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Supplementary Information

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Supplementary Information on:

Pressure influence on excitonic luminescence of $CsPbBr_3$ perovskite

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Luminescence as a function of temperature and different points of the sample

In most cases, excitons bound to defects exhibit a much faster temperature-induced quenching compared to free excitons. For instance, in the study of $FA_xMA_{1-x}PbI3$ [1], various spectral lines below the free exciton were attributed to different defect types, and the luminescence of these defects was observed to decay well below 100 K. In our investigation, as depicted in Fig.SI. 1, the line assigned to the Rashba exciton demonstrates a quenching rate similar to or even slower than that of the free exciton. Hence, despite the absence of substantial evidence supporting the Rashba effect assignment in this study, it was designated as the Rashba exciton. It is worth noting that the temperature dependence of the Rashba exciton's position aligns with the findings of [2]. In contrast, the authors of [2] concluded that $CsPbBr_3$ lacks Rashba splitting at temperatures below 90 K, contradicting our observations. However, the work [3] provides compelling evidence supporting the presence of the Rashba effect in $CsPbBr_3$ at low temperatures. In conclusion, the assignment of the 542 nm line remains contentious, necessitating further investigations to address this issue.

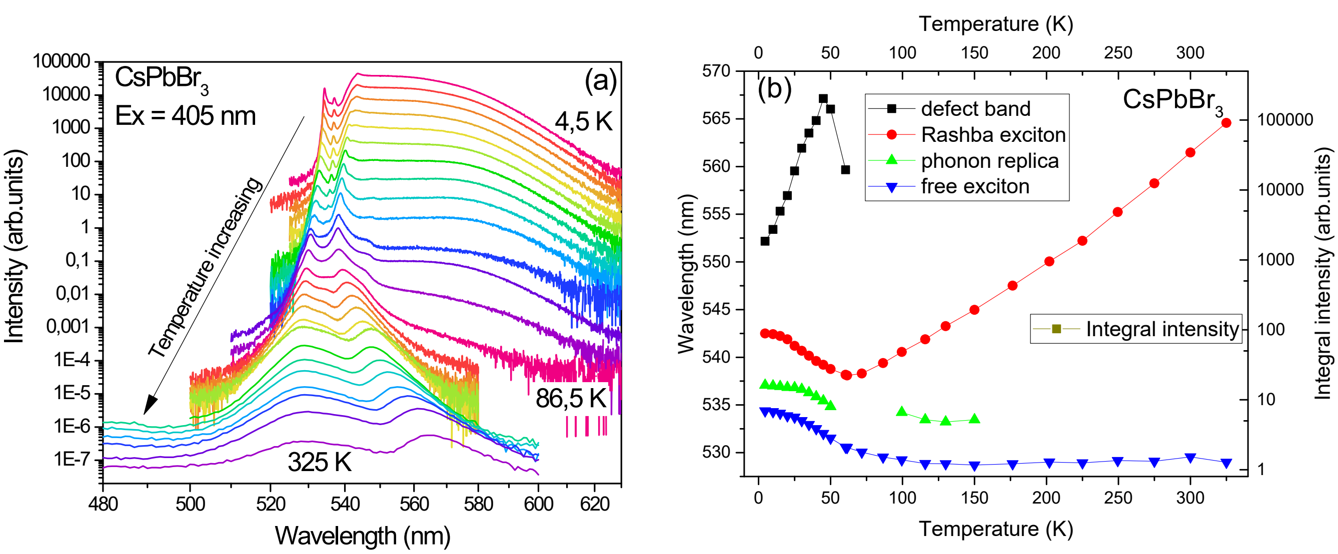

Fig.SI. 1. $CsPbBr_3$ luminescence dependence on temperature. (a) – luminescence spectra, (b) – position of the lines and the integral intensity of the luminescence.

The low-temperature spectra of the sample's luminescence are presented in Fig.SI. 2. These spectra were obtained by exciting the sample with a laser focused on various points. All spectra are normalized to the intensity of the free exciton. As depicted in Fig.SI. 2, different regions of the sample exhibit slightly different luminescence spectra, indicating sample inhomogeneity. The presence of the Rashba

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effect relies on the breaking of inversion symmetry within the $CsPbBr_3$ crystal structure. In the orthorhombic $CsPbBr_3$, lead (Pb) occupies a site that possesses inversion symmetry. However, if the sample is nonhomogeneous or contains defects, the symmetry may be disrupted in certain regions, thereby exhibiting Rashba luminescence.

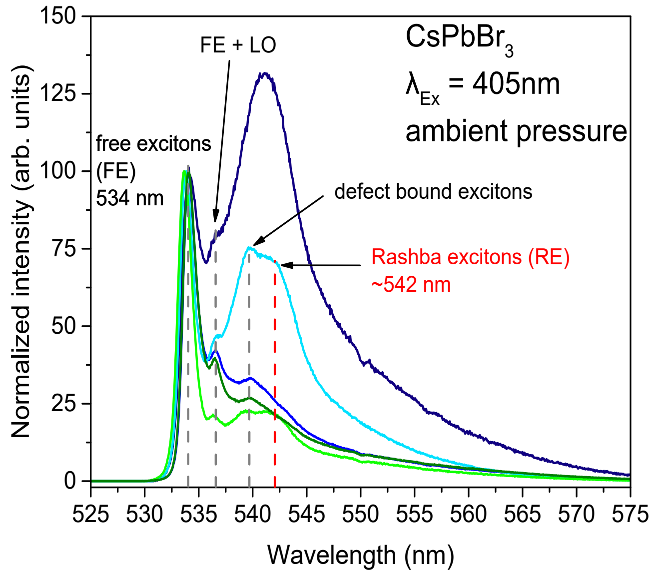

Fig.SI. 2. Comparison of the luminescence of different parts of the $CsPbBr_3$ sample at liquid helium temperature.

XRD Measurements of the $CsPbBr_3$

As shown in Fig.SI. 3, the single crystal X-ray diffraction (XRD) measurements confirmed the presence of the orthorhombic (Pbnm) phase in the sample, with the [002] orientation. It is important to note that the crystal was not intentionally oriented prior to the measurement, resulting in a random orientation. The powder diffraction analysis also exhibited distinct diffraction lines corresponding to the orthorhombic (Pbnm) phase.

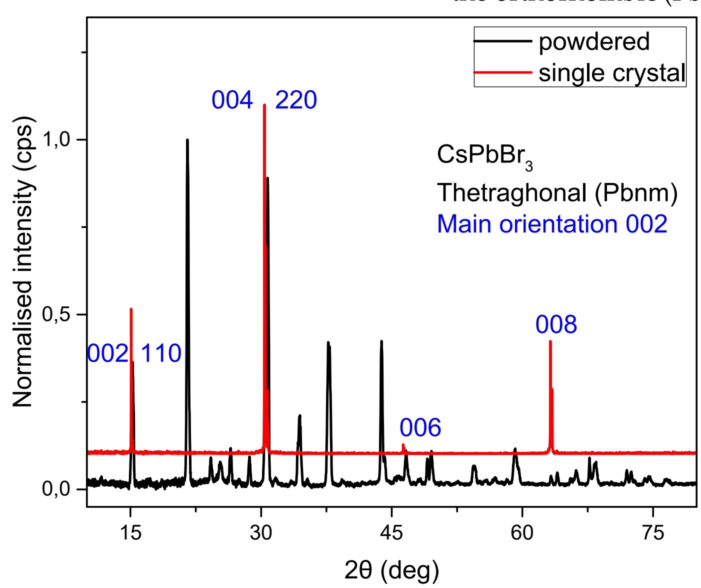

Fig.SI. 3. The results of the XRD measurements of single crystal and powdered $CsPBBr_3$.

Luminescence spectra

To assess the reproducibility of the experiment, multiple measurements of $CsPbBr_3$ under pressure were conducted. The data used in this study primarily came from two sets of measurements, as shown in Fig.SI. 4. Specifically, selected curves from Fig.SI. 4a are presented in the main text. It is worth noting that the spectra in panels a and b exhibit slight differences. This variation can be attributed to the fact that the measurements were performed on two different pieces of the same inhomogeneous sample. The presence of inhomogeneity in the sample is also evident in Fig.SI. 2.

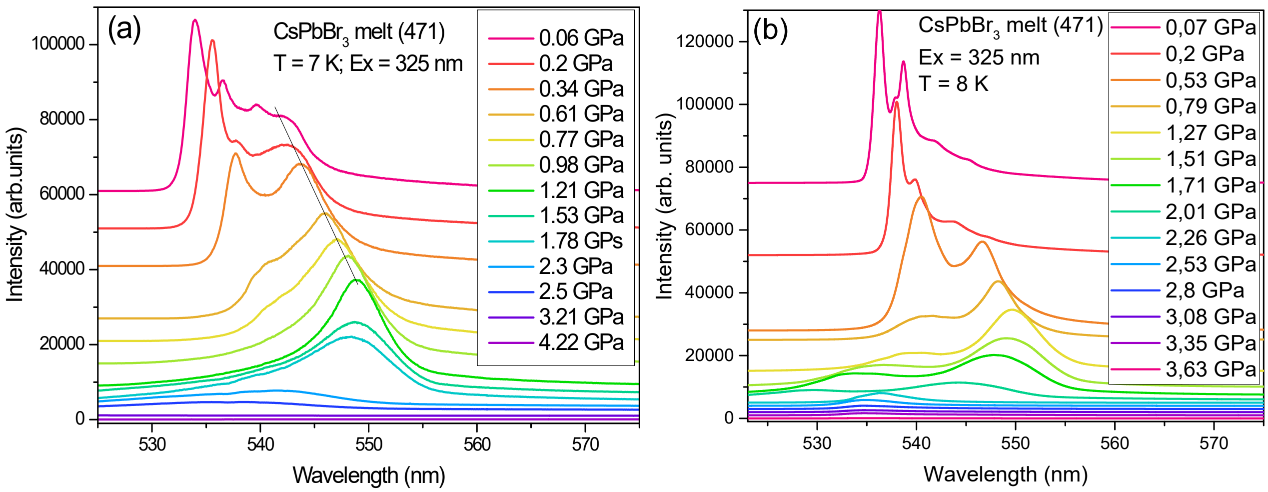

Fig.SI. 4. Low-temperature luminescence of $CsPbBr_3$ as a function of high pressure. (a) and (b) are two measurements of different pieces of the same sample (from the melt, number 471). Oil was used as a pressure-transmitting medium

Fittings of the spectra with Gaussian functions

Fig.SI. 6 illustrates several luminescence spectra along with their corresponding fittings. It can be observed that the phonon replicas and defect-bound excitons diminish rapidly with increasing pressure, whereas the intensity of the Rashba exciton exhibits an opposite trend by increasing. As the pressure rises, the accuracy of the fittings decreases, leading to multiple options of slightly different Gaussian fittings. This is demonstrated in Fig.SI. 5, which showcases two different fitting options at a pressure of 2.3 GPa. Initially, they may appear significantly distinct, but when the respective parameters are inserted into the dependencies shown in Fig.SI. 7, both options yield acceptable results due to the substantial scattering of the data points.

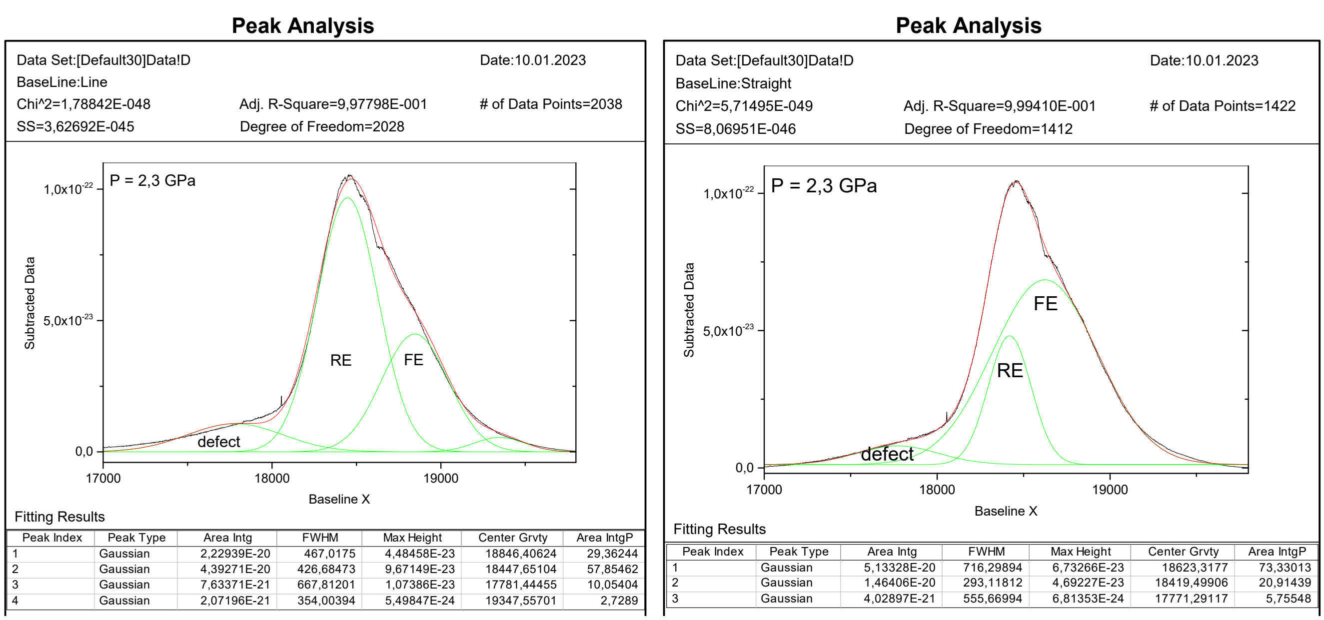

Fig.SI. 5. Two possible options for the fitting of the luminescence spectra at 2.3 GPa.

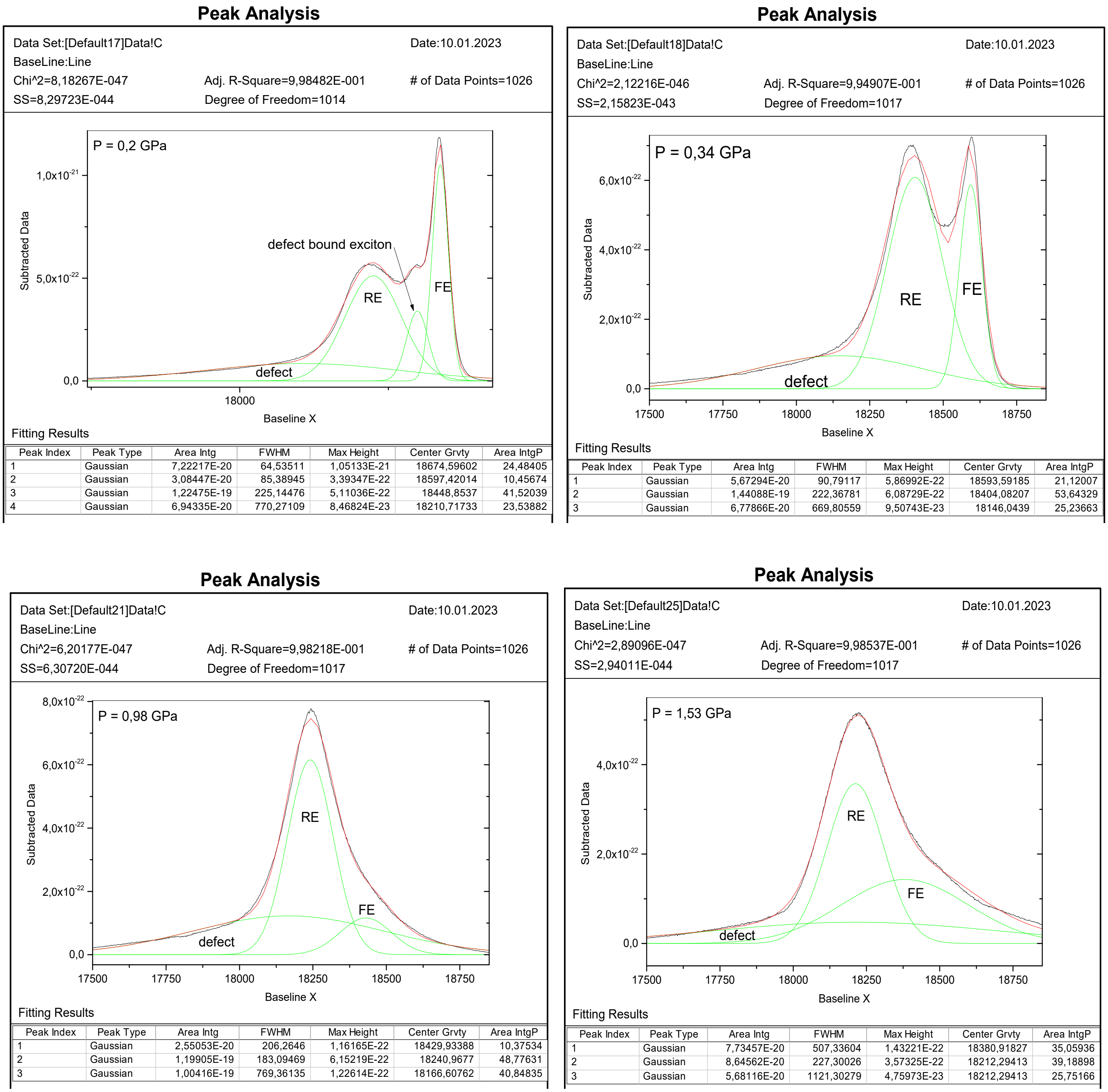

Fig.SI. 6. Fitting of some $CsPbBr_3$ high-pressure spectra (0.2, 0.34, 0.98, and 1.53 GPa).

Intensity and position of the luminescence lines as a function of pressure

If we consider all the data from both measurements (refer to Fig.SI. 4), the pressure dependence of the intensity would resemble that shown in Fig.SI. 7a. Consequently, the integral intensity was calculated by integrating under the luminescence spectrum. Subsequently, the intensity of the Rashba exciton was estimated by identifying the maximum intensity of the Rashba line. Similarly, the intensity of the free exciton was estimated as the difference between the integral intensity and the Rashba exciton intensity. This approach tends to overestimate the intensity of the free exciton, particularly in the low-pressure range (below 0.3 GPa), due to the presence of other lines in the spectra at that pressure range. Nevertheless, this approach yields qualitatively similar results to those obtained from the fitting in Fig.SI. 7 a. The fitting process involved additional data processing steps such as background subtraction, selecting the number of Gaussian functions for the fit, and occasionally manually adjusting or fixing certain fit parameters. In contrast, the second approach (Fig.SI. 7b) required less manual intervention. Considering the reduced need for manual adjustments, lower data scattering, and overall similarity of the results, the outcome of the second approach was presented in the main text of the study.

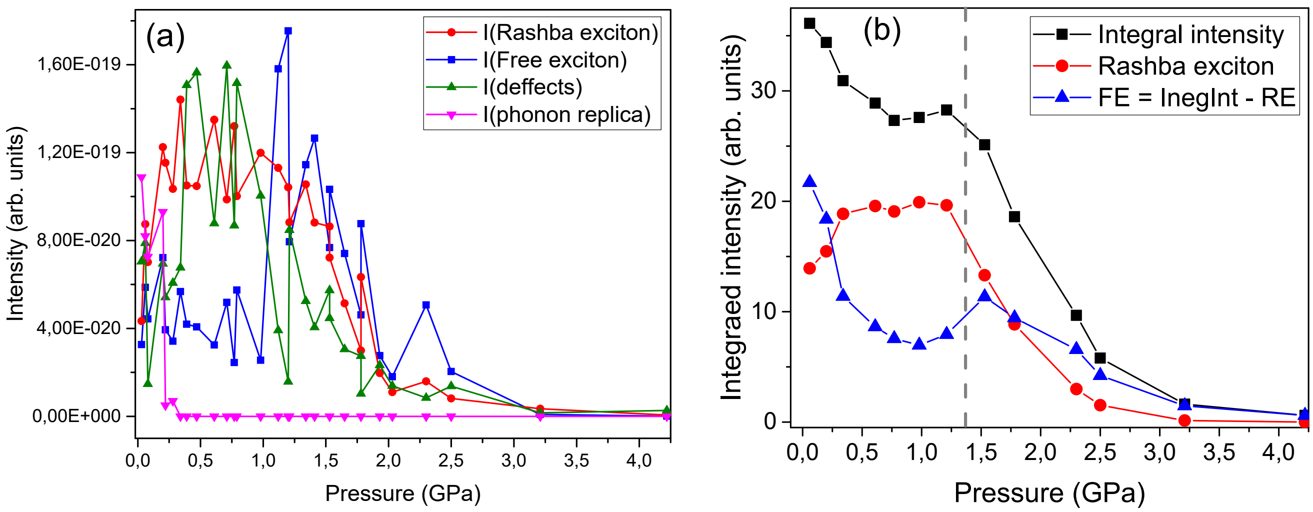

Fig.SI. 7. Intensity of the luminescence lines (a) – from fitting, (b) – a copy of Fig. 3 from the main text.

References

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