



New insight in the Am-O system by coupling experimental HT-XRD and CALPHAD modeling

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Context and Objectives

In the frame of **minor actinide recycling** in sodium cooled fast reactors, (**U, Am**)O₂ mixed oxides are promising transmutation targets. To assess the thermodynamic properties of the U-Am-O system, it is essential to have a thorough knowledge of the **binary phase diagrams**, which is difficult due to the lack of thermodynamic data on the Am-O system¹. Nevertheless, an **Am-O phase diagram** modeling has been recently proposed by Gotcu *et al.*¹ in which a fluorite-type dioxide, a sesquioxide and an intermediate phase are reported for an O/Am ratio ranging from 2 to 1.5. Here, we show an investigation of the Am-O system coupling thermodynamic modeling based on the **CALPHAD** method and *in situ* high temperature X-Ray Diffraction (XRD).

Methods

Experimental Setup

Powder XRD was performed with a Bragg-Brentano θ - θ Bruker D8 Advance X-ray diffractometer using Copper radiation and a LynX'Eye fast-counting PSD detector. The **heating stage** is constituted by a Pt strip and a radiant heating element. The **atmosphere is controlled** through a flowing gas whose partial oxygen pressure (**pO₂**) is measured and adjusted at the inlet of the chamber with a *GenAir* device (probe and pump oxygen) in order to have the desired **oxygen potential ΔG_{O_2}** .

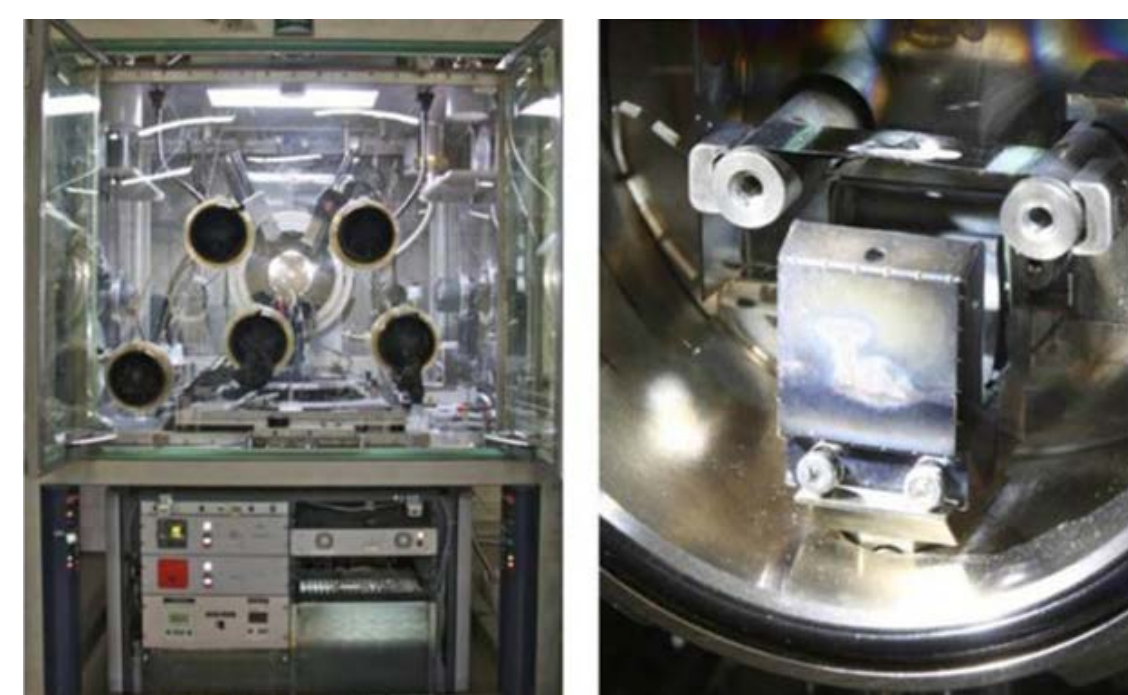
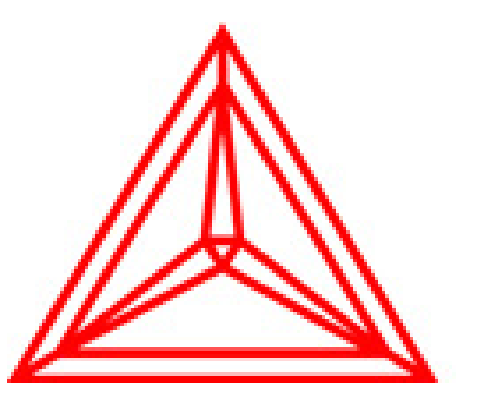


Fig. 1 The diffractometer glove box and the heating stage.

Thermodynamic Calculations

In order to set up the most interesting experimental conditions (temperature T and ΔG_{O_2}), thermodynamic calculations based on the CALPHAD method were performed, using the **TAF-ID** (Thermodynamic of Advanced Fuels-International Database)² containing the model¹.

A new improved thermodynamic assessment of the Am-O system was also performed. Both computations and modeling were performed using the *Thermo-Calc* software.



Thermo-Calc Software

CALPHAD

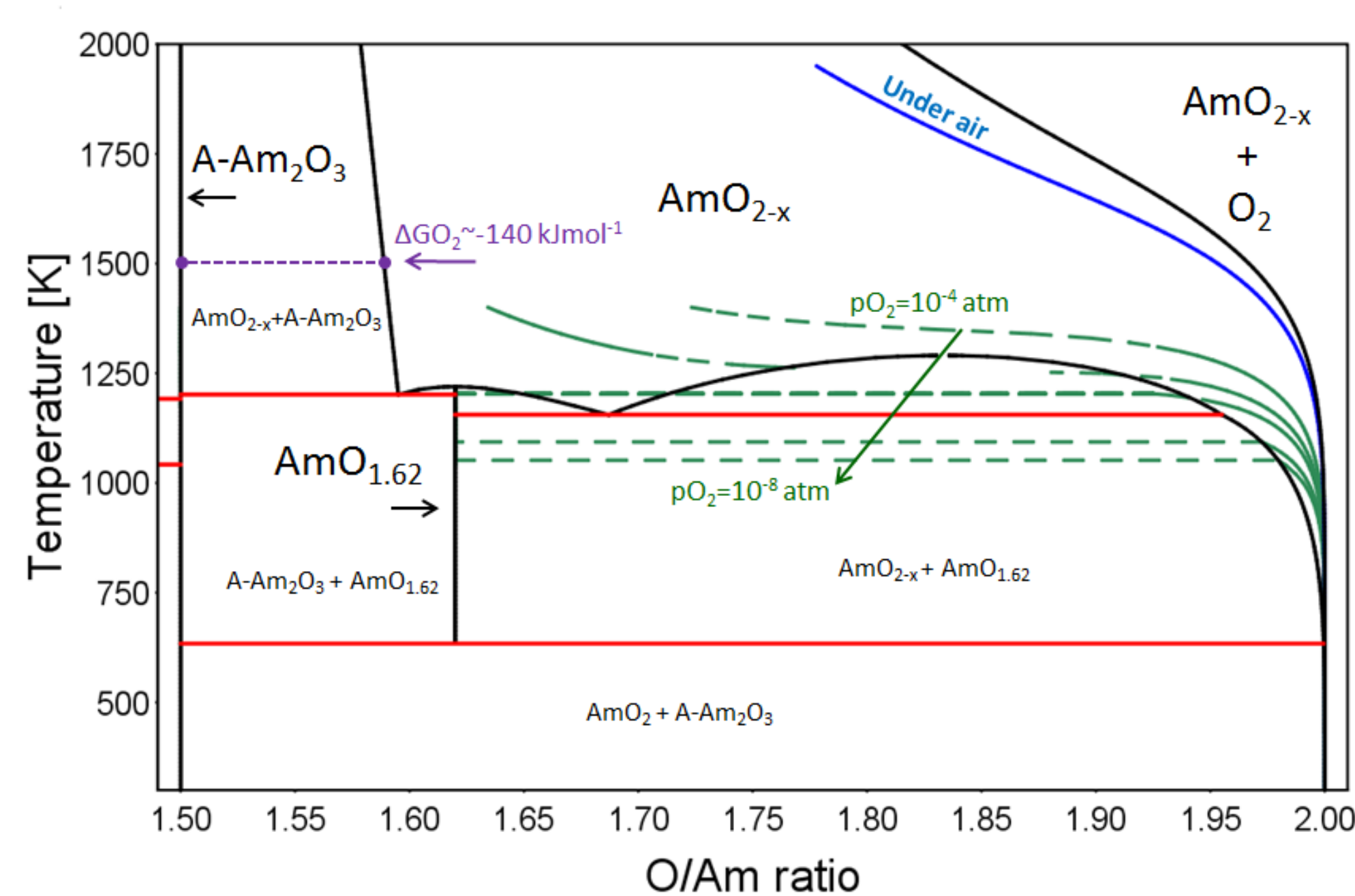
Calculations based on the literature model¹

Fig. 2: The phase diagram computed with the available model

Thermodynamic calculations were performed in order to foresee the explored regions of the phase diagram:

- Equilibria under air
- Equilibria under He with constant pO₂
- AmO_{2-x}/AmO_{1.62} two phase region at 1500 K

Improved CALPHAD assessment

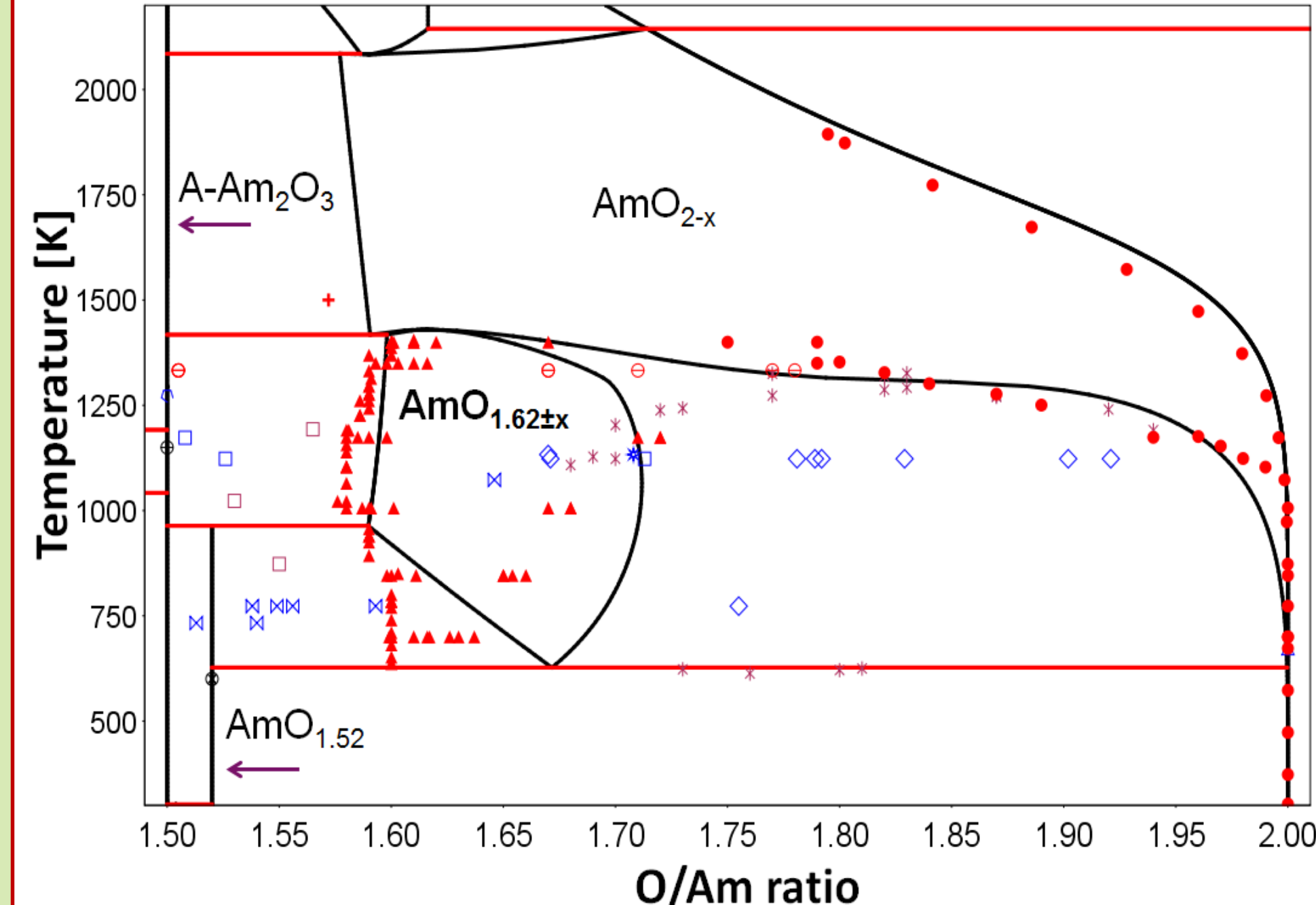


Fig. 7: The phase diagram computed with the new model

- The **AmO_{1.62}** composition domain was described
- The **AmO_{1.52}** phase was added
- The miscibility gap was not included in this model

EXPERIMENTAL RESULTS

Results in agreement with the literature model

The AmO_{2-x} behavior at HT under air

- The slope change of the thermal expansion at **T≈1200K** indicates the starting of the **AmO₂ reduction under air**, in agreement with the model previsions

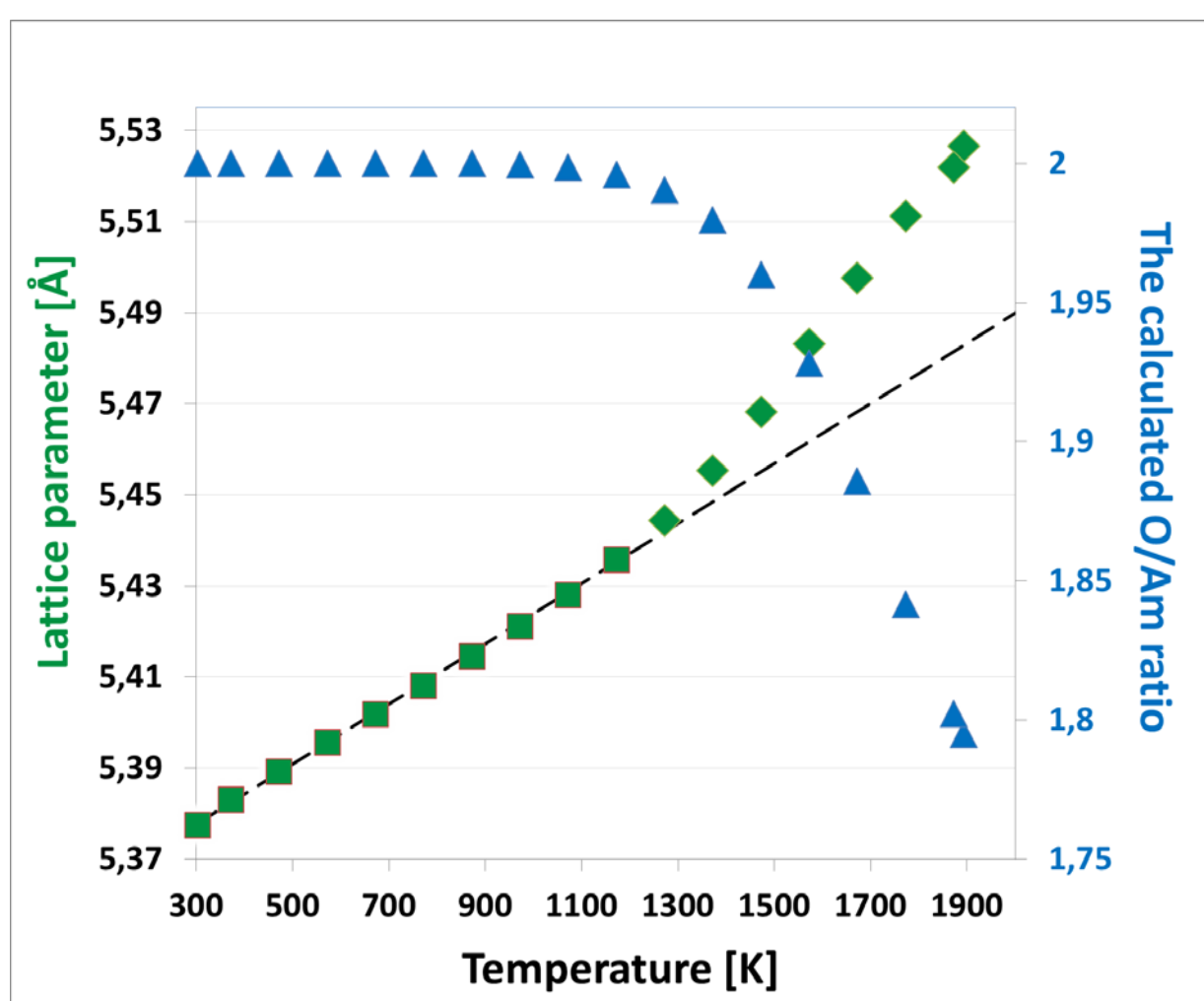
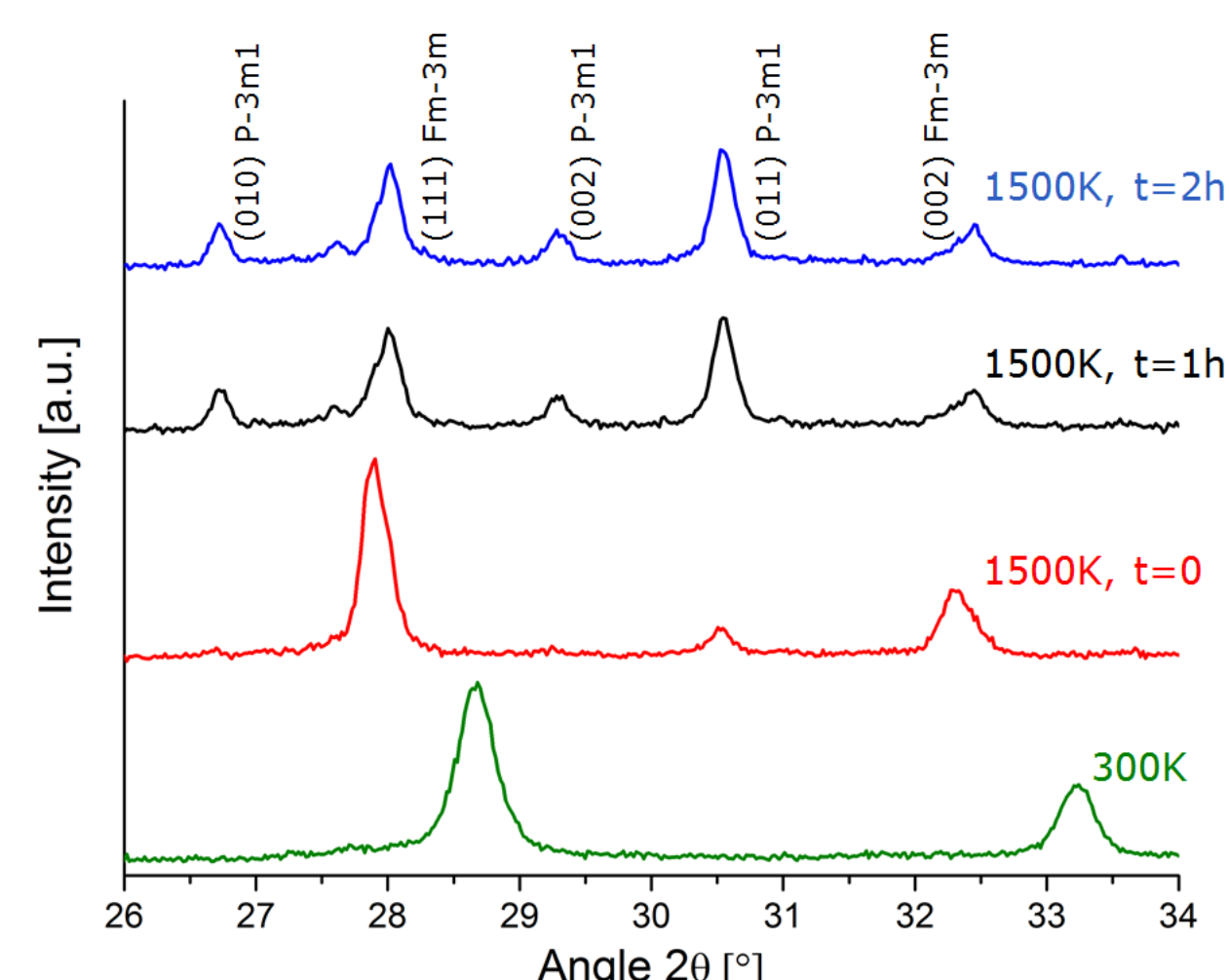


Fig. 3: Green points: measured lattice parameters during cooling from 1900K to RT under air; Blue points: the O/Am ratio calculated with ThermoCalc.

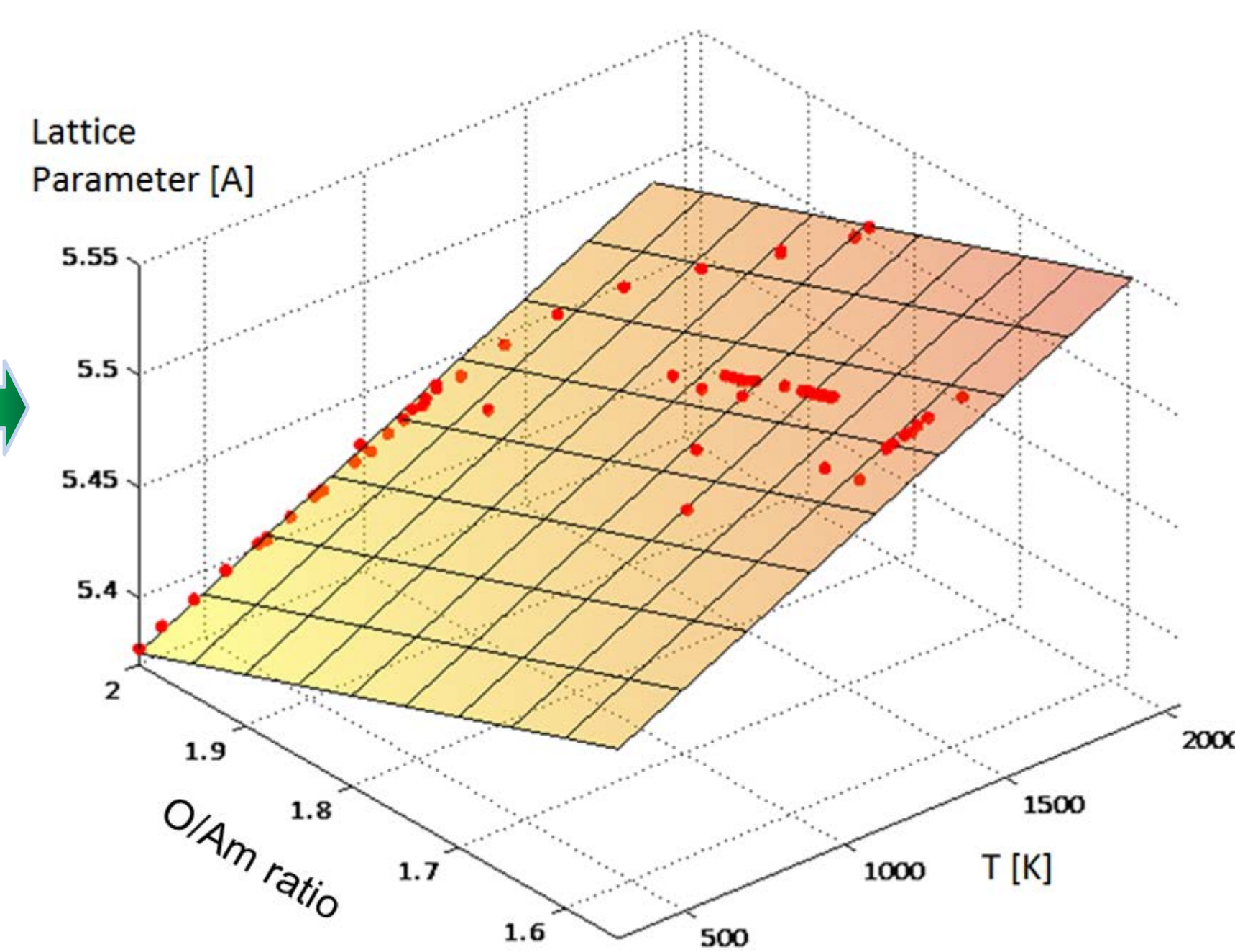
The AmO_{2-x}/A-Am₂O₃ two-phase region

- At **T=1500K**, the hexagonal **A-Am₂O₃** phase was observed by imposing the **ΔG_{O_2}** expected by the model (≈ -140 kJ/mol)

Fig. 4: Diffraction patterns acquired at RT and then at T=1500K for 2 hours under controlled atmosphere (pO₂=2 10⁻⁵ atm).

The *reliable* data were fitted using the least square minimization in order to find a linear relation between the **Lattice Parameter a**, the **O/Am ratio** and **Temperature**.

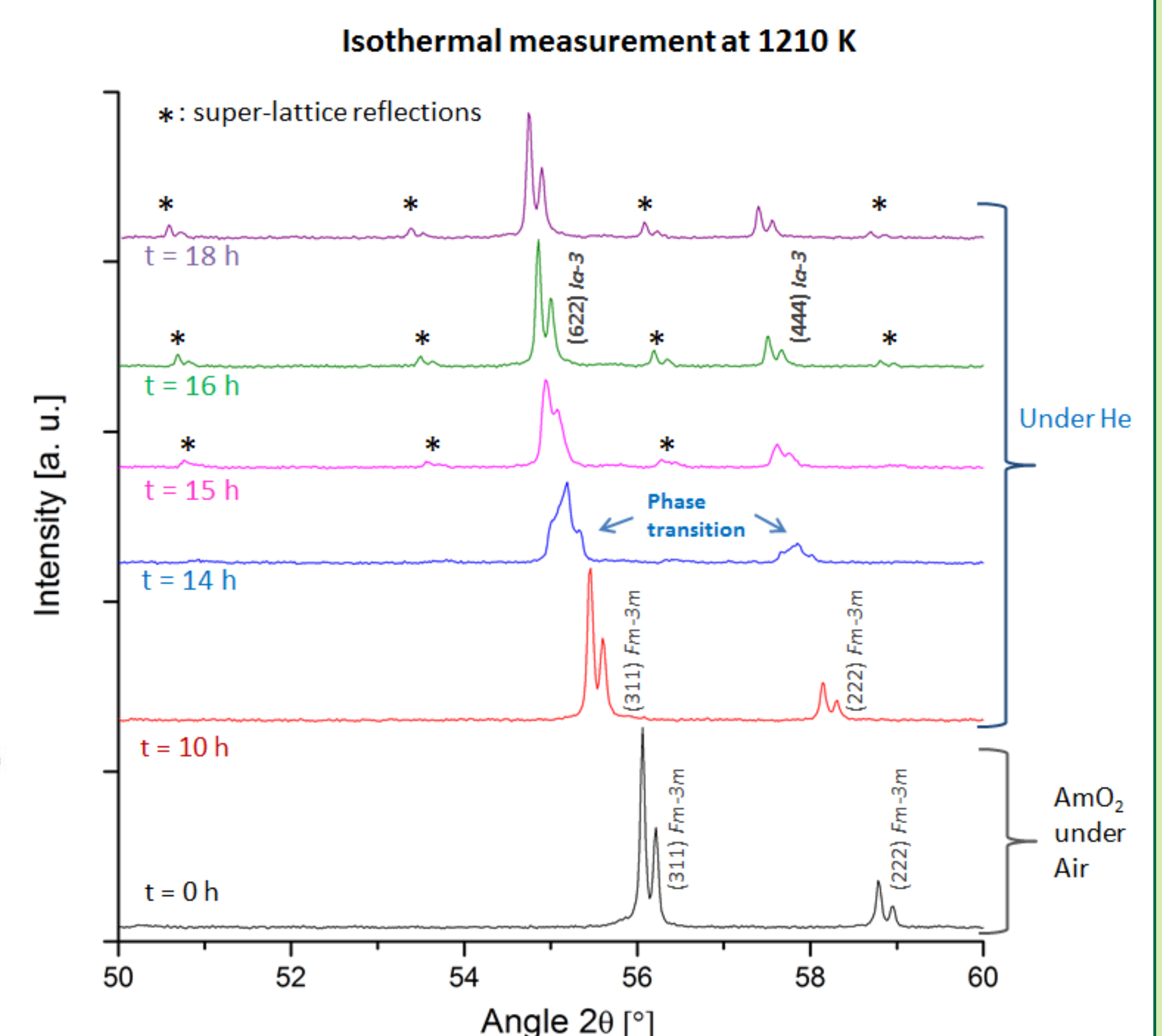
This relation allowed a **coherent interpretation** of all the experimental data and lead to the **re-definition of the phase boundaries** of the phase diagram.

Fig. 5: Fit of the "reliable" data: a as a function of T and O/Am

$$a(T, O/Am) = C_1 + C_2 T - C_3 O/Am$$

New insight

Contrary to the Pu-O system, Iso-T measurements at 1280 K and 1210 K have not shown the presence of a **miscibility gap**. The **AmO_{2-x} → AmO_{1.62±x}** phase transition was observed. **BCC AmO_{1.62±x}** was found to have a wide **composition domain**.

Fig. 6: Diffraction patterns from an iso-T measurement at **1210 K** under He. After 14 h, the **AmO_{2-x} → AmO_{1.62±x}** phase transition occurred. Then, the reduction of the **AmO_{1.62±x}** was observed (shift of the peaks to lower angles), proving the existence of a composition domain

Conclusions

In this work, an investigation of the Am-O system by HT-XRD was presented. The experimental conditions (T , ΔG_{O_2}) were chosen according to thermodynamic computations based on the Gotcu Calphad model [1], with the aim of verify its accuracy. A good agreement between experimental results and calculations was found for the AmO₂ in the slightly hypo-stoichiometric region (experiments under air). The model has also proven to be able to predict the appearance of the A-Am₂O₃ phase at HT (1500K), but the agreement between results and calculation was lost at lower temperature. Using the least square minimization method, a **lattice parameter - O/Am - T** relation was found, which allowed a coherent interpretation of all the data and the definition of the phase boundaries of a *new* BCC phase. Finally, thanks to the new data acquired, an improved **Calphad assessment** was performed and a **new phase diagram representation** was proposed.

1. P. Gotcu-Freis, J.-Y. Colle, C. Guéneau, N. Dupin, B. Sundman, R. J. M. Konings, J. Nucl. Mater. 414 (2011) 408-421.
2. www.oecd-nea/science/taf-id.com
3. H. Lukas, S. G. Fries, Bo Sundma, *Computational Thermodynamic: The Calphad Method*, 2007.