3D self-assembled chessboard-like microstructural evolution in CoFeMn and CoFeGaMnZn oxide spinels and $NdLiTiO_3$ 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

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I, **Avnish Singh Pal**, certify that the work embodied in this Ph.D. thesis is my own bonafide work carried out under the supervision of **Dr. Joysurya Basu** for a period from **Dec 2015** to **July 2022** at the "**Department of Metallurgical Engineering**", Indian Institute of Technology (BHU), Varanasi, India. The matter embodied in this Ph.D. thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports dissertations, thesis, etc., or available at websites and have not included them in this thesis and have not cited as my own work.

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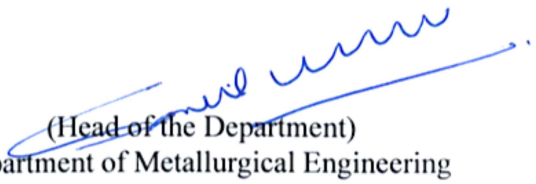

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Acknowledgement

I want to inaugurate my acknowledgement statement by offering my gratitude to the almighty God for the wisdom he has showered over me that has made my path easy to this attainment.

I am expressing my sincere gratitude to my supervisor Dr Joysurya Basu, for imparting his knowledge and expertise in this work. I am very fortunate to have learnt the basics of materials characterization techniques and crystallography from him. He has not only trained me on transmission electron microscopy but also introduced me with related advanced characterization techniques, such as in-situ TEM, EELS, HAADF-STEM-XEDS, etc. In combination with hands on experience, he has also made me familiar with essential analytical tools such as multislice image simulation (JEMS), crystal structure identification (Rietveld refinement) and other analytical software. His emphasis over squeezing the gathered data at the fullest, has implanted a sense of critical thinking and developed the ability of thinking out of the box. He has always advised me to prefer quality over quantity, which immensely benefited me in publishing my research work in reputed journals. In simple words, his amiable and enthusiastic nature and clear vision has helped me greatly in uplifting my understanding of such an intricate subject. I am extremely thankful to him for his untiring support throughout my Ph.D. journey, specially the push he gave me every time I have got stuck. It is my pleasure working under his guidance.

It is my privilege to express my heartfelt gratitude to him for giving me the latitude to perform various experiments irrespective of their success probability, which has immensely helped me in developing concept out of the book. His innovative approach towards research, always enhances my propensity toward research and inspired me to remain positive and be patient in all ups and downs. He is a thorough observer and a patient researcher, he listens to my all queries and tries to turn them into a logical discussions that always boosts up my confidence. His approach of putting the intricate things in simple and elusive manner has always inspired me to attain perfection in my work. I am indebted to him for inspiring guidance, persistent encouragement throughout the course of this work.

I would also like to convey my thanks to Prof. S. Lele, Prof. G.V.S. Sastry, Prof. N. K. Mukhopadhyay, Prof. Vakil Singh and Prof. R K Mandal for fruitful discussions and, former Heads of the Department for their kind support. I thank Prof. Sunil Mohan, the current Head of the Department for his valuable contribution.

I also want to show respect to the all faculty members of Department of Metallurgical Engineering, IIT (BHU) for creating such a wonderful environment for research. I would also like to express my gratitude to the entire non-teaching staff of the Metallurgical Engineering Department of IIT BHU.

I sincerely thank Dr K.G. Pradeep, Department of Metallurgical and Materials Engineering, IIT Madras, for extending me support for correlative microscopy and FIB sample preparation. It is my pleasure to thank Prof. Kevin M. Knowles, Department of Materials Science and Metallurgy, University of Cambridge, for involving in frequent and long discussion sessions, which has helped me improving my knowledge of crystallography to take my work up to next level. My heartedly thanks to Dr. Surendra Kr. Makineni, IISc, Bangalore, for providing me sophisticated instrumental facilities. I gratefully acknowledge Dr. Imteyaz Ahmed, Ceramic Engineering, IIT BHU, for letting me avail the high temperature furnaces for long heat treatment hours. I am extremely thankful to Prof. N. Ravishankar, IISc, Bangalore, for letting me avail the aberration corrected TEM (Titan 300) facility. Working with all of them have been a great learning experience.

I am grateful to my present and former labmates, Dr. Manish Singh, Dr. Vikas Shivam, Dr. Raj Bahadur, Dr. Vivek Pandey, Dr. Yagnesh, Dr. Raj, Dr. Asnit, Ankit, Shubham, Roopchand, Saarika, Soham, Saptarshi, Satyam, Sandeep, Urvashi, Deepak, Sujeet, Ankur, and Pavithra, for their cheerful company. I also want to convey my thanks to Lalit Kr. Singh and Aman for their unconditional support and readiness for any kind of help.

At personal front, I wish to express my sincere gratitude and indebtedness to my family for their blessings, care, encouragement and moral support throughout this journey.

I would also like to thank EMSI, Research & Development (IIT BHU), Mrs. Indira Anathachari endowment fund, and IIM Trust for extending me financial assistance for attending the national and international Conferences.

(Avnish Singh Pal)

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Abbreviations

CB	:	**C**hess**b**oard
SD	:	**S**pinodal **D**ecomposition
TEM	:	**T**ransmission **E**lectron **M**icroscope
APT	:	**A**tom **P**robe **T**omography
LEAP	:	**L**ocal **E**lectrode **A**tom **P**robe
TOF	:	**T**ime **of F**light
STEM	:	**S**canning **T**ransmission **E**lectron **M**icroscope
HAADF	:	**H**igh **A**ngle **A**nnular **D**ark **F**ield
SADP	:	**S**elected **A**rea **D**iffraction **P**attern
BF	:	**B**right **F**ield
DF	:	**D**ark **F**ield
DCI	:	**D**iffraction **C**ontrast **I**maging
FFT	:	**F**ast **F**ourier **T**ransform
XEDS	:	**X**-ray **E**nergy **D**ispersive **S**pectroscopy
NBD	:	**N**ano **B**eam **D**iffraction
HRTEM	:	**H**igh **R**esolution **T**ransmission **E**lectron **M**icroscopy
CTF	:	**C**ontrast **T**ransfer **F**unction
XRD	:	**X**-ray **D**iffraction
SA	:	**S**elf-**A**ssembly
SSA	:	**S**tatic **S**elf-**A**ssembly
DySA	:	**D**ynamic **S**elf-**A**ssembly
MM	:	**M**eta**m**aterial
ASSLBs	:	**A**ll **S**olid **S**tate **L**ithium-ion **B**attery
SSEs	:	**S**olid **S**tate **E**lectrolytes
SLRO	:	**L**ong **R**ange **O**rder **P**arameter
J-T	:	**J**ahn-**T**eller **D**istortion
CO	:	**C**harge **O**rdering
MCO	:	**M**ulti**c**omponent **O**xide

Symbols

θ	:	Bragg angle
λ	:	Wavelength
β	:	Peak broadening
t	:	Crystallite size
ΔH	:	Enthalpy of formation
ε	:	Misfit strain
ΔG	:	Free energy
d	:	Interplanar spacing
γ	:	Surface energy
a	:	Lattice parameter
^{0}	:	Degree
ϵ	:	Strain
c	:	Elastic constant
k	:	Shape factor
δ	:	Small fraction
Δ	:	Large fraction

Preface

An exponentially growing demand for materials, advanced in terms of directional-multi-functionality of physical properties, has been witnessed in modern days nano-electronics. Here the term 'directional' is intended to mean the anisotropy of physical properties along different directions. This implies that the single component made of such materials will exhibit physical properties in various possible combinations, e.g., multi-magnetism, multiferroicity, optoelectronic, thermoelectricity, piezoelectricity etc. along different crystallographic directions. In addition, some applications require the miniaturization of electronic devices in order to produce compact equipment. However, one way to meet this demand is to fabricate materials with exotic microstructures consisting of well-organized periodically distributed phases in complex geometries, i.e. chessboard (CB) nanodomains. Such well-organized microstructures are achievable not only via some modern and hard-to-scale up techniques such as e-beam lithography, templated chemical vapor deposition and pulsed laser deposition etc. but also with various classical phase transformation routes, such as spinodal decomposition, pearlitic transformation, order-disorder transformation (A1 to $L1_0$+$L1_2$), martensitic transformation, intergrowth, and 3D self-assembled checkerboard-like (CB) microstructural evolution etc. However, most of the above-mentioned techniques produce lamellae, well-organized precipitates and nanowires, which have been well understood and reported. Among all the techniques mentioned above, CB like microstructural evolution is found to be the most suitable for the given applications. It has unique potency to produce 3D well-organized interlacing of two chemically separable and structurally distinct cuboidal nanodomains, possessing functionality of the desired properties. Top of all, the CB-like microstructural domains are reportedly pretty homogeneous in terms of size, shape, and compositional distribution. The physical properties of a multiphase material depend not only on the atomic structure of each constituent phase but also on their shape, size, and morphological distribution. Herein, we have studied the mechanism of CB-like microstructural evolution in spinel and perovskite systems. CoFeMnO, ZnGaMnO and CoFeGaMnZnO multicomponent (MCO) spinel systems may evolve as CB microstructures consisting of well-organized nanodomains with differential functionality. In CB microstructure, well-organized alternative distribution of ferromagnetic and paramagnetic nanodomains builds up the decoupling effect of the magnetic

moments that provides the required anisotropy to upgrade ultrahigh density recording medium (> 1 Tb/inch^2) to a state-of-the-art stage. The square faceted domains improve the archivability of the memory device. On the other hand, CB-like microstructural evolution in $LiNdTiO_3$ perovskite system has been explored to comprehend its potential in all-solid-state lithium-ion battery (ASSLBs) applications. In this thesis, we have explored the evolution mechanism of CB-like microstructure in CoFeMn-based spinel, $LiNdTiO_3$ perovskite and its effects on the physical properties.

All samples were prepared by solid-state synthesis route due to its potency to produce the pure and certain end products, ease of material handling and better reproducibility. High purity precursors (> 99.9%) were mixed in appropriate stoichiometries and were put through specific heat treatments. For CoFeMnO, ZnGaMnO and CoFeGaMnZnO based CB systems, precursor powders of Fe_2O_3, Co_3O_4, Mn_2O_3, ZnO, and Ga_2O_3 were mixed and were pelletized in corresponding $Co_{0.6}Fe_xMn_{2-x}O_4$, $ZnGaMnO_4$ and $Co_{0.6}Fe_{0.8}GaMn_{2.6}ZnO_{8+x}$ stoichiometries. All the green pellets were sintered in air at 1250 °C for 24 hours, followed by quenching in ice water. The sintering process was repeated twice with an intermediate grinding of the first time sintered and quench pellets to ensure a homogeneous composition throughout the sintered pellet. In order to obtain sufficient diffusive rearrangement of ions, ageing treatment was given in air atmosphere at 375 °C. Similarly, to develop CB-like microstructure in $LiNdTiO_3$ perovskite system, ultra-high pure precursor powders of Nd_2O_3, TiO_2, and Li_2CO_3, were mixed and were pelletized in four stoichiometric ratios ($0.16>x>0.05$), $Li_{0.15}Nd_{0.5}TiO_3$, $Li_{0.24}Nd_{0.5}TiO_3$, $Li_{0.36}Nd_{0.5}TiO_3$ and $Li_{0.48}Nd_{0.5}TiO_3$. The pellets were sintered at 1250 ^{0}C for 24 hours and were cooled through two different routes namely: prolonged annealing and ice water quenching, in order to develop chessboard-like microstructure and disordered bulk microstructure, respectively. The electrochemical performance of the samples was evaluated against the Li reference electrode. The electrochemical performance of each obtained product was evaluated with a 2032 coin-type cell using a non-aqueous electrolyte (1M LiPF6/EC:DMC=1:1 in volume) and a polypropylene separator (Celgard 3501) against lithium metal. The cells were assembled in a glovebox filled with high purity argon. Electrochemical cycling was performed within the voltage range of 0.01–3V (vs. Li/Li^+) at the scan rate of 0.2mVs^{-1} at 25 ^{0}C.

It was speculated that the chessboard like nanostructure evolves through a series of phase transformations. In order to closely investigate these intermediate phase transformation events, total ageing time, from quenching to equilibrium, has been divided into four successive slots,

i.e., 0 hour, 5 minutes, 25 hours, 100 hours and 250 hours. In order to study these intermediate stages, samples at different stages of growth have been extensively investigated with XRD in combination with correlative microscopy of TEM and APT. In correlative microscopy, precise 2D information gathered by TEM investigations in various operating modes such as DCI, HAADF-STEM and HRTEM are complemented with the 3D information obtained by APT. The high-quality data has been processed with various software, i.e., Multislice image simulation, Rietveld refinement, and Vesta. Multislice image simulation has been performed with JEMS software to characterize complex structures, mainly interfacial arrangement of the nanodomains.

The XRD patterns corresponding to sintered and quenched conditions suggest that during the sintering treatment, the system was solutionized, which on quenching turned into unstable cubic $Co_{0.6}Fe_{0.8}Mn_{1.6}O_4$ spinel phase. The peak positions of this unstable phase closely match $CoFe_2O_4$ cubic spinel phase (JCPDS card number 00221086), which follows $Fd\bar{3}m$ space group. This cubic matrix turns into tetragonal through a fast cubic to tetragonal phase transformation. The XRD peaks corresponding to this tetragonal matrix match with $CoMn_2O_4$ tetragonal spinel phase (JCPDS card number 0011126), which follows $I4_1/amd$ space group. This cubic to tetragonal polymorphic phase transformation involves an exchange of interstitial position between Mn^{+3} and Fe^{+3} ions, which stabilizes the crystal field energy in the spinel structure. Once the Mn^{+3} ion occupies the B octahedral void it becomes J-T active ion. The diffusion of J-T (Jahn-Teller distortion) active Mn^{+3} ion introduces the anisotropy in the primary unstable cubic phase and turns it into a metastable tetragonal phase. That leads to a phase separation of the phases consisting of J-T active and inactive ions. Ideally, $CoFe_2O_4$ spinel structure possesses $Fd\bar{3}m$ space group, but after phase separation induced by J-T active Mn^{+3} ion, another $CoMn_2O_4$ tetragonal phase with $I4_1/amd$ space group comes into co-existence. The bright-field image along [100] zone shows chessboard like microstructure consisting of well-organized bright and dark nanodomains. This intriguing CB like contrast is the consequence of the mutual orientation of the neighboring cuboidal domains. The rotationally aligned electron diffraction pattern shows four split spots along 004 and 040 planes. These four spots represent two cubic and two tetragonal phase orientation variants, sharing twinned interfaces along (022) and $(02\bar{2})$. Tetragonal phase variants are in the twin relationship along (022) and $(02\bar{2})$; one tetragonal variant is rotated 180° around axis perpendicular to (022) or $(02\bar{2})$ planes of another tetragonal variant. The domains that have gone out of Bragg's diffraction condition appear bright, and those satisfying the condition

appear dark. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was performed on the post-annealed, phase-separated sample evidencing that these bright and dark nanodomains represent Fe-rich and Mn-rich phases. The orientation relationship between the cuboidal domains of cubic and tetragonal phases ought to be ~ 5.2° at the interface to minimize the strain induced by a misfit in lattice parameters. In the case of chessboard microstructure, $\gamma_{chemical} = 6a^2\gamma c$, $\gamma_{structure} = a^3.c\varepsilon.\gamma$, where c is elastic constant and ε is misfit strain and can be calculated by $\varepsilon = \frac{(a_c - a_t)}{(c_t - a_c)}$, here a_c ~ 8.3 Å, a_t ~ 8.1 Å and c_t ~8.8 Å. In some unique situations, the series of nanodomains lying in the identical Bragg's diffraction condition resembles a continuous rod. In this study, we have observed the formation of subdomains for the first time. Critical analysis of APT results has provided evidence of subdomains up to three-levels. At the First level CB microstructure shows domains of the order of 70nm x 70nm, while on the later levels, it shows subdomains of 10 nm x10 nm and 2 nm x 2 nm in the same sample. This observation suggests that CB-like microstructural evolution involves a recurring phase separation, where a coherent strain derives the 3D self-assembling of orientation variants. The facets of the domain generally grow normal to elastically soft directions of the crystal structure. In the same experiment, we have observed that spinodal decomposition leads to the formation of subdomains of higher compositional difference than their parental domains. Simultaneously, this compositional phase separation coalescence of parental domains along 040 or 004 directions turns cuboidal nanodomains into rods with facets along 022 and $(02\bar{2})$ planes. In the same line, ZnGaMnO and CoFeGaMnZnO were also investigated in order to understand CB evolution in them. Synthesis of a spinel based CoFeGaMnZnO MCO and formation of CB-like microstructure in any MCO is an entirely new observation. In the corresponding investigations we have found that the evolution mechanism in $ZnGaMnO_4$ and $Co_{0.6}Fe_{0.8}GaMn_{2.6}ZnO_{8+\delta}$ ($\delta << 1$) based spinel system is similar to $Co_{0.6}Fe_{0.8}Mn_{1.6}O_{4+x}$ ($x << 1$). However, the evolution kinetics is relatively sluggish in the case of MCO. In the $ZnGaMnO_4$ system, the system was separated into two coexisting phases having composition near to ~$ZnGa_2O_4$ and ~$ZnMn_2O_4$ phases. On the other side, $Co_{0.6}Fe_{0.8}Ga\mathit{Mn}_{1.6}^{+3}\mathit{Mn}_1^{+4}ZnO_{8+\delta}$ has formed CB nanodomains of the order of 7 nm x 7 nm in four different contrast. However, the HAADF-STEM-EDS maps could not differentiate the composition in the neighboring domains. These results refer to two different possibilities. First, the chemistry of cubic and tetragonal domains is of mixed nature. Second, there is only a subtle difference in the relative composition of four neighboring nanodomains that EDS detector is unable to distinguish.

A similar study shows that in sintered-quenched and annealed $Li_{0.48}Nd_{0.5}TiO_3$, Nd-ions, Li-ions, and vacancies are distributed in perovskite A-site and are ordered within alternate (001) planes. Ordering along 001 direction doubles the c-parameter of the primitive perovskite structure and turns it into a pseudo-tetragonal structure with Pmmm space group. The combined effect of the vacancy and aliovalent substitution slightly distorts the structure to pseudo-tetragonal (orthorhombic) with a minute difference in a and b lattice parameters a_p x 2 c_p (3.82 Å x 3.81 Å x 7.68 Å) that still can be considered as a tetragonal lattice with P4/mmm symmetry. In contrast, the crystal structure of a sintered and quenched $Li_{0.48}Nd_{0.5}TiO_3$ sample shows an orthorhombic crystal symmetry (Pmmm) with a_p x a_p x c_p (5.45 Å x 5.36 Å x 7.67 Å). Such a structural change is ascribed to the disordering of Nd-ions, Li-ions, and vacancies at A-site. In general, $LiNdTiO_3$ system shows four polymorphs A (primitive cubic), α′ (√2 a, √2 a+ δ, 2a-δ tetragonal, where δ is small distortion), C (orthorhombic distortion of α′), and β (tetragonal with a, a, 2a +Δ) where Δ is a large distortion. XRD analysis shows that $LiNdTiO_3$ sample, sintered at 1250 °C followed by quenching, acquires an orthorhombic α′ symmetry. On the other hand, same sample after sintering and annealing attains a tetragonal β symmetry through a polymorphic transformation. Rietveld refinement of sintered-annealed $Li_{0.48}Nd_{0.5}TiO_3$ confirms the formation of β phase in which ordering of aliovalent cations and vacancy distribution at A-site accounts for the variation in the Ti-O bond lengths. The difference in six Ti-O bond lengths introduces significant distortion in the unit cell, providing an off-center shift to Ti^{+4} cations that result in octahedral TiO_6 tilting. Bright-field image along the [001] zone axis shows two alternative bright and dark strip regions like nanodomains sharing interfaces along [100] and [010] directions. The corresponding electron diffraction pattern shows the superimposition of two mutually perpendicular diffraction patterns representing two domains having 001 direction perpendicular to each other. The interpenetration of these two striped nanodomains gives birth to CB-like microstructure. In addition, APT investigation of the same sample suggests the role of compositional phase separation in CB evolution. The iso-concentration surface maps suggest a difference in Ti, Li and Nd concentrations at both sides of isosurfaces of the corresponding element. From this correlative evidence, combined with these phase transformation complexities, spinodal decomposition gives birth to the nano chessboard-like microstructure consisting of 3D well-organized alternative domains.

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 in the beginning of the charging-discharging cycles, i.e. coulombic efficiency ~99% and specific capacity ~120 $mAhg^{-1}$. The coulombic efficiency and specific capacity of the sintered-annealed $Li_{0.48}Nd_{0.5}TiO_3$ sample remains constant at ~99% and ~120 $mAhg^{-1}$ even after 100 cycles. Whereas, for sintered-quenched $Li_{0.48}Nd_{0.5}TiO_3$ (disordered) sample-specific capacity reduces from 120 $mAhg^{-1}$ to 100 $mAhg^{-1}$ (~16%) with no change in coulombic efficiency. Compared to sintered-annealed $Li_{0.48}Nd_{0.5}TiO_3$ samples, the specific capacity of the $Li_{0.36}Nd_{0.5}TiO_3$ sample is relatively less (110 $mAhg^{-1}$) in the beginning of the charging and discharging cycle with ~99% coulombic efficiency. In sintered-annealed $Li_{0.36}Nd_{0.5}TiO_3$ sample, a drastic decrease in specific capacity was observed (27%) after 100 cycles.

The abovementioned investigations suggest that the mechanism of evolution for CB like microstructure is system dependent and for spinel systems, it is quite different from perovskite systems. However, the formation of the symmetry-breaking phase is common in both systems.