

Photofunctional Europium-Layered Double Hydroxides for efficient nitrogen oxides removal



UNIVERSIDAD
DE
CÓRDOBA

A. Pastor¹, C. Chen², M. Cruz-Yusta¹, I. Pavlovic¹, D. O'Hare², L. Sánchez¹, M. Sánchez¹.

¹Departamento de Química Inorgánica, Universidad de Córdoba, Campus de Rabanales, E-14071 Córdoba, Spain.

²Chemistry Research Laboratory, Department of Chemistry, University of Oxford, Oxford, OX1 3TA, United Kingdom

q92paesa@uco.es



VII JORNADAS IBÉRICAS DE FOTOQUÍMICA



FQM-214

INTRODUCTION

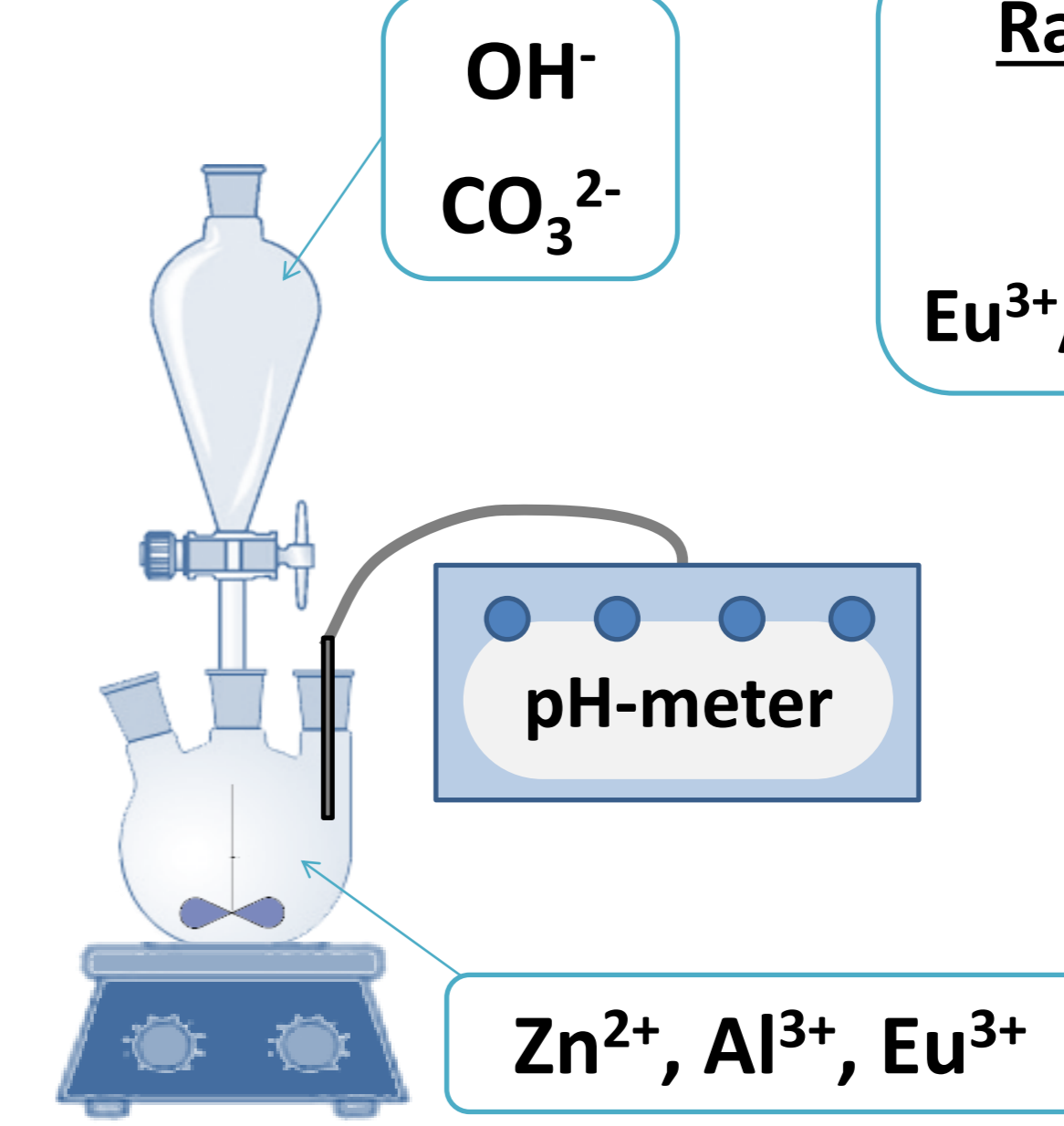
Nowadays there is great concern about NO_x gases pollution (NO_x = NO + NO₂) due to their hazardous effects on health and the environment. The concentration of these gases can be decreased directly from the air in cities through photocatalytic technology (**De-NO_x process**), by means of photocatalytic building materials.

In this regard, Layered Double Hydroxides (LDHs) are interesting compounds due to its high photocatalytic performance [1], low cost and chemical tuneability [2]. However, higher De-NO_x efficiencies are required, specially under Visible light, in order to boost the implementation of this technology in our cities.

Herein, ZnAl-LDH was doped with low amounts of Eu³⁺. The **substitution of Al³⁺ by Eu³⁺**, cations with quite different atomic radii, should induce some **disorder in LDH structure**, which may lead to the creation of defects [3]. These ones play a key role on the electron-hole recombination, light harvesting and thus the photocatalytic capacity is affected.

The LDHs were synthesised by the coprecipitation method. The obtained samples were characterized to analyse their structure, porosity, morphology and optical properties. Subsequently, De-NO_x photocatalytic tests were performed under both simulated solar light and Visible light irradiations.

LDH SYNTHESIS



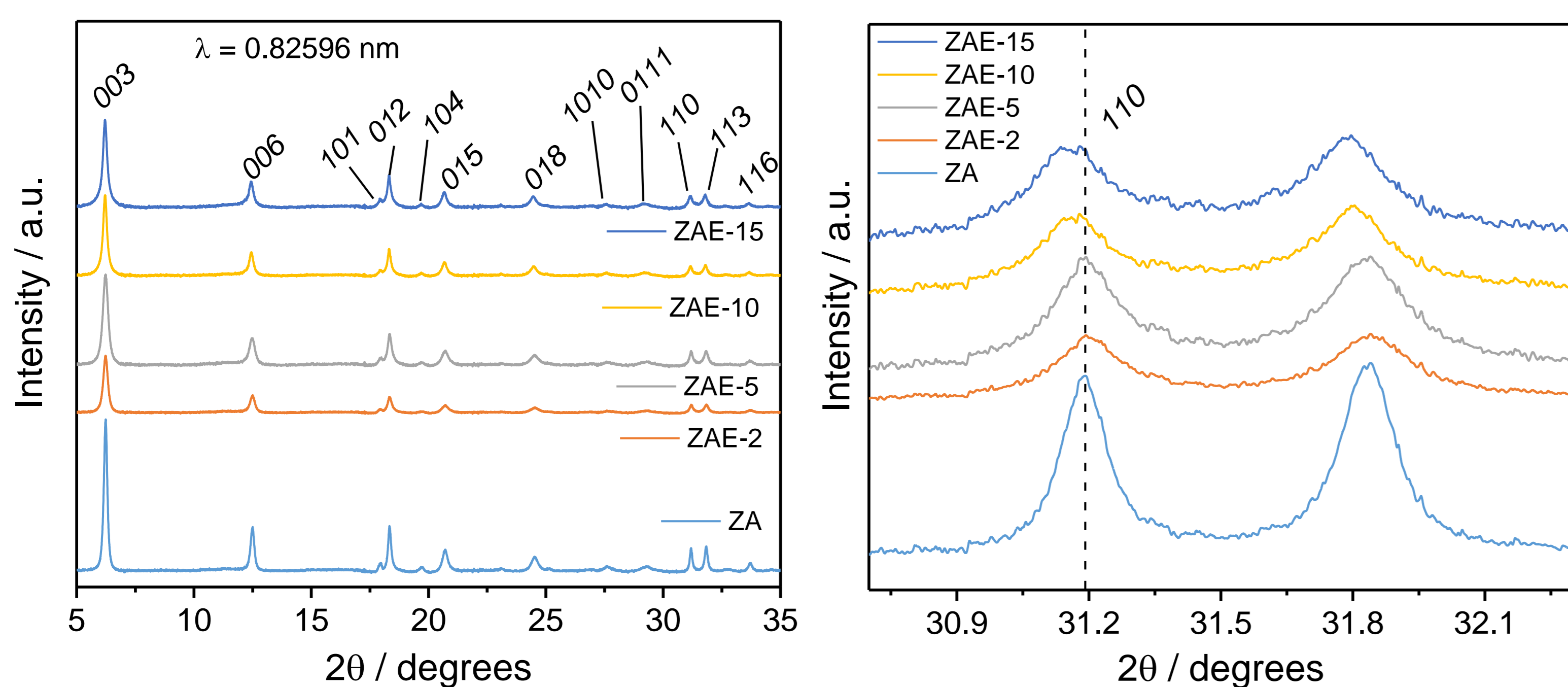
Ratio and doping level:

Zn²⁺ : Al³⁺ = 2 : 1
Eu³⁺/Al³⁺ = 0, 0.02, 0.05, 0.1

Samples:

ZA
ZAE-2
ZAE-5
ZAE-10
ZAE-15

RESULTS

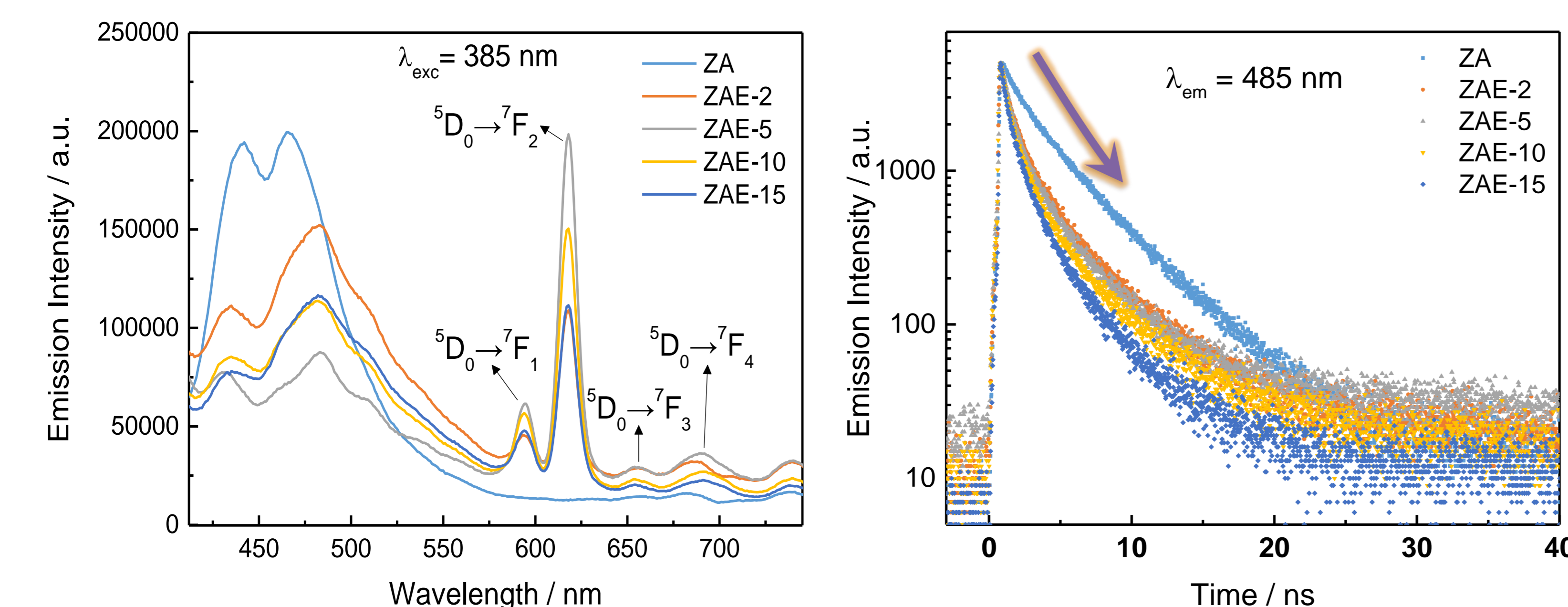


X-ray diffracción

- Typical patterns for LDH structure. No crystalline impurities are observed.
- Remarkable crystallinity decrease of the samples when Eu³⁺ doping takes place. In addition, the displacement of the (110) reflection to lower 2θ values, due to the larger atomic radius of Eu³⁺ vs Al³⁺, indicates that europium has been incorporated into the LDH structural framework.

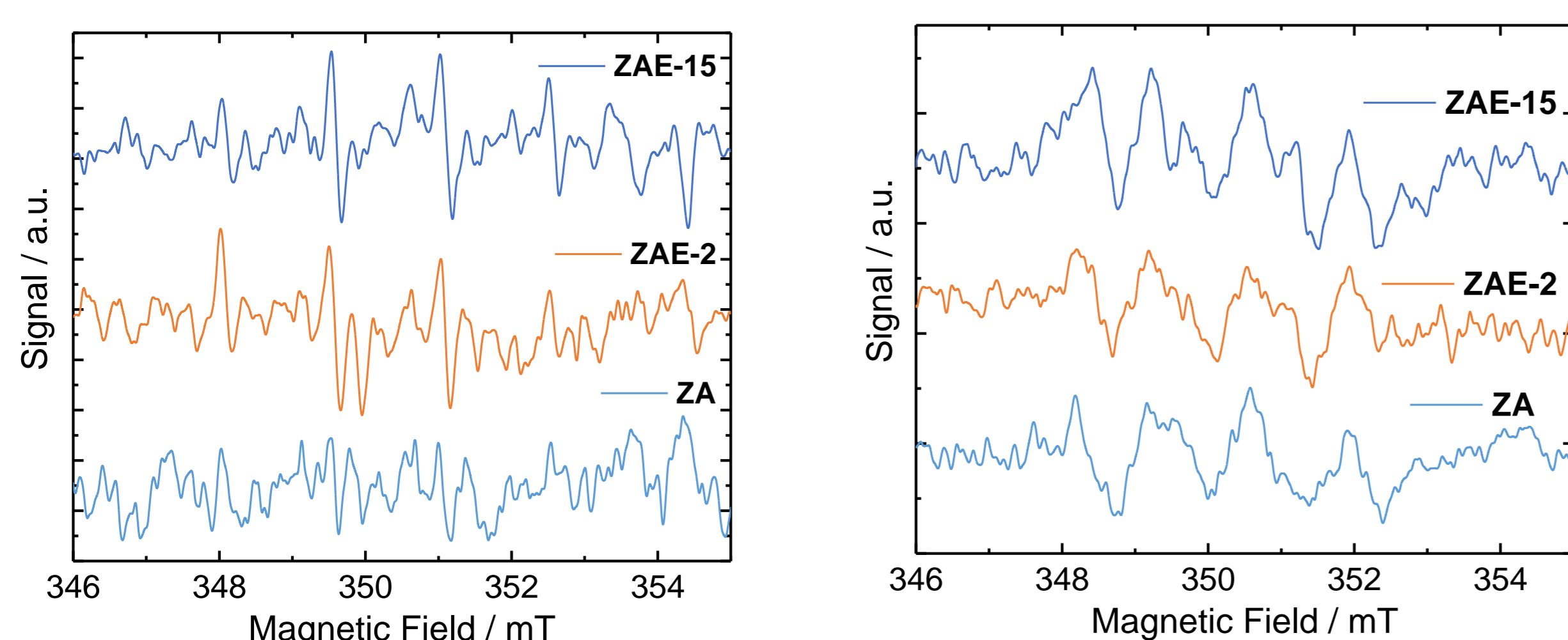
Photoluminescence measurements

- Broad bands < 500 nm → ZnAl structure; Narrow bands > 500 nm → Eu³⁺ f-f transitions
- ⁵D₀-⁷F₂ emission intensity >> ⁵D₀-⁷F₂ emission intensity → Eu³⁺ ions are located at site without an inversion centre (Judd-Ofelt theory) → Disordered LDH framework or structural defects
- PL intensity of ZnAl-LDH signal is quenched when LDH is doped. The lifetime of the ZnAl excited state is decreased.
- Quantum yield is decreased with Eu³⁺ doping (from 12 (ZA) to 2.2 % (ZAE-15))



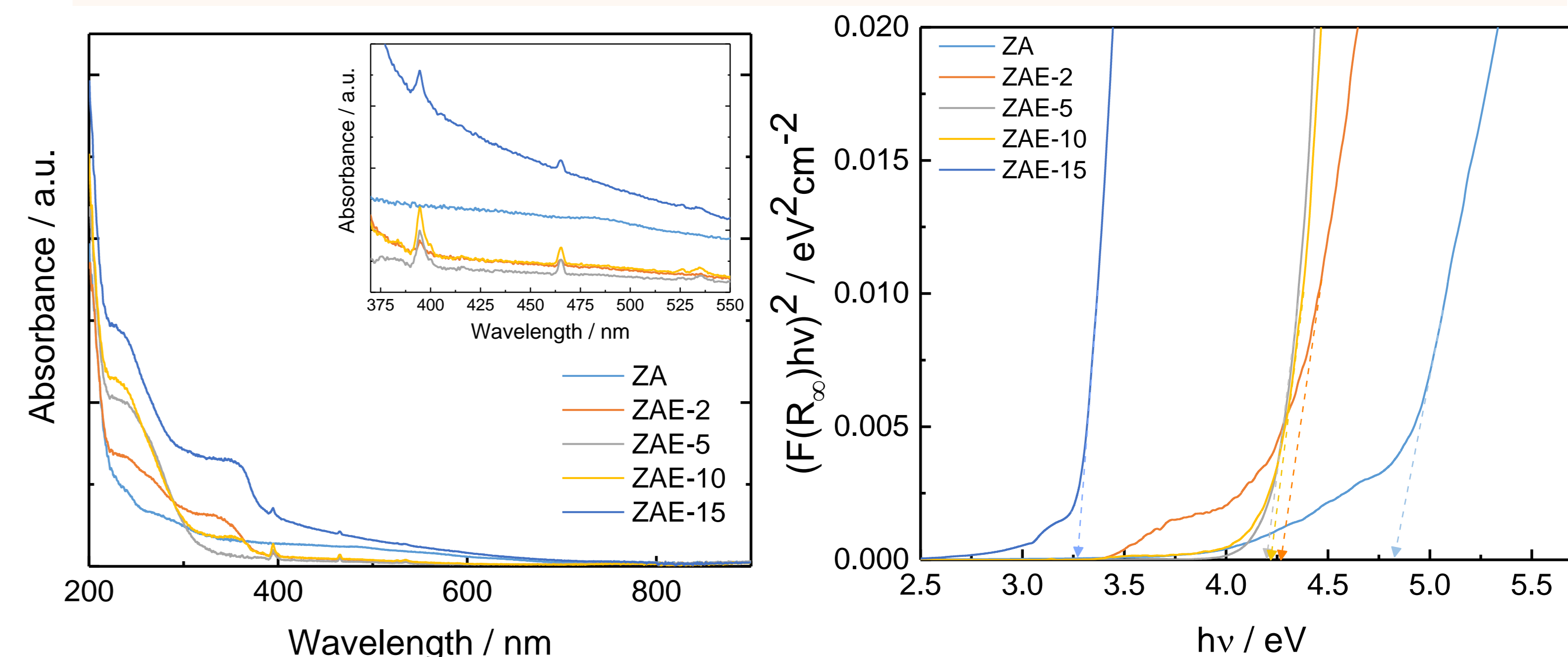
EPR spin-trapping experiments

The production of ·OH (left) and ·O₂⁻ (right) radicals was enhanced in Eu doped LDHs



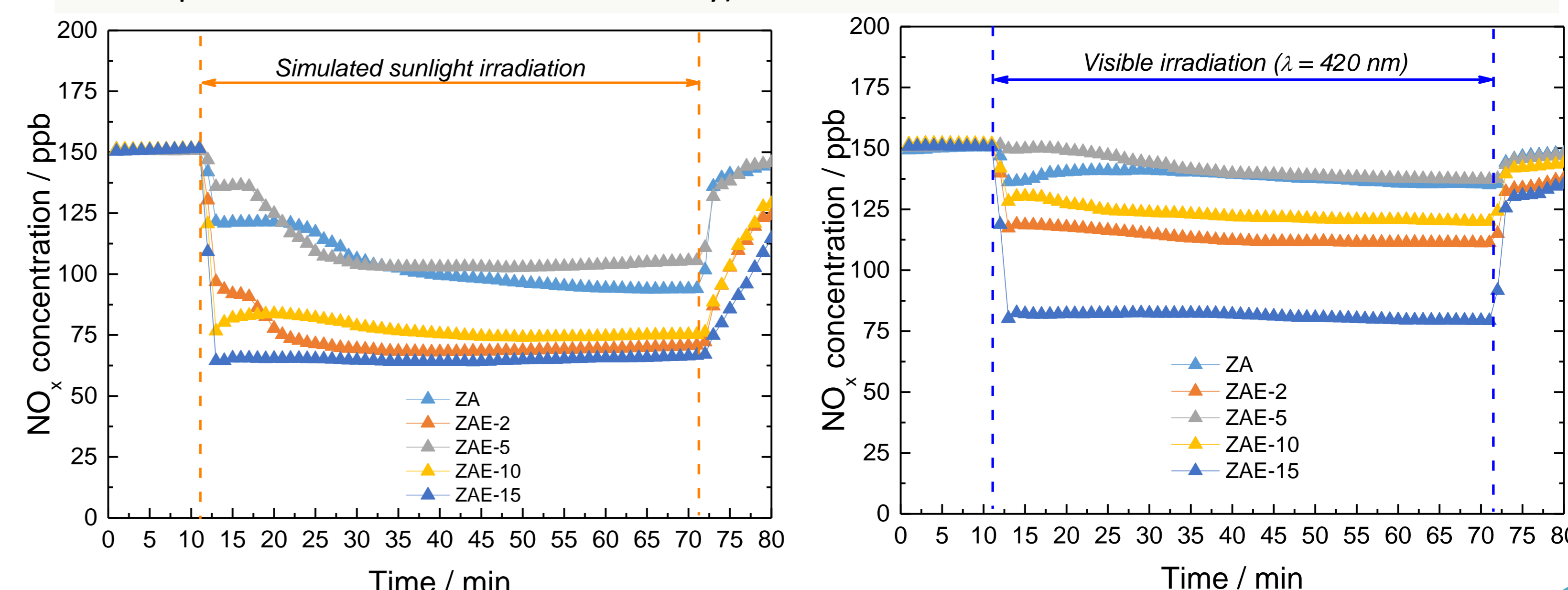
UV-Vis

- Increased absorption in the Visible spectrum range by Eu³⁺ doping.
- Low-intensity absorption peaks at 395, 465, 534 nm due to ⁷F₀ → ⁵L₆, ⁷F₀ → ⁵D₂ and ⁷F₀ → ⁵D₁ transitions from Eu³⁺
- Lower band gap for the Eu³⁺-doped LDHs → existence of empty energy levels.



Photocatalytic De-NO_x tests

- The NO_x concentration decreases when the samples are light irradiated.
- Under simulated sunlight irradiation: doped LDHs (except ZAE-5) show an enhanced De-NO_x efficiency compared to the undoped LDH → ZA ≈ ZAE-5 >> ZAE-10 ≈ ZAE-2 ≈ ZAE-15
- Under visible-light irradiation: De-NO_x efficiency of ZAE-15 is similar to that under simulated sunlight. On the other hand, the De-NO_x efficiency of the other LDHs is decreased
- The higher De-NO_x efficiency of ZAE-15 is explained by the adequate doping level (higher ·OH production and electron-hole delay).



CONCLUSIONS

ZnAl LDHs having diverse Eu³⁺ doping amounts were synthesized by coprecipitation at room temperature. The doping affected the LDH structure, since Eu³⁺ did not show the expected octahedral symmetry for a LDH cation. The shifts in the band gap, enhanced ·OH production and De-NO_x efficiency observed for the optimal composition (ZAE-15) were ascribed to an adequate energy/charge transfer from ZnAl conduction band to Eu³⁺ f levels.

REFERENCES

- [1] F. Rodríguez-Rivas, A. Pastor, C. Barriga, M. Cruz-Yusta, L. Sánchez, I. Pavlovic, *Chemical Engineering Journal*, **2018**, *346*, 151–158.
- [2] L. Mohapatra, K. Parida, *Journal of Material Chemistry A* **2016**, *4*, 10744-10766.
- [3] T. Stumpf, H. Curtius, C. Walther, K. Dardenne, K. Ufer, T. Fanghänel, *Environ. Sci. Technol.* **41** (2007) 3186–3191.

ACKNOWLEDGMENTS

This work was partly financed by FEDER 2014-2020 program (Consejería de Economía, Conocimiento, Empresas y Universidad de la Junta de Andalucía) and Agencia Estatal de Investigación (Spain; PID2020-117516GB-I00).

