Evolution of chessboard like nanodomains in Mn-doped $CoFe_2O_4$ spinel and $NdLiTiO_3$ based perovskite systems for nanoelectronic applications

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Well organized self assembled chessboard like nanostructures as evolves in some ceramic systems such as Mn-doped $CoFe_2O_4$ and $NdLiTiO_3$ can have potential applications in nanoelectronic devices, such as ultrahigh density recording medium (> 1 Tb/inch^2) and nano-batteries etc. Each chessboard like system facilitates construction of nanodevice having two identical and periodically distributed nanodomains possessing two distinct properties, like ferromagnetic-paramagnetic in case of $CoMnFe_2O_4$ and conductive-nonconductive in case of $NdLiTiO_3$. To convert this concept into realization, optimization of the growth mechanism is required. However, various attempts have been made so far, here a TEM based investigation is presented to establish the correlation between the two evolving mechanisms of chessboard like structure in the two different crystal systems.

The solid state synthesis route appeared most appropriate, due to its ease of material handling, cost effectiveness and success probability, in which high purity (>99.9%) powders of Li_2CO_3, Nd_2O_3 and TiO_2 for $Li_{2/3-x}Nd_{3x}TiO_3$ and Fe_2O_3, Co_3O_4, and MnO_2 for $Co_{0.6}Fe_xMn_{2.4-x}O_4$ were mixed in appropriate stoichiometric ratios, and pressed into pellets for sintering at specific temperature program for each system.

The evolution of chessboard like nanostructure in both of the systems has happened through various intermediate stages. In order to study these intermediate stages, samples at different stages of growth have been extensively investigated with various TEM techniques, such as diffraction contrast imaging, HAADF STEM, CBED, HRTEM and image simulation etc. The comprehensive investigation of interfaces has provided significant information about this phase separation event, which has shown that as because both of the chessboard systems have coherent twinning assisted interfaces between the two nanodomains, spinodal decomposition is the final stage of this microstructural evolution. Systematic tilting along appropriate zones excites various microstructural features in diffraction contrast imaging mode, like the contrast in nanodomain along a specific zone axis, thickness fringes in dark domains, simultaneous thickness fringes in both the nanodomains, and cuboidal shape of nanodomains etc. Dark domains are containing thickness fringes because, they have gone out of Bragg's diffraction condition, due to an orientation with respect to bright nanodomain. These two phases are oriented in such a manner so that they could minimize the interfacial energy, in turn reducing the free energy of the whole system. HAADF STEM and Nanodiffraction techniques were used for compositional mapping and crystal structure identification of these nanodomains. which has shown that one domain is Mn rich and another is Mn lean, in case of $CoMnFe_2O_4$, and similarly, Li rich and Li lean domains in case of $NdLiTiO_3$. Nanodiffraction patterns corresponding to Mn rich and Mn lean domains have shown that one domain is tetragonal and another is cubic and similarly for Li rich and Li lean domains. There are also few evidences of twinning at interfaces. Detailed microscopic investigation and the process of microstructure evolution would be presented.

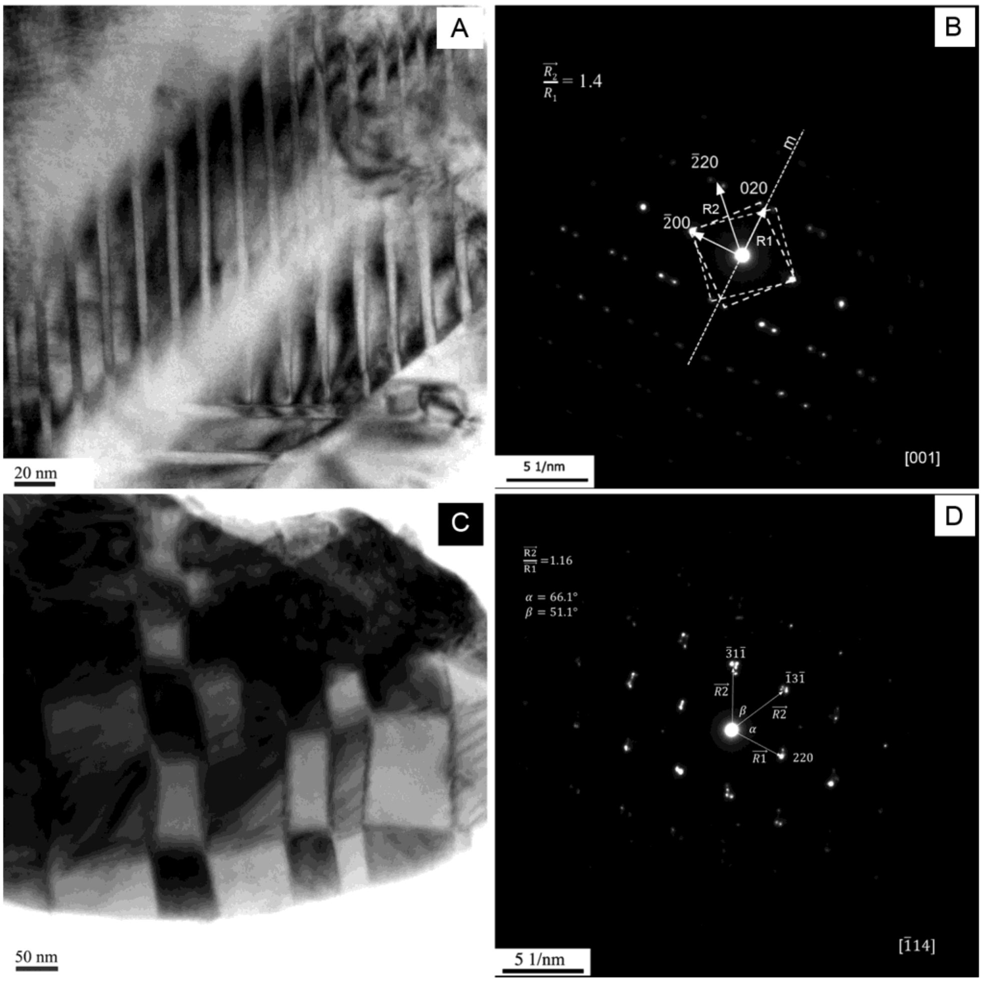

Fig. 1 Diffraction contrast bright field images of $Co_{0.6}Fe_{0.8}Mn_{1.6}O_4$, annealed for 250 h illustrating, (A) elementary stage of evolution of two phases in nanochessboard microstructure (B) corresponding SADP to the central area (C) final stage of chessboard like nanostructure (D) corresponding SADP from central area covering six domains.