Multiscale modeling of the crystallization of rare-earth nickelates $ReNiO_3$ from metastable amorphous phases

Perovskites of the $ReNiO_3$ type with Re= Pr, Nd, Sm and Eu are superconducting nickelates with a particularly interesting metal/insulator transition (MIT) that can be used in many fields such as thermochromic compounds or infrared furtivity. [1–3]. These compounds are nevertheless difficult to synthesize because they are metastable with respect to the corresponding elemental oxides and require drastic synthesis conditions in terms of temperature and pressure. [1,4]. One of the current challenges is to synthesize these compounds under near-ambient temperature and pressure conditions, which can be achieved using magnetron sputtering techniques. This technique produces amorphous "Re/Ni/3O" thin films which, when annealed under soft conditions (atmospheric pressure, temperature below 900 K), crystallize as $ReNiO_3$ perovskites.

An initial thermodynamic study of Samarium nickelate ($SmNiO_3$) crystallization showed that it was possible to predict optimum crystallization conditions and to determine a number of physical parameters associated with this solid-phase transformation (crystallization enthalpy, amorphous/crystal interfacial tension, amorphous phase shear modulus) [5,6]. This approach is based on the correlation between a solid-phase germination model derived from Volmer's capillary theory and experimental results from DRX and TEM analysis of partially crystallized samples at different temperatures. the full development of this model requires a microscopic approach to determine the atomic processes of atomic migration during crystallization, in particular the atomic diffusion of oxygen in the case of perovskites nucleation. As part of this thesis work will be devoted to develop a microscopic approach using Molecular Dynamic (MD) simulation to study the atomic migration within the amorphous phase, in order to determine the enthalpy and entropy of oxygen migration and any losses of this element during annealing. A machine-learning interatomic potential (MLIP) will also be developed in collaboration with the computational materials science group team (Pr. H. Zhang) from University of Alberta (UoA) for a model system, e.g., $SmNiO_3$, to investigate the atomistic mechanism for nucleation process from amorphous phase, in particular, to focus on the migration of oxygen.

The aim of this thesis is to generalize the thermokinetic approach to the whole nickelate family and to globalize the crystallization model by integrating the Goldsmith tolerance factor, which quantifies the structural modification linked to the rare earth change [3], and by including the MD approach to take account of atomic migration in the amorphous/crystalline perovskite phases.

The main objectives of the thesis are as follows:

- Cathodic magnetron sputtering synthesis of various metastable amorphous nickelates (ReNiO)

- $ReNiO_3$ crystallization during in situ TEM or XRD annealing

- MD approach for atomic migration modeling during the amorphous/crystalline transformation

- Reworking of the crystallization model (Volmer capillary approach) and extension to the entire $ReNiO_3$ family

- Generalization of the nucleation-growth modeling via the multiscale approach (thermodynamic and microscopic model)

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