EELS study of $SmNiO_3$ thin films deposited by magnetron sputtering with a soft air post-annealing

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Introduction

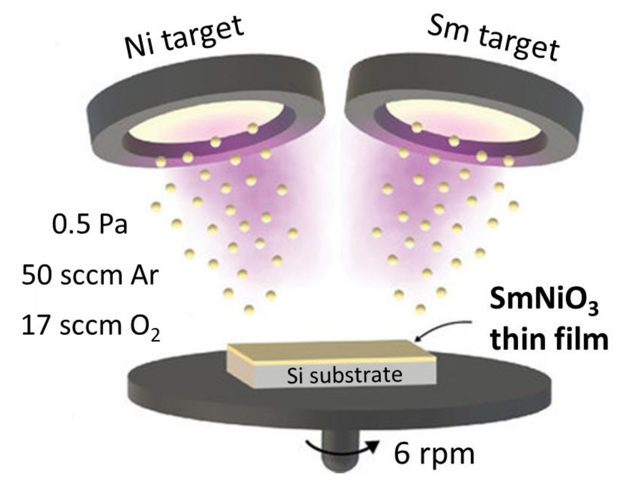
Samarium nickelate ($SmNiO_3$) exhibits a reversible metal-insulator transition (MIT) at 120 °C and remarkable structural, electronic, magnetic, and optical properties. However, its elaboration is challenging. Until recently, nickelates required extreme annealing conditions (for crystallization) under high oxygen pressures (~200 bar) to avoid oxygen loss and stabilize the Ni^{3+}, the less stable degree of nickel oxidation.

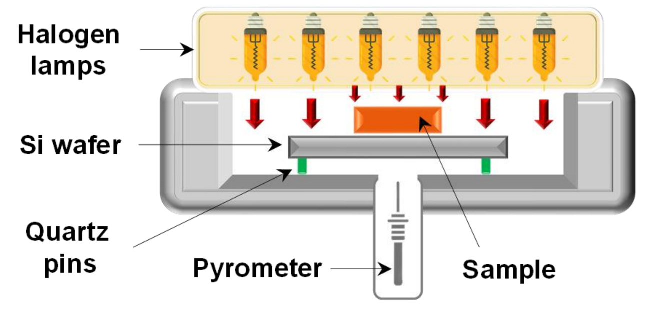
Electron energy loss spectroscopy (EELS) is a powerful method that can provide direct proof of the valency of elements ions. Here, we used it to show that $SmNiO_3$ thin films films can be grown under soft-annealing as the habitual orthorhombic perovskite structure. The importance of Ni^{3+} stabilization and orbital hybridization of *O 2p–Ni 3d* was demonstrated to synthesize the $SmNiO_3$ phase and not a Sm_2O_3 oxide.

Experimental details

Deposition by magnetron sputtering

The layers were deposited on silicon substrates in reactive mode. A current of 0.53 A was applied to the Sm target and 0.13 A to the Ni one. Deposition time was 90 min, resulting in 280 nm thick amorphous films.



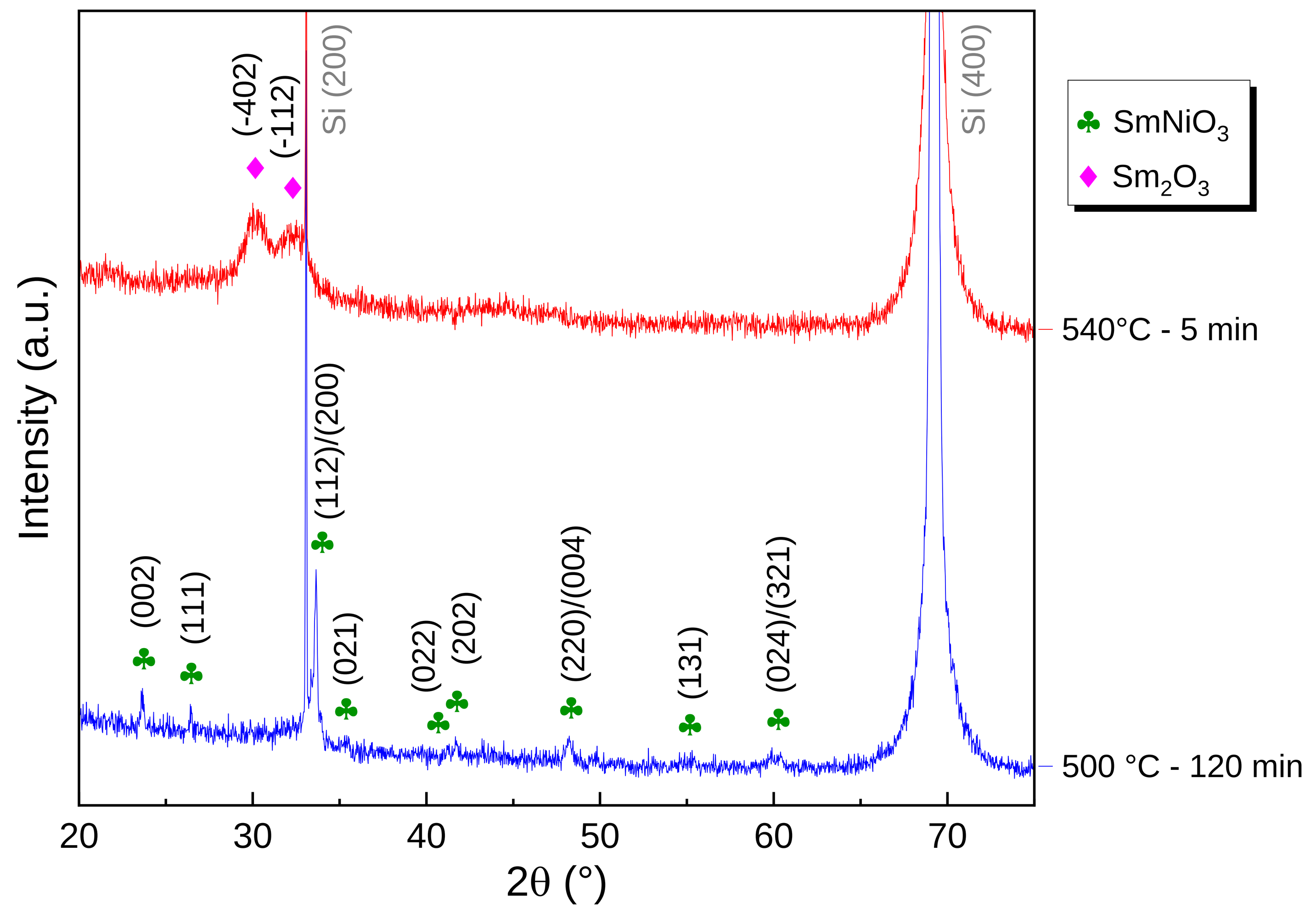


Crystallization by soft-annealing in air

The amorphous Sm-Ni-O films were annealed at atmospheric pressure in a rapid thermal annealing (RTA) furnace at 500 °C and 540 °C for 120 and 5 minutes, respectively.

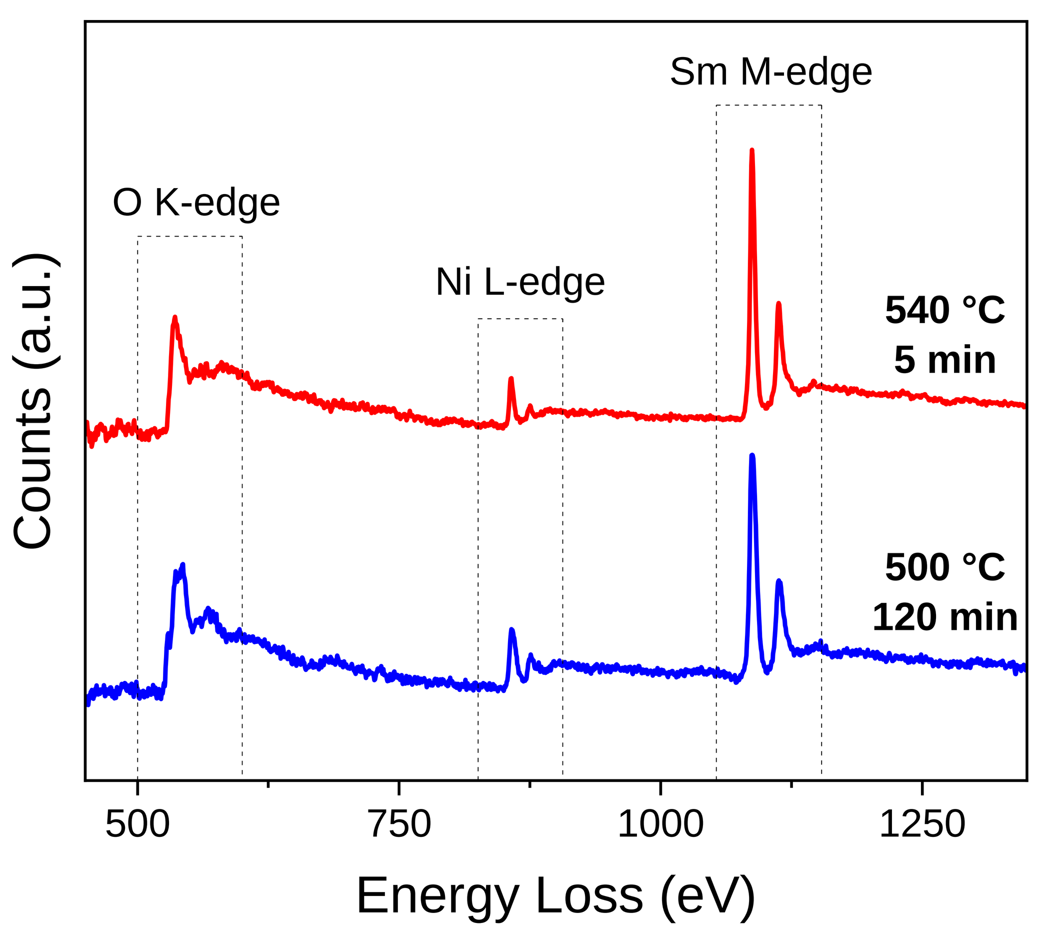
X-ray diffraction (XRD)

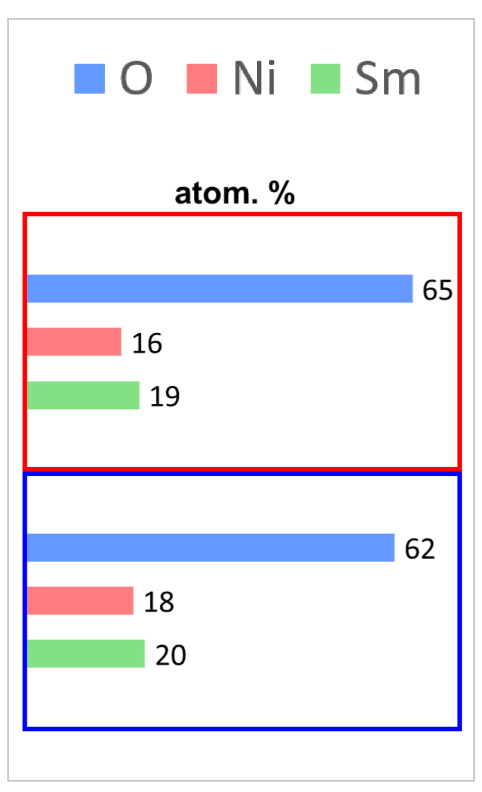
The samples annealed revealed different phases during crystallization. At 540 °C and 5 minutes the favored phase was Sm_2O_3, while at 500 °C and 120 minutes the most stable phase was $SmNiO_3$.



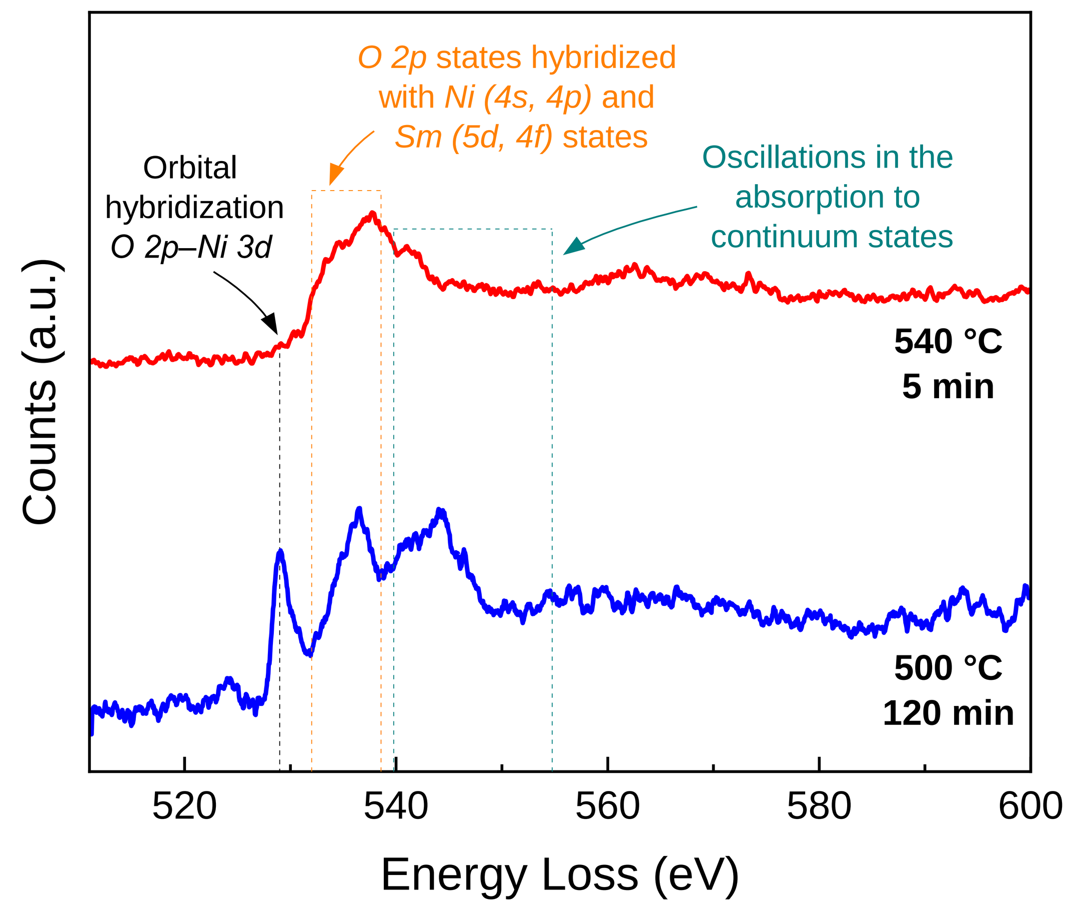
Chemical quantification by EELS

The chemical composition of the annealed samples was determined by EELS measurements. The core excitation edge of every element was identified and recovered in a broad spectrum of the film.





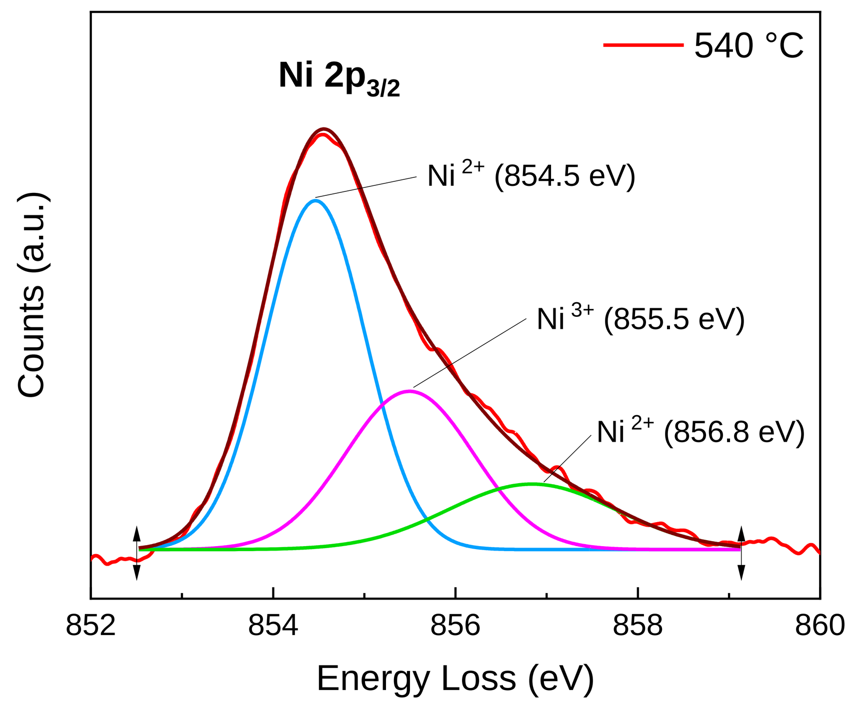
Oxygen K-edge EELS spectra

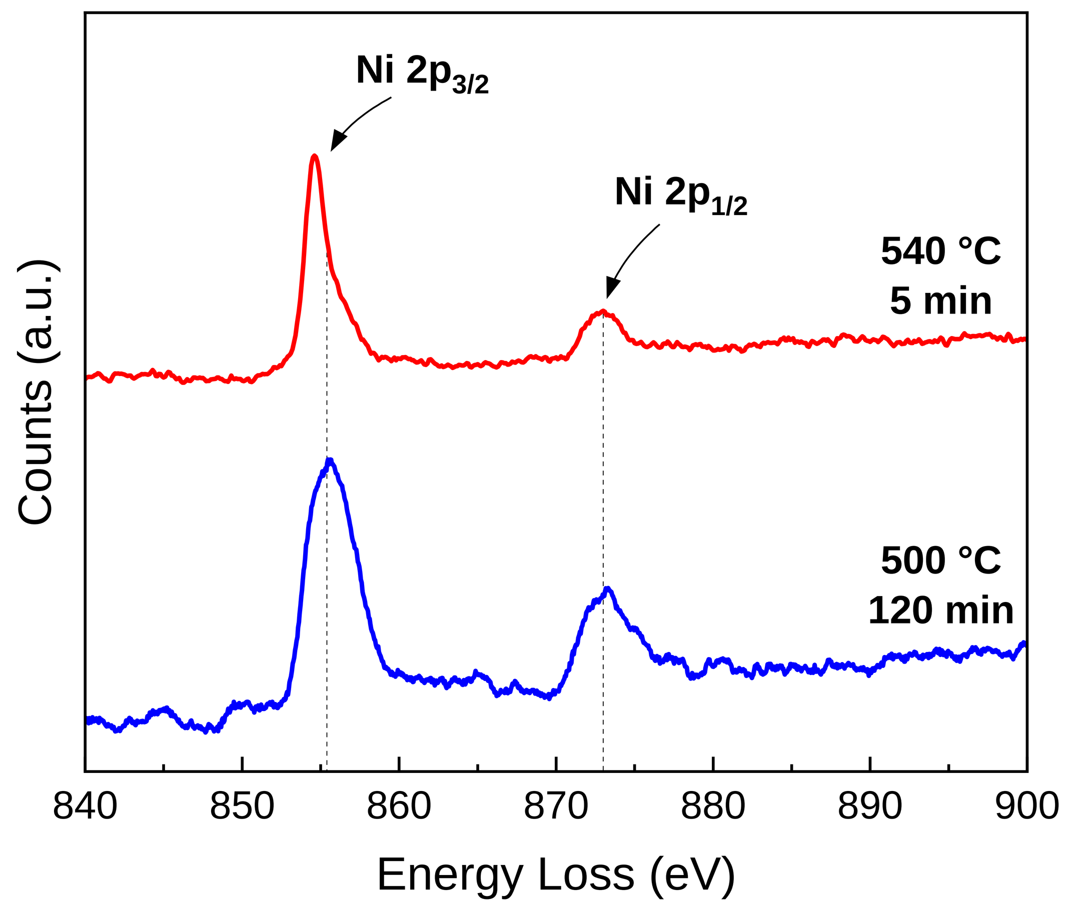


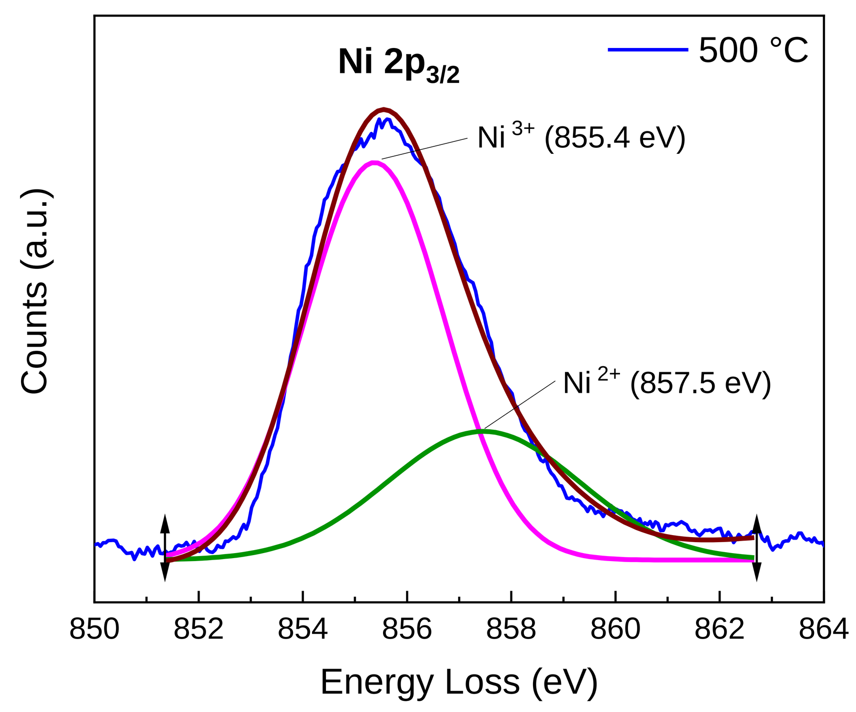
- Only the sample that crystallized in the $SmNiO_3$ phase shows the peak at 529 eV.
- This feature is due to the *O 2p* weight in states of predominantly *Ni 3d* character.
- For the sample annealed at 540 °C, perhaps because it does not show the hybridization between the Ni-O, the most favored phase to crystallize is that of Sm_2O_3.

Nickel L-edge EELS spectra

- The *2p*-states peaks of Ni are present.
- The deconvolution of the Ni $2p_{3/2}$ peak shows different intensities of the Ni^{2+} and Ni^{3+} oxidation degrees.
- For the sample annealed at 500 °C, a significant Ni^{3+} peak is observed, allowing crystallization in the $SmNiO_3$ phase. The prominent peaks of Ni^{2+} in the other sample favored the crystallization in the phase Sm_2O_3.

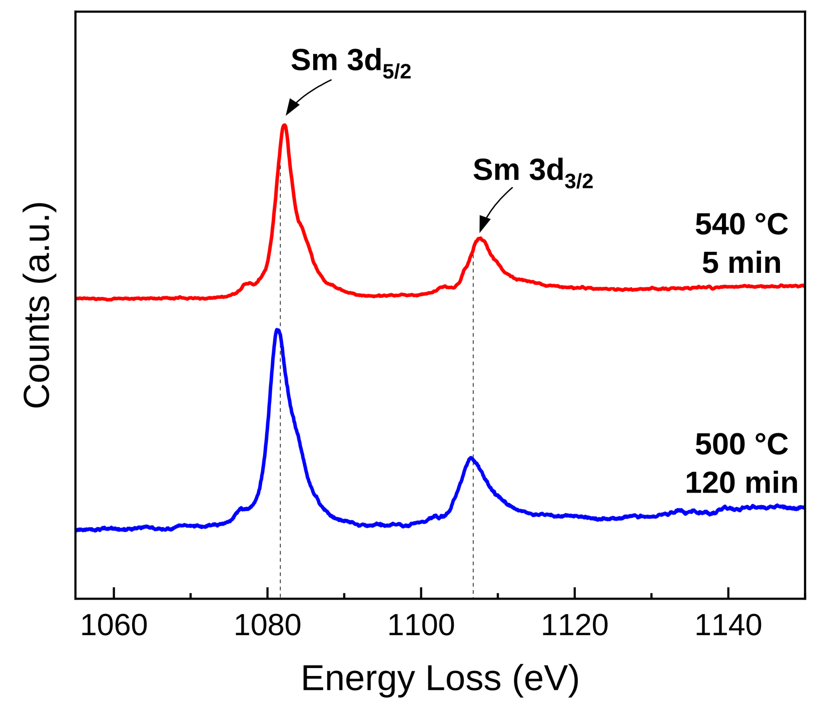






Samarium M-edge EELS spectra

- The two peaks corresponding to the *3d*-states of Sm are present. The spectra consist of two well separated line groups close to the $3d_{5/2}$ (M_V) and $3d_{3/2}$ (M_{IV}) edge positions.
- Given the positions and shapes of the peaks, we can conclude that samarium in the studied samples is trivalent (Sm^{3+}).
- Thus, both $SmNiO_3$ and Sm_2O_3 phases can be synthesized as shown by XRD results.



Conclusions

- The $SmNiO_3$ and Sm_2O_3 phases obtained by XRD were confirmed by EELS measurements.
- It was found that when the $SmNiO_3$ phase is well crystallized, it is possible to observe the orbital hybridization of *O 2p–Ni 3d* and a significant Ni^{3+} content.
- On the other hand, the trivalent samarium ion (Sm^{3+}) was identified in its corresponding positions. It allows crystallization of the two oxide phases: $SmNiO_3$ and Sm_2O_3.
- Finally, the chemical composition of both samples was quantified by EELS analysis.

References

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