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Supporting information for:

Huge Enhancement of Sm^{2+} Emission via Eu^{2+} Energy Transfer in SrB_4O_7 pressure sensor

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Experimental Section

Materials

All chemicals were used as received without further purification. Strontium carbonate - $SrCO_3$ (pure p.a.; 99.9%) was purchased from Sigma-Aldrich; boric acid - H_3BO_3 (pure p.a) was purchased from Chempur; europium oxide (Eu_2O_3) (99.99%) and samarium oxide (Sm_2O_3) (99.99%) were purchased from Stanford Materials.

Synthesis

The SrB_4O_7:0.01 Sm^{2+}, *x* Eu^{2+} (*x*=0, 0.005, 0.01, 0.03, 0.05, 0.07 and 0.09) and SrB_4O_7: 0.05 Eu^{2+}, y Sm^{2+} (y=0.005, 0.01, 0.02, 0.03 and 0.05) micro-particles were synthesized by means of a facile, reproducible and cheap method, i.e. a solid-state method in the air. Stoichiometric amounts of Eu_2O_3, Sm_2O_3, H_3BO_3 and $SrCO_3$ were weighted and ground together in an agate mortar. Then the mixtures were transferred to porcelain crucibles covered with a lid, then heat-treated at 700 °C for 5 h and then ground, subsequently further heat-treated at 850°C for 5 h. Then they were ground again in a mortar, and then heat-treated at 850 °C for another 5 h. All grinding must last more than 15 minutes to ensure that the powder is evenly mixed. It is crucial to cover the crucibles with lids to limit the amount of oxygen from the air in the system.

Characterization

X-ray diffraction patterns (XRD) were recorded using a Bruker AXS D8 Advance diffractometer in Bragg-Brentano geometry, with Cu Kα1 radiation (λ=1.5406 Å) in the 2θ range from 6°to 60°, with 0.05° step scan mode. The reference data for XRD were taken from ICDD (International Centre for Diffraction Data). Scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX) were obtained with a scanning electron microscope FEI Quanta 250 FEG, using an EDAX detector. The excitation spectra of the prepared samples were collected using a Hitachi F-7000 spectrofluorometer, at ambient conditions. The studies of the emission properties in ambient (in quartz holder) and under high-pressure conditions (in the DAC, with methanol/ethanol/water medium) were carried out by using Andor Shamrock 500i spectrograph

with iDus CCD camera as a detector. The excitation source for high-pressure luminescence measurements was a focusable, 280 nm LED device.

DAC loading procedure

High-pressure measurements were performed in a Merrill-Bassett diamond anvil cell (DAC), modified by mounting the anvils directly on steel supporting plates. The pressure in DAC was adjusted by the use of three metal screws. The gaskets used were made of stainless-steel sheets 250 μm thick, with the aperture of ≈150 μm (hole size). The gaskets were pre-indented to ≈70 μm thick (sample thickness). The DAC chamber was loaded with sample (white powder), one small ruby sphere (<10 μm diameter) and filled with methanol/ethanol/water (16:3:1 vol.) solvent system (pressure transmitting medium), to provide hydrostatic or quasi-hydrostatic conditions, in the whole range of measurements.

Pressure calibration

Pressure in the system was determined monitoring the ruby R_1 fluorescence line shift, using Andor Shamrock 500i spectrograph with iDus CCD camera as a detector, and a 100 mW 532 nm laser, as an excitation source. The pressure values in DAC were determined using the standard ruby calibration curve, available at: http://kantor.50webs.com/ruby.htm.

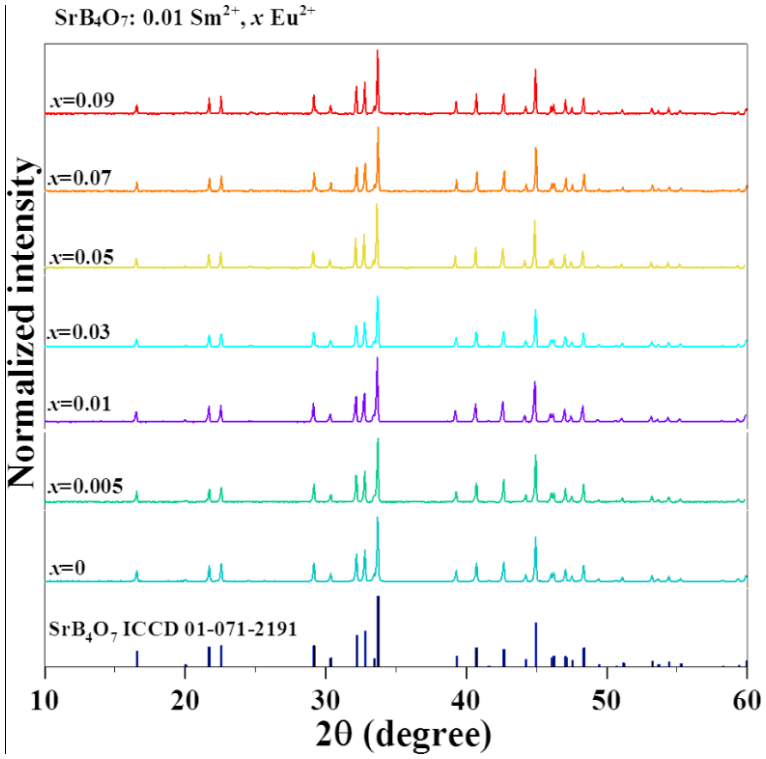

Figure S1 (a) XRD patterns of the SrB_4O_7:0.01 Sm^{2+}, *x* Eu^{2+} (*x*=0, 0.005, 0.01, 0.03, 0.05, 0.07 and 0.09) micro-particles.

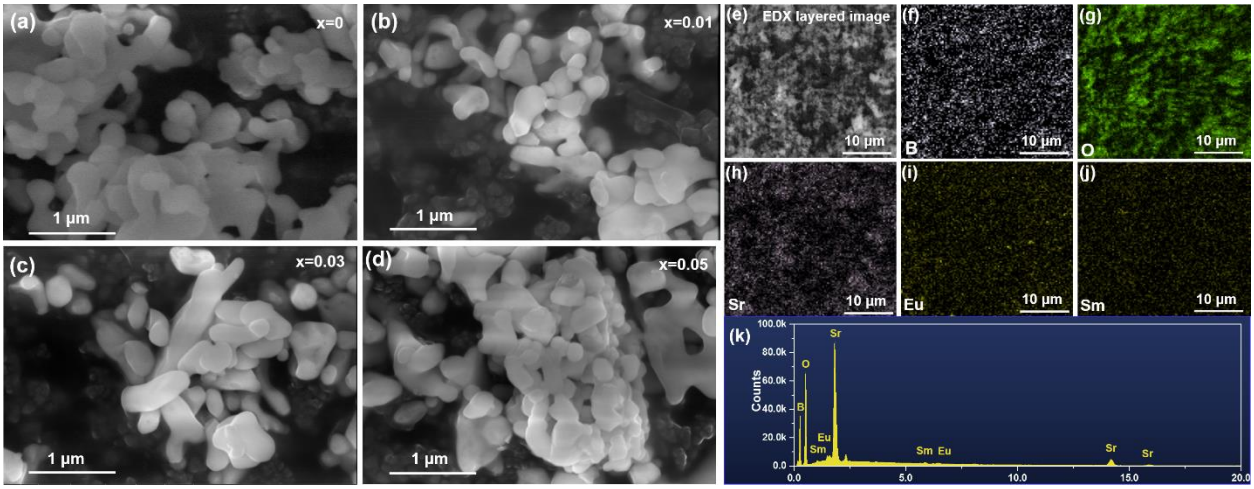

Figure S2. SEM images of SrB_4O_7:0.01 Sm^{2+}, *x* Eu^{2+} micro-particles obtained: (a) *x* = 0, (b) *x* = 0.01, (c) *x* = 0.03 and (d) *x* = 0.05. (e)–(j) Elemental mappings and (k) EDX spectrum of the SrB_4O_7:0.01 Sm^{2+}, 0.03 Eu^{2+} micro-particles.

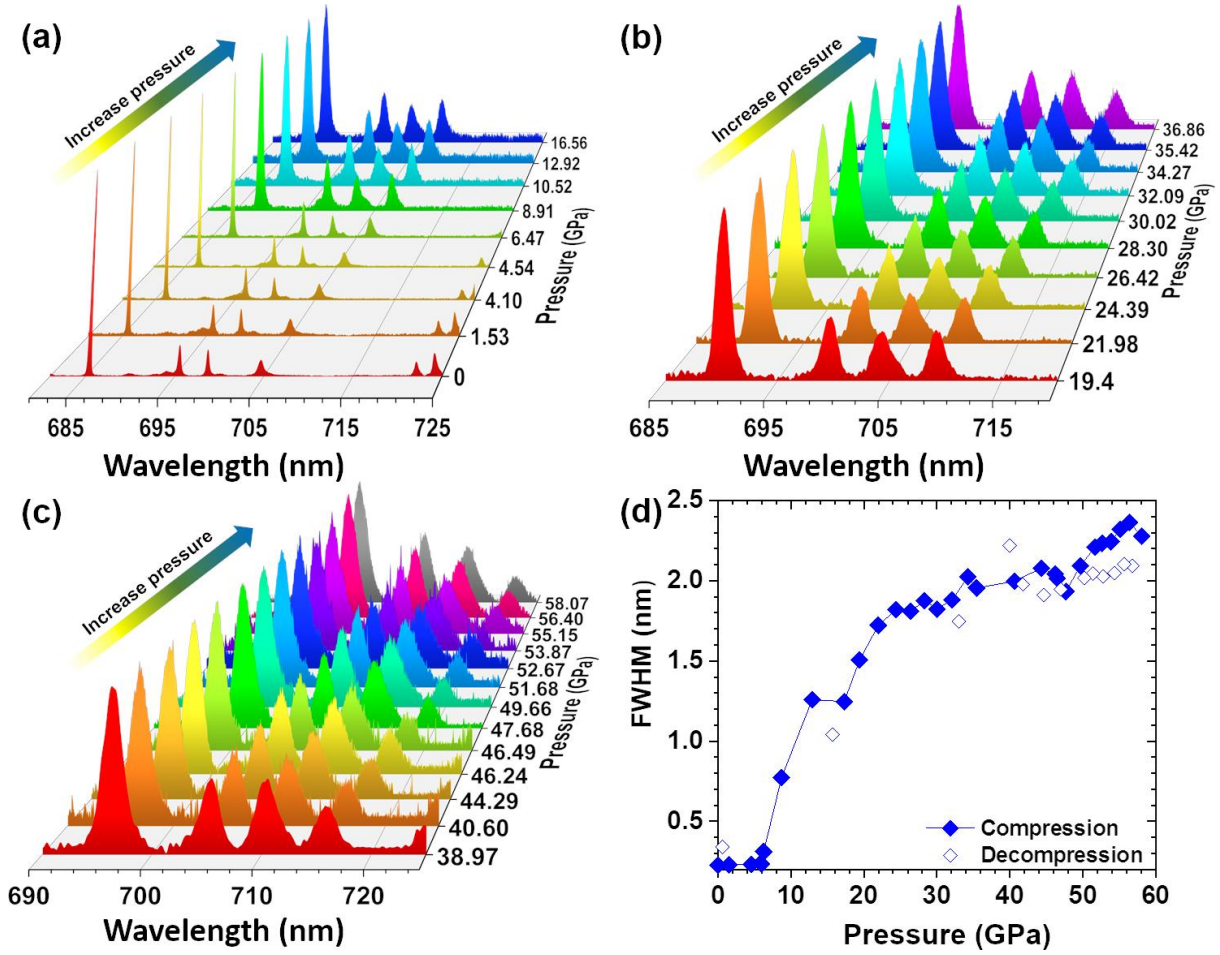

Figure S3. The emission spectra of SrB_4O_7: $0.01Sm^{2+}$, $0.03Eu^{2+}$ micro-particles at every measured pressure (a) 0 - 16.56 GPa, (b) 19.40 - 36.86 GPa and (c) 38.97 - 58.07 GPa normalized at 0-0 line of Sm^{2+}. (d) The linewidth Γ (FWHM) of $^5D_0 \rightarrow {}^7F_0$ emission peaks as a function of pressure. The filled symbols represent the compression and the empty ones decompression data.

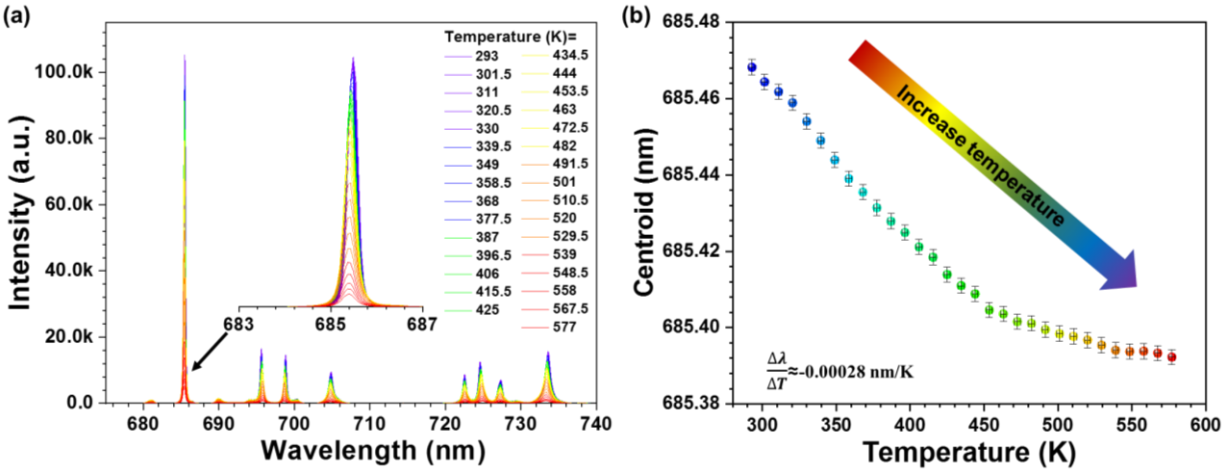

Figure S4 (a) non-normalized emission spectra of Sm^{2+} the SrB_4O_7: $0.03Eu^{2+}$, $0.01Sm^{2+}$ micro-particles at high temperature. The inset of (a) shows the magnified emission spectra of 0-0 line at various temperatures; (b) Peak centroid of 0-0 line of the sample as a function of temperature.

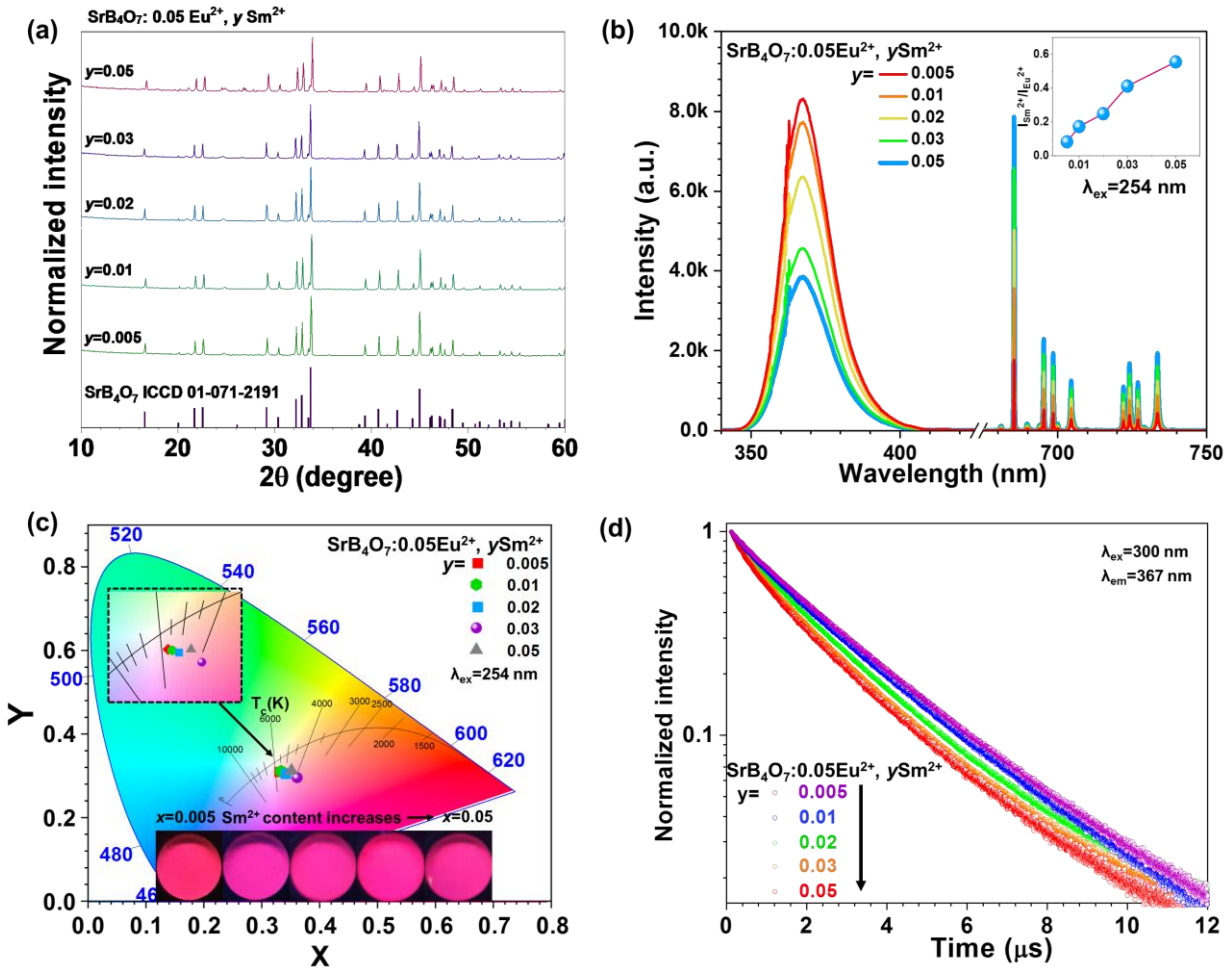

Figure S5 (a) XRD patterns of the SrB_4O_7: y Sm^{2+}, 0.005 Eu^{2+} (*y*=0.005, 0.01, 0.02, 0.03 and 0.05) micro-particles. (b)The emission spectra with excitation wavelength λ_{ex}=254 nm. The inset of (b) shows the corresponding Sm^{2+}/Eu^{2+} integrated intensity ratio as a function of Sm^{2+} content. (c) CIE chromaticity diagram and luminescent images excited at 254 nm LED light. These samples are white powders at daylight. (d) The luminescence decay curves recorded for the Eu^{2+} ($4f^65d \rightarrow 4f^7$ transition) of obtained samples.

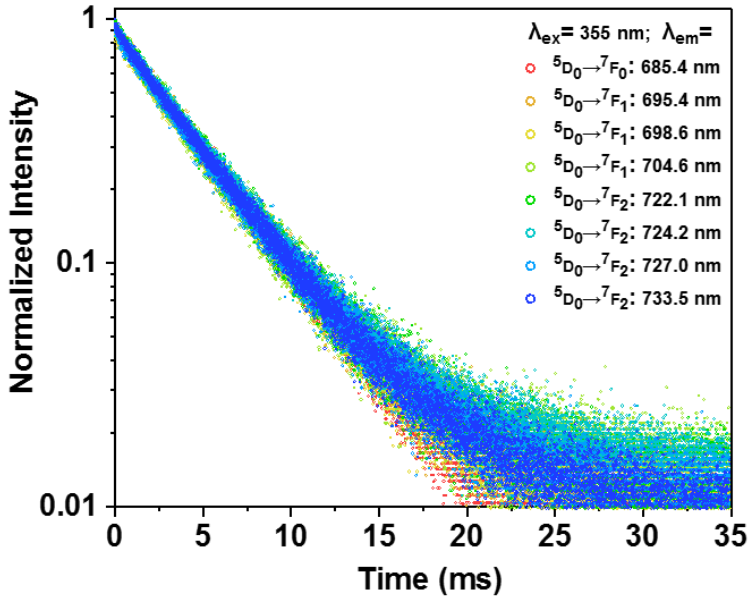

Figure S6. The luminescence decay curves recorded for the Sm^{2+} ($^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$ transitions) of obtained samples.

Table S1. The integrated emission intensity of Sm^{2+} ($I_{Sm}{}^{2+}$) and Eu^{2+} ($I_{Eu}{}^{2+}$), corresponding multiples of the increase in Sm^{2+} emission at different Eu^{2+} concentration and the integrated intensity ratio of Eu^{2+}/Sm^{2+} ($I_{Eu}{}^{2+}/ I_{Sm}{}^{2+}$) of the SrB_4O_7:0.01 Sm^{2+}, *x* Eu^{2+} (*x*=0, 0.005, 0.01, 0.03, 0.05, 0.07 and 0.09) micro-particles.

Eu^{2+} content	0	0.005	0.01	0.03	0.05	0.07	0.09
I_{Eu}^{2+}	0	60241.7	104373.6	140794.4	184633.8	192050.6	200760.0
I_{Sm}^{2+}	119.5	1870.3	3694.5	7211.2	6502.0	6427.7	5808.9
Enhancement	-	15.7	30.9	60.4	54.4	53.8	48.6
I_{Eu}^{2+}/ I_{Sm}^{2+}	-	3.6	3.8	4.2	4.3	4.7	4.3

Table. S2. The determined color coordinates of the SrB_4O_7:0.01 Sm^{2+}, *x* Eu^{2+} (*x*=0, 0.005, 0.01, 0.03, 0.05, 0.07 and 0.09) micro-particles under 254 nm excitation.

Eu^{2+} doping concentration	Color coordinates (x,y)
0	(0.48158, 0.37176)
0.005	(0.32549, 0.30865)
0.01	(0.33005, 0.32013)
0.03	(0.32868, 0.31012)
0.05	(0.32469, 0.3051)
0.07	(0.32691, 0.31423)
0.09	(0.32218, 0.30554)

Table. S3. The determined color coordinates of the SrB_4O_7:0.01 Sm^{2+}, 0.03Eu^{2+} micro-particles under excitation wavelength from 250-350 nm.

excitation wavelength (nm)	Color coordinates (x,y)
250	(0.33001, 0.32544)
280	(0.33547, 0.30388)
300	(0.33822, 0.30787)

320	(0.35061, 0.29726)
340	(0.35453, 0.31118)

Table S4. Calculated spectral positions (peak centroids) of the $^5D_0 \rightarrow {}^7F_0$ and $^5D_0 \rightarrow {}^7F_1$ emission peaks, and the corresponding pressure-induced wavelength shift rates.

	Peak centroid (nm) ambient conditions	Peak centroid (nm) at 58.07 GPa	$d\lambda/dP$ (nm/GPa)
$^5D_0 \rightarrow {}^7F_0$	685.3784	702.3325	0.291959
$^5D_0 \rightarrow {}^7F_1$	695.4777	710.5647	0.259807
	698.7308	716.3253	0.302988
	704.6798	722.3945	0.305058

Table. S5. The determined color coordinates of the SrB_4O_7: y Sm^{2+}, *x* Eu^{2+} (*x*=0.005, 0.01, 0.02, 0.03 and 0.05) micro-particles under 254 nm excitation.

Sm^{2+} doping concentration	Color coordinates (x,y)
0.005	(0.32933, 0.31220)
0.01	(0.33337, 0.31083)
0.02	(0.33986, 0.30815)
0.03	(0.36112, 0.29559)
0.05	(0.35130, 0.31231)

Table. S6. Determined luminescence lifetimes for the emission bands (Stark sublevels) of Sm^{2+}:$^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions in the SrB_4O_7: 0.01 Sm^{2+}, 0.03 Eu^{2+} system, obtained under λ_{ex} = 355 nm.

λ_{em} (nm)	*Transitions*	τ (ms)	R^2
685.4	$^5D_0 \rightarrow {}^7F_0$	4.17 5± 0.009	0.998
695.4	$^5D_0 \rightarrow {}^7F_1$	4.236 ± 0.013	0.996
698.6	$^5D_0 \rightarrow {}^7F_1$	4.243 ± 0.013	0.995
704.6	$^5D_0 \rightarrow {}^7F_1$	4.227 ± 0.006	0.995
722.1	$^5D_0 \rightarrow {}^7F_2$	4.294 ± 0.006	0.996
724.2	$^5D_0 \rightarrow {}^7F_2$	4.342 ± 0.005	0.997
727.0	$^5D_0 \rightarrow {}^7F_2$	4.278 ± 0.006	0.996
733.5	$^5D_0 \rightarrow {}^7F_2$	4.286 ± 0.004	0.998