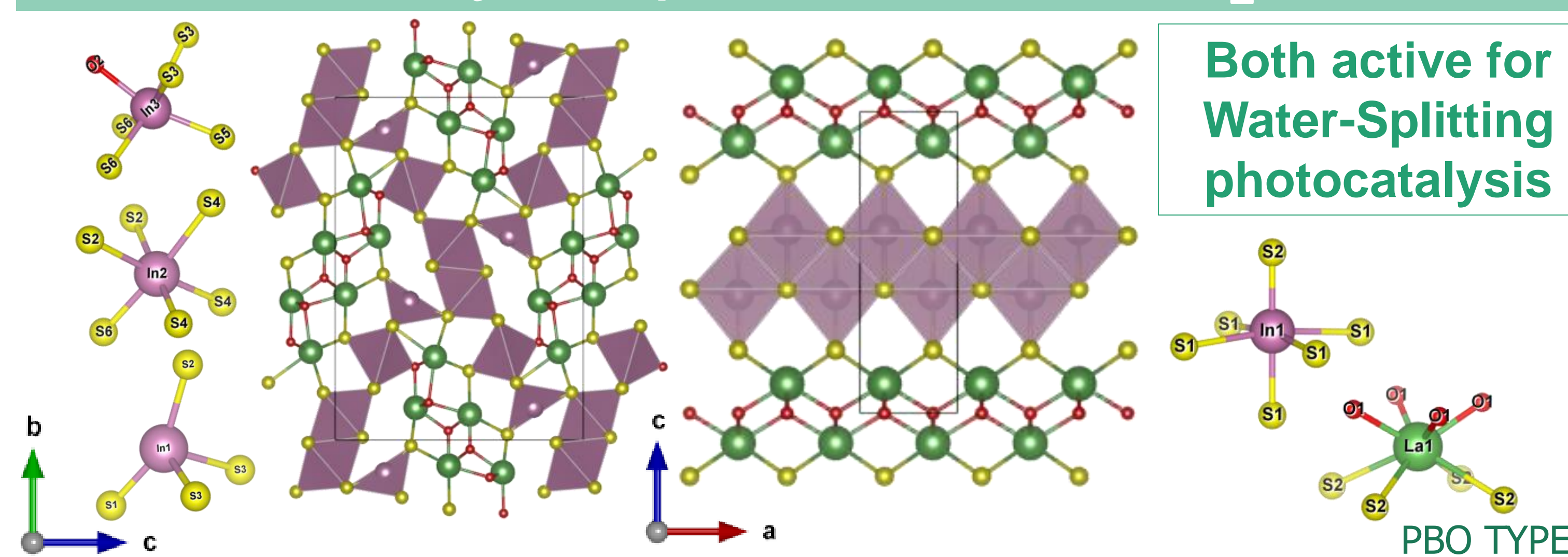


Introduction and objectives

The search for new functional phases is a major task in inorganic chemistry. Mixed anion compounds are ideal to design materials with great control and tunability of the properties. Oxychalcogenides are promising to design sustainable and efficient photocatalysts for the overall water-splitting reaction. Here, we present new phases in the system LaOInS_2 by substituting S by Se and study the impact on the polymorphism and on the photoconduction properties which are crucial for the photocatalytic activity.

Polymorphism of LaOInS_2



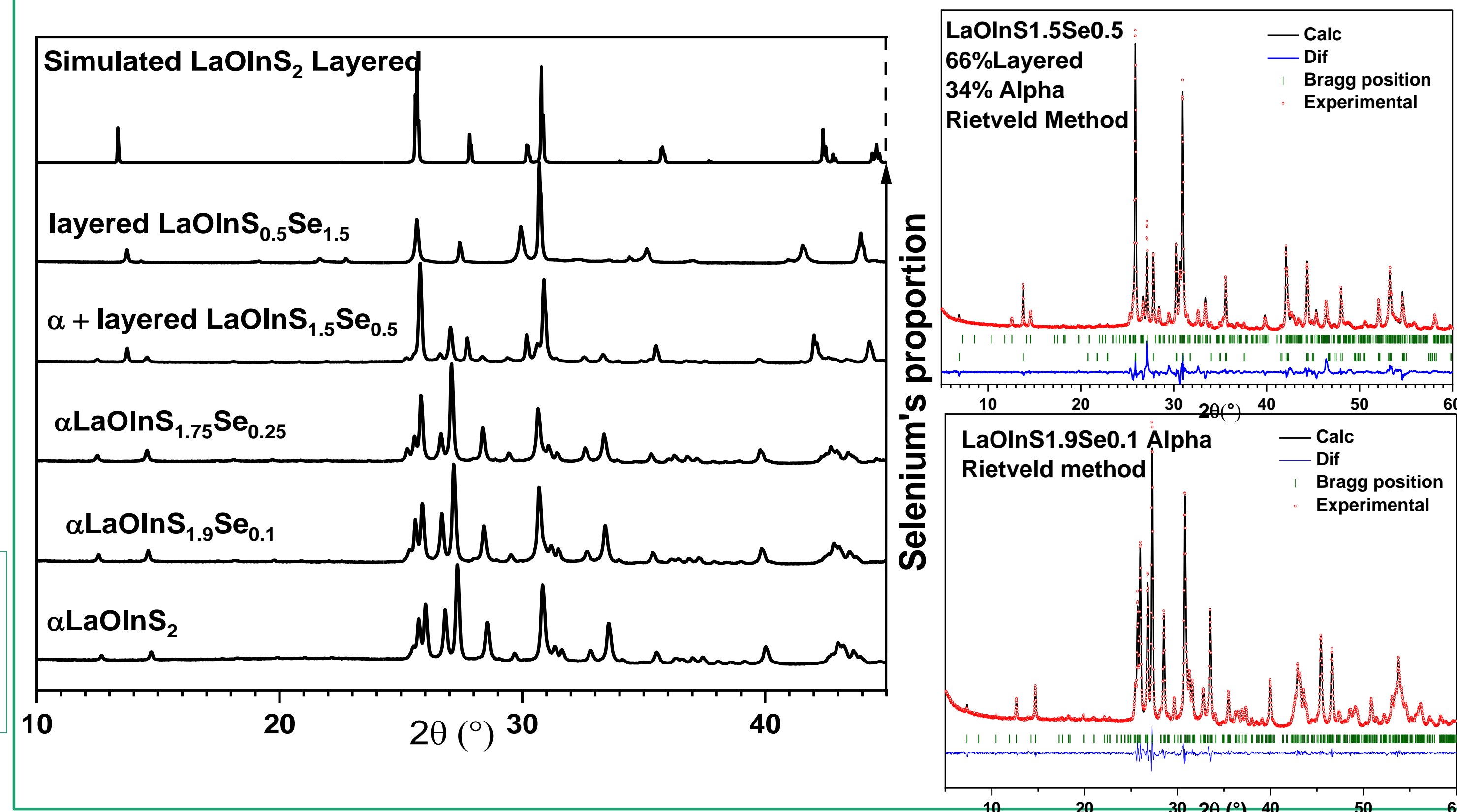
Two synthesis pathways: two different polymorphs:

- Thermodynamically stable α -phase via direct solid-state reaction in sealed quartz tube at 800°C of In_2S_3 , La_2S_3 and La_2O_3
- The layered via metathesis from LaOCl and NaInS_2
- LaOCl and NaInS_2 heated at 850°C yield Layered phase and transform to α at higher temperatures (ref. 2)

- Kabbour, H & Al. (2020). Structure of the water-splitting photocatalyst oxysulfide α - LaOInS_2 and ab initio prediction of new polymorphs. *Chemical Communications*, 56(11), 1645–1648. H. Kabbour, L. Cario & al. *J. Solid State Chem.*, (2004), 177, 1053–1059
- Miura, A & Al. (2017). Synthesis, structure and photocatalytic activity of layered LaOInS_2 . *Journal of Materials Chemistry A*, 5(27), 14270–14277.

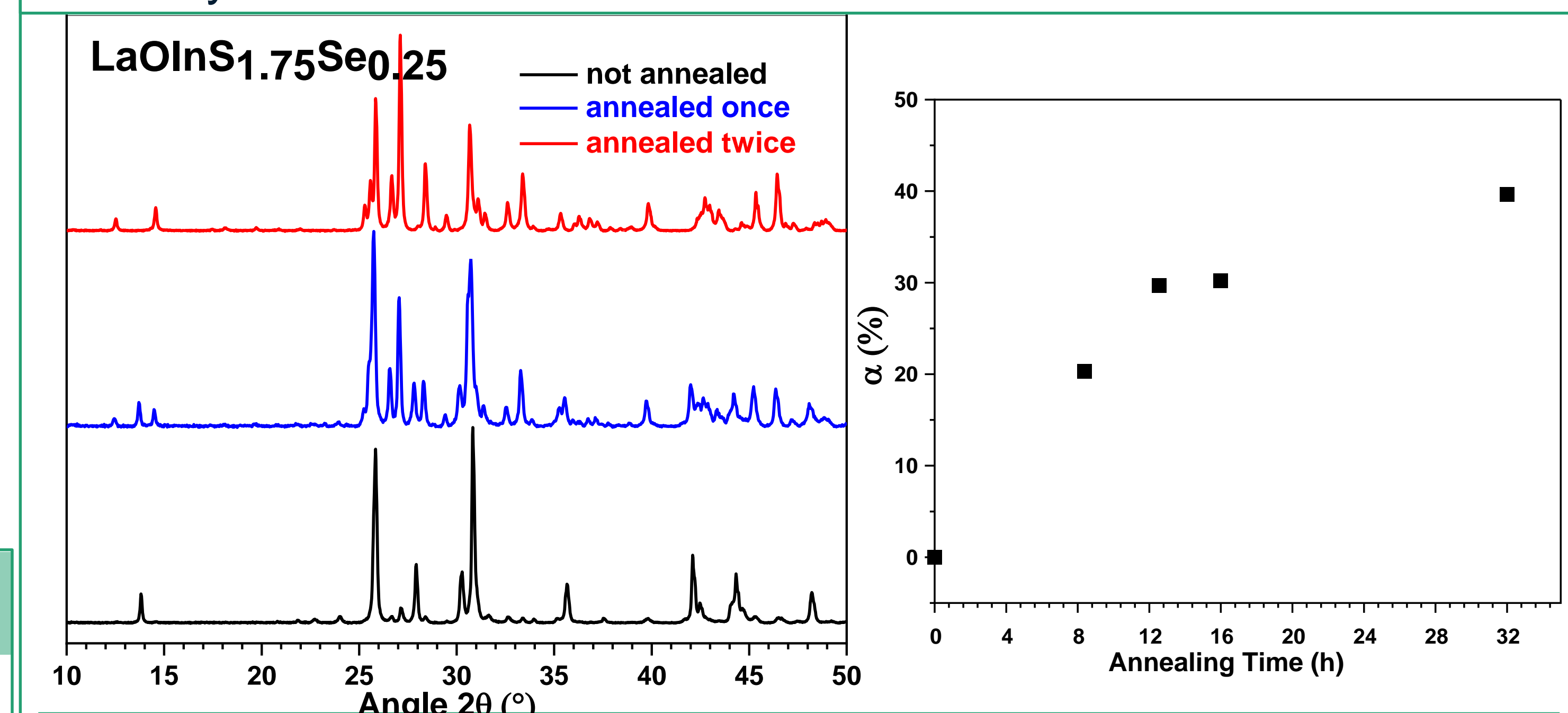
Selenium's impact on structure

- Selenium substitution stabilize the layered phase
- Limit of insertion of selenium is below 75% in α



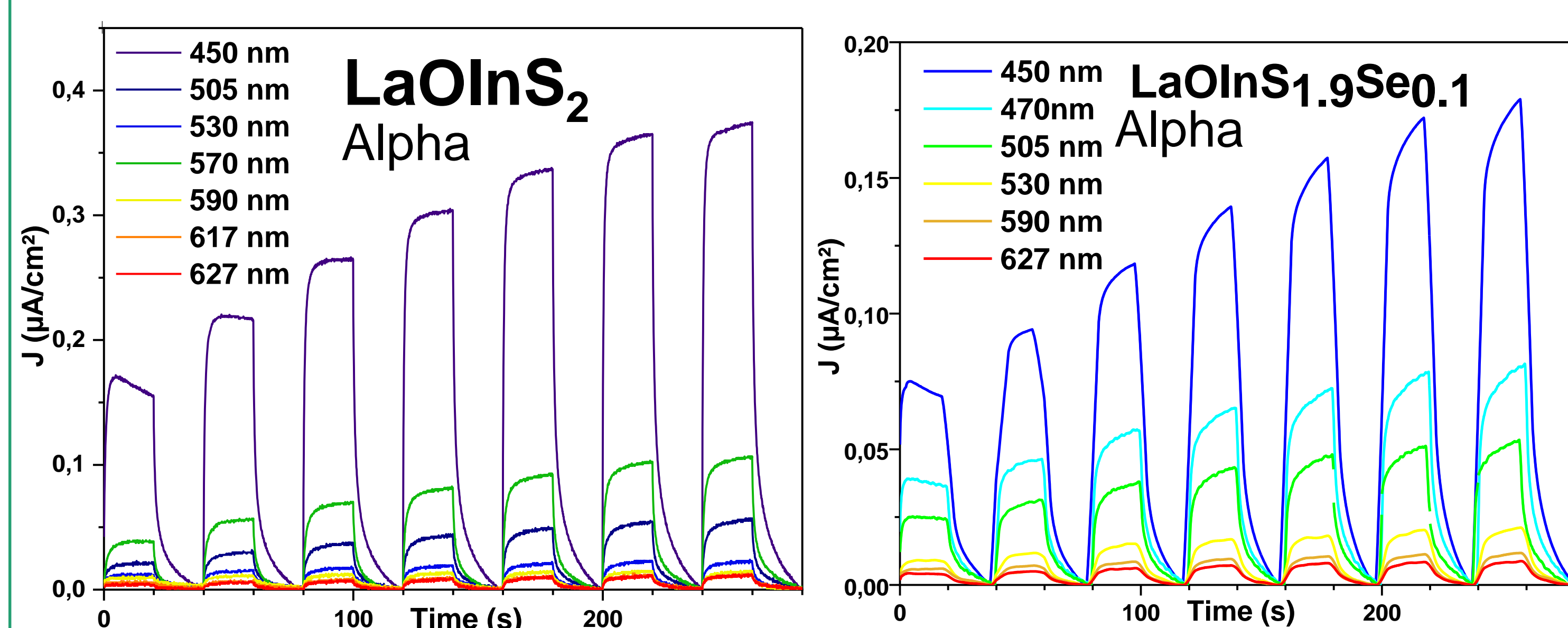
Kinetic and thermodynamic competition

- Both pure layered and α can be obtained depending on the thermal treatment for 12,5% and 25% of selenium
- The grinding between annealing has a huge impact on the reactivity



- Bandgap of 2,68eV determined by the S 3p and O 2p orbitals in α - LaOInS_2
- Chalcogenide substitution achieved to narrow the bandgap to 2,54eV

Optical and photocatalytical properties



- Selenium substitution decreases photocurrent but shift the efficiency spectral zone to higher wavelength
- Layered structure (2D) has a better response
- Faster separation of charge carriers in layered

