

**3D self-assembled chessboard-like microstructural evolution in
CoFeMn and CoFeGaMnZn oxide spinels and NdLiTiO₃
perovskites for nano-electronics/energy devices**



**Thesis submitted in partial fulfilment for the
Award of Degree**

Doctor of Philosophy

By

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2022

Chapter 7

Conclusions and suggestions for future work

7.1 Conclusion

To give a broader perspective of CB-like microstructural evolution in ceramic systems, in this thesis author has studied this phenomenon in two different ceramic systems, i.e., spinel, perovskite. Based on well-planned investigations, it can be concluded that the mechanism of CB-like microstructural evolution is a system-dependent phenomenon. However, a symmetry-breaking phase transition is standard in every mechanism. In spinel systems, the primary emphasis was to elucidate this phenomenon in manganite spinels, i.e., CoFeMnO, ZnGaMnO and CoFeGaMnZnO systems. Whereas in perovskites CB-like evolution in LLnTO based LiNdTiO₃ perovskite system is explored. XRD and TEM investigations of spinel manganites have confirmed that such microstructural evolution occurs through a series of phase transformations. To study CB-like microstructural evolution in continuation, a specific interrupted growth experiment was planned for every material system. XRD and TEM investigations of all the spinel manganite samples collected after each such interruption have suggested J-T distortion's role as a driving force for a symmetry-breaking phase transformation. A fast cubic to tetragonal phase transformation is identified as the primary transition step in the series of phase transformations. This cubic to tetragonal phase transition incubates tetragonal domains twinned along (022) planes, and interpenetration of these twin-related domains gives birth to a CB-like self-assembled microstructure. In second transition step, a slow pseudospinodal decomposition turns the microstructure into a well-organized disposition of Mn-rich and Mn-lean square domains arranged as chessboard squares forming {022} interfaces. After sintering and ageing, chessboard nanodomains of CoFe₂O₄ and CoMn₂O₄, and ZnGa₂O₄ and ZnMn₂O₄ spinel phases evolve in the CoFeMn and ZnGaMn oxides, respectively. After similar heat treatment, similar CB-like microstructure was observed in the CoFeGaMnZn multicomponent oxide, with comparatively smaller domains of similar phases. These spinel phases are all likely to have mixed chemistry. Nanobeam diffraction pattern taken from individual nanodomains along [100] zone axis confirms the presence of a cubic phase (Fd $\bar{3}m$) and a tetragonal phase (I4₁/amd) each with two orientation variants interlaced with complex crystallographic relationship. A mutual in-plane and out-of-the-plane $\sim 5.2^\circ$ solid-body rotation between the nanodomains occurs during prolonged ageing treatment may relate to minimization of misfit in lattice parameters of cubic and tetragonal phases. To reconstruct a 3D perspective model, TEM and APT-based correlative microscopy were done. For correlative microscopy, CoFeMnO was taken as a system of interest. In this

correlative microscopy, APT analysis has reconfirmed the presence of subdomains captured in diffraction contrast imaging and HAADF-STEM-EDS Z-contrast imaging up to three orders. This study shows that within the first order decomposed parental cuboidal/octahedral domains (~70 nm), subdomains with similar shape (~7-12 nm) evolve with a preferential orientation, i.e., 45° with respect to parental domains. These subdomains evolve with {022} interface parallel to [004] directions of parental domains. In the same line, these second-order subdomains again go under the decomposition process and work as parental domains for third-order subdomains (~2nm). The evolution of domains inside the domains up to third-order indicates that CB-like microstructural evolution in spinel manganite is a recurrent phase separation process. In this process, the orientation relationship between the parental and product domains is expected to be preserved until the relative concentration of the two phases reaches to equilibrium. A more critical observation of iso-concentration surfaces of Fe and Mn ions constructed by APT data helped to visualize further stages of phase transformations of CB-like microstructural evolution. The correlation of iso-concentration surface maps to TEM images confirms that CB-like microstructural evolution in spinel manganites involves recurrent phase separation with a simultaneous concatenation of cuboidal/octahedral nanodomains along <004> directions. This concatenation of the domains with like composition turns the 3D CB-like microstructure of well-organized nano cuboidal/octahedral into a 2D arrangement of well-organized rod-like morphology of Mn-rich and Mn-lean phases.

In addition to ternary spinel systems, an attempt to design a CoFeGaMnZn-based MCO system with CB-like microstructure has been made. TEM diffraction contrast imaging confirms that nanodomains developed in CoFeGaMnZn are significantly smaller than those seen in CoFeMn and ZnGaMn ternary oxides because the pseudo-spinodal segregation of ionic species is diffusion mediated, and this becomes slower with an increase in the number of cationic species present. Minimization of strain energy in the multicomponent MCOs appear to be the driving forces behind systematic twinning in the spinel tetragonal I structure and the subsequent diffusive separation within this structure. However, in MCO system both the square and rod-like domains share interface along {022} planes similar to other manganites spinels, their frequency of alternation of contrast and width is not consistent with other ternary manganites. Contrary to ternary manganites, the repetition in contrast is observed after every four nanorods. The variation in the width of every nanorod is the subject of further elucidation.

Here, we have clearly shown that the earlier report by Ni and Khachatryan (2009) is only partially complete. The interpenetration of twin regions initially defines the CB morphology, which occurs to reduce the strain energy introduced by J-T distortion in the cubic matrix. The kinetics of all these processes are fundamental in the predictive design of the nanostructure. In addition, two different phases with distinct magnetic states could be suitably tailored to design the functionality or differential flux permeability that this material is poised to exhibit. The concept of CB nanostructure evolution presented in this thesis could also be extended to design other materials for desired applications.

A-site deficit LiLnTiO_3 ($\text{Ln} = \text{La}, \text{Nd}, \text{Sr}, \text{Pr}, \text{etc.}$) based perovskites are considered as forerunner in all the material systems contesting in pursuit of ASSLBs. $\text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_5$ is proven to be the best material for the solid-state electrolyte to date with an ionic conductivity near to $\lambda=1.5 \times 10^{-3} \text{ S/cm}^{-1}$. These systems have been reported to evolved as CB-like microstructure. In this thesis, the author has explored the LiLnTiO_3 -based LiNdTiO_3 perovskite system to study CB-like microstructural evolution and its consequence on electrochemical properties. This thesis also addresses the debate over the involvement of compositional phase separation in the CB-like microstructural evolution of LiNdTiO_3 . XRD analysis shows that the LiNdTiO_3 sample, sintered at 1250°C followed by quenching, acquires an orthorhombic α' symmetry. On the other hand, the same sample, after sintering and annealing, attains a tetragonal β symmetry through a polymorphic transformation. Rietveld refinement of sintered-annealed $\text{Li}_{0.48}\text{Nd}_{0.5}\text{TiO}_3$ confirms the formation of the β phase in which ordering of aliovalent cations and vacancy distribution at the A-site accounts for the variation in the Ti-O bond lengths. Bright-field image along the $[001]$ zone axis from the sintered-annealed $\text{Li}_{0.48}\text{Nd}_{0.5}\text{TiO}_3$ sample shows two alternative bright and dark strip regions with 5-10 nm wide nanorods sharing interfaces along $[100]$ and $[010]$ directions. The two domains have 001 direction perpendicular to each other. The interpenetration of these two striped nanodomains gives birth to CB-like microstructure. The CB-like appearance of these well-organized rods results from a perpendicular cross-penetration of the striped rods. Later, an APT and TEM-based correlative investigation confirms that these rods consist of Li-rich and Nd-rich, two or more different phases.

Parallel to the abovementioned microstructural investigation, we have also studied how the CB-like microstructural evolution affects the electrochemical properties of the LiNdTiO_3 samples. The coulombic efficiencies and specific capacities of both the samples are almost equal at the beginning of the charging-discharging cycles, i.e. coulombic efficiency $\sim 99\%$

and specific capacity $\sim 120 \text{ mAhg}^{-1}$. The coulombic efficiency and specific capacity of the sintered-annealed $\text{Li}_{0.48}\text{Nd}_{0.5}\text{TiO}_3$ sample remain constant at $\sim 99\%$ and 120 mAhg^{-1} even after 100 cycles. Whereas, for sintered-quenched $\text{Li}_{0.48}\text{Nd}_{0.5}\text{TiO}_3$ (disordered) sample-specific capacity reduces from 120 mAhg^{-1} to 100 mAhg^{-1} ($\sim 16\%$) with a constant coulombic efficiency from $\sim 99\%$. Compared to sintered-annealed $\text{Li}_{0.48}\text{Nd}_{0.5}\text{TiO}_3$ samples, the specific capacity of the $\text{Li}_{0.36}\text{Nd}_{0.5}\text{TiO}_3$ sample are relatively less 110 mAhg^{-1} in the beginning with a coulombic efficiency ($\sim 99\%$). In sintered-annealed $\text{Li}_{0.36}\text{Nd}_{0.5}\text{TiO}_3$ sample, a drastic decrease in specific capacity was observed 110 mAhg^{-1} to 80 mAhg^{-1} (27%) after 100 charging and discharging cycles.

7.2 Suggestions of future work

Although the author has tried to elucidate the evolution of CB-like microstructure in ceramic systems to the best of his competencies, this research domain still has many open areas for further research. With advanced instrumentations and characterization techniques, e.g., High-resolution HAADF-STEM-XEDS, EELS, in-situ TEM, Lorentz microscopy, AFM, etc., it is possible to take this work up to the next level. A critical TEM-based investigation in HR-STEM mode may provide new insight regarding the nature of the interface. Especially for complex systems, i.e., Li^+ containing LLnTOs, MCOs, HR-STEM-XEDS coupled with EELS may facilitate an in-depth information of atomic distribution in CB-like domains. As done for Mn-doped CoFe_2O_4 (Chapter 4), an APT and TEM-based correlative microscopy can be extended for LiNdTiO_3 and MCO systems to reconstruct 3D-microstructure. In addition, Lorentz microscopy and AFM techniques may be utilized to characterize the magnetic properties of CB systems, i.e., CoFeMnO , CoFeGaMnZnO up to the domain level.

Apart from improved characterization, a combination of existing literature and this thesis may lay a roadmap to develop an entirely new range of advanced patterned materials consisting of domains/basic building blocks down to $\sim 1\text{-}10 \text{ nm}$. In addition, this thesis informs that through CB-like microstructural evolution, not only binary patterned materials but also more complex ones can be fabricated. This thesis reports that the CB-like microstructural evolution is a series of phase transformations, which involves various structural and compositional modifications during the process. Basic components/domains of CB-like microstructure alter their shape (from cuboid to the rod) and size (increases with time) as the transformation kinetics proceeds. A new range of materials may be designed by controlling the evolution kinetics.

In addition, CB-like systems may be utilized to fabricate complex 1D, 2D and 3D nanoelectronics devices. A layer of material with CB-like microstructure may be used as a template for alternative preferential growth of other materials over it. The CB-like template is expected to serve as a substrate that provides an alternative 2D arrangement of two different substrates. Here a well-organized tiling of material possessing two distinct structures/compositions may behave differently for a to be deposited material. For instance, an Mn-doped CoFe_2O_4 spinel system-based CB-like microstructure may be used as a substrate to grow ZnO nanowires. The CB-like microstructure developed in CoFeMnO system may facilitate as 2D alternative tiling of the Mn-rich phase and Mn-lean phase. Different crystal structures, compositions and orientation (As explained in Chapter 3 and Chapter 4) of these phases will affect the growth differently. Consequently, an alternative arrangement of two types of ZnO nanowire may be achieved (Figure 7.1).

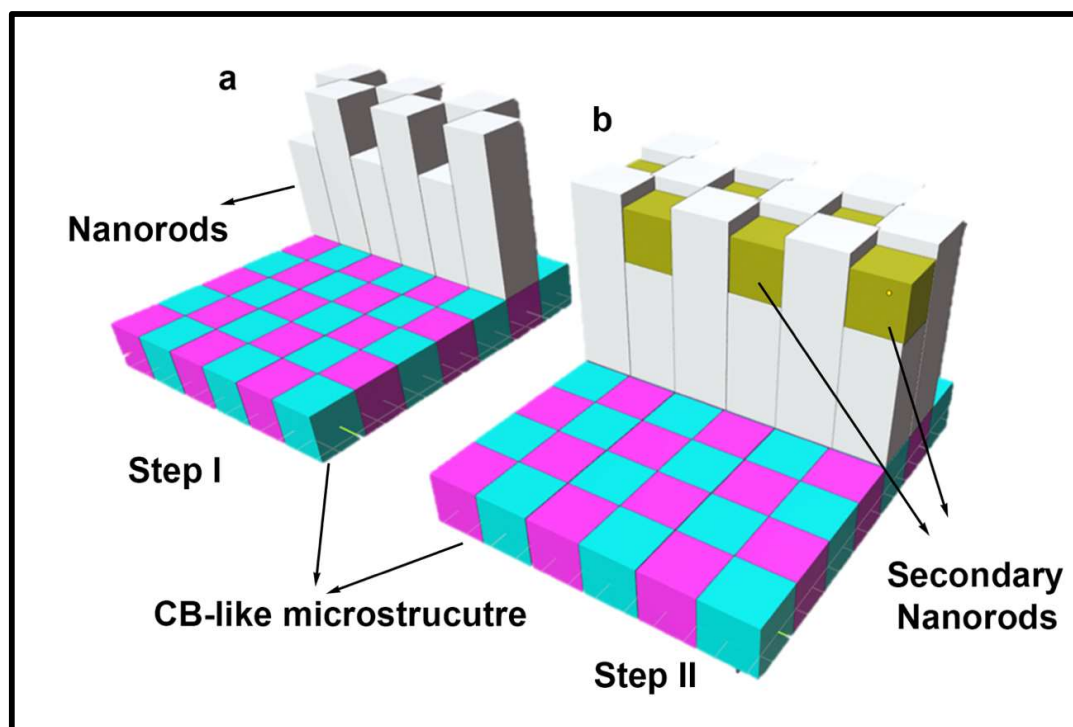


Figure 7.1: Schematic illustrates design procedure for 2D alternative growth of different nanorods using CB-like microstructure as a template. (a) the first step of the process shows selective growth of one type of nanorods (white) (b) the second step shows secondary deposition for another kind of nanorods (yellow).