

The discovery of new efficient Hydrogen Evolution Catalysts (HEC) is critical in the transition to a zero carbon economy. In this work multiple layered oxides have been prepared and tested. Their HEC activity is compared against the known HEC KCa₂Nb₃O₁₀, as shown in Figure 1. KLaTiO₄, illustrated in Figure 2, was found to be a good HEC with a H₂ evolution rate of 9.54 (11) μmol.hr⁻¹.

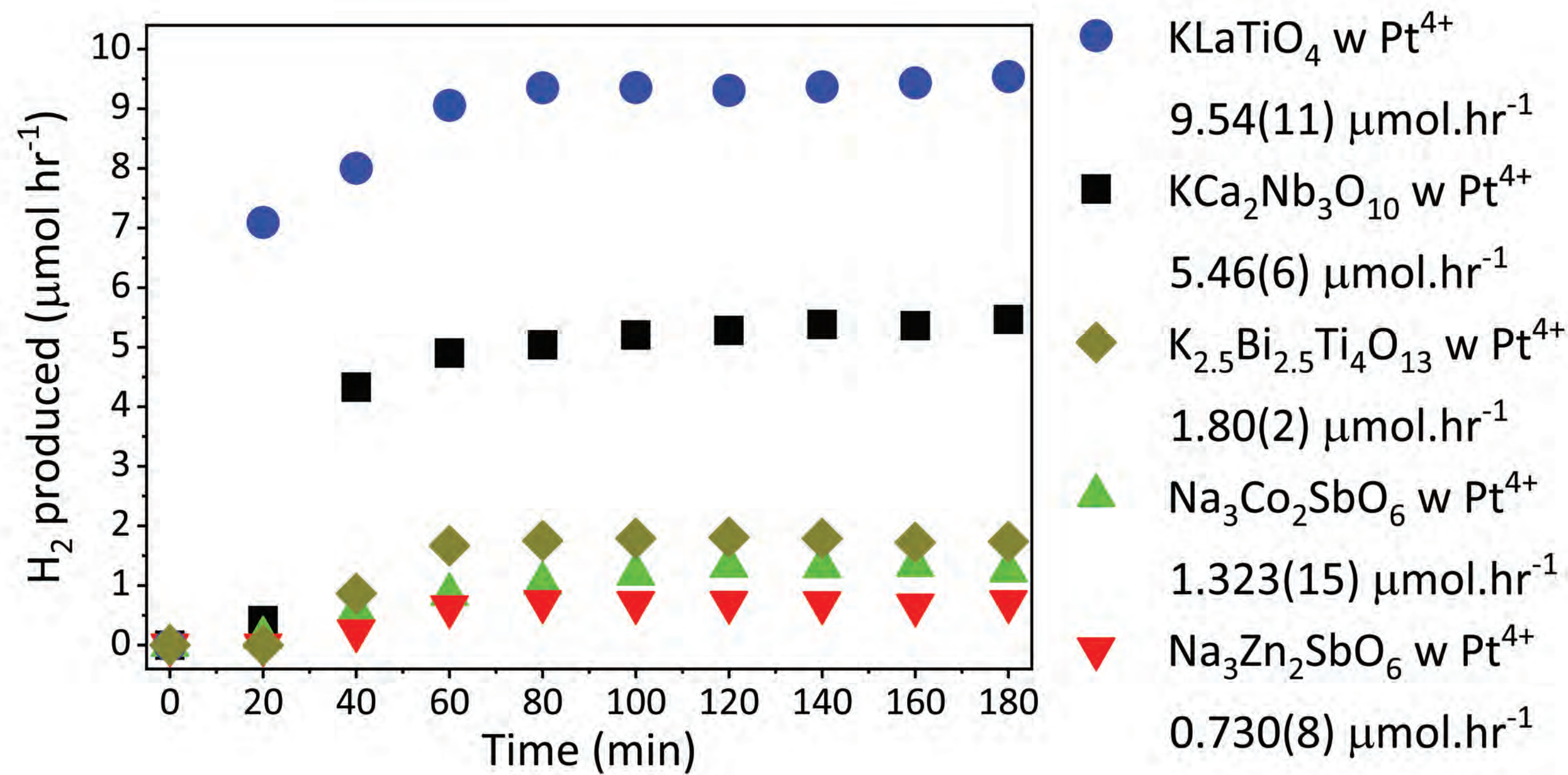


Figure 1: Hydrogen evolution rate of six different catalyst candidates, all tested with the following conditions: 20 mg powder sample dispersed in 20 mL 1:3 methanol:water solution, with addition of 40 μL of 26 mM H₂PtCl₆. The solution was irradiated using 350 Hg lamp with a 305 nm cut-off filter.

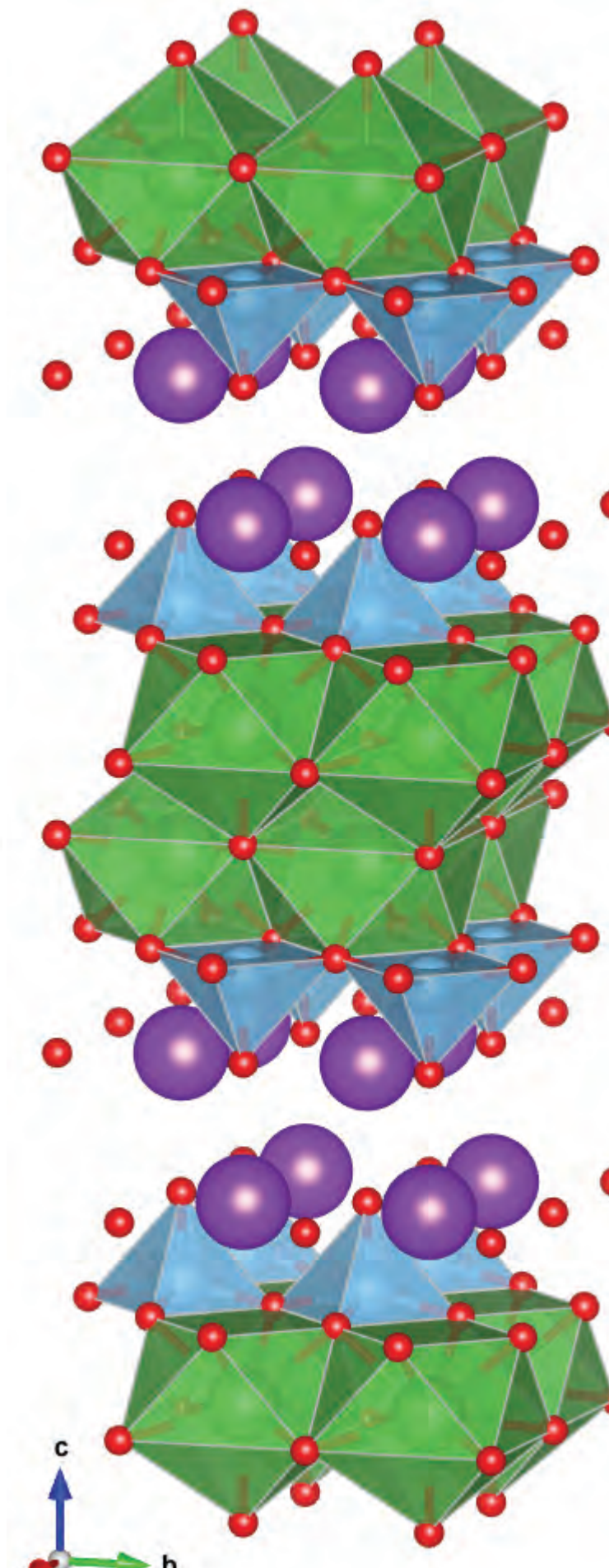


Figure 2: Structure of KLaTiO₄.

A significant problem with KLaTiO₄ as a HEC lies in its high bandgap of 4.09(13) eV. Thus, it cannot absorb across the UV-Vis spectra of sunlight, as illustrated in Figure 3.

We have sought to reduce the bandgap of KLaTiO₄, by Nitrogen doping using TiN as a reagent to synthesise KLaTiO₃N.

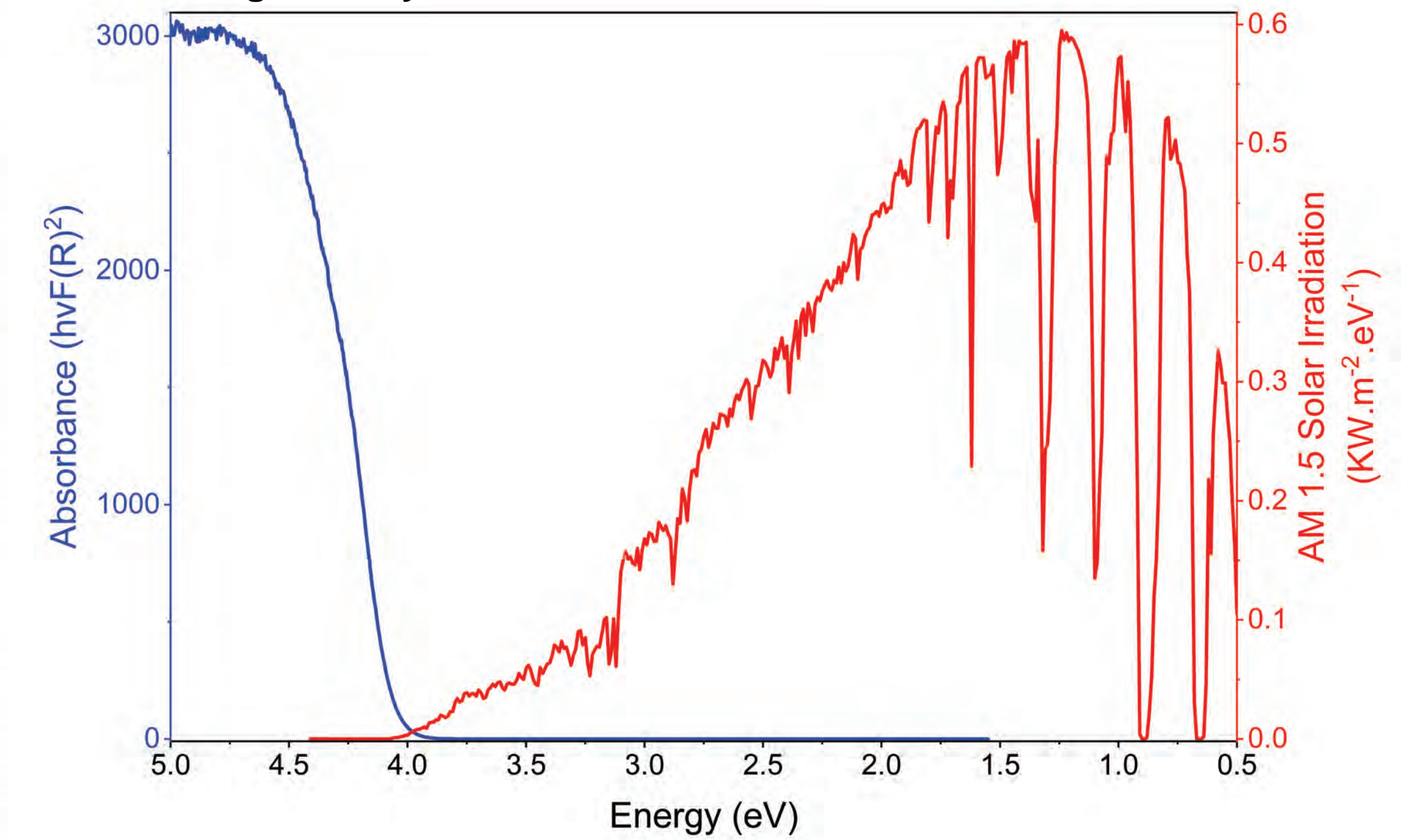


Figure 3: Tauc plot of KLaTiO₄ (blue) with the solar irradiation on the Earth's surface (red),¹ showing a lack of overlap between the two. This is problematic as the KLaTiO₄ absorbance spectrum of KLaTiO₄ does not overlap, it cannot act as a direct solar active HEC.

NaLaTiO₄ was prepared by reacting Na₂CO₃, La₂O₃ and TiO₂ at 4:1:2 molar ratio, with annealing duration set for 16 hours.² 100 % Na₂CO₃ excess was used to counteract sodium volatility. Synthesis experiments at varying temperatures, summarised in Figure 4, shows sample purity was optimized when annealed at 800 °C.

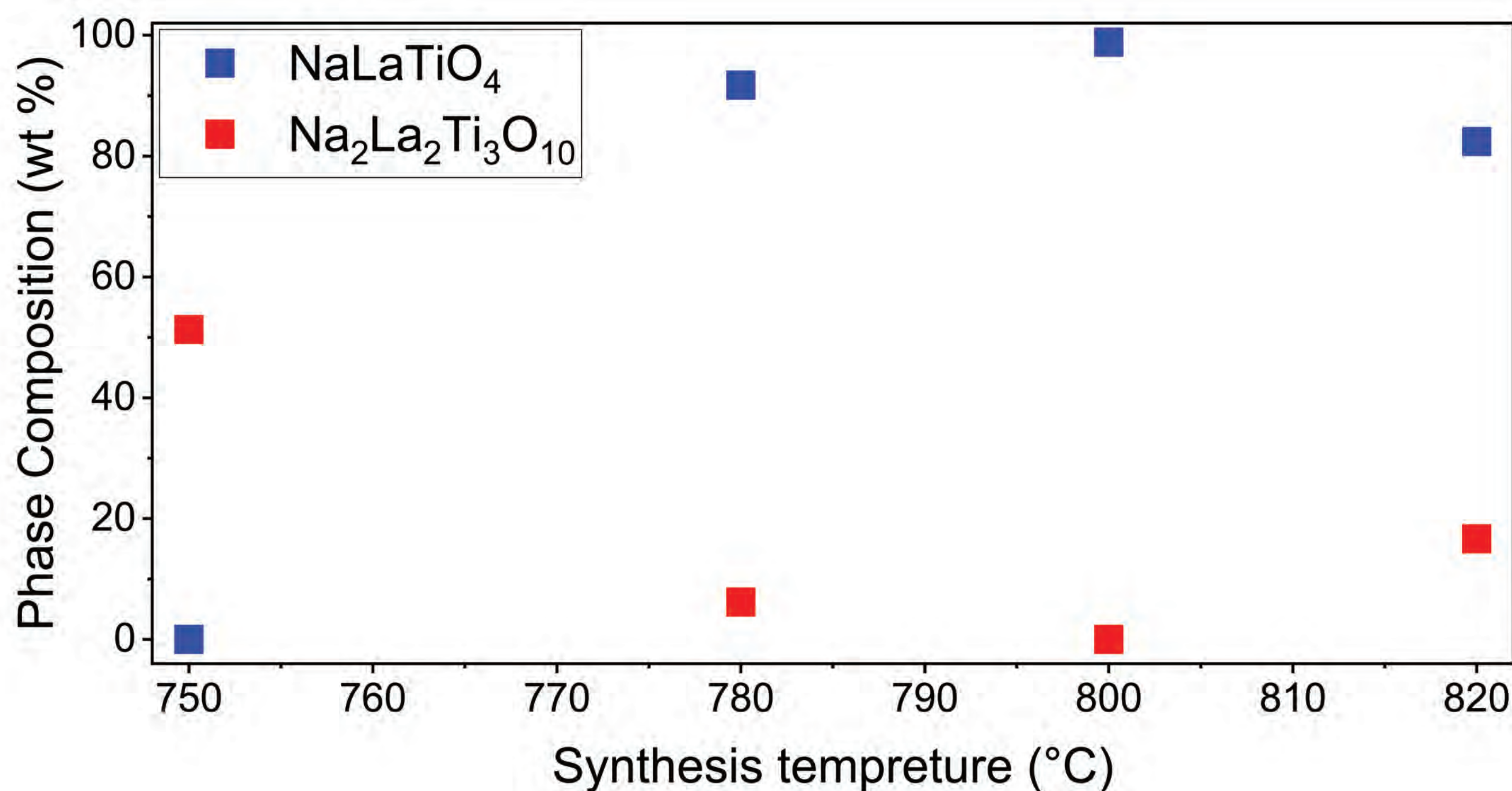


Figure 4: Weight percentage composition of NaLaTiO₄ and Na₂La₂Ti₃O₁₀ for NaLaTiO₄ samples made at different annealing temperatures.

It was hypothesised that isostructural KLaTiO₄ and NaLaTiO₄ could be prepared under similar conditions. KNO₃ excess and annealing temperature were varied to test the optimal condition to prepare phase pure KLaTiO₄, Figure 5. KLaTiO₄ made using 100 % KNO₃ excess and annealed at 800 °C.

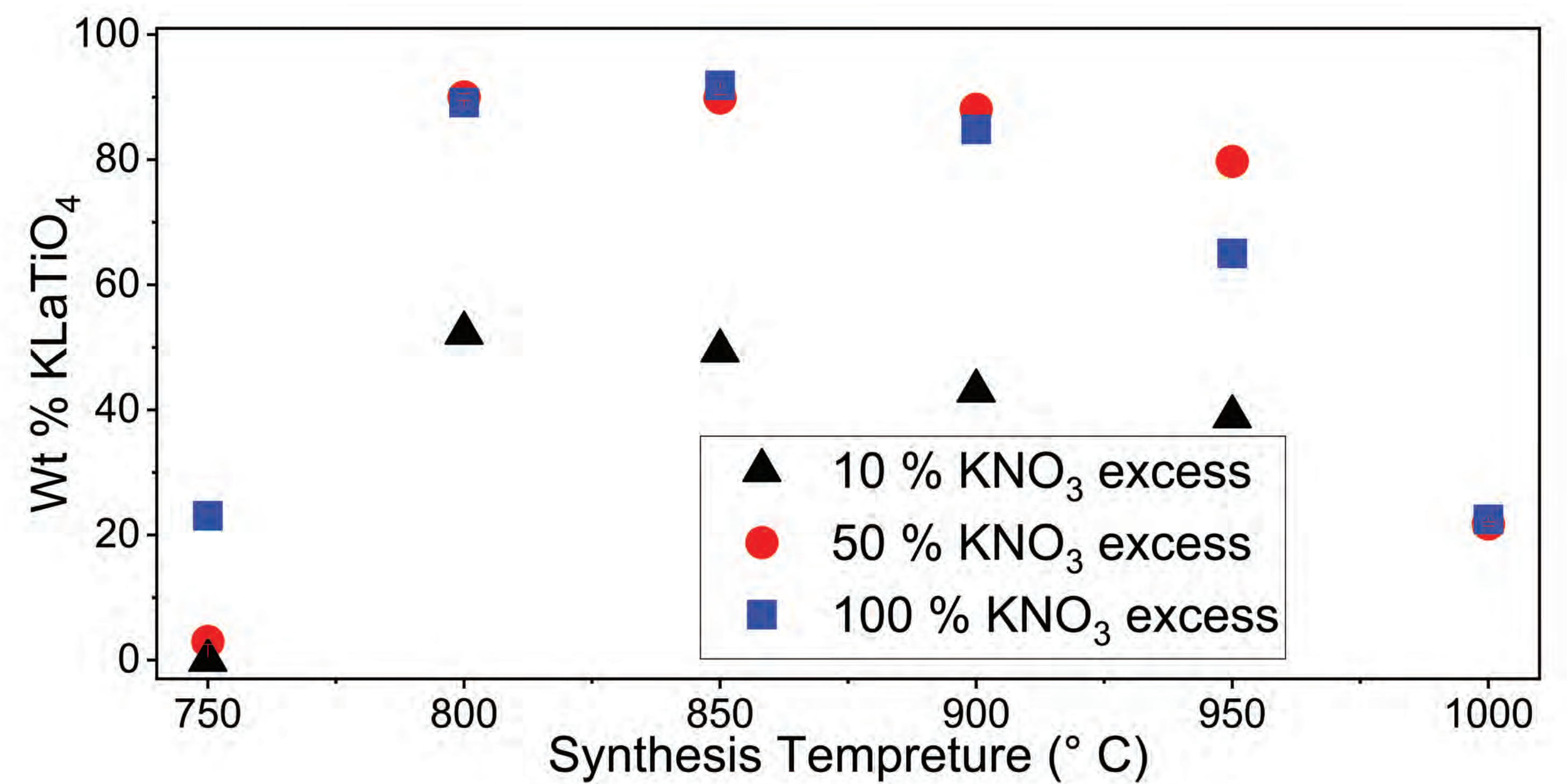


Figure 5: Weight percentage composition of KLaTiO₄ for KLaTiO₄ prepared under different annealing temperatures, using mixtures that contained 10 %, 50 % and 100 % KNO₃ reagent excess.

The S-XRD diffraction pattern of N-doped KLaTiO₄ (obtained at the Australian Synchrotron BL 10) shows KLaTiO₃N (Figure 6) to have comparable crystallinity to undoped KLaTiO₄ (Figure 7).

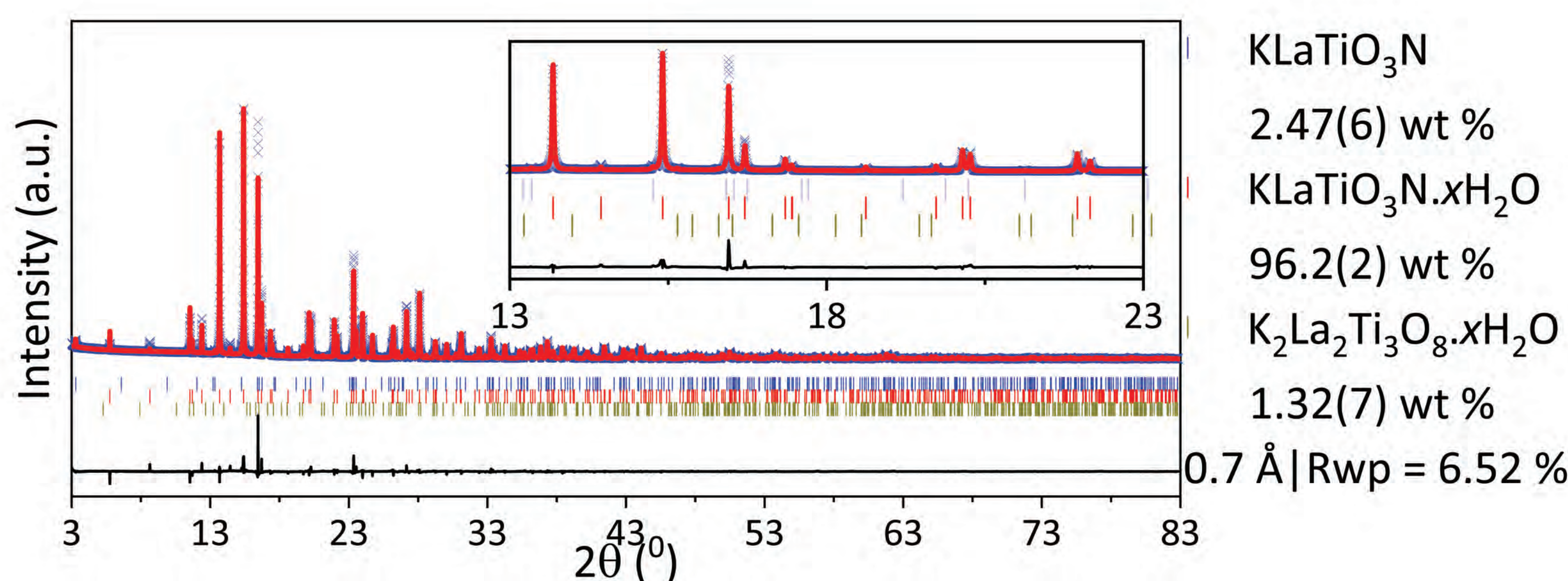


Figure 6: S-XRD pattern of KLaTiO₃N, with phase and weight composition shown in the legend on the right.

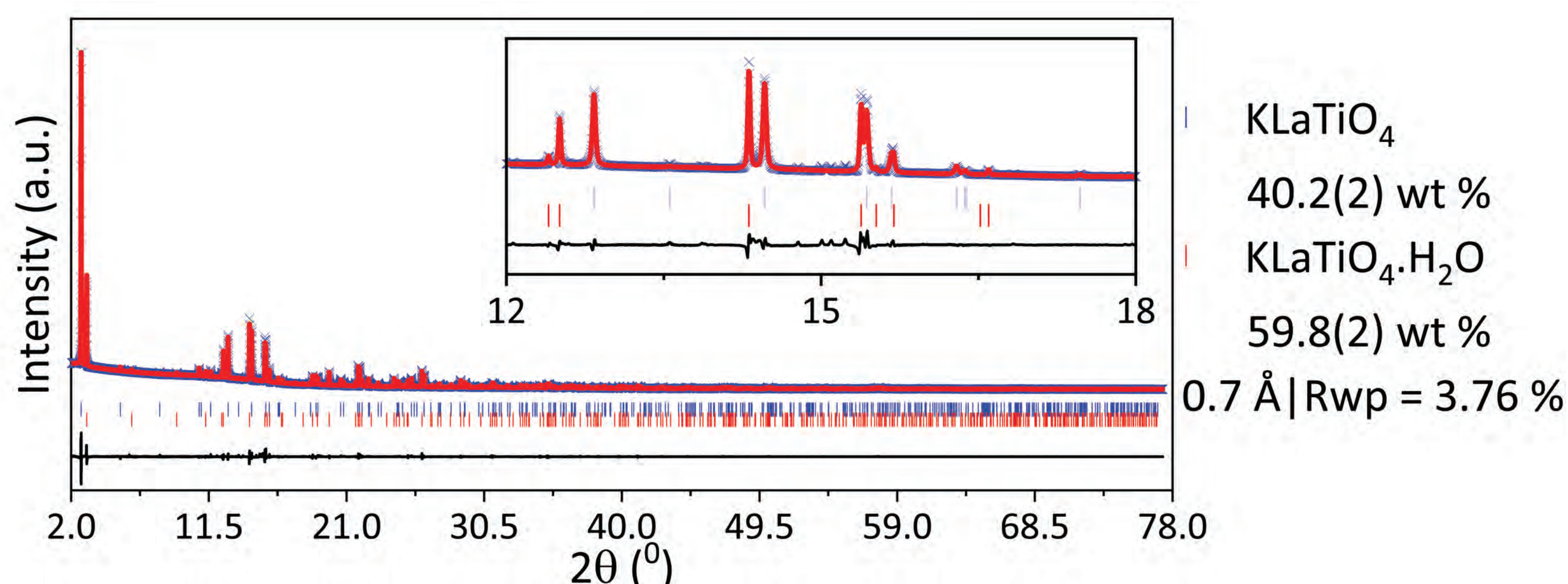


Figure 7: S-XRD pattern of KLaTiO₄, with phase and weight composition shown in the legend on the right.

Tauc plot of the N-doped samples demonstrating a reduction in bandgap in the KLaTiO_{3-x}N_x samples in comparison to undoped KLaTiO₄. In testing KLaTiO₃N as a photocatalyst the rate of hydrogen evolution was found to be 1/3 that of the undoped KLaTiO₄.

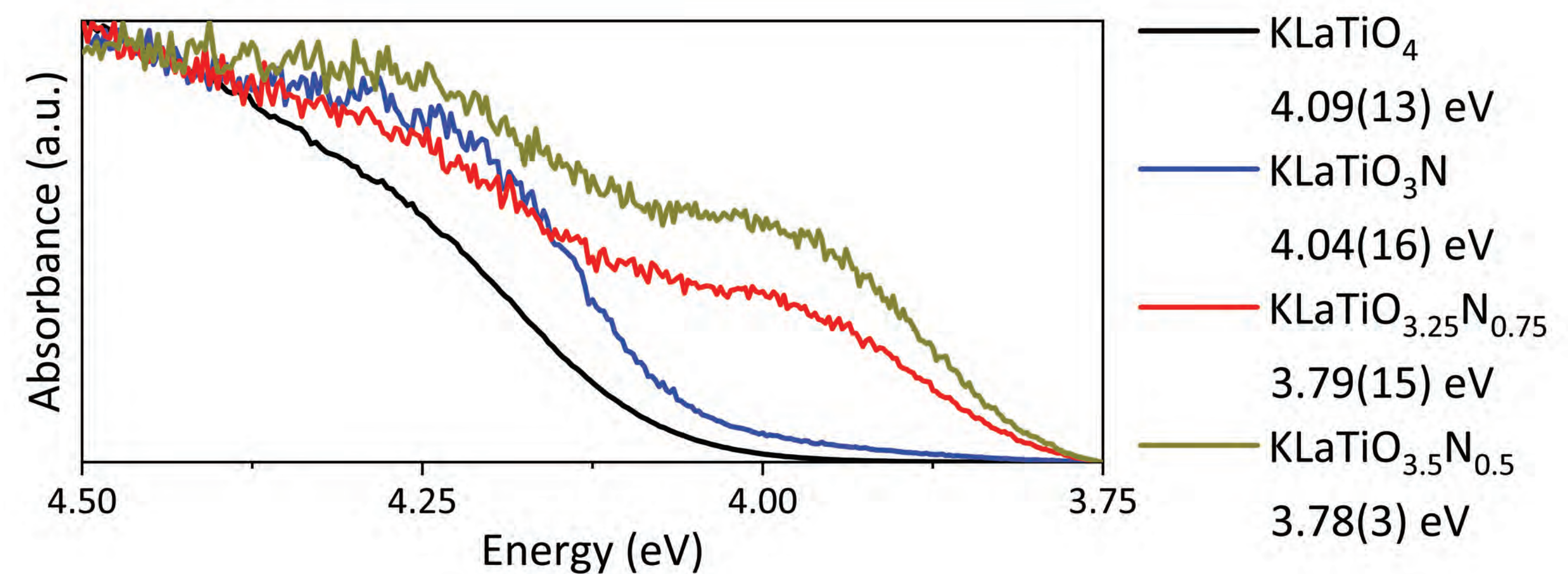


Figure 8: Tauc of KLaTiO_{3-x}N_x, with bandgap of each sample shown in the legend on the right.

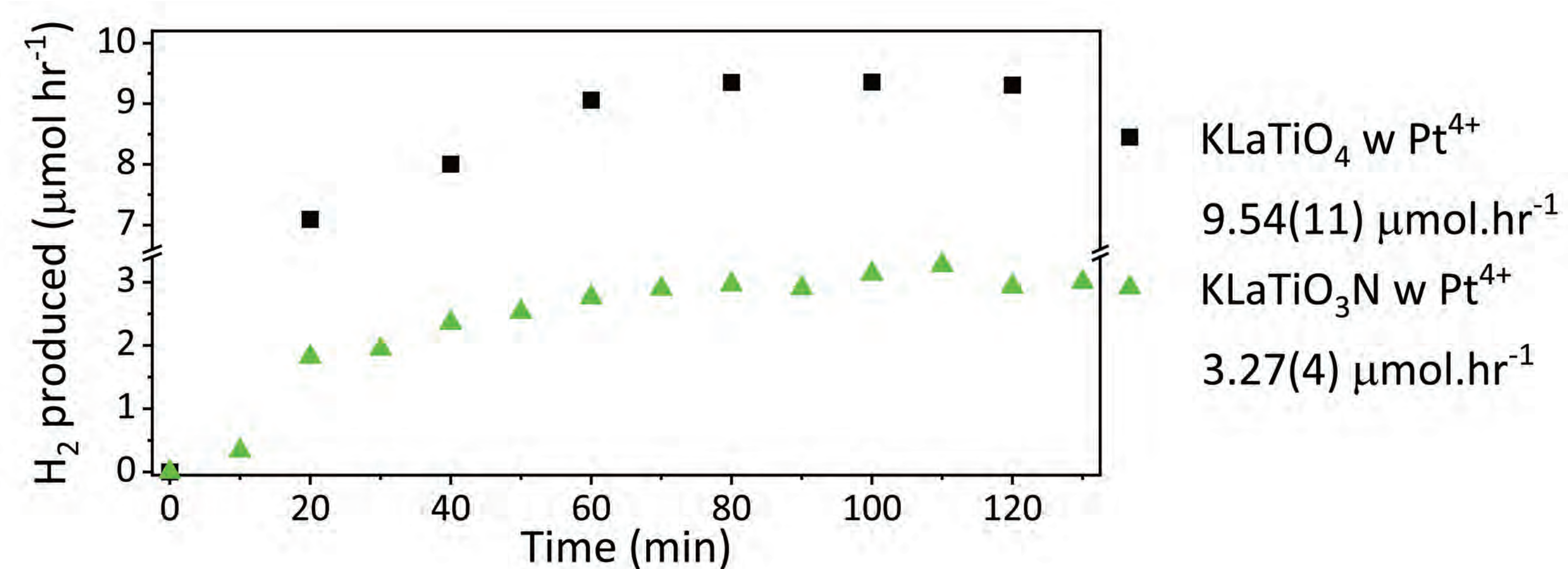


Figure 9: Hydrogen evolution rate of KLaTiO₃N, compared against KLaTiO₄, with maximum hydrogen evolution rate shown in the legend on the right.

1. Appendix E: AM1.5 Reference Solar Spectrum. In Physics of Solar Energy, pp 307-312.

2. Petrov, A. A.; Melnikova, N. A.; Petrov, A. V.; Silyukov, O. I.; Murin, I. V.; Zvereva, I. A., Experimental investigation and modelling of the Na⁺ mobility in NaLnTiO₄ (Ln = La, Nd) ceramics. Ceramics International 2017, 43 (14), 10861-10865