

# Spectroscopic studies of Bi<sup>3+</sup>-doped Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub> garnet

V. Tsiurma<sup>1,2,\*</sup>, A. Krasnikov<sup>3</sup>, Ya. Zhydachevskyy<sup>1,4</sup>, Yu. Hizhnyi<sup>5</sup>, S.G. Nedilko<sup>5</sup>, Ł. Wachnicki<sup>1</sup>, L. Vasylechko<sup>4</sup>, S. Zazubovich<sup>3</sup>, A. Suchocki<sup>1,6</sup>

<sup>1</sup> Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, Warsaw, 02-668, Poland

E-mail: [tsiurma@ifpan.edu.pl](mailto:tsiurma@ifpan.edu.pl)

<sup>2</sup> Ivan Franko National University of Lviv, Kyryla and Mefodiya 8a, Lviv 79005, Ukraine

<sup>3</sup> Institute of Physics, University of Tartu, W. Ostwaldi 1, Tartu 50411, Estonia

<sup>4</sup> Lviv Polytechnic National University, 12 Bandera, Lviv 79646, Ukraine

<sup>5</sup> Taras Shevchenko National University of Kyiv, Ukraine

<sup>6</sup> Institute of Physics, University of Bydgoszcz, Weyssenhoffa 11, Bydgoszcz 85-072, Poland

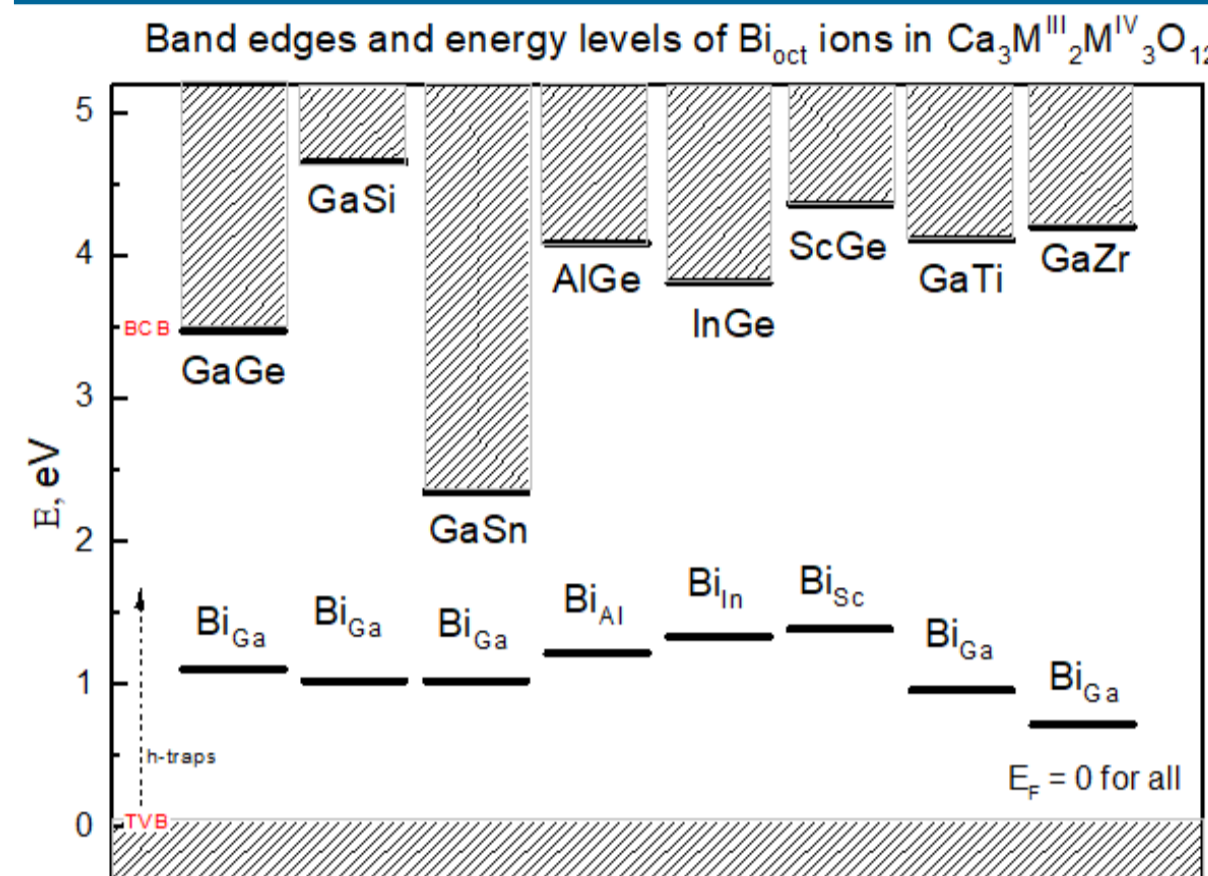


## Motivation and aim of the work

In this study, the possibility of Bi<sup>3+</sup> activation was studied in Ca-(Al, Ga, In, Si, Ge, Sn, Ti, Zr, Hf)-based garnets. The DFT-based theoretical calculations with use of the Plane-Wave Pseudopotential method were carried out in order to establish the band structures of the crystals and positions of the Bi<sup>3+</sup> states relatively to the band edges.

The Ca<sub>3</sub>Ga<sub>2</sub>Ge<sub>3</sub>O<sub>12</sub> (CGGG) both pure and Bi-doped were chosen to be studied experimentally by luminescence techniques. CGGG possesses low melting point (T<sub>melt</sub> = 1370 °C), a broad defect-related absorption and luminescence which makes them of interest to be studied as the phosphors for WLED.

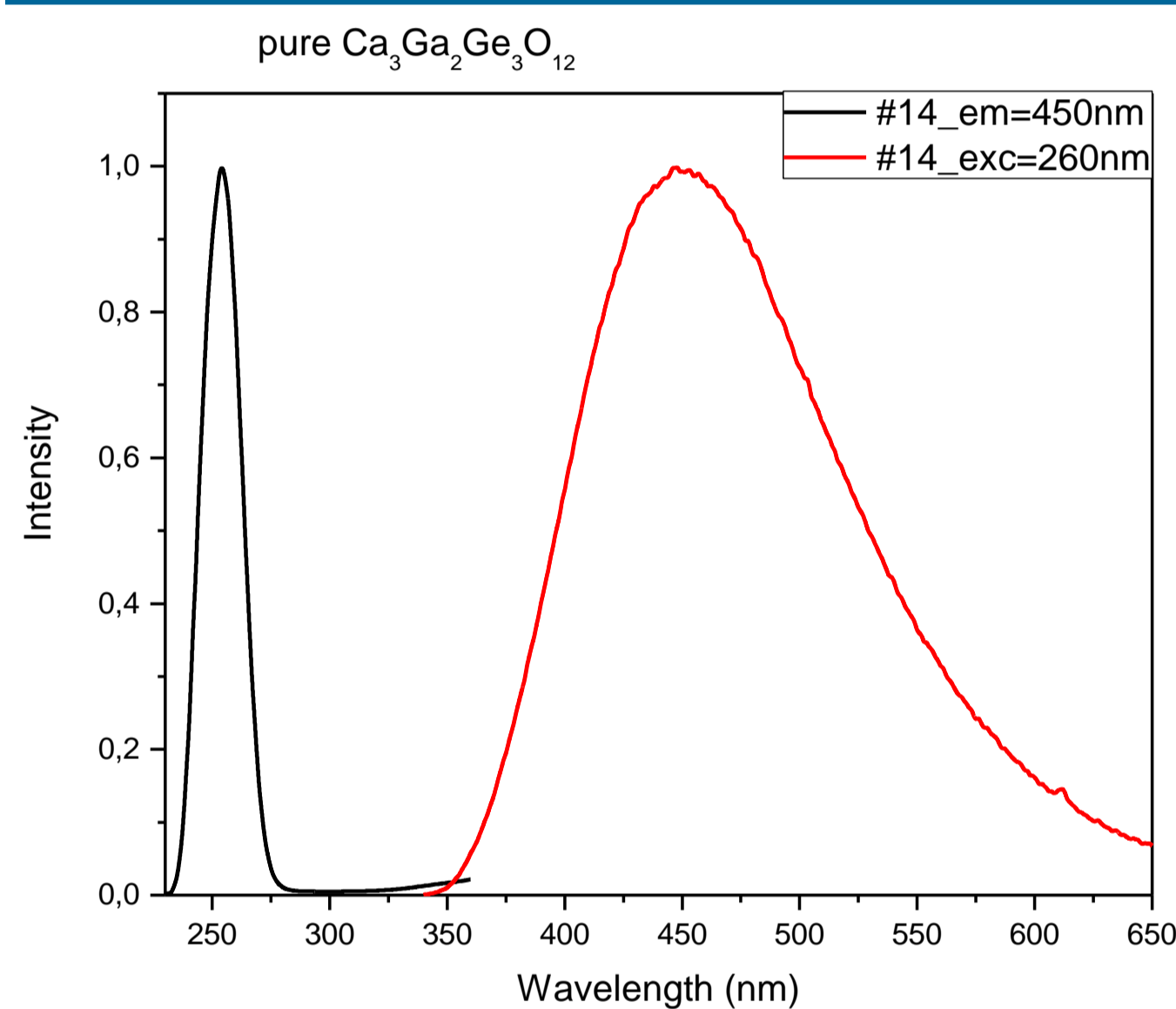
## Band structure calculations



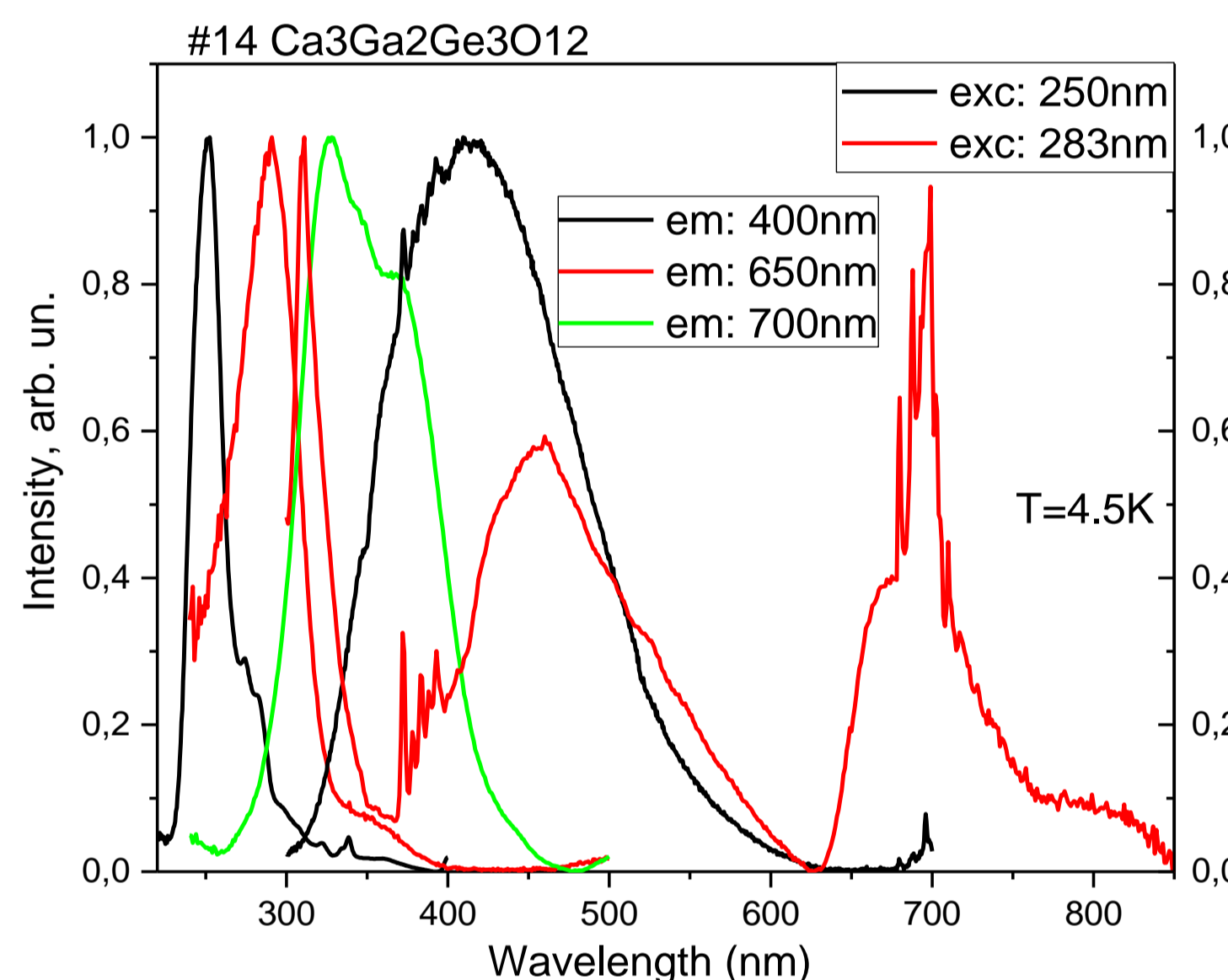
## Phase composition

	Phase composition	Lattice parameter
14 - Ca <sub>3</sub> Ga <sub>2</sub> Ge <sub>3</sub> O <sub>12</sub> , 1250 °C	Almost pure garnet	a = 12.2514(1)
16 - Ca <sub>3-x</sub> Ga <sub>2+x</sub> Ge <sub>3-x</sub> O <sub>12</sub> :Bi (5%), 1150 °C	Garnet + Bi <sub>2</sub> O <sub>3</sub> + Ga <sub>2</sub> O <sub>3</sub> + GeO <sub>2</sub>	a = 12.2548(2)
17 - Ca <sub>3</sub> Ga <sub>2-x</sub> Ge <sub>3</sub> O <sub>12</sub> :Bi (5%), 1150 °C	Garnet + Ga <sub>2</sub> O <sub>3</sub> + Ca <sub>5</sub> Ge <sub>3</sub> O <sub>11</sub>	a = 12.2553(2)
18 - Ca <sub>3</sub> Ga <sub>2</sub> Ge <sub>3</sub> O <sub>12</sub> :Bi (5%) excess, 1150 °C	Garnet + Bi <sub>2</sub> O <sub>3</sub> + Ga <sub>2</sub> O <sub>3</sub> + GeO <sub>2</sub>	a = 12.2568(1)

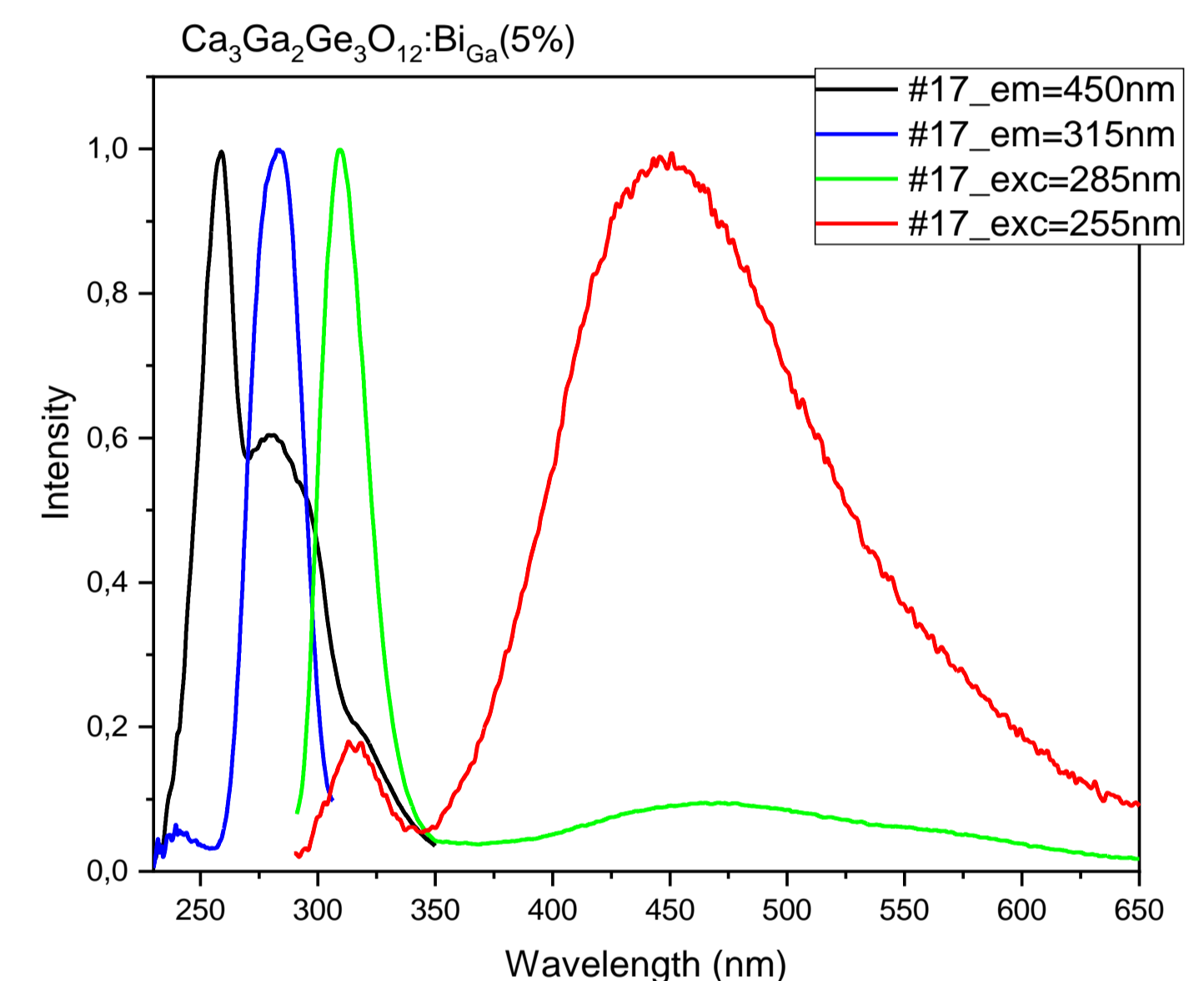
## Luminescence of the pure and Bi-doped CGGG microcrystals



Normalized PL and PLE spectra of pure CGGG microcrystals at room temperature

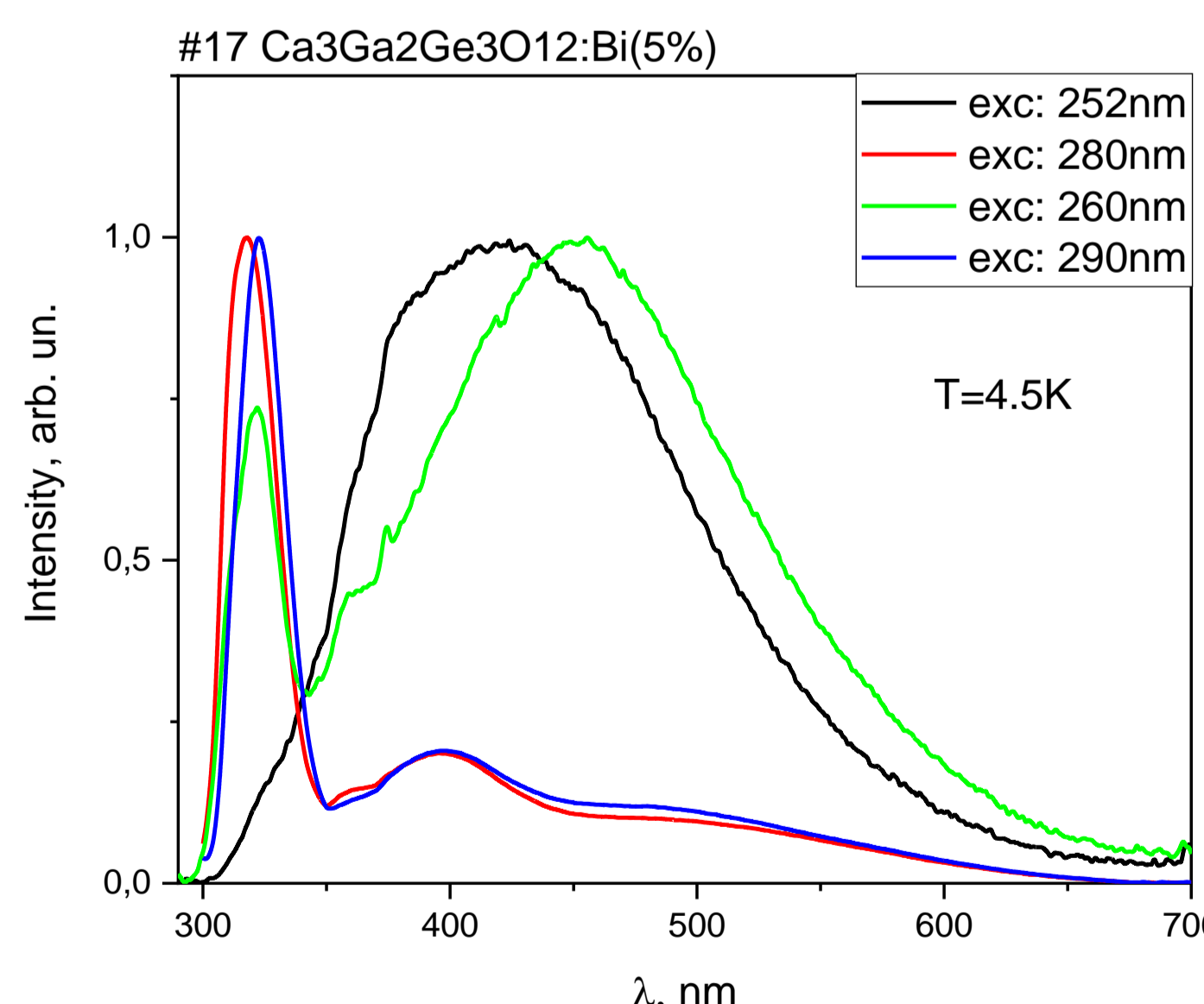
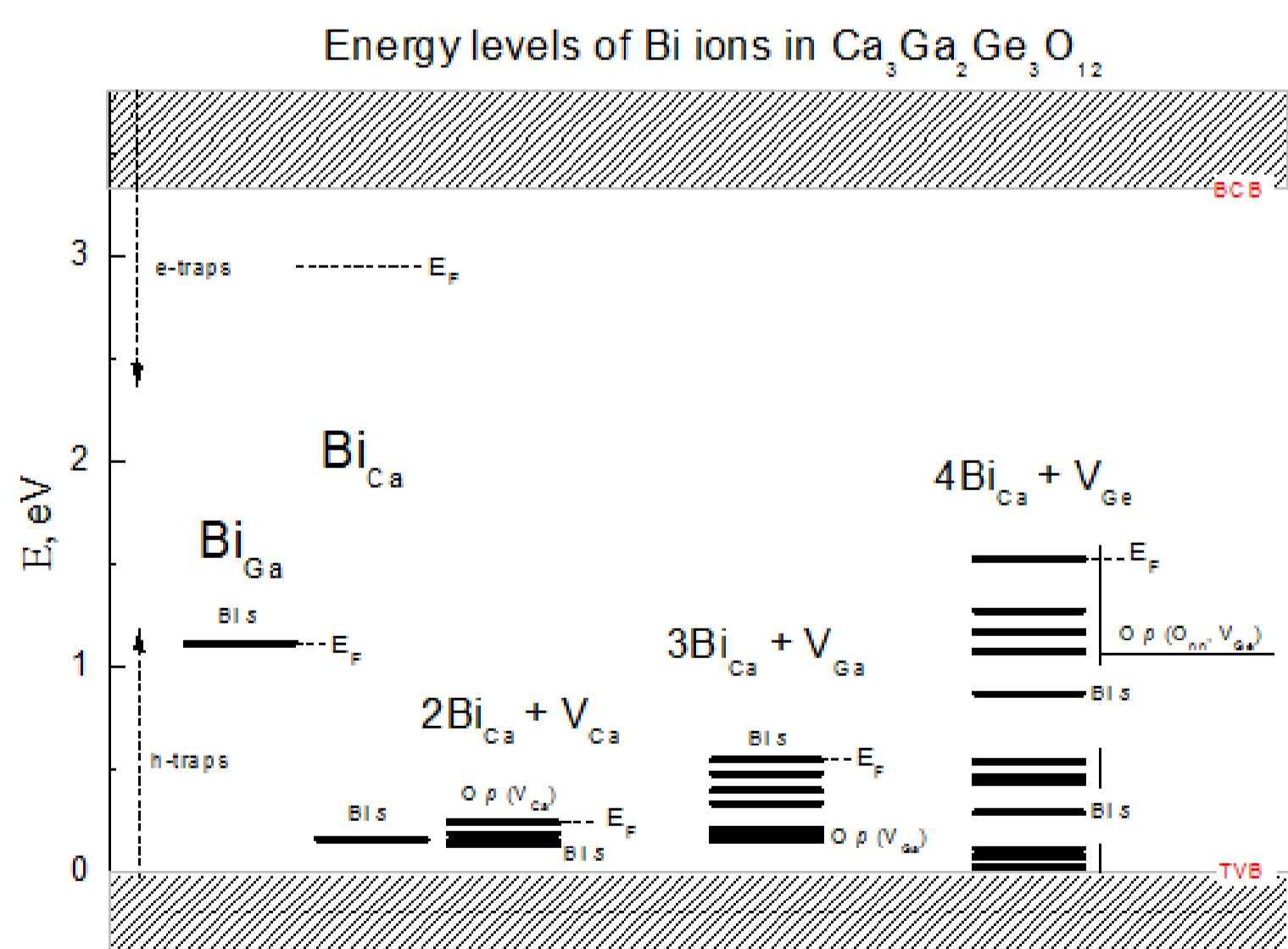


The steady-state emission and excitation spectra of CGGG measured at 4.2 K

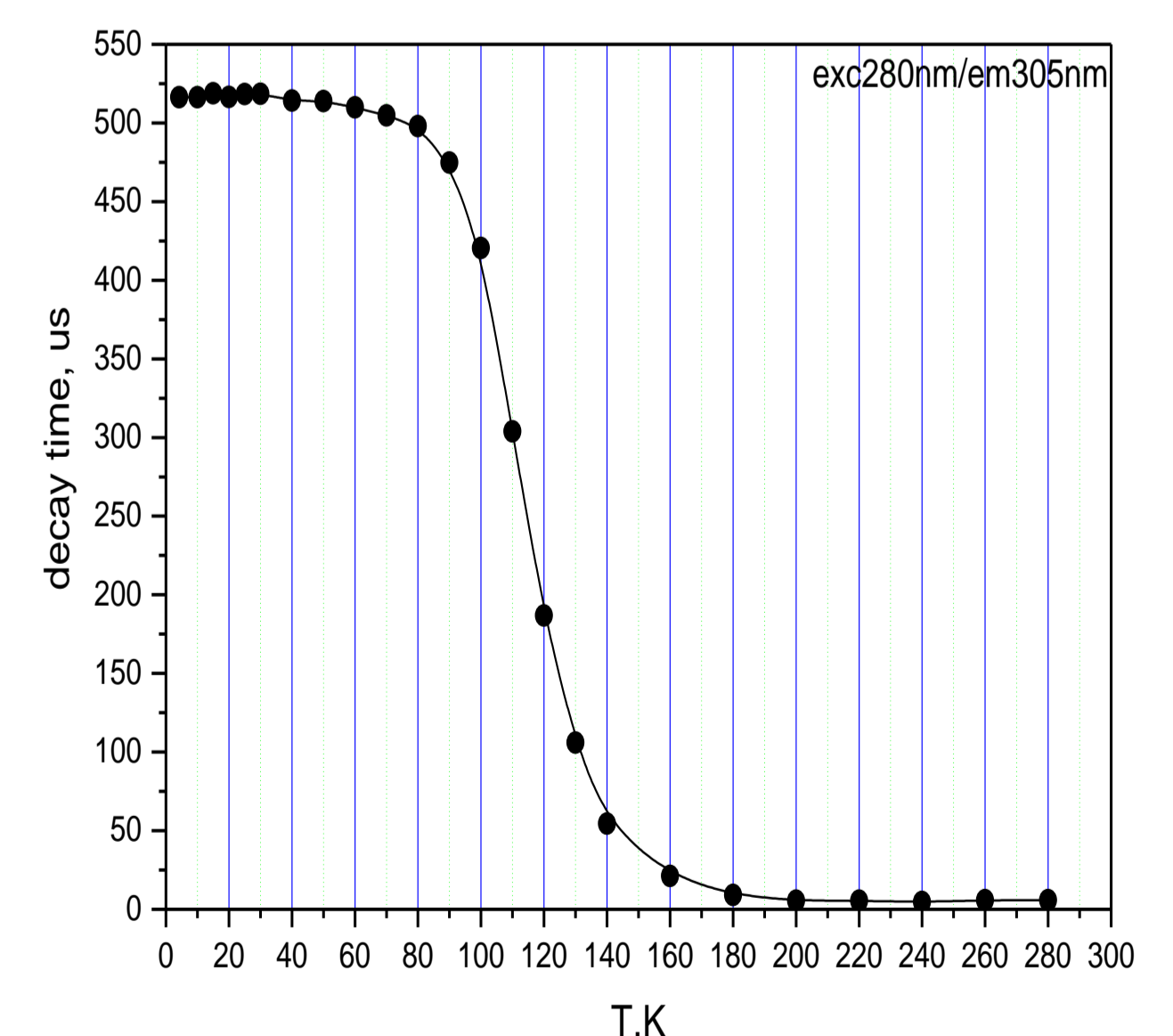


Normalized PL and PLE spectra of Bi-doped CGGG microcrystals at room temperature

## Luminescence decay studies



Emission spectra of CGGG:Bi(5%) measured at 4.2 K



Temperature dependence of the 305 nm emission decay time

## Conclusion

The obtained results testify that besides the intrinsic luminescence, CGGG:Bi<sup>3+</sup> shows two complex Bi<sup>3+</sup>-related emission bands located in the ultraviolet and visible spectral ranges.

The narrow ultraviolet emission with the small Stokes shift arises from the electronic transitions from the triplet relaxed excited state of a Bi<sup>3+</sup> ion, while the broad visible emission with the large Stokes shift arises from an exciton localized around the Bi<sup>3+</sup> ion. The complex structure of both emission bands is probably caused by the presence, besides single Bi<sup>3+</sup> ions, also of Bi<sup>3+</sup> ions associated with their excess charge compensating defects.

## Acknowledgements

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