Influence of Chromium and Cobalt Doping On Structural Properties and Magnetic Imaging of $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ and $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$

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Abstract: Mixed-valence manganese oxide has a variety of properties such as colossal magnetoresistance, dense granular magnetoresistance and optically induced magnetic phase transitions. To get a better comparison, a technique called doping technique were used. The doping happened at Mn-site with a chromium and cobalt. With a report from previous research, such as the changing of charge ordering, and ferromagnetic transition it will compare the results of all samples. The samples were prepared using solid state reaction method and the structural properties and magnetic imaging of chromium and cobalt doped at Mn site of perovskite manganite $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ (x= 0, 0.02, and 0.05) and $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ (y= 0.0.2 and 0.05) have been investigated to do a comparison. The XRD measurement has showed the samples are crystallised in a single phase in orthorhombic structure with a space group of *Pnma*. In comparison with the chromium and cobalt, Co^{3+} ion has a larger ionic radius than Cr^{3+}, therefore affecting the unit cell volume (*V*). The spectral RMS amplitude reading in magnetic topology of $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ (x= 0, 0.02, and 0.05) and $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ (y= 0.0.2 and 0.05) revealed a different number of readings.

Keywords: Pevovskite Maganite, Rare-Earth Elements , Doping, Structural Properties, Magnetic Imaging

1. Introduction

Mixed-valence manganite with the formula of $R_{1-x}A_xMnO_3$, where x is an unknown variable that indicates the amount of doping and can be replace with other letters, R is the rare-earth element such as La, Nd, Pr and A is the divalent dopant such as Ca, Ba, and Sr has gained interest by many researchers since they are found in 1950 by Jonner and Van Santen. What make this material special is it possessed an interesting and unique physical property. This includes the metal to insulator transition, colossal magneto resistance, paramagnetic to ferromagnetic transition, charge and orbital ordering and a series of structural transitions [1]. Moreover, the doping in Mn site of the manganite with a magnetic cation such as chromium, cobalt, nickel, and ruthenium has the possibility to convince ferromagnetism and metal like behaviour in an insulating CE-type antiferromagnetic [2]. In addition, a phase separation occurs due to the ferromagnetic clusters around the magnetic doping elements by adding the doping content [2]. Previous study [3] on the structural, electrical transport and magnetic properties of $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ has found out the sample are crystallised in orthorhombic crystal with a space group of *Pnma*, these properties are shared by $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ as it has been reported by the previous research [4]. However, there are lack of research done by the previous researcher in comparing both samples and differentiate their magnetic topology since the previous research only done to get structural properties of the chromium and cobalt doped in Mn site of perovskite manganite [1][2][3][4] but not the magnetic topology of the samples. In this paper, it will be comparing the crystal structure and magnetic topology for $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ (x= 0, 0.02, and 0.05) and $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ (y = 0.0.2 and 0.05) to get the confirmation of the presence of chromium and cobalt in the samples.

2. Methods

2.1 Sample Preparation

The manganite sample of $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ (x= 0, 0.02, and 0.05) and $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ (y = 0.0.2 and 0.05) sample was prepared using a standard conventional solid state reaction method. A stoichiometric amount of MnO_2, Nd_2O_3, Na_2O_3 and Cr_2O_3 for $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ and MnO_2, Nd_2O_3, Na_2O_3 and Co_2O_3 for $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ with a high purity ($\geq$ 99.99%) in a powder form were mixed and ground by using agate mortar with pestle for approximately 2 hours to became homogenous powders. All the samples that have been grind are taken to Protherm furnace model PLF130/15 for calcination in air, the process will use a temperature of 1000ºC with a duration of 24 hours, the temperature is slowly increase with a rate of 15ºC/min and then the samples are cooled to a room temperature with a cooling rate of 1ºC/min. After it has been cooled, the samples are grinded for another 2 hours. The samples that in powder form are compacted and pellet under a load of 5 tons with a diameter of 13 mm and thickness of 3mm. The samples that in pellet form are proceed through a sintering process using the same Protherm Furnace with a temperature of 1200ºC for 24 hours and heating rate of 15ºC/min and cooled into a room temperature with a cooling rate of 1ºC/min.

2.2 Sample Characterisation

The characterisation of the samples in the form of powder was study by X-ray diffraction using X-ray diffractometer XRD Bruker D8. The radiated radiation was $CuK\alpha$ (λ= 1.5440 Å) and it was run under the voltage, V = 40kV with a current, I = 40mA at room temperature. The sample was constantly scanned with a scanning range between $20º \leq 2\theta \leq 80º$ and a scanning rate of 2º/min. The reflected radiation on the sample was scanned by goniometer. All the XRD patterns for the samples are analysed using X'pert High Score software to authenticate the crystalline phase of the samples. The magnetic topology for the samples was carried out by using Bruker Dimension Edge Atomic Force Microscope with a magnetic force microscopy mod. The tapping was adjusted to record the height sensor forward, height sensor backward, tapping phase forward, tapping phase backward and tapping amplitude

forward. On the scanning menu, the scanning range was adjusted to 50 μm with a lift height of 0.3 μm and frequency of 0.5 Hz. The recorded data for height sensor forward, height sensor backward, tapping phase forward, tapping phase backward and tapping amplitude forward were analysed to find a magnetic pattern on the sample's surface. Another scanned was performed on the pattern with a smaller scanning range which is 500 nm to get a better pattern of the magnetic topology. All the analysation of the data were made using NanoScope Analysis software.

2.3 Equations

To find the lattice parameter of the samples for confirmation of the crystalline phase, miller indices for each peak of the XRD data were determined by using a Bragg's law [5]

$$n\lambda = 2d \sin(\theta) \qquad Eq.1$$

where,

$n = 1,2,3, \ldots$

λ = wavelength of the rays

θ = angle between incident rays and surface of crystal

d = spacing between layers of atoms

After getting the miller indices, lattice parameter can be find using a UnitCell software [6].

$$\frac{1}{d^2_{hkl}} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \qquad Eq.2$$

where,

d = spacing between layers of atoms

h, k, l = miller indices

a, b, c = lattice parameter

3. Results and Discussion

3.1 Structural Analysis

Figure 1 and Figure 2 shows the XRD pattern of the samples $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ ($x = 0, 0.02, 0.05$) and $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ ($y = 0.02, 0.05$) respectively. From the analysis of the data that has been collected, it appeared that all samples are were crystallised in orthorhombic crystal system with space group of *Pnma*. Furthermore, it can be found that the crystal is in single phase without any appearance of impurity peaks which is similar as reported in the previous study [7][8]. The lattice parameter and unit cell volume (V) were tabulated in the Table 1. From the table it can be concluded that for samples that is doped with Cr, the unit cell volume (V) showed a decreasing number as the composition of Cr increase. This trend was suggested due to the high ionic radius of Mn^{3+} (0.645Å) ion is being replaced by a smaller ionic radius of Cr3+ (0.615Å) ion which has been stated in past study [7]. The unit cell volume (V) for samples that was doped by Co also can be seen to have a reduced value as the content of the Co increasing. This happened also due to the small Co^{3+} ion substituting the large Mn^{3+} ion. To compare the Cr and Co doped manganite, it turned out that the Co^{3+} has a slightly larger ionic radius than the Cr^{3+} [8] ions as the Table 1 revealed that Co has higher unit cell volume (V) with the same composition as Cr.
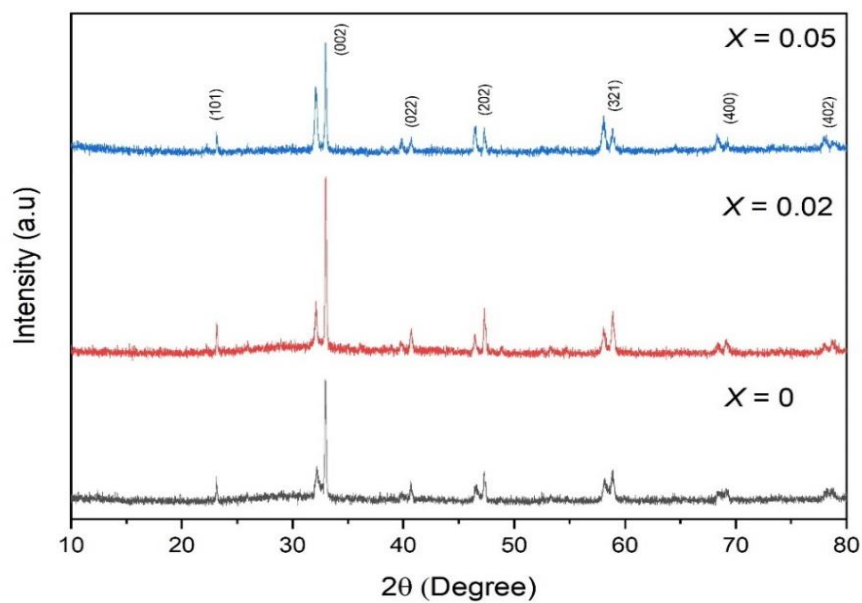
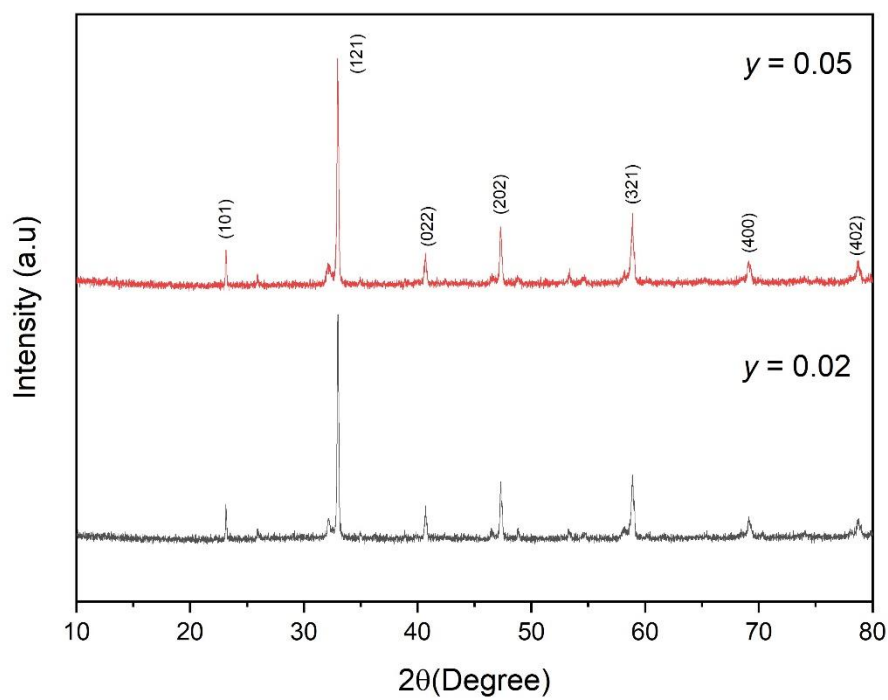**Figure 1: X-ray Diffraction for the sample $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ ($x = 0, 0.02, 0.05$).**

Figure 2: X-ray Diffraction for the sample $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ ($y = 0.02, 0.05$).

Table 1: Lattice parameter and unit cell volume of $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ ($x = 0$, 0.02, 0.05) and $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ ($y = 0.02$, 0.05).

Samples	Lattice parameter (±0.001)			V (Å) (±0.1)
	a (Å)	b(Å)	c(Å)	
$x = 0$	5.440	7.696	5.440	227.7
$x = 0.02$	5.443	7.653	5.444	226.8
$x = 0.05$	5.417	7.698	5.424	226.2
$y = 0.02$	5.441	7.676	5.440	227.2
$y = 0.05$	5.443	7.661	5.441	226.9

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3.2 Atomic Microscope Analysis

The magnetic topology of $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ ($x = 0$, 0.02, 0.05) and $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ ($y = 0.02$, 0.05) were produced in Bruker Dimension Edge Atomic Force Microscope using Magnetic Force Microscopy mod with lift height was set to 0.3 μm and the scanning rate at 0.5 Hz. Figure 3 show all the picture of magnetic topology of the samples where tapping phase is at 500nm for all the samples. The images produce was further analysed using NanoScope Analysis 1.7 software.

Figure 3 show all the images of magnetic topology for the samples produced by the magnetic tip of MFM. The brightness contrast in the images indicates the interaction between the magnetic cation and the tip [9]. The brighter the contrast, the strong interaction happened, and it affect the amplitude of the magnetic topology. So, the elements in the samples can be identified by analysing the contrast variation of the images. The measurement of phase shift can be done by using spectral root mean square (RMS) amplitude of images by selecting a certain area and figuring the distance it shifted upward or downward. The upward shift or positive shift is indicator to show a strong repulsive magnetic interaction meanwhile the downward shift or negative shift prove that samples has a strong attractive magnetic interaction [9].
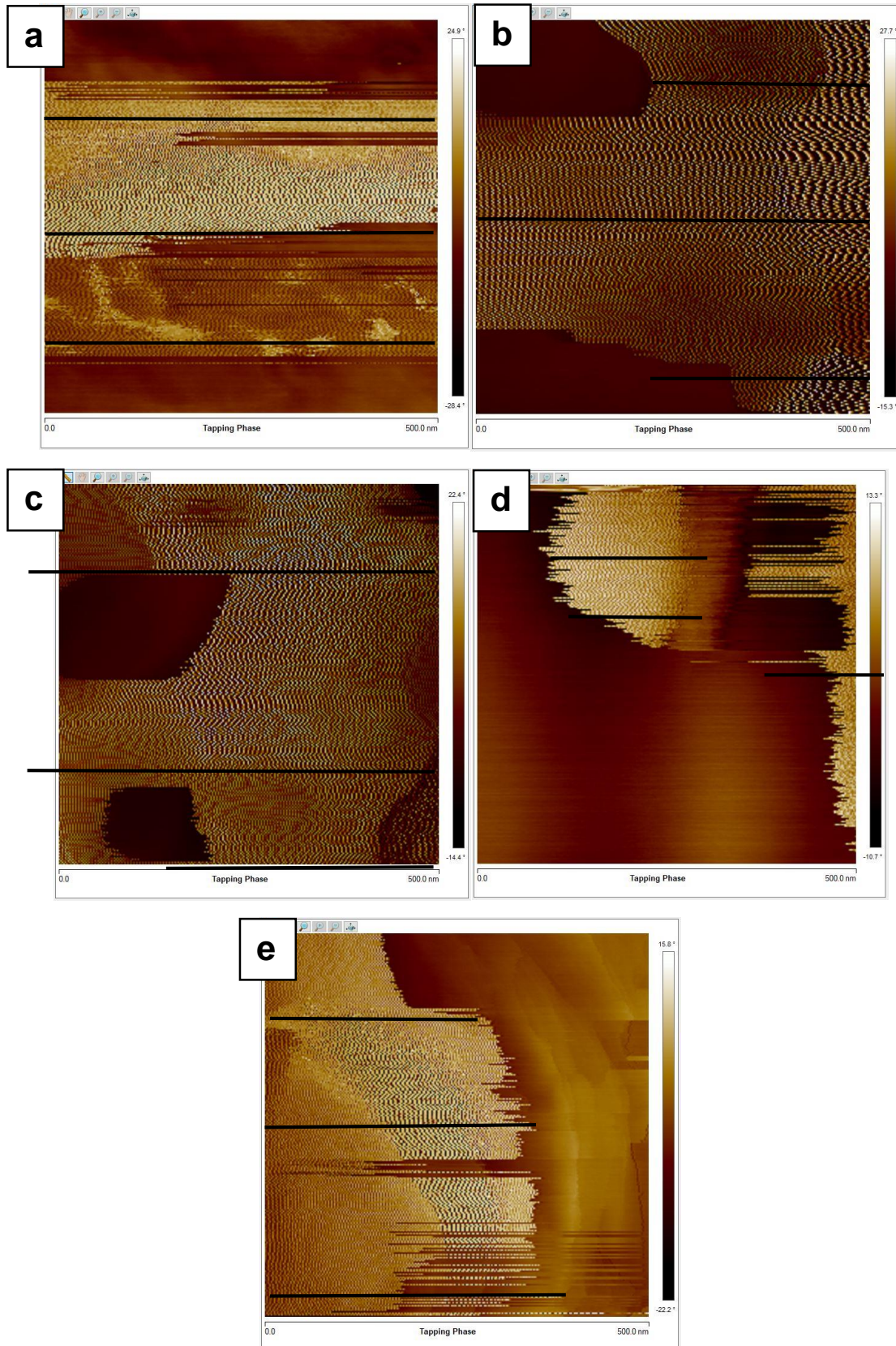
Figure 3: Magnetic Topology of the $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ (a) $x = 0$, (d) $x = 0.02$, (e) $x = 0.05$ and $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ (b) $y = 0.02$ (c) $y = 0.05$ by using magnetic tip in tapping mode.

On Figure 4, the spectral RMS amplitude is 20° appear on the bright contrast. This is happened due to the high repulsion of magnetic interaction between the tip and the sample. The same thing happened in Figure 5, as the line move to the brighter side, the spectral shift to the higher degree 15° and shift downward as it moved to the darker side. In comparison, chromium with composition y = 0.02 has a better repulsion compared to the $y = 0.05$.
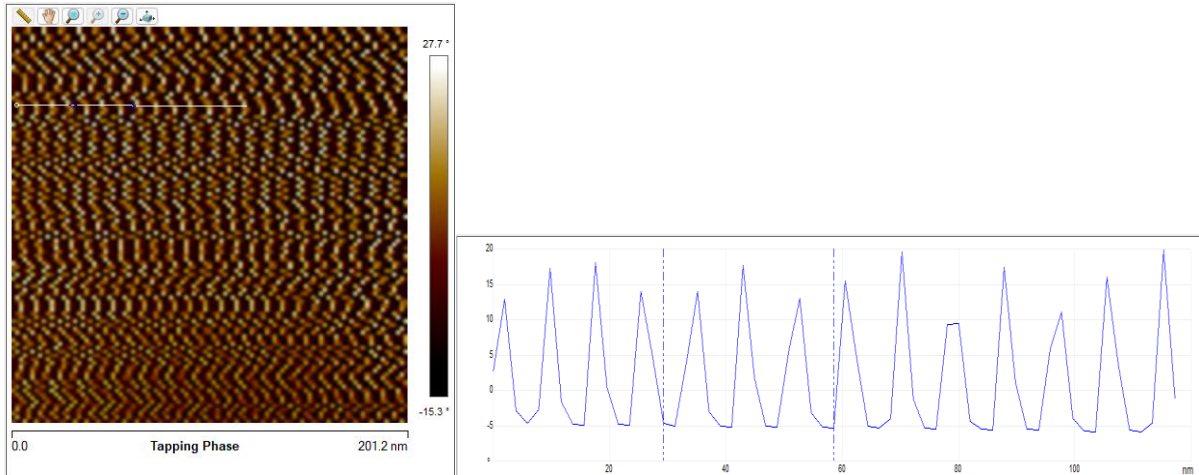

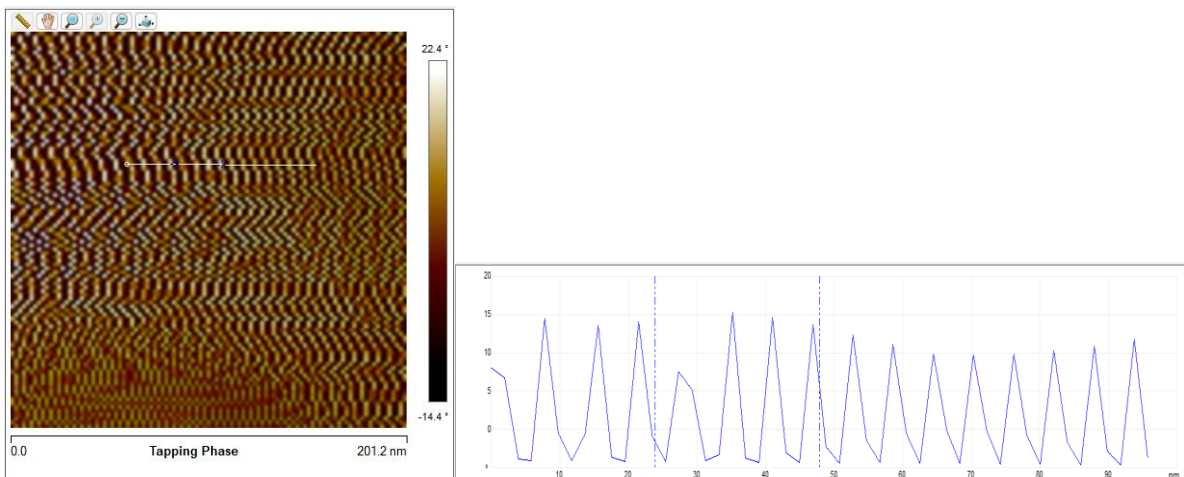**Figure 4: The spectral RMS amplitude of $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ ($y = 0.02$)**

Figure 5: The spectral RMS amplituse of $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ ($y = 0.05$)

Figure 6 and 7 show the spectral RMS amplitude for $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ ($x = 0.02$) and $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ ($x = 0.05$) respectively. The contrast for chromium shows to be brighter than the cobalt. The amplitude for the chromium sample is lie in between 8° to 10° as the line approach the bright side. In comparison with cobalt, the amplitude for cobalt is more than the chromium because of the stronger magnetic force possessed by cobalt than chromium.
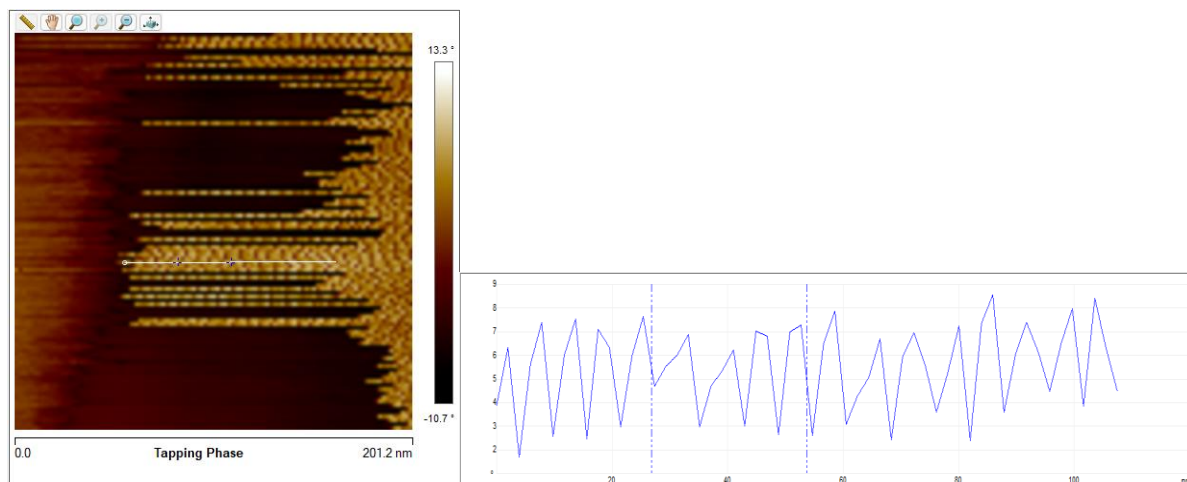
Figure 6: The spectral RMS amplitude of $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ (x = 0.02)

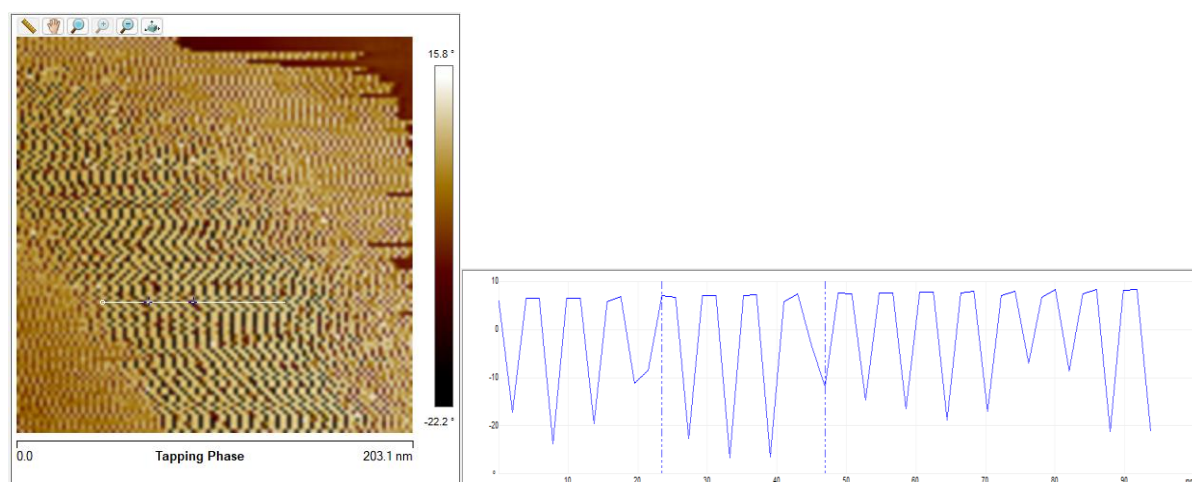**Figure 7: The spectral RMS amplitude of $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ (x = 0.05)**

4. Conclusion

In conclusion, the effect of Cr and Co doping at Mn site of $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ (x = 0, 0.02, 0.05) and $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ (y = 0.02, 0.05) on structure and magnetic topology have been investigated. Based on the study, the crystalline phase of all samples was found in orthorhombic which has axes of two-fold symmetry so that the cell can be rotated by 180⁰ without changing its appearance with space group of *Pnma* in a single phase. The size of ionic radius affects the unit cell volume (V) of samples. The change in unit cell volume (V) prove the presence of chromium and cobalt. The spectral RMS amplitude are changed for each sample, it also shows a different unique pattern after doping with a chromium. From the information it can be said that the chromium and cobalt are presence. In comparison, the cobalt has a stronger repulsive interaction which indicate a stronger magnetic interaction than chromium as the phase shifted higher. All results for structural properties and magnetic topology can be further analyse to get the pole information on the samples.

Acknowledgement

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