

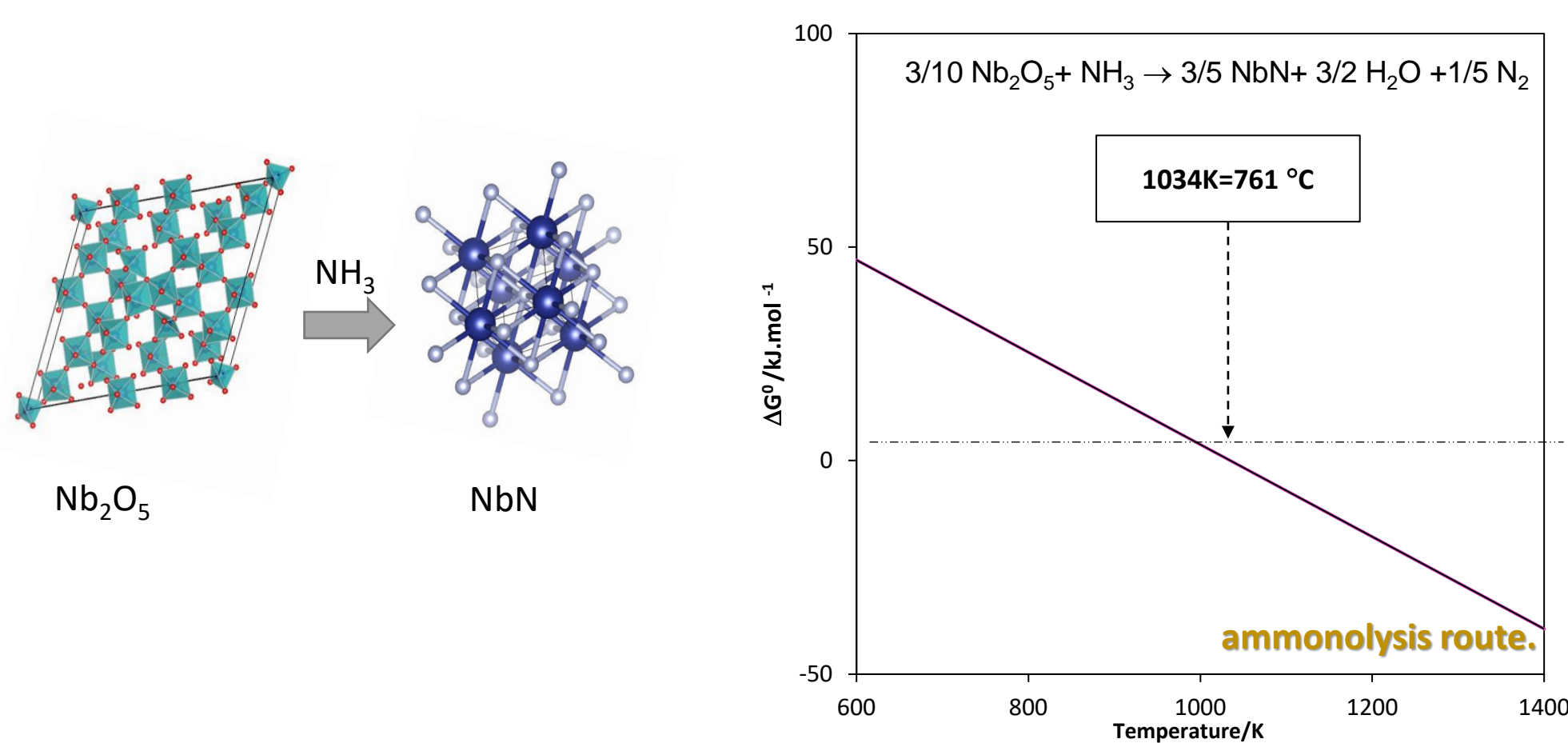
# The influence of time and temperature on the preparation of niobium nitride by ammonolysis route.

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## INTRODUCTION

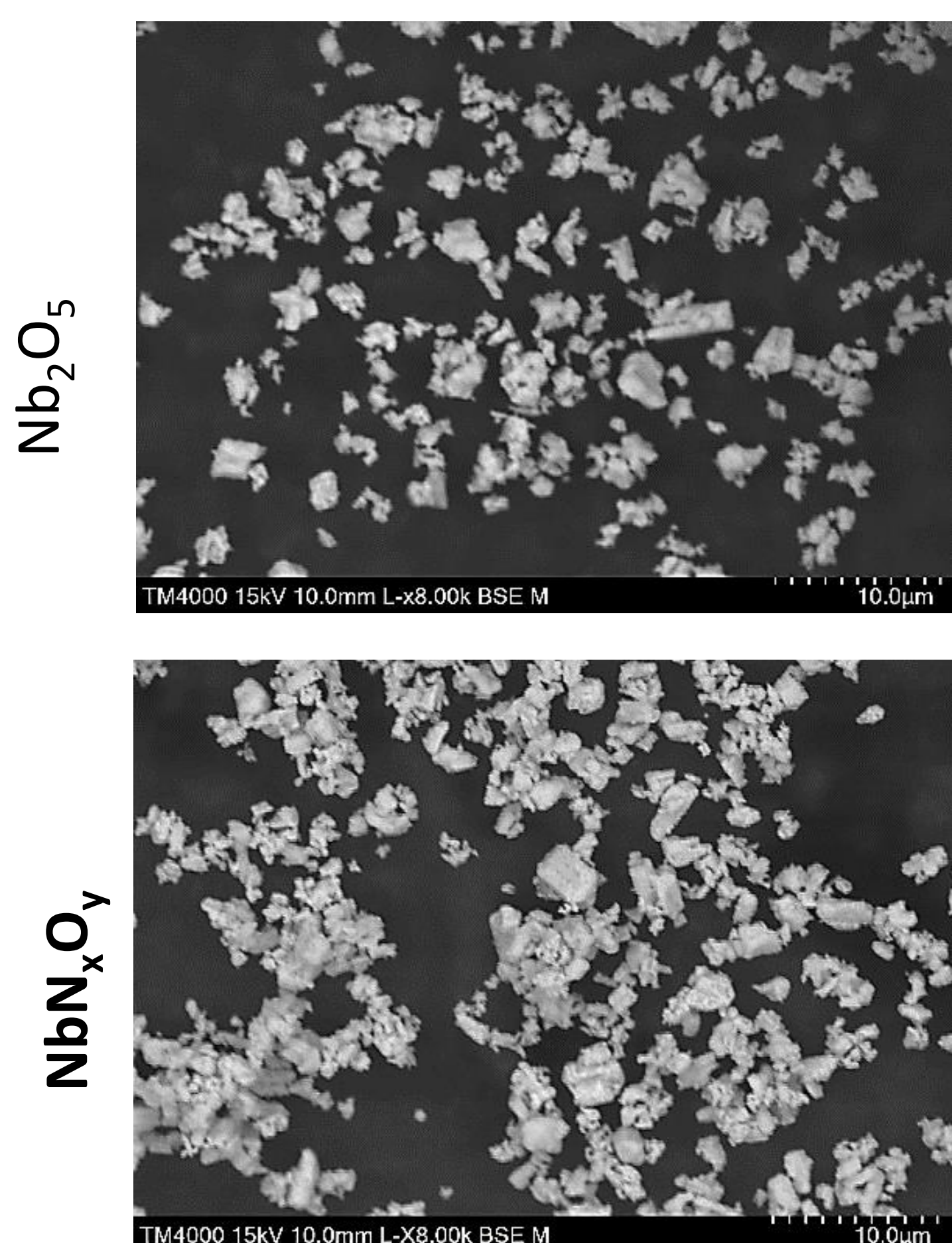
The current industrial process for NH<sub>3</sub> synthesis is the Haber-Bosch process (HBP). However, it is estimated to be responsible for 2.5 % of worldwide greenhouse-gas CO<sub>2</sub> emissions<sup>1</sup>. Electrochemical ammonia synthesis offers a promising green alternative by the direct synthesis of NH<sub>3</sub> from steam and nitrogen. The key to the success of this process is to find a proper electrocatalysts for the nitrogen reduction reaction (NRR). Transition metal nitrides, namely, niobium nitride (NbN) have been highlighted by DFT calculations to potentially offer high catalytic activity for the ammonia formation reaction<sup>2</sup>. A pure phase of the cubic NbN composition can be obtained from niobium pentoxide (Nb<sub>2</sub>O<sub>5</sub>) by the thermal ammonolysis route. In this work, we, therefore, study the influence of temperature and time on the crystal structure, microstructure, and nitrogen content of niobium nitride, using different techniques such as X-ray diffraction, X-ray photoelectron spectroscopy, scanning Electron Microscopy and thermogravimetry.



Thermodynamic data of  $\Delta G^\circ$  vs. temperature for the reaction of ammonia formation with niobium pentoxide precursor. Ammonolysis reactions show a negative slope indicating more favorable reaction with increasing temperature. The reaction becomes spontaneous at  $\sim 1034\text{K}$  ( $761^\circ\text{C}$ )

## Powder morphology- SEM

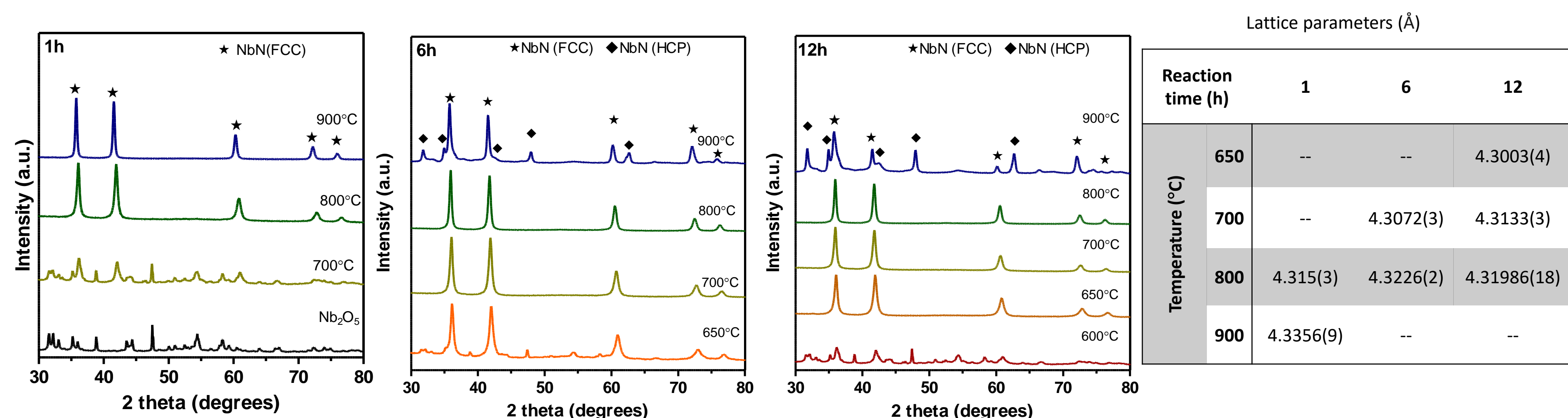
From the micrographs obtained is possible to conclude that the ammonolysis route does not significantly alter the morphology of the powder, due to the similar morphologies of the oxide precursor (Nb<sub>2</sub>O<sub>5</sub>) and formed nitride powders.



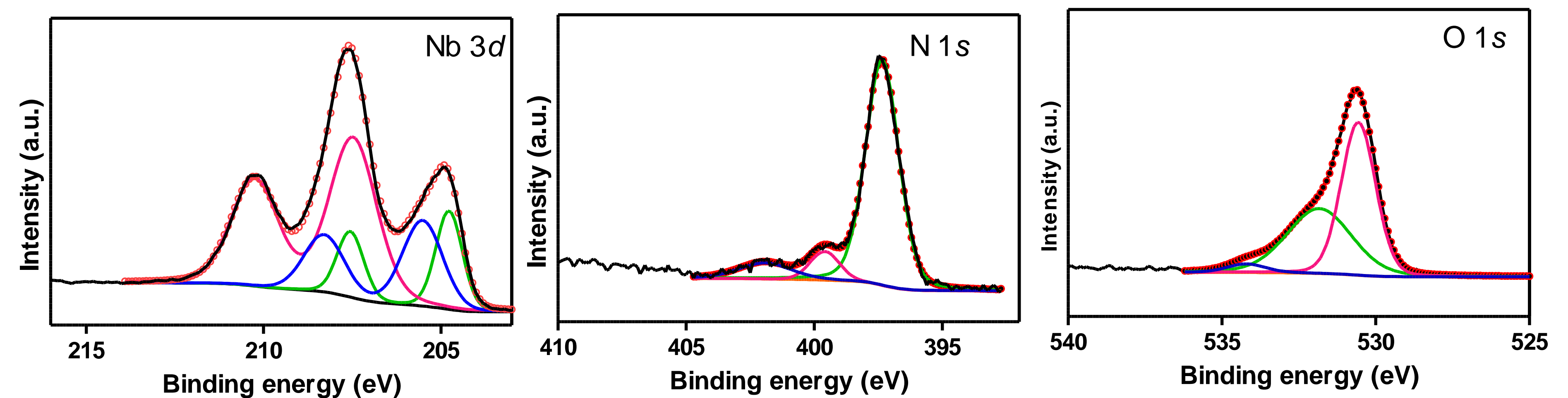
## RESULTS

### Structural characterization- XRD and XPS

The XRD results show that the pure cubic phase of NbN<sub>x</sub>O<sub>y</sub> can be obtained with 1h of dwell time at 800°C and 900 °C. Longer dwell times of 6 and 12 hours can permit a reduction of the sintering temperature to 700°C and 650 °C, respectively. However, the obtained lattice parameters of NbN<sub>x</sub>O<sub>y</sub> phase are shown to be dependent on the synthesis conditions.

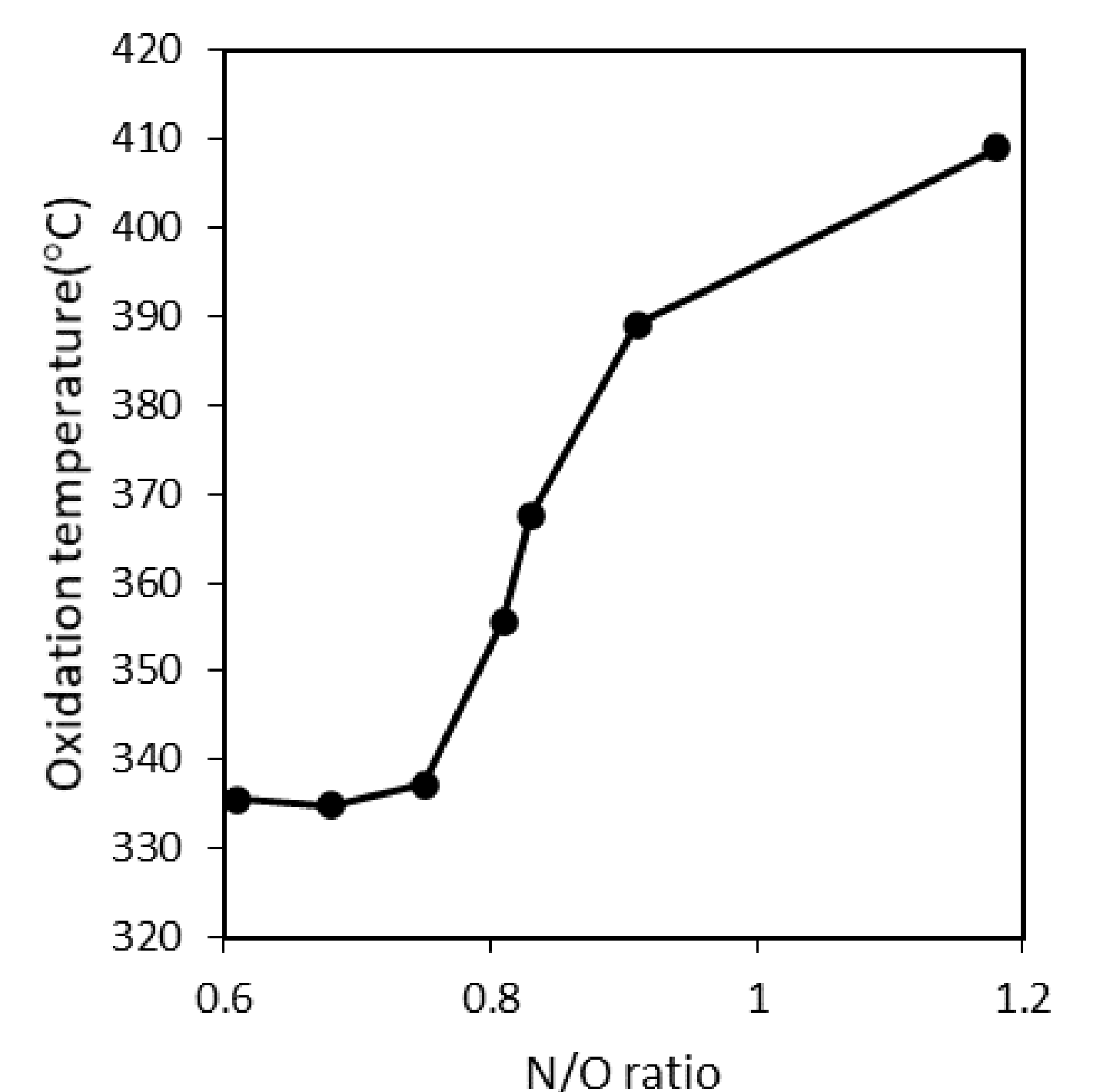
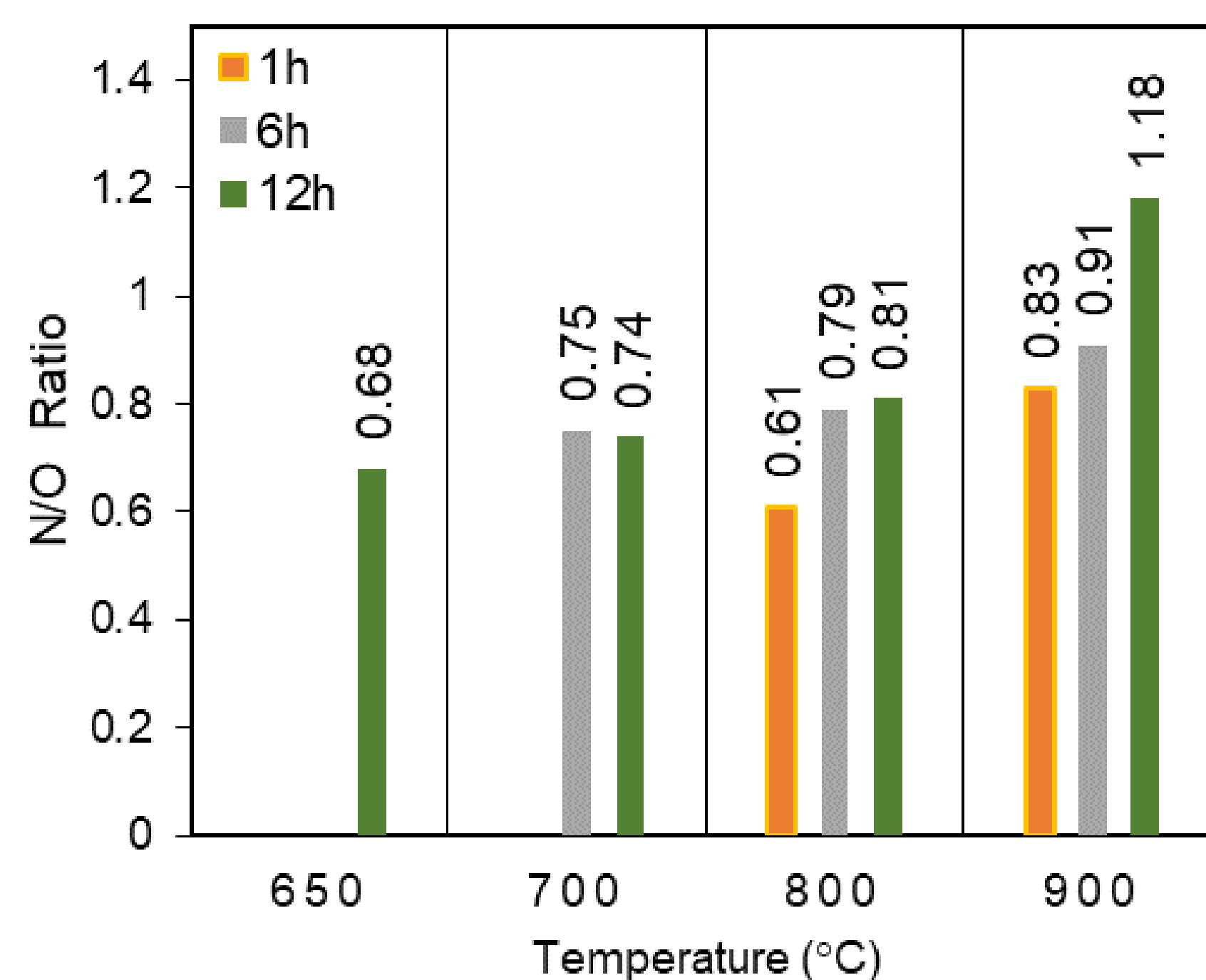


XPS spectra of Nb 3d, O 1s and N1s bands obtained for the powder prepared at 800 for 1h. Three doublets can be observed in the Nb 3d high resolution XPS spectra. The higher binding energy (BE) at  $\sim 207.47$  eV can be associated with the presence of Nb<sup>5+</sup>-O, while the BE at  $\sim 204.76$  eV can be ascribed for a mixture of Nb<sup>2+</sup>/Nb<sup>3+</sup> and can be associated with NbO<sub>x</sub>N<sub>y</sub>. The BE at  $\sim 205.6$  eV can be associated with Nb<sup>3+</sup>-N.



### Nitrogen and oxygen content

The N/O ratio of the obtained powders is shown to increase with increasing temperature and dwell time, explaining the aforementioned sensitivity of lattice parameters on preparation conditions. Interestingly, the N/O ratio is shown to also have influence on the initiation temperature for oxidation of the NbN<sub>x</sub>O<sub>y</sub> powder.



## MATERIALS & METHODS

Niobium nitride was prepared by the ammonolysis route from a niobium pentoxide precursor (Sigma-Aldrich). Nb<sub>2</sub>O<sub>5</sub> was nitrided using an alumina boat in a tubular furnace under 50 ml/min of NH<sub>3</sub> in the temperature range of 650-900°C during different dwell times (1, 6 and 12h). After cooling to room temperature, all samples were purged with N<sub>2</sub>.

The phase purity and structure analysis of the materials were examined by X-ray diffraction (XRD, Rigaku SmartLabSe diffractometer) and x-ray photoelectron spectroscopy (XPS, JPS9010TR, JEOL). Nitrogen and oxygen content were measured by using elemental analysis (Truspec 630-200-200) and TGA/DSC (Netsch). Microstructures of the final powders were assessed using SEM/EDS (Hitachi Tabletop microscope TM4000Plus).

## ACKNOWLEDGMENTS

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