Evolution of a self-assembled chessboard nanostructure spinel in a

CoFeGaMnZn multicomponent oxide

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Abstract

Mixed oxides of CoFeMn, ZnGaMn and CoFeGaMnZn have been pelletized, sintered at 1250 °C for 24 hours, and then quenched and aged at 375 °C for 150 hours to determine their phase compositions and microstructure evolution. After sintering and ageing, chessboard nanodomains of CoFe₂O₄ and CoMn₂O₄, and ZnGa₂O₄ and ZnMn₂O₄ spinel phases evolve in the CoFeMn and ZnGaMn oxides, respectively. In the CoFeGaMnZn multicomponent oxide, chessboard nanodomains of similar phases are also observed after sintering and ageing. These spinel phases are all likely to have mixed chemistry, and this often causes polymorphic transformations from spinel crystal structures with cubic *F* Bravais lattices (FCC) to ones with tetragonal *I* (BCT) Bravais lattices, often described in the literature in terms of crystal structures with tetragonal *F* (FCT) Bravais lattices. The nanodomains have specific orientation relationships with respect to one another, with {220} planes as their boundary planes with respect to a FCT unit cell description. The nanodomain size in the multicomponent oxide is significantly smaller than in the ternary mixed oxides because of the slower diffusion kinetics in this multicomponent oxide.

Keywords: chessboard nanodomains, electron microscopy, multicomponent oxide, spinel, twinning, X-ray diffraction

1. Introduction

Multicomponent high entropy metallic alloys have emerged over the last two decades as materials of both fundamental scientific interest and technological promise [1–4]. A number of possible areas of application ranging from structural applications to alternative energy and electronics have been identified for this class of alloys. However, the phase and microstructural stability of these alloys, any consequential changes in properties while in service, and service lifetime predictions for these alloys are still all active areas of research. By comparison, high entropy oxides are a more recent innovation; these too have their scientific challenges and technological opportunities [5]. Their electronic and electrochemical properties are also promising. A clear understanding of their microstructure and properties at the atomic scale is also an area of active research.

Initially, high entropy metallic alloys were defined as single-phase solid solutions or intermetallic-based alloys. However, the number of metallic alloy systems with a single solid solution phase is limited [6], and instead many such alloys have been found to be multiphase. In addition, time- and temperature-dependent composition changes have been observed in multicomponent high or medium entropy metallic alloys [7]. Therefore, the scientific community is now more inclined to term these materials as multicomponent alloys (MCAs) or complex concentrated alloys [8]. In the case of high entropy oxides, single phase materials have been observed upon quenching. However, so-called 'high entropy oxides' also tend to form multiple phases upon ageing, and so such materials are better regarded as multicomponent oxides (MCOs). MCOs are potential candidate materials for high-density memory devices, nanoscale batteries and thermo-electric devices [9–10]. Although microstructural design and stability has been discussed extensively in the MCA literature [11–12], there is much less discussion of these topics in the MCO literature [13–14]. MCOs

in which the cation sublattice is occupied with multiple cations have been reported in a number of crystal structures such as rock salt, fluorite, perovskite and spinel [5,15]. Recently, both single and multiple oxide phase formation have been reported in MCOs [16–17]. However, the morphology of these phases, their distribution, the evolution of the final microstructure and the stability of the microstructure are all far from being completely understood.

In the work presented here, the evolution of self-assembled and functionally different chessboard nanostructures has been explored. Chessboard nanostructures may find applications in high density memory storage, thermoelectric devices and in energy storage devices. CoFeMn and ZnGaMn oxides have been reported elsewhere to form self-assembled chessboard nanostructures from CoFe₂O₄ and CoMn₂O₄ spinels, and ZnGa₂O₄ and ZnMn₂O₄ spinels, respectively, after suitable heat treatment because of the diffusive separation of the ions into two different spinel phases [18–20]. In CoFeMn oxide, the two spinel domains are ferromagnetic and paramagnetic respectively. In ZnGaMn oxide, the two phases are thermoelectric and non-thermoelectric. In the present work, the microstructural evolution in a CoFeGaMnZn MCO has been studied, and a comparison has been made with the microstructural evolution of the ternary CoFeMn and ZnGaMn oxides prepared in a similar manner.

2. Experimental Procedure

Self-assembled chessboard (CB) nanostructures in mixed CoFeMn, ZnGaMn and CoFeGaMnZn oxides have been produced through a solid-state synthesis route chosen for ease of materials handling, its cost effectiveness, and its probability of success in producing pure end products. Ultra-high pure precursor powders of Co₃O₄, ZnO, Mn₂O₃, Ga₂O₃ and

Fe₂O₃, each more than 99.99% purity (Sigma Aldrich & Alfa Aesar) were mixed and pelletized in stoichiometric proportions to obtain mixed oxides with compositions of $Co_{0.6}Fe_{0.8}Mn_{1.6}O_{4+x}$ (x << 1), ZnGaMnO₄ and $Co_{0.6}Fe_{0.8}GaMn_{2.6}ZnO_{8+x}$ (x << 1). In these stoichiometric calculations the oxidation states of Fe, Mn and Ga have been taken to be +3, while the oxidation states for Zn and Co have been taken to be +2. However, the oxidation states of the transition metals Co, Fe, Mn and Zn can vary, and this will clearly affect the defect chemistry and oxygen non-stoichiometry of the final phases. By contrast, the oxidation state of Ga can be taken to be +3 in both the oxide and in the spinel phases produced.

All the green pellets were sintered in air at 1250 °C for 24 hours followed by quenching into ice water. This heat treatment temperature and time was chosen to enable pellet densification and encourage diffusion of the various transition metal ions at this heat treatment temperature. To try and encourage further, more local, diffusive rearrangement of the cations below the phase transition temperatures of the constituent spinel phases, ageing treatments for all three mixed oxides were undertaken in air at 375 °C for 150 hours. Phase identification was undertaken by X-ray diffraction (XRD) in a Panalytical Empyrean highresolution X-ray diffractometer operated at 40 kV with 40 mA current. For X-ray diffraction experiments Co-K $_{\alpha}$ radiation with wavelength of 1.78 Å was used. For transmission electron microscopy (TEM) observations, slices were obtained from both the periphery and the centre of the sintered and aged pellets and then ground separately into powder. For each TEM sample, the powder was suspended in ethanol and subjected to ultrasonication for about 20 minutes before it was drop cast onto a carbon coated copper grid. TEM observations were made at 200 kV in a Tecnai G2 T20 transmission electron microscope. Compositional mapping of the heat-treated oxide samples was obtained by scanning transmission electron microscopy (STEM) and X-ray energy dispersive spectroscopy (XEDS).

3. Results and Discussion

Powder XRD patterns from the sintered and aged pellets of CoFeMn, ZnGaMn and CoFeGaMnZn oxides are shown in Figure 1. The pattern from CoFeMn oxide can be indexed in terms of two spinel phases: CoFe₂O₄ (JCPDS card No. 00-022-1086) (space group $Fd\overline{3}m$ with $a \approx 8.3$ Å [18]) and CoMn₂O₄ (JCPDS card no. 00-001-1126) ($I4_1$ / and with a = 5.72Å and c = 9.27 Å), which have the cubic inverse spinel structure with a cubic F (FCC: Face centred cubic) Bravais lattice and a tetragonal I (BCT: Body centred tetragonal) spinel structure, respectively [21]. This indexing is not unique because there is a possibility that the phase(s) in the CoFeMn oxide pellet have mixed chemistries, altering subtly the nature of the phases present and their lattice parameters [19]. Similarly, the ZnGaMn oxide powder after sintering and ageing can be indexed in terms of two spinel phases: ZnGa₂O₄ (JCPDS card no. 00-038-1240) ($Fd\overline{3}m$ with a = 8.33 Å [19]) and ZnMn₂O₄ (JCPDS card no. 00-024-1133) ($I4_1$ / amd with a = 5.66 Å and c = 9.34 Å [21]), also with crystal structures with cubic F and tetragonal I Bravais lattices respectively. Here too, the indexing is not unique because of the possibility that the mixed chemistries within the pellet changes the nature of the phase(s) present and their lattice parameters [20]. The quinary CoFeGaMnZn oxide also produces an XRD pattern similar to those from CoFeMn oxide and ZnGaMn oxide. The diffraction peaks match quite closely those attributed to CoFe₂O₄, CoMn₂O₄, ZnMn₂O₄ and ZnGa₂O₄. The crystal structures of transition element-based spinel phases are sensitive to the cationic ratio, heat treatment temperature and cooling rate. In the case of manganate spinels, those with high manganese content tend to form tetragonal phases, while those with low manganese content tend to form cubic spinel phases at room temperature. Heat treatment temperatures and cooling rates also alters the cationic distribution in the interstitial sites that in turn can change the crystal symmetry [21]. However, the X-ray diffraction peaks are often quite broad, apart from the 111 and 222 peaks. This broadening of the peaks suggests that the microstructure is on a fine scale and that there may be a number of spinel phases present. The possibility of strain as an origin of the peak broadening is unlikely because the pellets were aged for a significantly long period of time. Some spinel peaks in the quinary oxide powder are shifted from the originally reported spinels: this might indicate the formation of novel mixed spinel phase(s) in the quinary oxide. In summary, it is evident that the X-ray diffraction information from the multicomponent oxide is difficult to deconvolute with confidence into individual spinel phases; this is why TEM is required in conjunction with X-ray diffraction for phase identification.

Bright field images and corresponding electron diffraction patterns of the sintered and aged CoFeMn mixed oxide are shown in Figure 2. For these and the other TEM observations that we have made, it is convenient to use a tetragonal *F* (FCT) Bravais lattice description for the tetragonal structures observed, as others have also done [18,19], so that $a_{f.c.t.} = \sqrt{2}a_{b.c.t.} \approx 8 - 8.1$ Å, with a 45° rotation of the *x*-and *y*-axes highlighting the close structural relationship between the cubic FCC and tetragonal FCT forms of the spinels observed.

The bright field image from the central region of the sintered and aged CoFeMn mixed oxide powder in Figure 2(a) has $\{022\}_{FCT}$ planes almost parallel to the electron beam. From the corresponding electron diffraction pattern along $[100]_{FCT}$ in (b), it is apparent that these $\{022\}_{FCT}$ planes are twin planes and that in (a) there are two sets of co-existing tetragonal domains twinned with respect to one another by a 180° rotation about the normal to the plane whose reflection in Figure 2(b) is labelled as $0\overline{2}2$. Reflections in Figure 2(b) from one set of tetragonal domains are arrowed in white and reflections from the other set of domains are

arrowed in light blue. Had a tetragonal BCT unit cell description been used, these twinning planes would have been indexed as $\{112\}_{BCT}$ twins. While others have described such twinning planes in phases with tetragonal *I* lattices as $\{011\}_{FCT}$, such as in In–Tl martensite [22], we have chosen here to describe these twin planes as $\{022\}_{FCT}$ planes rather than $\{011\}_{FCT}$ planes because $\{011\}_{FCT}$ planes have fractional indices with respect to the conventional tetragonal *I* unit cell.

High angle annular dark field STEM (HAADF-STEM) Z-contrast compositional mapping (XEDS) of these twinned regions is shown in Figure 2(c). This shows evidence of segregation of Fe and Mn to alternating twinned regions. This segregation can be rationalized in terms of the pseudo-spinodal decomposition model described by Ni and Khachaturyan [20]. However, here, this is with respect to decomposition within a twinned tetragonal FCT spinel phase where there would seem to be no changes in lattice parameter between the twinned regions as a consequence of the chemical ordering. In addition, it is worth noting that the width of the twinned domains in Figure 2(a) is ~30 nm, while the width of the compositionally separated domains in Figure 2(c) is ~70 nm. The composition map represents a different projection view of the sample, as the sample is tilted by $\sim 19^{\circ}$ with respect to the bright field image in Figure 2(a) towards the detector while collecting the composition map. Furthermore, as we have noted, the composition separation might well be incomplete, and this might result in incommensurate observations of widths between the twinned domains and compositionally separated domains. A STEM-HAADF-EDS map of the similar twinned region with no tilt is shown in Figure 3. It is apparent in Figure 3(a) that the twinned regions are ~70 nm wide and the compositionally separated Fe and Mn domains (Figures 3(b) and 3(c), respectively) are also ~70 nm wide. These differing width observations can be attributed both to the tilting of the specimen and also to the

incompleteness of the composition separation process. In addition, it is observed that oxygen and cobalt (Figures 3(e) and 3(f), respectively) are uniformly distributed in the sample. Nanobeam electron diffraction patterns obtained from the white spot in Figure 3(a), such as that given in Figure 3(d) indicates that the spinel phase that forms is a tetragonal phase.

A bright field image and the corresponding electron diffraction pattern from the peripheral region of the pellet are shown in Figures 2(d) and 2(e), respectively. In the bright field image rectangular alternating bright and dark domains are observed, similar to chessboard (or checkerboard) regions seen in Mg-doped CoFe₂O₄ spinel by Zhang et al. [18] and interpreted by them in terms of coexisting cubic and tetragonal domains. The size of the domains in Figure 2(d) are ~80-100 nm and the boundaries between adjacent domains are nearly edge-on. The prominent electron diffraction pattern in Figure 2(e) can be indexed as [100]_{FCT}, so that, as is evident in the electron diffraction pattern, the 022 and $02\overline{2}$ systematic rows of reflections are not perpendicular to one another. The reflection arrowed in blue has an interplanar spacing consistent with it being from the FCC cubic spinel phase. The lattice parameters for the FCT tetragonal spinel phase calculated from the electron diffraction patterns are $a \approx 8.1$ Å and $c \approx 8.8$ Å, similar to the reported lattice parameters of CoMn₂O₄, but with a smaller 'c'. This difference can be attributed to the existence of mixed chemistries in the tetragonal domains. The HAADF-STEM compositional map (XEDS) in Figure 2(f) from the region shown in Figure 2(d), shows that alternate domains are preferentially rich in Fe and Mn respectively. There is incomplete segregation of Fe and Mn within these nanodomains similar to observations made elsewhere by Zhang et al. [18].

Bright field images from the central and peripheral regions of the sintered and aged pellet of ZnGaMn oxide and the corresponding diffraction patterns and HAADF-STEM composition maps (XEDS) from the central region are shown in Figure 4. As with Figure 2(b), the electron diffraction pattern in Figure 4(b) can be interpreted straightforwardly in terms of twinned tetragonal regions present in Figure 2(a) where the twin plane is $\{022\}_{FCT}$. Here, the common zone axis can be labelled as $[31\overline{1}]$ and the twins can be labelled as (022)_{FCT} planes. Other than the common 022 set of reflections, reflections in Figure 4(b) from one set of twins are highlighted in blue and reflections from the other set of twins are highlighted in red. The HAADF-STEM composition maps (XEDS) from the central region shown in Figures 4(c) and 4(f) show that there is preferential segregation within these twinned tetragonal regions of Mn and Ga, while the Zn composition is almost uniform. A HAADF, diffraction contrast bright field image and STEM-HAADF-XEDS composition maps from a similar area of the ZnGaMnO₄ sample are given in Figure 5. Similar banded contrast arising from the composition separation between Mn and Ga can be observed in the HAADF image in Figure 5(a). In the diffraction contrast bright field image (Figure 5(b)) similar bands arising from composition separation could also be observed. The width of the bands is ~ 70 nm. In the composition maps (Figures 5(d) and 5(e)), it is observed that Zn is homogeneously distributed, whereas Mn and Ga are distributed in alternate bands. The composite composition map for Mn and Ga is given in Figure 5(c). As with the situation found in the centre of the CoFeMn oxide pellet, the lattice parameters in the twinned regions seem unchanged by the chemical ordering.

A bright field image and the corresponding rotationally aligned diffraction pattern from the peripheral region of the sintered and aged pellet are given in Figure 4(d) and Figure 4(e) respectively. In the bright field image chessboard-like contrast is observed, but the alternating bright and dark domains are not rectangular in appearance, but instead rhombus-like with an internal angle of $\approx 60^{\circ}$. The electron diffraction pattern shown in Figure 4(e) is consistent with the presence of only FCT tetragonal domains. The lattice parameters measured from Figure 4(e) are $a \approx 8.2$ Å and $c \approx 8.7$ Å. These match with those of ZnMn₂O₄ with a suitable change in chemical composition to modify the lattice parameters. The domain structure seen in Figure 4(d) is reminiscent of interpenetrating twin morphologies reported in the tetragonal *F* In–Tl phase with a $c/a \approx 1.04$ [23] and also in the tetragonal *I* Ni–Mn–Ga phase which has an equivalent $c/a \approx 1.20$ when described in terms of a FCT tetragonal unit cell [24].

Bright field images and the corresponding electron diffraction patterns from the central and peripheral regions of the sintered and aged CoFeGaMnZn mixed oxide pellet are shown in Figure 6. In Figure 6(a) tetragonal F domains twinned on $\{022\}_{FCT}$ planes are visible, confirmed by the electron diffraction pattern in Figure 6(b). The peripheral region of the sintered and aged pellet seen in Figure 6(c) has a chessboard nanostructure with alternative bright and dark contrast similar to that seen in Figure 2(d), but on a much finer scale than in Figure 2(d). The electron diffraction pattern from Figure 6(c) shown in Figure 6(d) suggests that, as in Figure 4(e), there are only tetragonal FCT domains present in Figure 6(c). A HAADF image and STEM-HAADF-XEDS composition maps from the central region of the sintered and aged CoFeGaMnZn mixed oxide are shown in Figure 7. In the HAADF image linear contrast arising out of the twin formation is observed. However, in the composition maps, in contrast to the ternary oxides, no visible segregation of the chemical elements is observed. The area XEDS spectrum from the same sample is shown in Figure 8. In this spectrum, the presence of all the metallic elements, i.e. Co, Fe, Ga, Mn and Zn can be established. The composition after background correction is given at the side of the spectrum. This is consistent with the starting composition.

This MCO based on a five component CoFeGaMnZn oxide is a new observation, as is the chessboard microstructure in this system seen here in the periphery of the 150 hours aged pellet. While after 150 hours of ageing at 1250 °C, the microstructure is dominated by a

twinned tetragonal phase, in line with the relative intensities of the 112t and 220c diffraction peaks in Figure 1 from this five-component oxide, after far longer ageing times there is more of a 50:50 mixture of cubic and tetragonal spinel phases, as we will report elsewhere. At this stage of ageing, composition separation is not significantly seen because no distinct separation of the elemental species is observed in the STEM-EDS composition maps for Co, Fe, Ga, Mn and Zn. This is consistent with the XRD pattern shown in Figure 1, where splitting of the diffraction peaks is not a prominent feature. However, the splitting of the major XRD peaks is visibly present in Figure 1 for the CoFeMn and ZnGaMn ternary oxides, for which compositional separation has progressed and the compositionally separated domains have also grown significantly after 150 hours of ageing at 1250 °C. A detailed study on composition separation within this five component CoFeGaMnZn oxide as it evolves over far longer hours of ageing will be published elsewhere. The mechanism behind the evolution of the chessboard nanostructure in this five-component oxide would seem to be similar to that discussed in the literature for oxides with fewer components [18-20], with the additional consideration that very similar nanostructures can also be produced by interpenetrating twins of a single phase, with or without a pseudo-spinodal decomposition process. The twinning seen in the tetragonal phase can be described in the formal theory of deformation twinning [25] as being either defined by $K_1 = (101), K_2 = (10\overline{1}), \eta_1 = (10\overline{1}), \eta_2 = [101], s = (c/a) - (c/a)$ (a/c) using a tetragonal F lattice description [22] or by $K_1 = (112), K_2 = (11\overline{2}), \eta_1 = (11\overline{1}),$ $\eta_2 = [111], s = (\sqrt{2} c/a) - (a/\sqrt{2} c)$ using a tetragonal *I* lattice description [24], where K_1, K_2, η_1, η_2 and s have their usual meanings in deformation twinning crystallography [25].

In the mixed oxides it is reasonable to assume that the twinning seen in the tetragonal spinels is a consequence of the degree of strain energy within the crystal. The strain energy in

the CoFeGaMnZn MCO is likely to be quite high because of the presence of several different ionic species in the lattice. In order to minimize the strain energy, the lattice twins. The formation of multiple interpenetrating twins with different variants leads to the evolution of a chessboard morphology, with or without a second cubic spinel phase. It is relevant that stacking faults were not seen in any of these oxide systems. As the tetragonal spinel structures twin and also exhibit pseudo-spinodal decomposition, the nanodomains are quite similar in terms of lattice parameters as a consequence. Furthermore, there was no evidence of extensive arrangements of dislocation networks at interfaces within the nanostructure. It could reasonably be expected that the long heat treatment time at elevated temperatures would help to minimize any interfacial strain through the annihilation of defects at interfaces. The chessboard nanodomains in the MCO are significantly smaller than those in the ternary oxides. We attribute this to the lower diffusivity of ionic species in the MCO, which makes it resistant to grain growth, and we note that this is consistent with the recent report of grain growth resistance in high entropy alloys [26].

4. Conclusions

The CoFeGaMnZn multicomponent oxide is observed to produce chessboard nanodomains after a long-term ageing treatment. The mechanism of chessboard nano domain formation is similar to that reported in ternary oxides in which multiple twinning-induced diffusive separation of ionic species takes place. The nanodomains 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 and overall free 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.

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Disclosure statement

The authors declare that there is no potential conflict of interest.

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Figure 1: Multiple display of powder XRD patterns of ZnGaMnO₄, Co_{0.6}Fe_{0.8}Mn_{1.6}O_{4+x} (x << 1) and Co_{0.6}Fe_{0.8}GaMn_{1.6}ZnO_{8+x} (x << 1) after sintering at 1250 °C for 24 hours followed by ageing at 375 °C for 150 hours. The XRD patterns indicate the presence of the cubic $Fd\overline{3}m$ ZnGa₂O₄ and tetragonal $I4_1$ / amd ZnMn₂O₄ phases in the pattern of ZnGaMnO₄, and the presence of the cubic $Fd\overline{3}m$ CoFe₂O₄ and tetragonal $I4_1$ / amd CoMn₂O₄ phases in the Co_{0.6}Fe_{0.8}Mn_{1.6}O_{4+x} pattern. The cubic spinel peaks are marked with black dotted lines with reference to cubic CoFe₂O₄ and the tetragonal spinel peaks are marked with red dotted lines with reference to tetragonal CoMn₂O₄. These two patterns have been indexed with respect to the conventional unit cell descriptions for the two tetragonal phases. The XRD pattern of Co_{0.6}Fe_{0.8}GaMn_{1.6}ZnO_{8+x} (x << 1) also shows signs of separation of similar cubic and tetragonal phases. Shifting in the (103)_t and (224)_t peaks of the tetragonal phase in the XRD pattern of Co_{0.6}Fe_{0.8}GaMn_{1.6}ZnO_{8+x} with respect to ZnMn₂O₄ and CoMn₂O₄ is indicative of slight changes in the a and *c* lattice parameter.



Figure 2: (a) TEM diffraction contrast bright field image from the centre of the $Co_{0.6}Fe_{0.8}Mn_{1.6}O_{4+x}$ pellet sintered at 1250 °C for 24 hours followed by ageing at 375 °C for 150 hours showing two sets of co-existing tetragonal domains. Domain boundaries are parallel to $(0\overline{2}2)$ interface planes of the FCT unit cell. (b) Electron diffraction pattern from (a) showing twinning on the common $(0\overline{2}2)$ planes of the two domains. (c) HAADF-STEM-XEDS Z-contrast compositional mapping showing the segregation of Fe and Mn to alternating twinned regions. (d) Bright field image from the periphery of the Co_{0.6} Fe_{0.8}Mn_{1.6}O_{4+x} pellet after sintering and ageing as described for (a) showing cuboidal nanodomains observed slightly off axis from a [100] zone. (e) Electron diffraction pattern from the region in (d) consistent with the presence of cubic and tetragonal phases. The interfaces of the squared nanodomains are along {022} family of planes with respect to the FCC and FCT unit cells of the cubic and tetragonal phase. (f) HAADF-STEM-XEDS Z-contrast compositional map from the cuboidal nanodomains showing the onset of separation of Fe and Mn in two neighbouring nanodomains.



Figure 3: (a) Diffraction contrast image of the $Co_{0.6}Fe_{0.8}Mn_{1.6}O_{4+x}$ (x<<1) after heat treatment at 1250 °C for 24 hours followed by quenching in ice water. Subsequently it was aged at 375 °C for 150 hours. In the diffraction contrast image alternate bands of Fe-rich and Mn-rich domains are observed. The width of the individual bands is ~70 nm. STEM-HAADF-EDS mapping is shown for (b) Fe, (c) Mn, (e) O and (f) Co. Co and O are uniformly distributed while Fe and Mn are alternately distributed in the bands. (d) Nano-beam electron diffraction pattern from the white point in the dark band in (a). In the diffraction pattern the tetragonal symmetry of the band is clearly observed.



Figure 4: (a) TEM bright field image from the centre of the ZnGaMnO₄ pellet after sintering at 1250 °C for 24 hours and subsequent ageing at 375 °C for 150 hours. A striped microstructure is apparent arising from the presence of two sets of domains. (b) Electron diffraction pattern from (a) indexed with respect to the doubly primitive FCT unit cell showing that twinning has occurred on (022) interface planes. (c) HAADF-STEM-XEDS Zcontrast compositional map showing the segregation of Ga and Mn to alternating twinned regions. (d) Bright field image from the periphery of the same pellet showing a chessboardlike morphology with ($\overline{022}$) and ($\overline{202}$) twin planes denoted by dotted lines. (e) Split in the {202} family of spots in the corresponding rotationally oriented diffraction pattern along the [111] zone axis showing the twinned orientation relationship between the domains. (f) HAADF-STEM-XEDS Z-contrast compositional mapping of Zn in the region shown in (c). It is evident that the Zn is almost uniformly distributed within the two twinned regions.



Figure 5: (a) HAADF image (b) diffraction contrast bright field image of the ZnGaMnO₄ after heat treatment at 1250 °C for 24 hours followed by quenching in ice water. Subsequently this was aged at 375 °C for 150 hours. In the HAADF and the bright field image an alternate banded structure is observed. STEM-HAADF-EDS maps are shown for (c) Ga+Mn overlay (d) Zn (e) Mn and (f) Ga. The alternate bands of Mn and Ga rich domains are ~70 nm wide.



Figure 6: (a) TEM bright field image from the centre of the $Co_{0.6}Fe_{0.8}Mn_{1.6}ZnGaO_{8+x}$ (x<<1) pellet after sintering at 1250 °C for 24 hours and subsequent ageing at 375 °C for 150 hours. Twinned regions are evident. Each region is internally twinned on $\{202\}_{FCT}$ planes. (b) Electron diffraction pattern from (a) along a [$\overline{2}33$] direction. (c) Bright field image from the periphery of the pellet showing a chessboard-like morphology, with alternating dark and bright nanodomains. (d) electron diffraction pattern from (c) indicating that within this chessboard-like morphology twinning has occurred on (202)_{FCT} planes in (c).



Figure 7: STEM-HAADF-EDS mapping of the $Co_{0.6}Fe_{0.8}GaMn_{2.6}ZnO_{8+X}$ (x << 1) after heat treatment at 1250 °C for 24 hours followed by quenching in ice water. Subsequently this was aged at 375 °C for 150 hours. In the HAADF image in (a) very faint linear contrast corresponding to the twins can be observed. EDS maps corresponding to (b) O (c) Mn (d) Fe (e) Co (f) Ga and (g) Zn show uniform distribution, indicating that the MCO after this aging treatment does not undergo significant composition separation.



Figure 8: XEDS spectrum of the $Co_{0.6}Fe_{0.8}GaMn_{2.6}ZnO_{8+X}$ (x << 1) after heat treatment at 1250 °C for 24 hours followed by quenching in ice water. Subsequently this was aged at 375 °C for 150 hours. Compositions in wt% and in at% obtained after the background correction are given to the right of the spectrum. These are consistent with the starting composition, so that the relative ratios of different elements are also maintained.