Role of Ni substitution on structural, magnetic and electronic properties of epitaxial CoCr$_2$O$_4$ spinel thin films

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Abstract
Cubic spinel CoCr$_2$O$_4$ has recently attained attention due to its multiferroic properties. However, the Co site substitution effect on the structural and magnetic properties has rarely been studied in thin film form. In this work, the structural and magnetic properties of Co$_{1-x}$Ni$_x$Cr$_2$O$_4$ ($x = 0, 0.5$) epitaxial thin films deposited on MgAl$_2$O$_4$ (100) and MgO (100) substrates to manipulate the nature of strain in the films using pulsed laser deposition (PLD) technique are presented. The epitaxial nature of the films was manifested through x-ray diffraction (XRD), reciprocal space mapping (RSM) and Rutherford backscattering spectrometry (RBS) measurements. Raman measurements revealed a disappearance of characteristic $A_{1g}$ and $F_{2g}$ modes of the CoCr$_2$O$_4$ with increase in the Ni content. Atomic force microscopy (AFM) and field emission scanning electron microscopy (FE-SEM) studies show a modification of the surface morphology upon Ni substitution. Magnetic measurements disclose that the ferrimagnetic Curie temperature ($T_C$) of the CoCr$_2$O$_4$ in thin film grown on MgAl$_2$O$_4$ (100) and MgO (100) substrates were found to be 100.6 ± 0.5 K and 93.8 ± 0.2 K, respectively. With Ni substitution the $T_C$ values were found to be enhanced to 104.5 ± 0.4 K for MgAl$_2$O$_4$ (100) and 108.5 ± 0.6 K for MgO (100) substrates. X-ray photoelectron spectroscopy (XPS) suggests Cr$^{3+}$ oxidation states in the films, while Co ions are present in a mixed Co$^{2+}$/Co$^{3+}$ oxidation state. The substitution of Ni at Co site significantly modifies the line shape of the core level as well as the valence band. Ni ions are also found to be in a mixed 2+/3+ oxidation state. O 1s core level display asymmetry related to possible defects like oxygen vacancies in the films.

Keywords: chromites, pulsed laser deposition (PLD), thin films, Raman, XPS

(Some figures may appear in colour only in the online journal)

1. Introduction
CoCr$_2$O$_4$ is a ferrimagnetic spinel compound with complex magnetic interactions at low temperatures [1]. The magnetic transitions Co$^{2+}$ and Cr$^{3+}$ ions occupy the tetrahedral A and octahedral B sites, respectively, of the spinel structure [1]. Below Curie temperature ($T_C = 93$ K), a collinear ferrimagnetic ordering occurs, with further lowering the temperature
to 26 K ($T_S$) the compound develops a short-range-ordered (SRO) spiral component [1]. Theoretical calculations has also evidenced the feature at $T_S$ due to the nesting of the Fermi surface having high degree of magnetic instability in the system associated with the nesting vector $q$ along the [110] direction [2]. Recent experiments have shown the size dependence of these magnetic transitions [3]. Below a critical particle size of $d_{\text{critical}} = 4.4$ (1) nm, the spiral ordering vanishes [3] and for size less than $d_{\text{col}} = 3.3$ (1) nm, the collinear magnetic order disappears [3]. A lock-in transition at a temperature $T_L = 15$ K appears because of the incommensurate-to-commensurate magnetic phase transition [1]. At $T_L$, the period of the spin spiral eventually ‘locks-in’ to the lattice parameter [1]. This spiral component is responsible for inducing the multiferroicity in CoCr$_2$O$_4$ [1]. Structurally, CoCr$_2$O$_4$ is stable and remains cubic with space group Fd3m at all temperatures as the sample is cooled down to 10 K [4].

On the other hand for NiCr$_2$O$_4$ the crystal structure of the system reduces from cubic to tetragonal at 310 K [5, 6]. In NiCr$_2$O$_4$ the cubic-to-tetragonal phase transition is first order in nature [7]. It is driven by a cooperative Jahn-Teller (J-T) effect in the array of Ni$^{2+}$ cations in tetrahedral position [7]. For the Cr$^{3+}$ ($3d^3$) cations the J-T effect in the octahedral crystal field is absent [7]. The tetragonal structure further transforms to an orthorhombic phase, driven by a magnetostructural coupling at the Néel temperature ($T_N$) at about 65 K [8, 9]. Both magnetic susceptibility and heat capacity measurements indicate anomalies at $T = 30$ K, resulting from the distortion occurring within the orthorhombic structure [10].

Investigations into the structural properties of CoCr$_2$O$_4$ thin films deposited on MgAl$_2$O$_4$ (001) substrates reveal a self-organized three dimensional isolated pyramidal architecture and hut-clusters with [111] facets [11]. The anisotropy of the surface energy in the spinel is the driving force for the growth of the [111] faceted structure [11]. Aqeel et al [12] reported spin-Hall magnetoresistance (SMR) and spin-Seebeck effect (SSE) in multiferroic CoCr$_2$O$_4$ thin films with Pt contacts indicating a large enhancement of both the signals occurring below the $T_S$ and $T_L$ transitions. These results indicated that the spin transport at the Pt/CoCr$_2$O$_4$ interface is sensitive to the magnetic phases, but this cannot be explained solely by the magnetic properties observed in the bulk samples [12]. The magnetic anisotropy in the spinel structure of CoCr$_2$O$_4$ thin films demonstrate a strain dependence which was supported by theoretical calculations predicting a tensile strain that favors the spin orientation in the film plane whereas a compressive strain induces an out-of-plane magnetic easy axis which is in contradiction with what is reported for CoFe$_2$O$_4$ [13].

Guzman et al [14] found that the deposition of CoCr$_2$O$_4$ thin films on MgAl$_2$O$_4$ (100) and MgO (100) substrates show optimum growth, with good quality films on the spinel MgAl$_2$O$_4$ substrate, despite the large lattice mismatch of about 3%. On the contrary, CoCr$_2$O$_4$ thin films deposited on MgO (100) substrate, with a rock-salt structure with lower lattice mismatch (~1%), degrades the crystal quality of the pristine films by forming antiphase boundaries (APBs). The type and number of APBs can be manipulated by changing the growth temperature that will ultimately help to partially recover the magnitude of magnetization [14]. By using soft x-ray techniques Windsor et al [15] have shown that the magnetic behavior of a strained [110] oriented CoCr$_2$O$_4$ film is a type-II multiferroic. The resonant soft x-ray diffraction (RXD) signal of the $(q,q,0)$ reflection appeared below $T_S$, the same ordering temperature as the conical magnetic structure in the bulk, indicating that this phase remains multiferroic even under strain [15]. However, reports on doped CoCr$_2$O$_4$ thin films are lacking. Recently, magnetic and electronic properties of (Ni$_{1-x}$Co$_x$)Cr$_2$O$_4$, with $0 \leq x \leq 1$, were reported [16, 17]. Substituting Co at the Ni site effectively changed the magnetic transition temperatures [16, 17]. In case of nanoparticles of (Co$_{1-x}$Ni$_x$)Cr$_2$O$_4$, with $x = 0.5$ and 0.25, showed modified magnetic transition temperatures along with wasp-waist like features observed in the magnetization as a function of applied magnetic field measurements at low temperatures [18]. In addition, temperature dependent infrared (IR) studies revealed anomalous behavior of phonons below $T_C$ for Co$_{0.9}$Ni$_{0.1}$Cr$_2$O$_4$, attributed to spin-phonon coupling [19].

Having similar molecular formula, both CoCr$_2$O$_4$ and NiCr$_2$O$_4$ differs significantly for their distinct properties. Beside ferrimagnetic $T_C$, CoCr$_2$O$_4$ has different magnetic transitions at low temperatures without any change in its cubic crystal structure. On the other hand, NiCr$_2$O$_4$ has temperature dependent structural as well as magnetic phase transitions significantly different from that of CoCr$_2$O$_4$. NiCr$_2$O$_4$ demonstrates tetragonal crystal structure at room temperature whereas CoCr$_2$O$_4$ has cubic structure. At present, there is no report on the structural and magnetic properties of Ni doped CoCr$_2$O$_4$ thin films. While depositing thin films, the role of selection of substrate to manipulate the type of the strain in the film has also been explored in this work. In the present paper, the structural properties and magnetic phase transitions in Co$_{1-x}$Ni$_x$Cr$_2$O$_4$ (with $x = 0, 0.5$) thin films on MgAl$_2$O$_4$ (100) and MgO (100) single crystal substrates are discussed.

2. Experimental details

Co$_{0.9}$Ni$_{0.1}$Cr$_2$O$_4$, with $x = 0, 0.5$, powder samples were prepared using the sol-gel technique, following the procedure reported earlier [18]. The amorphous powders were then calcined at 900°C. The Co$_{0.1}$Ni$_{0.9}$Cr$_2$O$_4$ ($x = 0, 0.5$) targets for pulsed laser deposition (PLD) were then prepared by pressing calcined powder samples into a pellet and sintering these at 1100 °C for 12 h in a programmable tubular furnace. The thin films were deposited from these targets using PLD. After loading the ceramic target and substrates into the PLD chamber, the chamber was evacuated to obtain a base pressure about 10$^{-5}$ Torr prior to the deposition. The ceramic targets were ablated using a KrF excimer laser (Lambda Physik COMPex 201 Model, Germany) at constant laser energy of 220 mJ and 10 Hz repetition rate. The target to substrate distance was kept constant at four centimeters. Commercial (100) oriented MgAl$_2$O$_4$ and MgO single crystal substrates with dimensions 10 $\times$ 10 $\times$ 0.5 mm were used. The samples were deposited for 30 min at 100 mTorr oxygen partial pressure to compensate the oxygen loss from the targets during the ablation process and to make the films stoichiometric. During deposition, the substrate temperature was maintained at 750 °C and the target was rotated continuously during the laser ablation process.
Figure 1. XRD patterns of the $(\text{Co}_{1-x}\text{Ni}_x)\text{Cr}_2\text{O}_4$ $(x = 0, 0.5)$ films grown on (a) MgAl$_2$O$_4$ (100) and (b) MgO (100) substrates.

Table 1. Lattice parameters of the thin film samples deposited on various substrates as calculated from XRD results.

| Sample                  | Lattice parameter $(a)$ for the films deposited on | Lattice parameter $(a)$ for the films deposited on |
|-------------------------|--------------------------------------------------|--------------------------------------------------|
|                        | $\text{MgAl}_2\text{O}_4$ (100)                  | $\text{MgO}$ (100)                              |
| CoCr$_2$O$_4$           | 8.36 Å                                          | 8.25 Å                                          |
| $(\text{Co}_{0.5}\text{Ni}_{0.5})\text{Cr}_2\text{O}_4$ | 8.24 Å                                          | 8.21 Å                                          |
| CoCr$_2$O$_4$           | 8.58 Å                                          | 8.17 Å                                          |

After deposition the films were cooled down to room temperature under the same oxygen partial pressure in order to avoid the formation of cracks.

Structural characterizations of these samples were carried out by utilizing x-ray diffraction (XRD) techniques, with a Bruker D 8 x-ray diffractometer and using a Cu–$K_\alpha$ radiation ($\lambda = 1.54056$ Å). The maximum thickness that can be determined through x-ray reflectivity (XRR) measurements is 200 nm. Raman measurements (JOBIN YVON HORIBA HR 800) were performed using a diode laser having wavelength $\lambda = 473$ nm (Power 25 mW, grating 1800, spectral resolution of about 1 cm$^{-1}$). Atomic force microscopy (AFM) measurements were done using a Mutimode Atomic Force Microscope employing a Si$_3$N$_4$ tip (length $\geq$ 1 nm and Z (height) $\approx$ 2–5 µm). Field emission scanning electron microscopy (FE-SEM) was used to explore the surface morphology of the films (length $\approx$ 1 nm at 500 V). The magnetic measurements were performed using a SQUID-VSM from Quantum Design (USA) with sensitivity $\approx 10^{-8}$ emu. The compositions of the films were determined by the Rutherford backscattering spectrometry (RBS) measurements using $\alpha$-particles (He$^{2+}$) of energy 2 MeV and the accumulated charge on the film was 20 µC (Resolution: 20–25 KeV). X-ray photoemission spectroscopy (XPS) measurements were acquired at room temperature using a SPECS XR 50 M monochromatised x-ray source equipped with an Al $K_\alpha$ anode ($h\nu = 1486.71$ eV) and a SPECS PHOIBOS 150 hemispherical electron energy analyser. The base pressure of the experimental chamber was smaller than 2 $\times$ 10$^{-10}$ mbar. Surface charge compensation was obtained by using a low-energy electron flood gun (electron energy = 3 eV, electron flux = 20 µA). The overall energy resolution of the XPS spectra was set to 0.7 eV for the survey scans, and to 0.55 eV for all the other spectra presented in this work.

3. Results and discussion

The motivation for using two different types of substrates such as MgO and MgAl$_2$O$_4$ for the deposition of films was to induce two different types of strain in the films [13]. In case, the lattice parameter of the film matches exactly with the lattice parameter of the substrate, then epitaxial growth of the film occurs. Depending on the type of lattice mismatch consequent strain can be of two types such as compressive and tensile. If the film having lattice parameter higher than that of the substrate is forced to match the lattice parameter of the substrate, the nature of strain would be compressive [13]. On the other hand, the film having lattice parameter smaller than the substrate if compelled to match the lattice parameter of the substrate, the type of strain in the film will be termed as tensile strain [13]. MgAl$_2$O$_4$ has a spinel structure analogue to that of CoCr$_2$O$_4$ but with a smaller lattice parameter that causes a lattice mismatch of 3.1% that induces a large in-plane compressive strain in the films [13]. On the other hand, MgO (100) has a rock-salt crystal structure that has a lattice mismatch of 1.1% with CoCr$_2$O$_4$ which will induce a tensile strain in the films [13]. Despite having a significant lattice mismatch between both the substrates and the $(\text{Co}_{1-x}\text{Ni}_x)\text{Cr}_2\text{O}_4$ (with $x = 0, 0.5$), that can create strain, good quality thin films have been grown on
both MgAl$_2$O$_4$ (100) and MgO (100) substrates, as will be discussed later. It is also noted that as the ionic radii of Ni$^{2+}$ (0.55 Å) is very similar to that of the Co$^{2+}$ (0.58 Å) [20], it is expected that Ni substitution at the Co site will not result in a dramatic change in the lattice parameter.

The effect of inducing strain in the spinel material by depositing on substrates having lattice mismatch was also previously investigated for the case of CoFe$_2$O$_4$ where the role of strain plays the opposite role as in the case of CoCr$_2$O$_4$ [13, 21]. CoCr$_2$O$_4$ thin films were previously grown on [001]-oriented MgAl$_2$O$_4$ and MgO substrates by Heuver et al [13]. These studies [13, 21] revealed the structure and magnetism of these films through experimental results but also included theoretical estimations of the strain to support their results. However, the effect of Ni substitution on the crystal structure, magnetic and electronic properties has not been reported as yet.

The XRD patterns of both MgO (100) and MgAl$_2$O$_4$ (100) substrates are also shown in order to visualize the peak in each pattern related to these substrates (figure 1). The splitting seen in the most intense peaks of both the substrates are attributed to the Cu–K$_{\alpha 1}$ and Cu–K$_{\alpha 2}$ split [23]. The out-of-plane lattice constants of the films are given in table 1, where the lattice parameter of bulk CoCr$_2$O$_4$ and NiCr$_2$O$_4$ are 8.33 Å and 8.32 Å, respectively [9, 13]. The lattice parameter for both the compositions has a smaller value (table 1) for the films deposited on the MgO (100) substrate when compared to that obtained for the films grown on MgAl$_2$O$_4$ (100). This is in line with the findings of Heuver et al [13]. Upon Ni substitution the (400) reflection shifts toward higher 2$\theta$ values for all the films prepared, irrespective of the substrates used. This indicates that the addition of Ni results in a decrease in the lattice parameter (see figure 1). As Ni has smaller atomic radius compared to Co, the shifting of peak towards higher diffraction angle resulting decrease in lattice parameters corroborates the incorporation of Ni at Co site.

In order to calculate the thickness of the films x-ray reflectivity (XRR) measurements were conducted (figure 2). The oscillations observed in the XRR are attributed to the interference of the x-ray beam reflected from the surface of the film, as well as from the film-substrate interface. Figure 2 also depicts fits to the measured data for the (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ thin films prepared on MgO (100) and MgAl$_2$O$_4$ (100) substrates have shown the phi-scan results of CoCr$_2$O$_4$ thin films grown on [001]-oriented MgAl$_2$O$_4$ and MgO substrates and confirmed this can produce films that are epitaxial nature. In addition, Heuver et al [13] also referred CoCr$_2$O$_4$ thin films as epitaxial when grown on [001]-oriented MgAl$_2$O$_4$ and MgO substrates as evidenced from HRXRD and reciprocal space mapping (RSM) data. In line with this, this paper also reflects on RSM data (see below) that supports the epitaxial nature of the films used in the present investigation.

![Diagram](image.png)

**Figure 2.** X-ray reflectivity (XRR) of the (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ films grown on MgAl$_2$O$_4$ (100) and MgO (100) substrates.

| Sample                  | Thickness of films grown on MgAl$_2$O$_4$ | Thickness of films grown on MgO |
|-------------------------|-------------------------------------------|---------------------------------|
| CoCr$_2$O$_4$            | ~394 Å                                    | ~666 Å                          |
| (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ | ~235 Å                                    | ~344 Å                          |

The XRD patterns of the Co$_{1-x}$Ni$_x$Cr$_2$O$_4$ (x = 0, 0.5) films deposited on MgAl$_2$O$_4$ (100) substrates are shown in figure 1(a) and those for the MgO (100) substrates in figure 1(b). It indicates a reflection corresponding to the (400) plane of the CoCr$_2$O$_4$ on the two different substrates. The presence of only (400) reflection peaks suggest preferentially oriented films along $a$-direction. Previously, Lüders et al [22] have shown the phi-scan results of CoCr$_2$O$_4$ thin films grown on [001]-oriented MgAl$_2$O$_4$ and MgO substrates and confirmed this can produce films that are epitaxial nature. In addition, Heuver et al [13] also referred CoCr$_2$O$_4$ thin films as epitaxial when grown on [001]-oriented MgAl$_2$O$_4$ and MgO substrates as evidenced from HRXRD and reciprocal space mapping (RSM) data. In line with this, this paper also reflects on RSM data (see below) that supports the epitaxial nature of the films used in the present investigation.

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**Figure 2.** X-ray reflectivity (XRR) of the (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ films grown on MgAl$_2$O$_4$ (100) and MgO (100) substrates.

| Table 2. Thickness of films as calculated from the XRR measurements. |
|--------------------|-----------------|-----------------|
| Sample             | Thickness of films grown on MgAl$_2$O$_4$ | Thickness of films grown on MgO |
| CoCr$_2$O$_4$      | ~394 Å          | ~666 Å          |
| (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ | ~235 Å          | ~344 Å          |
Figure 3. XRD Reciprocal space maps (RSMs) around: (a) (115) and (200) reflections of the CoCr$_2$O$_4$ film grown on MgAl$_2$O$_4$ (100), (b) (115) reflection of the CoCr$_2$O$_4$ film grown on MgO (100), (c) (115) and (200) reflections of the (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ film grown on MgAl$_2$O$_4$ (100) and (d) (115) reflection of the (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ film grown on MgO (100).
Reciprocal space mapping (RSM) measurement is used to exactly determine properties, including the strain state and the in-plane lattice parameters of the thin films [25, 26]. This is performed by analyzing the distribution of the diffraction intensity near a reciprocal lattice point of a substrate and film [25, 26]. The reciprocal space of an epitaxial film grown on single crystal substrates would have a well-defined reciprocal lattice points (rlp). Therefore, in order to ascertain the epitaxy one needs to measure the diffracted intensity around such lattice points. Conventionally the RSM measurements would be carried out about such rlp’s, which can give reasonable diffracted intensity, so as to cover $q_x-q_z$ space. Reciprocal space maps (RSM) were collected along both symmetric (002) reflections and asymmetric (115) reflections. Considering the symmetric (002) reflections, the contour related to the film exactly coincides with that of the substrate along $q_z = 0$ direction (figures 3(a) and (c)), as one expects. Upon considering the asymmetric (115) reflection the center of the contour related to the film is slightly displaced from the line passing through the contour related to the substrate. This indicates although the lattice parameters of the film follows the substrate’s lattice parameters when considered the symmetric (002) reflection (out-of-plane lattice parameter), there is still a mismatch when asymmetric (115) reflection is considered (in-plane lattice parameter). An idea regarding the strain state of the film can be formed from such an asymmetric scan [13]. It is to be noted that if the film is fully strained then one would expect the lattice point corresponding to film to occur at the same $q_z$ as that of substrate [13]. This is indicated by a dashed line in figures 3(c) and (d). The reciprocal lattice point of the film move away from this corresponding $q_z$ line as film relaxes and for fully relaxed film then the film reciprocal lattice point lies along the line of relaxation corresponding to the lattice parameter of the bulk value. The present data suggests that
all the films are partially strained. However, it is evident that the (Co_{0.5}Ni_{0.5})Cr_{2}O_{4} film grown on MgAl_{2}O_{4} (100) substrate exhibiting more strain as compared to the remaining samples (figure 3).

As CoCr_{2}O_{4} crystallizes in Fd\bar{3}m crystal structure, Raman modes are predicted by group theory for this space group \[27\]. Group theory calculations predict 17 fundamental lattice vibration modes \[27\]. The representations of these modes are expressed as \[27\]:

\[ \Gamma = A_{1g} + E_{g} + 3F_{2g} + 2A_{2u} + 2E_{u} + 5F_{1u} + 2F_{2u} \] (1)

Among these modes, \(A_{1g}\), \(E_{g}\), \(3F_{2g}\) modes are Raman active, whereas \(4F_{1u}\) modes are IR-active \[26\]. Experimentally, only five Raman modes at 692 cm\(^{-1}\) (\(A_{1g}\)), at 457 cm\(^{-1}\) (\(E_{g}\)), and at 610, 515 and at 186 cm\(^{-1}\) (\(F_{2g}\)) \[28\] were observed for ZnCr_{2}O_{4} single crystal analogous to the crystal structure of CoCr_{2}O_{4} \[28\].

In figures 4(a) and (b) the Raman spectra are shown for CoCr_{2}O_{4} and Co_{0.5}Ni_{0.5}Cr_{2}O_{4} films deposited on MgAl_{2}O_{4} (100) and MgO (100) substrates, respectively. The Raman modes related to the substrate are observed at 409 cm\(^{-1}\), 667 cm\(^{-1}\), 720 cm\(^{-1}\), and 766 cm\(^{-1}\) for MgAl_{2}O_{4} (100), while no modes are observed for the MgO (100) substrate. No noticeable Raman modes up to 900 cm\(^{-1}\) wave number range and relatively low background intensity makes MgO one of the most suitable substrate in this prospect \[29, 30\]. For the CoCr_{2}O_{4}, deposited on both substrates, significant Raman modes are observed at 551 cm\(^{-1}\) related to \(F_{2g}\) mode. The peak observed at 551 cm\(^{-1}\) is found to be shifted by \(\sim 35\) cm\(^{-1}\) towards higher wavenumber in comparison to the reported \(F_{2g}\) mode located at 515 cm\(^{-1}\). This shift to higher wave numbers in the \(F_{2g}\) mode was also previously observed in CoCr_{2}O_{4} nanoparticles and is attributed to the size effect \[31\]. The observed Raman modes for CoCr_{2}O_{4} \[31\] are labeled in figure 4. For Co_{0.5}Ni_{0.5}Cr_{2}O_{4} films deposited on both substrates no Raman modes are observed. This can be attributed to the fact that phonons are sensitive to the finite length scale effects due to the long range order that can be influenced by the strain, cation redistribution, phonon confinement effects, directional nature and other factors \[31, 32\]. In addition, Raman spectra

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**Figure 5.** AFM images of thin films grown on various substrates: (a) CoCr_{2}O_{4} on MgAl_{2}O_{4} (100), (b) CoCr_{2}O_{4} on MgO (100), (c) (Co_{0.5}Ni_{0.5})Cr_{2}O_{4} on MgAl_{2}O_{4} (100), (d) (Co_{0.5}Ni_{0.5})Cr_{2}O_{4} on MgO (100).
Figure 6. FE-SEM images of thin films grown on various substrates: (a) CoCr$_2$O$_4$ on MgAl$_2$O$_4$ (100), (b) CoCr$_2$O$_4$ on MgO (100), (c) (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ on MgAl$_2$O$_4$ (100), (d) (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ on MgO (100).
are sensitive to pressure, whether it is applied externally or produced internally through the addition of a dopant ion known as ‘chemical pressure’ [33]. It is known that in the present case the samples containing 50 at.% Ni do not form a tetragonal structure as is the case for NiCr$_2$O$_4$ below 310 K [9], but rather stabilizes in a cubic phase due to the presence of Co [1] and the cubic substrates used [13]. Thus, it is considered that in the present case the disappearance or weakening of Raman modes can be attributed to a combined effect of chemical pressure, as well as stress or strain effects as a consequence of substituting Ni at Co site [33, 34].

In order to investigate the surface morphology of the thin films, AFM measurements were performed and the results are shown in figure 5. Considering for the CoCr$_2$O$_4$ thin films prepared on MgAl$_2$O$_4$ (100) and MgO (100) substrates similar morphology with distinct grains are observed in figures 5(a) and (b). Upon Ni substitution, the quality of the surface degrades resulting in a quite hazy AFM image as can be seen in figures 5(c) and (d). The average roughness of the CoCr$_2$O$_4$

**Table 3. Thickness of films as calculated from RBS results.**

| Sample                  | Thickness of films grown on MgAl$_2$O$_4$ (100) | Thickness of films grown on MgO (100) |
|-------------------------|-------------------------------------------------|--------------------------------------|
| CoCr$_2$O$_4$           | ~700 Å                                          | ~700 Å                               |
| (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ | ~700 Å                                          | ~800 Å                               |
thin films grown on MgAl\textsubscript{2}O\textsubscript{4} (100) and MgO (100) substrate ranges from 0.8 to 1.2 nm. Upon Ni substituting the average roughness was found to decrease to values ranging from 0.5 to 0.7 nm. However, upon careful observation, it can be seen that the grain size has remarkably increased with Ni substitution (figure 5). Despite the fact that the surface morphology of the Ni doped CoCr\textsubscript{2}O\textsubscript{4} thin films is not sharply defined, clear cubic spots corresponding to larger grains are observed in figure 5. To substantiate this FE-SEM of the four thin films were measured as shown in figure 6. On increasing the magnification (thus, zooming in further) these images became indistinct and unclear, thus, the present magnification was maintained. However, figures 6(c) and (d) shows an increase in the sizes of the grains observed, supporting the AFM results.

In order to explore the elemental distribution, thickness and epitaxial nature of the deposited thin films Rutherford backscattering spectrometry (RBS) was performed under both random and channeling conditions using $\alpha$-particles. RBS measurement of an Au film was taken for the calibration before the sample measurements were started. The RBS results are depicted in figure 7. The desired elements present in the thin films, as well as in the substrate, were identified in the spectra, where the width of each peak corresponds to the relative thickness of that material in the film. RBS techniques are commonly

**Figure 8.** RBS data shown in black and fitted curves obtained using RUMP simulation code for CoCr\textsubscript{2}O\textsubscript{4} thin film grown on (a) MgAl\textsubscript{2}O\textsubscript{4} (100) and (b) MgO (100) substrates.
Figure 9. XPS survey scan for (a) CoCr$_2$O$_4$ on MgAl$_2$O$_4$ (100), (b) (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ on MgAl$_2$O$_4$ (100), (c) CoCr$_2$O$_4$ on MgO (100), and (d) (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ on MgO (100).

used for the estimation of the chemical composition, thickness and atomic distribution of the elements throughout the film thickness and composition [35]. If the material of the film is oriented along the substrate and the direction of $\alpha$-particles is aligned in the substrate orientation direction, most of the alpha particles will pass through the channel or empty space available within the crystal lattice leading to lower yield [36]. The fundamental principle is that the energetic ions can move into the crystals, penetrating much deeper if the atoms in the crystal are directed in some specific crystal directions [37]. This phenomenon is termed as a 'channeling effect' and it can be utilized in specific ion beam analysis methods for the analytical and atomistic simulations based on molecular dynamics (MD) approaches [37]. Comparing the red and black curves shown in the various panels shown in figure 7 it is clear that the yield has decreased significantly when the film is aligned and channeling occurs. However, this kind of decrease in yield cannot be observed for a polycrystalline thin film which has not grown along a preferred orientation [38]. Hence, the decrease in yield in the RBS channeling measurements is a manifestation of the epitaxial character of the films, thus, corroborating the XRD results suggesting the epitaxial nature of the films. The peak profile of Ni doped CoCr$_2$O$_4$ on MgO (100) substrates (see figure 7(d)) showed a diffused nature indicating a non-uniform distribution of both Ni and Co throughout the film thickness. The thicknesses of the films were calculated by fitting the RBS random spectra using the RUMP simulation code [39]. The values obtained are tabulated in table 3. Except for the estimated thickness obtained for the CoCr$_2$O$_4$ grown on MgO (100) substrate, all other values are almost double the value predicted from the XRR measurements. These discrepancies arise because of the different principles that are involved in XRR and RBS. In literature, often these techniques yield different results for the same film [40, 41]. For instance, the thickness of HfO$_2$ film was determined to be 0.21 nm from RBS, whereas XRR showed the thickness to be 1.2 nm [40]. However, it is believed that XRR can be considered to evaluate the thickness more precisely when compared to the RBS technique due to its high-density contrast [40]. The typical simulated curves for CoCr$_2$O$_4$ thin film grown on two substrates are also depicted in figure 8 (see red curves). In addition from figure 8 it is evident that the presence of Co is somewhat non-uniform in the films and has higher concentration at the film surface. For the doped samples the fitting became rather difficult due to complex nature of Co and Ni distribution in the film as well as the fact that the Co and the Ni have nearly similar atomic masses. The yield from the film is reduced because the channeling was performed along the substrate, thereby confirming the epitaxial nature of the films.

XPS measurements were performed in order to investigate the electronic structure and the oxidation states of the different chemical elements in the thin films. Figure 9 shows the wide survey spectra for the four investigated samples. Figure 10 shows the O 1s XPS spectra for the investigated thin films. In addition to a Shirley background, each spectrum has been fitted with three Voigt-type single components, labeled as O(1), O(2) and O(3), as shown in figure 10. This is consistent with what is published in the literature for similar systems [42, 43]. Component O(1), on the lower binding energy side of the spectrum, is attributed to stoichiometric...
Figure 10. O 1s XPS core level spectra for (a) CoCr$_2$O$_4$ on MgAl$_2$O$_4$ (100), (b) (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ on MgAl$_2$O$_4$ (100), (c) CoCr$_2$O$_4$ on MgO (100), and (d) (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ on MgO (100).

Table 4. Fit results for O 1s core level.

| Sample                          | O(1) BE (eV) | O(2) BE (eV) | O(3) BE (eV) | O(1)% area | O(2) % area | O(3)% area |
|---------------------------------|--------------|--------------|--------------|------------|------------|------------|
| CoCr$_2$O$_4$ on MgAl$_2$O$_4$ (100) | 529.82       | 531.51       | 533.20       | 58         | 38         | 4          |
| (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ on MgAl$_2$O$_4$ (100) | 529.88       | 531.79       | 533.21       | 55         | 41         | 4          |
| CoCr$_2$O$_4$ on MgO (100)      | 529.85       | 532.42       | 533.30       | 62         | 35         | 3          |
| (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ on MgO (100) | 529.87       | 531.53       | 533.22       | 61         | 36         | 3          |

oxygen in the oxide main matrix. The second component O(2), is ascribed to oxygen vacancies or defects in the lattice [42, 43], while the O(3) component can be ascribed to residual chemisorbed oxygen [44]. The fitted binding energy (BE) and the relative percentage area of each component are reported in table 4.

Fitted Cr 2p core level spectra are shown in figure 11. The Cr 2p BE region is composed of two main asymmetric peaks located at ~576 eV and ~586 eV, corresponding to the Cr 2p$_{3/2}$ and Cr 2p$_{1/2}$ spin orbit components, respectively. Each spectrum was fitted with three spin-orbit doublets, labeled as Cr(1), Cr(2) and Cr(3) and a Shirley-type background, a broad satellite structure at about 597 eV BE. These, together with the overall fit to the data, are all reported in figure 11. This fine multiplet structure, composed of three multiplet lines, is consistent with Cr ions being in a 3+ oxidation state, as was previously reported [45, 46] for many Cr-based oxides. The fitted binding energy (BE), the spin orbit energy splitting ($\Delta_{SO}$)
and the relative percentage area for Cr(1), Cr(2) and Cr(3) are reported in table 5.

Figure 12 shows the fitted Ni 2p core level spectra for (Co<sub>0.5</sub>Ni<sub>0.5</sub>)Cr<sub>2</sub>O<sub>4</sub> grown on (a) MgAl<sub>2</sub>O<sub>4</sub> (100) and (b) MgO (100). The line shape of this core level is composed of two main peaks with centroids located at about 855 eV and 873 eV, corresponding to Ni 2p<sup>3/2</sup> and Ni 2p<sup>1/2</sup> spin-orbit components respectively. The two main doublets correspond to Ni ions in 2+ and 3+ oxidation states; these have therefore been labeled as Ni<sup>2+</sup> and Ni<sup>3+</sup> in figure 12. The fit parameters for this core level are reported in table 6. It is important to note that the area ratio Ni<sup>3+</sup>:Ni<sup>2+</sup> is 2:1 for both thin films. Interestingly, this ratio is slightly smaller than the corresponding component in nanoparticle form [18].

A comparison of Co 2p core level spectra is reported in figure 13. The line shape of this core level is composed of two main peaks at ~780 eV and ~795 eV, corresponding to Co 2p<sub>3/2</sub> and Co 2p<sub>1/2</sub> spin-orbit components. For both CoCr<sub>2</sub>O<sub>4</sub> thin
Figure 12. Ni 2p XPS core level spectra for (a) (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ on MgAl$_2$O$_4$ (100), and (b) (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ on MgO (100).

films-spectra (a) and (c) in figure 13-the line shape of the Co 2p core level resembles that of Co$_3$O$_4$ [47, 48]. The intensity maxima for 2p$_{3/2}$ and 2p$_{1/2}$ are located at 780 eV and 795 eV, respectively. The observed double feature in the 2p$_{1/2}$ satellite is a fingerprint of a mixed Co$^{2+}$/Co$^{3+}$ oxidation state for Co ions. Substitution of Ni at Co site quite drastically modifies the line shape of this core level, as shown in figures 13(b) and (d). The centroid of the main peaks shifts to a 0.5 eV higher
Table 6. Fit results for Ni 2p core level.

| Sample                                      | Ni$^{2+}$ 2p$_{1/2}$ BE (eV) | Ni$^{3+}$ 2p$_{1/2}$ BE (eV) | Ni$^{2+}$ $\Delta$SO (eV) | Ni$^{3+}$ $\Delta$SO (eV) | Ni$^{2+}$ % area | Ni$^{3+}$ % area |
|---------------------------------------------|-----------------------------|-----------------------------|---------------------------|---------------------------|-----------------|-----------------|
| (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ on MgAl$_2$O$_4$ (100) | 854.45                      | 855.91                      | 17.40                     | 17.50                     | 37              | 63              |
| (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ on MgO (100)     | 854.62                      | 856.13                      | 17.40                     | 17.50                     | 35              | 65              |

Figure 13. Co 2p XPS core level spectra for (a) CoCr$_2$O$_4$ on MgAl$_2$O$_4$ (100), (b) (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ on MgAl$_2$O$_4$ (100), (c) CoCr$_2$O$_4$ on MgO (100), and (d) (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ on MgO (100).
Figure 14. Valence band spectra for (a) CoCr$_2$O$_4$ and (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ on MgAl$_2$O$_4$ (100), and (b) CoCr$_2$O$_4$ and (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ on MgO (100).
Figure 15. Magnetization as a function of temperature for thin films grown on various substrates: (a) \( \text{CoCr}_2\text{O}_4 \) on \( \text{MgAl}_2\text{O}_4 \) (100), (b) \( \text{CoCr}_2\text{O}_4 \) on \( \text{MgO} \) (100), (c) \( \text{(Co}_{0.5}\text{Ni}_{0.5})\text{Cr}_2\text{O}_4 \) on \( \text{MgAl}_2\text{O}_4 \) (100), (d) \( \text{(Co}_{0.5}\text{Ni}_{0.5})\text{Cr}_2\text{O}_4 \) on \( \text{MgO} \) (100). Blue symbols represent the data measured under ZFC and red symbols indicate FC conditions.
Figure 15. Magnetization as a function of temperature for thin films grown on various substrates: (a) CoCr$_2$O$_4$ on MgAl$_2$O$_4$ (100), (b) CoCr$_2$O$_4$ on MgO (100), (c) (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ on MgAl$_2$O$_4$ (100), (d) (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ on MgO (100). Blue symbols represent the data measured under ZFC and red symbols indicate FC conditions.
BE. Furthermore, the difference in energy between the main peaks and their satellites is now ~5.3 eV, as opposed to 6.2 eV in spectra (a) and (c). Spectra (b) and (d) resemble more the line shape of the typical charge-transfer-type compound CoO [49], indicating the presence of the Ni that has induced a pronounced change in the local electronic structure of the Ni-doped thin films, favoring a situation in which the 3d electrons for Co are more localized and possibly an increase in the presence of Co ions in a 2+ oxidation state. This is seen in the increase in the intensity of the charge-transfer satellite in the Co 2p core level).

Finally, figure 14 shows a comparison of the valence band region for the four investigated thin films. The line shape of the valence band for both CoCr$_2$O$_4$ thin films consists of a sharp feature located between the Fermi level ($E_F$, BE = 0 eV) and 2 eV BE, which can mainly be ascribed to a superposition of Cr 3d and Co 3d partial density of states [50–52]. This peak is separated from a wider structured region between ~2 eV and ~8 eV, where O 2p states are expected to be located [51]. The broad region between ~8 eV and ~12 eV is likely to derive from Co/Cr 4s states. The partial substitution of Co by Ni ions in both (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ thin films have two effects; firstly, a slight depletion of the spectral weight of the above-mentioned near-$E_F$ feature, due to the decreased contribution and increased localization of Co 3d states, in agreement with the analysis of the Co 2p core level spectra reported above. Secondly, an increase in the spectral weight in the BE region from 1 eV to 3 eV, where the Ni 3d states are generally located [53]. Although the valence bands are measured at 300 K, the significant change in the line shape upon Ni substitution is somehow related to enhancement of the $T_C$ for the (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ thin films grown on MgAl$_2$O$_4$ (100) and MgO (100) substrates. To further explore the magnetic properties of the thin films, in-plane magnetic measurements were carried out using a SQUID-VSM.

Temperature dependent in-plane magnetization measurements, shown in figure 15, were performed with a probing magnetic field of 100 Oe. Films deposited on MgAl$_2$O$_4$ substrates, having compressive strain, show a ferrimagnetic $T_C$ of 100.6 ± 0.5 K; whereas the film prepared under tensile strain on MgO (100) show $T_C$ = 93.8 ± 0.2 K for CoCr$_2$O$_4$ (figure 15); comparable to the bulk $T_C$ value of CoCr$_2$O$_4$ that is 93 K [1]. The transition is prominent for the CoCr$_2$O$_4$ film prepared on the MgO (100) substrate. In order to obtain $T_C$, $dM/dT$ as function of $T$ plots were used and the $T_C$ values were taken as the temperature associated with the minimum (see insets of figures 15(a) and (c)). The values of $T_C$ were found to be 88.4 K for the film deposited on the MgAl$_2$O$_4$ (100) substrate and 91.9 K for the film grown on the MgO (100) substrate. However, upon substituting Ni at Co site, the transitions appeared to be smeared out (see figures 14(a) and (b)). The $T_C$ values were determined to be 104.5 ± 0.4 K and 108.5 ± 0.6 K for films grown on the MgAl$_2$O$_4$ (100) and MgO (100) substrates, respectively. These values were determined, using knee point method as described previously [16, 17] (see insets of figures 15(b) and (d)). The $T_C$ values found for the films are given in table 7 for comparison with those obtained for the powder samples previously measured and also determined using the knee-point method as reported previously [16, 17]. The reported $T_C$ values for CoCr$_2$O$_4$ films grown on MgAl$_2$O$_4$ (100) and MgO (100) substrates were previously [13] found to be ~81 K and ~80 K, respectively, using a 0.01 T probing field along [100] in plane direction. The order of magnitude of magnetic moments (figure 15) of the films is relatively small, as the material in the films is only a very thin layer. Magnetic properties are greatly influenced by cationic site occupancy and anisotropy induced by the substrate [13]. The difference in $T_C$’s for CoCr$_2$O$_4$ and (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ thin films for different substrates is significant compared to the earlier reports [13]. It is interesting to note that upon Ni substitution causes the reverse in magnitude of the $T_C$ when the substrates are changed. This clearly indicates the magnetic properties are controlled by the anisotropy in addition to the dopants [16].

This is the first report of $T_C$ values for thin films where Co is substituted with Ni in CoCr$_2$O$_4$. However, there are quite a few reports that depicts enhancement of $T_C$ in epitaxial thin films [54]; including that of CoCr$_2$O$_4$ films prepared on MgAl$_2$O$_4$ (100) and MgO (100) substrates given as ± 81 K and 82 K, respectively [13]. These values are actually substantially smaller than the reported value of $T_C$ for the bulk CoCr$_2$O$_4$ of 93 K [1]. In the present case the $T_C$ values obtained for the CoCr$_2$O$_4$ films are 100.6 ± 0.5 K for the MgAl$_2$O$_4$ (100) substrate and 93.8 ± 0.2 K for the film on MgO (100). These values are quite similar to the bulk values. However, on substituting Ni at Co site, the $T_C$ values were found to be enhanced to 104.5 ± 0.4 K for MgAl$_2$O$_4$ (100) and 108.5 ± 0.6 K for MgO (100) substrates. The increase in $T_C$ in the present case is possibly due to the effect of the substrates as well as the dopants that can each affect the nature of strain in a different way [13, 17]. NiCr$_2$O$_4$ favors a tetragonal crystal structure at room temperature due to Jahn-Tellor distortion [5, 6]. Upon 50 at.% substitution of Ni at Co site it is found to retain the cubic structure in the present work. It is proposed that this is the result of the chemical pressure due to doping that have induced strain within the crystal, in addition to the strain induced by the selected substrates. A similar enhancement of the $T_C$ value of BiMnO$_3$ thin films, to a value of 176 K which is 70 K higher than the

### Table 7. Curie temperatures ($T_C$) determined from $M(T)$ measurements for the various samples.

| Sample | $T_C$ value for film on MgAl$_2$O$_4$ (100) substrate | $T_C$ value for film on MgO (100) substrate | $T_C$ values for powder samples [16] |
|--------|-----------------------------------------------|-----------------------------------------------|-----------------------------------------------|
| CoCr$_2$O$_4$ | 100.6 ± 0.5 K | 93.8 ± 0.2 K | 99.5 ± 0.5 K |
| (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ | 104.5 ± 0.4 K | 108.5 ± 0.6 K | 89.2 ± 0.7 K |
| CoCr$_2$O$_4$ | 81 K [13] | 80 K [13] | |


Figure 16. Magnetization as a function of applied magnetic field for thin films grown on various substrates: (a) CoCr$_2$O$_4$ on MgO (100) ($T = 20$ K), (b) CoCr$_2$O$_4$ on MgO (100) ($T = 60$ K), (c) CoCr$_2$O$_4$ on MgAl$_2$O$_4$ (100) ($T = 60$ K), (d) (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ on MgAl$_2$O$_4$ (100) ($T = 60$ K) and (e) (Co$_{0.5}$Ni$_{0.5}$)Cr$_2$O$_4$ on MgO (100) ($T = 60$ K).
bulk value, was obtained by manipulating the strain through the selection of different single crystal substrates [54]. The $T_C$ was strongly enhanced by improving the (pseudo-) tetragonal distortion in BiMnO$_3$ [54]. As NiCr$_2$O$_4$ prefers to adopt a tetragonal structure and this phase has been inhibited due to preferential growth in the present case, the enhancement in $T_C$ can be attributed to the complex interplay between the strains induced by the various substrates and the nature of strain resulting from the site substitution.

Further, to explore the magnetism below $T_C$, $M$ versus $\mu_0 H$ measurements were performed (figure 16). Figure 16(a) shows the hysteresis loop measured at 20 K for the CoCr$_2$O$_4$ film grown on MgO (100) substrate. The constricted loop around the low field region is possibly due to the spiral ordering of the spins [1, 2]. When the measurement temperature is increased to 60 K (figure 16(b)), the irreversibility of the loop still persists indicating the ferrimagnetic ordering as observed in the bulk [1, 2]. The diamagnetic tailing of the hysteresis loop is due to the contribution from the substrate. As the magnetic moment of the film is rather small, the substrate constrictions dominate. The hysteresis loop measured for the CoCr$_2$O$_4$ thin film grown on MgAl$_2$O$_4$ (100) substrate at 60 K also shows irreversibility (figure 16(c)). Upon Ni substitution at Co site retains the ferrimagnetic order below $T_C$ as shown in figures 16(d) and (e) measured at 60 K. Hence, the magnetic properties are significantly modified either by selecting appropriate substrates or by substituting suitable cation at Co site.

4. Conclusions

Thin films of Co$_{1-x}$Ni$_x$Cr$_2$O$_4$ ($x = 0, 0.5$) were deposited on MgAl$_2$O$_4$ (100) and MgO (100) substrates using PLD technique. The films demonstrate phase purity without any contamination. With Ni substitution, characteristic Raman modes disappear indicating disorder or possible structural changes. XRD and RBS measurements confirm oriented epitaxial nature of the thin films. The observation of oscillations in the x-ray reflectivity of the films suggest the deposition of the thin films that causes the interference fringes. AFM and FE-SEM studies reveal the change of surface morphology upon Ni substitution. XPS studies demonstrate the complex nature of the oxidation states of Co and Ni. Magnetic measurements reveal the ferrimagnetic transition temperature, $T_C$, of the CoCr$_2$O$_4$ is modified when grown on different substrates that have induced different types of anisotropies into the films. In addition substitution of Co site with Ni has found to change the $T_C$ of the films which is also evidenced from the change in the line shape of the valence band.

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References

[1] Yamasaki Y, Miyasaka S, Kaneko Y, He J-P, Arima D and Tokura Y 2006 Phys. Rev. Lett. 96 207704
[2] Ganguly S, Chimata R and Sanyal B 2015 Phys. Rev. B 92 224417
[3] Zakutna D, Alemajhebu A, Vlcek J, Nemkovski K, Grams C P, Niznansky D, Honecker D and Disch S 2019 Phys. Rev. B 100 184427
[4] Lawes G, Melot B, Page K, Ederer C, Hayward M A, Proffen T and Seshadri R 2006 Phys. Rev. B 74 024413
[5] Dunitz J D and Orgel L E 1957 J. Phys. Chem. Solids 3 20
[6] Kocsis V, Bordács S, Varjas D, Penc K, Abouelsayed A, Kunther C A, Ogushi K, Tokura Y and Kézsmárkí I 2013 Phys. Rev. B 87 064416
[7] Bush A A, Shukuratov V Y, Kamentsev K E, Prokhvorov A S, Zhubkova E S, Gorschunov B P and Torgashev V I 2012 Phys. Rev. B 85 214412
[8] Ishibashi H and Yasumi T 2007 J. Magn. Magn. Mater. 310 e610
[9] Suchomel M R, Shoemaker D P, Rihaud L, Kemei M C and Seshadri R 2012 Phys. Rev. B 86 054406
[10] Sparks T D, Kemei M C, Barton P T, Seshadri R, Mun E-D and Zapf V S 2014 Phys. Rev. B 89 024405
[11] Luders U, Sanchez F and Fontcuberta J 2004 Phys. Rev. B 70 045403
[12] Aquil A, Vlieststra N, Heuer J A, Baurer G E W, Noheda B, van Wees B J and Palstra T M 2015 Phys. Rev. B 92 224440
[13] Heuer J A, Scaramucci A, Blickenstorfer Y, Matzen S, Spaldin N A, Ederer C and Noheda B 2015 Phys. Rev. B 92 214429
[14] Guzman R, Heuer J, Matzen S, Magen C and Noheda B 2017 Phys. Rev. B 96 104415
[15] Windsor Y W et al 2017 Phys. Rev. B 95 224413
[16] Mohanty P, Sheppard C J, Prinsloo A R E, Roos W D, Olivi L and Aulagni G 2018 J. Magn. Magn. Mater. 541 20
[17] Mohanty P, Venter A, Sheppard C J and Prinsloo A R E 2020 J. Magn. Magn. Mater. 498, 166127
[18] Mohanty P, Prinsloo A R E, Doyle B P, Carleschi E and Sheppard C J 2018 Adv. Mat. 8 056424
[19] Ptak M, Maczka M, Pikul A, Tomaszewski P E and Hanuza J 2014 J. Solid State Chem. 212 218
[20] Shannon R D 1976 Acta Crystallogr. A32 751
[21] Gatel C, Varot-Fournou B, Matzen S and Moussy J-B 2013 Appl. Phys. Lett. 103 092405
[22] Luders U, Sanchez F and Fontcuberta J 2004 Mater. Sci. Eng. B 109 200
[23] Cullity B D 1956 *Elements of X-ray Diffraction* (Reading, MA: Addison-Wesley)

[24] Parratt L G 1954 *Phys. Rev.* **95** 359

[25] Saito K, Ulyanenkov A, Grossmann V, Ress H, Bruegeman L, Ohta H, Kurosawa T, Ueki S and Funakubo H 2006 *Jpn. J. Appl. Phys.* **45** 7311

[26] Liu G, Wang H, Makino H, Ko H-J, Hanada T and Yao T 2002 *Appl. Surf. Sci.* **190** 408

[27] Saito K, Ulyanenkov A, Grossmann V, Ress H, Bruegeman L, Ohta H, Kurosawa T, Ueki S and Funakubo H 2006 *Jpn. J. Appl. Phys.* **45** 7311

[28] Liu G, Wang H, Makino H, Ko H-J, Hanada T and Yao T 2002 *Appl. Surf. Sci.* **190** 408

[29] Gasparov L, Jegorel T, Loetgering L, Middey S and Chakhalian J 2014 *J. Raman Spectrosc.* **45** 134107

[30] Irie M N, Abrashev M V, Popov V N and Hadjiev V G 2003 *Phys. Rev. B* **65** 134107

[31] Tian Z, Zhu C, Wang J, Xia Z, Liu Y and Yuan S 2015 *J. Magn. Magn. Mater.* **377** 176

[32] Mohanty P, Saravanakumar S, Saravanan R and Rath C 2013 *J. Nanosci. Nanotechnol.* **13**

[33] Djuradze E, Bouch F, Dezanneau G and Bouvier P 2003 *J. Phys. Chem. B* **107** 8321

[34] Iliev M N, Abrashev M V, Popov V N and Hadjiev V G 2003 *Phys. Rev. B* **67** 212301

[35] Mohanty P, Singh V P, Mishra N C, Ojha S, Kanjilal D and Rath C 2014 *J. Phys. D: Appl. Phys.* **47** 315001

[36] Wendler E, Becker G, Rensberg J, Schmidt E, Wolf S and Wiesch W 2016 *Nucl. Instrum. Methods B* **379** 195

[37] Nordlund K, Djurabekova F and Hobler G 2016 *Phys. Rev. B* **94** 214109

[38] Hobler G 1996 *Radiat. Eff. Def. Sol.* **139** 21

[39] Doolittle L R 1985 *Nucl. Instrum. Methods B* **9** 344

[40] Kitahara A, Yasuno S and Fujikawa K 2009 *Trans. Mater. Res. Soc. Jpn.* **34** 613

[41] Kang H Y, Lim J D, Peranantham P and Hwangbo C K 2013 *J. Opt. Soc. Korea* **17** 38

[42] Rath C, Mohanty P, Pandey A C and Mishra N C 2009 *J. Phys. D: Appl. Phys.* **42**

[43] Dolla T H, Pruessner K, Billing D G, Sheppard C, Prinsloo A, Carleschi E, Doyle B and Ndungu P 2018 *J. Alloys Compd.* **742** 78

[44] Pendashteh A, Palma J, Andersona M and Marcilla R 2016 *RSC Adv.* **6** 28980

[45] Biesinger M C, Payne B P, Grosvenor A P, Lau L W M, Gerson A R and Smart R S C 2011 *Appl. Surf. Sci.* **257** 2717

[46] Choudhary B, Paul D, Singh A and Gupta T 2017 *Environ. Sci. Pollut. Res.* **24** 16786

[47] Bingwa N et al 2018 *Appl. Catal. A* **555** 189

[48] van Elp J, Wieland J L, Eskes H, Kuiper P, Sawatzky G A, de Groot F M F and Turner T S 1991 *Phys. Rev. B* **44** 6090

[49] Shen Z-X et al 1990 *Phys. Rev. B* **42** 1817

[50] Carleschi E, Malvestuto M, Zacchigna M, Nicolaou A, Brouet V, Hébert S, Muguerra H, Grebille D and Parmigiani F 2009 *Phys. Rev. B* **80** 035114

[51] Singh D J 2000 *Phys. Rev. B* **61** 13397

[52] Yokobori T et al 2013 *Phys. Rev. B* **87** 195124

[53] Panda S K, Thunström P, Marco I D, Schött J, Delin A, Dasgupta I, Eriksson O and Sarma D D 2014 *New J. Phys.* **16**

[54] Choi E-M, Kleibeuker J E and MacManus-Driscoll J L 2017 *Sci. Rep.* **7** 43799