3P_0{\rightarrow}^3H_6$, $^3P_1{\rightarrow}^3F_2$
646	15500	$^3P_0{\rightarrow}^3F_2$
681	14700	$^3P_1{\rightarrow}^3F_3$
703	14200	$^3P_1{\rightarrow}^3F_4$

As the concentration of Pr^{3+} increases, some emission peaks disappear. For example, just four peaks in LaBr₃(16% Pr³⁺, 0.15% Ce³⁺) are found: 531nm, 619 nm, 643 nm and 678nm. The 479 nm ($^3P_1{\rightarrow}^3H_4$), 491 nm ($^3P_0{\rightarrow}^3H_4$), 600 nm ($^3P_1{\rightarrow}^3H_6$) and 703 nm ($^3P_1{\rightarrow}^3F_4$) emission peaks are missing, which can be partly explain by fluorescence trapping effect, and exhibited by the single crystal absorption spectrum (Fig. 3). There are notable transmission valleys near 479 and 491 nm. It's hard to see the 479 nm and 491 nm emission peaks while the Pr^{3+} concentration is more than 4%.
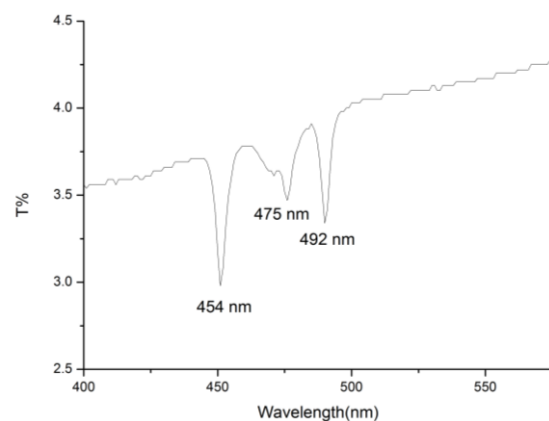

Fig. 3. The absorption spectrum of a 1.90 mm single crystal LaBr₃(0.5% Pr³⁺).

The excitation spectra of six emission peaks were measured (Fig. 4). The most easily to excite emission peaks are 454 nm (22026 cm^{-1}), 492 nm (20325 cm^{-1}) and 475 nm (21053 cm^{-1}), which correspond to the energy level of $^3P_2$, $^3P_0$, $^3P_1$, respectively.

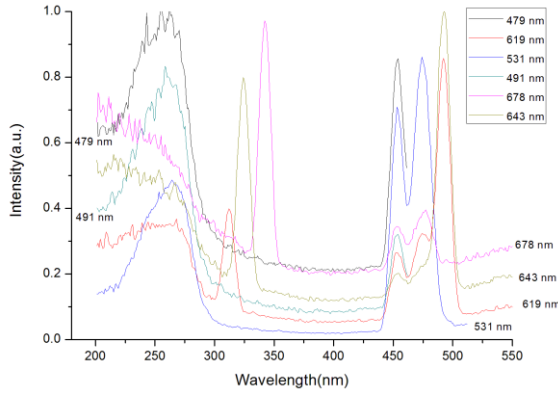*Fig. 4.* *The excitation spectra of six emission peaks in polycrystalline power LaBr$_3$(1% Pr^{3+}).*

Besides such three wavelengths that can excite several emission peaks, there are also several wavelengths that can just excite one emission peak. The 312, 324 and 343 nm wavelength can excite 619, 643 and 678 nm peak, respectively, which is due to the secondary scattering effect.

Table 2. The excitation peaks of fluorescence emission peaks in LaBr$_3$(Pr^{3+}), arranged in the order of intensity from left to right.

Emission peak(nm)	Max1 (nm)	Max2 (nm)	Max3 (nm)	Max4 (nm)	Max5 (nm)
479	453.8	WP[b]			
491	453	WP			
531(532)[a]	474.8	453.4	WP		
619(621)	492.4	312	474.8	452.8	WP
643.4(646)	492.6	324.2	453.4	WP	
678(681)	342.6	476.6	453.2	WP	
Note:					
[a] The data in the bracket come from Ref. 4					
[b] WP: Wave packet between 200 and 300 nm					

In Table 2, the exciting peaks of the emission peaks observed except for 600 and 703 nm are list by the intensity from left to right. It's found that the emission peaks are easily excited by 454 nm (the 479 and 491 nm peaks), 492 nm (the 619 and 643 nm peaks), and 475 nm

(the 531 nm peak). The excitation band between 200 and 300 nm in LaBr$_3$(Pr^{3+}) is caused by the CT (charge transfer) from the valence band of Br$^-$ to Pr^{3+} [4].
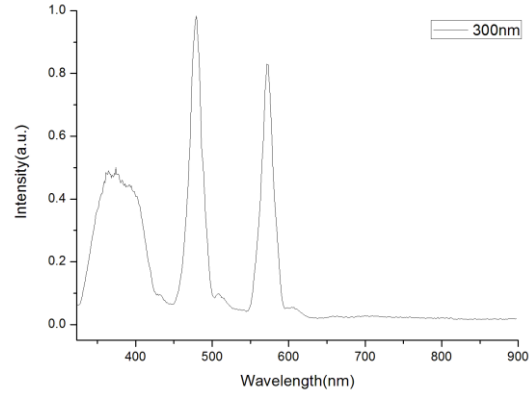

Fig. 5. *The emission spectrum of polycrystalline power LaBr$_3$(31% Dy^{3+}). The excitation wavelength is 300 nm.*

Some deviations between the experimental and literature data[4] are found. For example, 531 and 532 nm, 601 and 600 nm, 619 and 621 nm, 643 and 646 nm. Some of them can just be attributed to system error while the deviation is 1 or 2 nm. But 3 nm large may can't simply be attributed to system error while the error rate is nearly 0.5%, which should be attributed to different crystal fields.

As exhibited above, the absorption spectrum of single crystal LaBr$_3$(0.5% Pr^{3+}) was measured (Fig. 3). Three absorption peaks (or transmission valley) are found: 454 nm, 475 nm and 492 nm. They are exactly the wavelengths which are most easily to excite the emission peaks, and correspond to the energy level of $^3P_2$, $^3P_1$, $^3P_0$, respectively.

We use the absorption spectra and Judd-Ofelt theory[1] to calculate the phenomenological intensity parameters $\Omega_\lambda (\lambda = 2, 4, 6)$ of Pr^{3+} in LaBr$_3$(Pr^{3+}). The experimental oscillator strength

$$f_{exp} = f_{ed} + f_{md}$$

While f_{ed} and f_{md} is the oscillator strength of electric and magnetic dipole transition, respectively.

Because $f_{md} = 0$ in LaBr$_3$(Pr^{3+}), $f_{exp} = f_{ed}$.

$$f_{ed} = \frac{8\pi^2 mc\sigma}{3h(2J+1)} \chi_{ed} \sum_{\lambda=2,4,6} \Omega_\lambda < 4f^N \psi J \| U^\lambda \| 4f^N \psi' J' >^2$$

$$f_{exp} = \frac{2303mc^2}{N\pi e^2} \int \varepsilon(\sigma) d\sigma = 4.318 \times 10^{-9} \int \varepsilon(\sigma) d\sigma$$

$$\varepsilon(\sigma) = \frac{2.303 \lg \frac{1}{T(\sigma)}}{c\Delta x}$$

With the three equations above, we can get

$$\Omega_4 = 1.17 \times 10^{-20} cm^2 , \quad \Omega_6 = 13.14 \times 10^{-20} cm^2$$

Pr^{3+} in $LaBr_3$ just has three group of absorption lines (every group contains a series of Stark splitting lines), which correspond to the transition of energy level $^3P_0 \rightarrow {}^3H_4$, $^3P_1 \rightarrow {}^3H_4$, and $^3P_1 \rightarrow {}^3H_4$, respectively[5]. But the reduced matrix element $U(2)$ of such three transitions are zero (or approximate to zero), so Ω_2 can't be calculated through the current absorption spectrum.

The emission spectra of $LaBr_3(31\%Dy^{3+})$, $LaBr_3(22\%Eu^{2+}, 0.89\%Ce^{3+})$, $LaBr_3(14.2\%Nd^{3+})$, $HoBr_3$, $LuBr_3$ and $ErBr_3$ were measured. Ref. 6 points out that La^{3+} and Lu^{3+} can't exhibit fluorescence, for they are rare earth cations with inert structure. Eu^{3+} and Dy^{3+} can exhibit strong fluorescence, and Pr^{3+}, Nd^{3+}, Ho^{3+}, Er^{3+} have low fluorescence efficiency[2], which can be checked through our experiments. The fluorescence spectra and corresponding energy level information are listed in a table for every sample.

Table 3. Emission wavelengths, wave numbers, and assignments of Dy^{3+} emission lines in $LaBr_3(31\% Dy^{3+})$.

λ(nm)	ν(cm⁻¹)	Transition[2]
356	28090	$^6P_{7/2} \rightarrow {}^8S_{7/2}(4f \rightarrow 4f)$
430	23256	$5d \rightarrow 4f$

Table 4. Emission wavelengths, wave numbers, and assignments of Eu^{2+} emission lines in $LaBr_3(22\%Eu^{2+}, 0.89\%Ce^{3+})$.

λ(nm)	ν(cm⁻¹)	Transition
479	20868	$^4F_{9/2} \rightarrow {}^6H_{15/2}$
507	19716	$^4G_{11/2} \rightarrow {}^6H_{13/2}$
571	17507	$^4F_{9/2} \rightarrow {}^6H_{13/2}$

It's found that Dy^{3+} has two main emission bands, one is blue (479 nm) and the other is yellow (571 nm). The blue band is stronger than the yellow one. The $^4G_{11/2} \rightarrow {}^6H_{13/2}$ transition is a hypersensitive transition[1], whose emission intensity has a notable change in

different host crystals, while the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition is a normal one, whose emission intensity changes little in different host crystals. Besides this, at least three small peaks near 340, 500 and 600 nm exist.
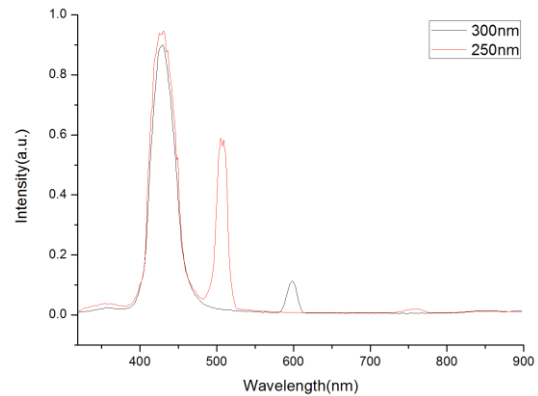

Fig. 6. The emission spectra of polycrystalline power $LaBr_3(22\%Eu^{2+}, 0.89\%Ce^{3+})$. The excitation wavelength is 250 and 300 nm, respectively.
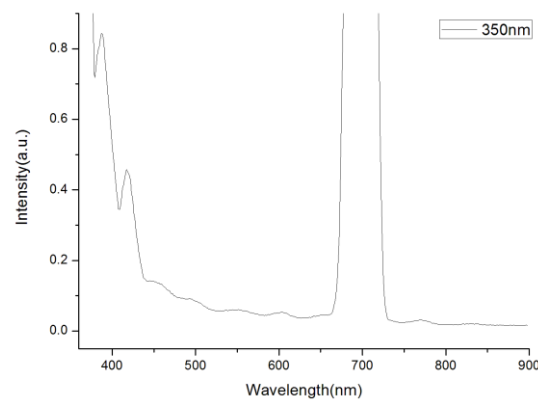

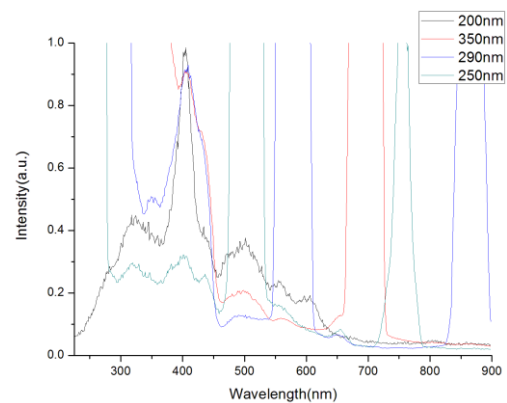Fig. 7. The emission spectrum of polycrystalline power $LaBr_3(14.2\%Nd^{3+})$. The excitation wavelength is 350 nm.

Fig. 8. The emission spectra of polycrystalline power $HoBr_3$. The excitation wavelength is 200, 250, 290 and 350 nm, respectively.

Table 5. Emission wavelengths, wave numbers, and assignments of Nd^{3+} emission lines in $LaBr_3(14.2\%Nd^{3+})$.

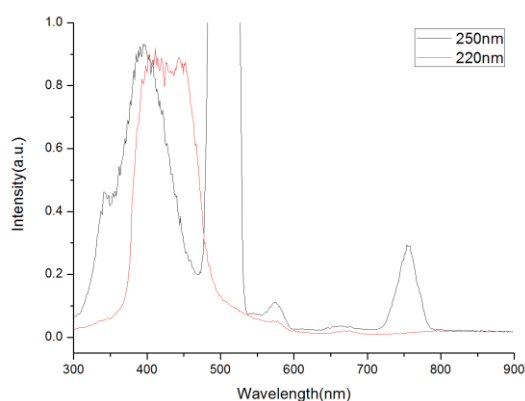| λ(nm)	ν(cm⁻¹)	Transition[2]
387.2	25826	$^2P_{3/2} \rightarrow ^4I_{9/2}$
417.2	23969	$^2D_{5/2} \rightarrow ^4I_{9/2}$
445.2	22462	$^2P_{1/2} \rightarrow ^4I_{9/2}$
480.2	20825	$^4G_{9/2} \rightarrow ^4I_{9/2}$
551.2	18142	$^4G_{7/2} \rightarrow ^4I_{9/2}$
604.2	16551	$^4G_{5/2} \rightarrow ^4I_{9/2}(^4D_{3/2} \rightarrow ^4F_{3/2})$

Fig. 9. The emission spectra of polycrystalline power $LuBr_3$. The excitation wavelength is 220 and 250 nm, respectively.

Table 6. Emission wavelengths, wave numbers, and assignments of Ho^{3+} emission lines in $HoBr_3$.

λ(nm)	ν(cm⁻¹)	Transition
319.2	31328	$^5G_2 \rightarrow ^5I_8$
405.2	24679	$^5G_4 \rightarrow ^5I_8$
436.2	22925	$^5F_1 \rightarrow ^5I_8$

The energy level information of Lu^{3+} isn't acquired from literature, so the energy level of transition can't be identified.

Table 7. Emission wavelengths, wave numbers, and assignments of Er^{3+} emission lines in $ErBr_3$[7].

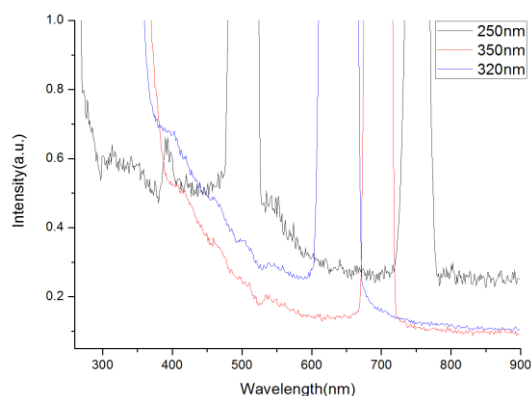| λ(nm)	ν(cm⁻¹)	Transition
390	25641	$^2P_{3/2} \rightarrow ^4I_{13/2}$

Fig. 10. The emission spectra of polycrystalline power $ErBr_3$. The excitation wavelength is 250, 320, and 350 nm, respectively.

There is only one obvious emission peak acquired from Fig. 10, but many energy levels in Er^{3+} should have been observed. Maybe excessive moisture had contaminated the sample during preparation, which influenced the fluorescence emission of Er^{3+}.

4. Conclusion

The UV fluorescence spectra and energy level information of $LaBr_3(Pr^{3+})$, $LaBr_3(Pr^{3+}, Ce^{3+})$, $LaBr_3(Nd^{3+})$, $LaBr_3(Eu^{2+}, Ce^{3+})$, $LaBr_3(Dy^{3+})$, $HoBr_3$, $LuBr_3$ and $ErBr_3$ were acquired. The excitation and absorption spectra of polycrystalline power and single crystal $LaBr_3(Pr^{3+})$ were measured, and the phenomenological intensity parameters of Pr^{3+} in $LaBr_3(Pr^{3+})$ can be calculated through the latter.

Acknowledgements

Reference

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