Unexpected Phonon Behaviour in BiFe\(_x\)Cr\(_{1-x}\)O\(_3\), a Material System Different from Its BiFeO\(_3\) and BiCrO\(_3\) Parents

Cameliu Himcinschi \(^{1,*}\), Felix Drechsler \(^{1}\), David Sebastian Walch \(^{2,3}\), Akash Bhatnagar \(^{2,3}\), Alexei A. Belik \(^{4}\) and Jens Kortus \(^{1}\)

1 Institute of Theoretical Physics, TU Bergakademie Freiberg, D-09596 Freiberg, Germany; felix.drechsler@student.tu-freiberg.de (F.D.); jens.kortus@physik.tu-freiberg.de (J.K.)
2 Zentrum für Innovationskompetenz SiLi-nano, Martin-Luther-Universität Halle-Wittenberg, D-06120 Halle (Saale), Germany; david.knoche@physik.uni-halle.de (D.S.W.); akash.bhatnagar@physik.uni-halle.de (A.B.)
3 Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, D-06120 Halle (Saale), Germany
4 International Center for Materials Nanoarchitectonics (WPI-MANA), National Institute for Materials Science (NIMS), Namiki 1-1, Ibaraki, Tsukuba 305-0044, Japan; alexei.belik@nims.go.jp
* Correspondence: himcinsc@physik.tu-freiberg.de

Abstract: The dielectric function and the bandgap of BiFe\(_{0.5}\)Cr\(_{0.5}\)O\(_3\) thin films were determined from spectroscopic ellipsometry and compared with that of the parent compounds BiFeO\(_3\) and BiCrO\(_3\). The bandgap value of BiFe\(_{0.5}\)Cr\(_{0.5}\)O\(_3\) is lower than that of BiFeO\(_3\) and BiCrO\(_3\), due to an optical transition at ~2.27 eV attributed to a charge transfer excitation between the Cr and Fe ions. This optical transition enables new phonon modes which have been investigated using Raman spectroscopy by employing multi-wavelength excitation. The appearance of a new Raman mode at ~670 cm\(^{-1}\) with a strong intensity dependence on the excitation line and its higher order scattering activation was found for both BiFe\(_{0.5}\)Cr\(_{0.5}\)O\(_3\) thin films and BiFe\(_x\)Cr\(_{1-x}\)O\(_3\) polycrystalline bulk samples. Furthermore, Raman spectroscopy was also used to investigate temperature induced structural phase transitions in BiFe\(_{0.5}\)Cr\(_{0.5}\)O\(_3\).

Keywords: Raman spectroscopy; thin films; spectroscopic ellipsometry; charge transfer; phase transition; multiferroics; BiFe\(_x\)Cr\(_{1-x}\)O\(_3\)

1. Introduction

Bi\(_2\)FeCrO\(_6\) was first theoretically proposed as a bismuth-based multiferroic material having large spontaneous magnetisation and polarisation by means of first principle studies by Baettig et al. [1,2]. Following this theoretical prediction, Bi\(_2\)FeCrO\(_6\) epitaxial films have also been synthesised and its multiferroic character demonstrated [3,4]. Consequently, a lot of attention was dedicated to the characterisation of structural, ferroelectric and multiferroic properties of the material, and to the optimisation of the growth parameters for thin films [5–8]. Promising photovoltaic properties, the low bandgap and the possibility to tune it by the growth conditions, cationic ordering, and the domain size have attracted a lot of attention in recent years [9–13]. Various heterostructures or BiCrO\(_3\)/BiFeO\(_3\) superlattices with different thicknesses and repetitions have been proposed for designing efficient ferroelectric photovoltaic devices [14–16].

Raman spectroscopy is an established method to detect subtle structural changes induced by strain or temperature and it has been already very successfully applied to the study of the lattice dynamics in the class of oxides with perovskite structures. However, in the case of Bi\(_2\)FeCrO\(_6\) there are very few Raman or infrared spectroscopic studies reported [17–19].

In the present paper Raman spectroscopy was used in combination with spectroscopic ellipsometry for the characterisation of BiFe\(_{0.5}\)Cr\(_{0.5}\)O\(_3\) thin films and polycrystalline...
BiFe$_x$Cr$_{1-x}$O$_3$ materials. It was thus possible to provide the evidence of light induced phonon modes and to follow the temperature induced phase transitions by Raman spectroscopy in these material systems. It should be mentioned that Bi$_2$FeCrO$_6$ is commonly used in literature for double perovskite structure with alternating Fe and Cr in the unit cell [14]. BiFe$_{0.5}$Cr$_{0.5}$O$_3$, although an equivalent representation of the same stoichiometry, allows for some deviation from the ideal 1:1 ordering expected from a typical Bi$_2$FeCrO$_6$ unit cell. In this paper, for the sake of simplicity and consistency, BiFe$_{0.5}$Cr$_{0.5}$O$_3$ (BFCO) is used for the stoichiometry of the films which also allows us to address other investigated stoichiometries for BiFe$_x$Cr$_{1-x}$O$_3$ bulk samples.

2. Materials and Methods

Epitaxial BiFe$_{0.5}$Cr$_{0.5}$O$_3$ films with thickness of 120–200 nm were grown on SrTiO$_3$ (001) c substrates using pulsed laser deposition (SURFACE systems + technology PLD-Workstation (Hueckelhoven, Germany), Coherent KrF excimer laser (Santa Clara, CA, USA)). A stoichiometric ceramic BiFe$_{0.5}$Cr$_{0.5}$O$_3$ target was placed 60 mm below the substrate. During the deposition the substrate was kept at a temperature of 700 °C and exposed to 0.01 mbar oxygen partial pressure inside the chamber. The laser pulses were set to a pulse energy of 136 mJ with a repetition rate of 2 Hz. After finishing the deposition, the film was cooled at a high oxygen partial pressure (>200 mbar) with a rate of 5 °C/min. The crystallinity and phase purity of the BFCO films were confirmed by X-ray analysis (see Figure S1 in Supplementary Materials). BiFe$_x$Cr$_{1-x}$O$_3$ (x = 0.3, 0.4, 0.6, 0.7) bulk polycrystalline samples were prepared from stoichiometric mixtures of Bi$_2$O$_3$ (99.9999%), Fe$_2$O$_3$ (99.999%), and Cr$_2$O$_3$ (99.9%) (Rare Metallic Co. Ltd., Tokyo, Japan) at high-pressure, high-temperature conditions of about 6 GPa. The sample with x = 0.7 was annealed at about 1550 K in an Au capsule for 90 min. The samples with x = 0.3, 0.4, 0.6 were annealed at about 1700 K in Pt capsules for 60 min. After annealing, quenching was performed by turning off heating current, and then pressure was slowly released.

The ellipsometric measurements were performed at room temperature at four angles of incidence (55°, 60°, 65° and 70°) using a M2000 ellipsometer from J.A. Woollam Company (Lincoln, NE, USA).

The micro-Raman measurements were performed with a LabRam Horiba Jobin Yvon spectrometer (Villeneuve d’Ascq, France) using 325, 442, 532, and 633 nm laser lines for excitation. A 50× magnification objective (N.A. 0.55) was used to focus and collect the scattered light, while the laser power was set low enough (below 1.5 mW for all lasers) in order to avoid damage of the samples surface and any influence of laser induced heating on the Raman spectra. All spectra were recorded in backscattering geometry. Temperature-dependent Raman measurements from 90 K up to 700 K were carried out using a Linkam THMS-600 cooling stage (Salfords Redhill, UK) and a Linkam TS 1200 heating chamber (Salfords Redhill, UK) placed under the Raman microscope.

3. Results and Discussions

3.1. Ellipsometry Dielectric Function

First, a bare SrTiO$_3$ substrate was measured using ellipsometry, its optical response being modelled using a sum of Gaussian oscillators which ensures the Kramer–Kronig consistency of the real and imaginary parts of dielectric function. The determined dielectric function of the SrTiO$_3$ substrate was further used for the evaluation of the film/substrate system. In a second step, the absorption free energy range (below 1.75 eV) was used in order to estimate the thickness of the BFCO films using a four-layer model (substrate/film/roughness layer/ambient). The procedure used here was also applied previously for the determination of the optical constants of BiFeO$_3$ films [20]. The equations relating the ellipsometric parameters to the dielectric function can be found in [21]. The optical response of the film was modelled by a Cauchy dispersion relation ($n = A_n + B_n/\lambda^2$) (describing the refractive index in this spectral range. In a third step, using the thickness and the roughness obtained in the second step as an initial guess, the ellipsometric data were evaluated in the energy
range up to 6 eV describing the line shape of the imaginary part of the dielectric function of the film as a sum of Gaussian oscillators, while its real part is generated according to the Kramers–Kronig relation.

Using the method mentioned above a thinner (~120 nm) and a thicker (~200 nm) film with an optical roughness of ~4 nm, were evaluated using a multi-sample analysis method in order to avoid correlations between the fit parameters of the dielectric function and the thickness. Evaluating the films separately delivered nearly the same results, with an error in the determination of the thickness and roughness of ±1 nm, which indicate that both films have the same optical properties. The thickness values obtained from ellipsometry were in good agreement with the expected nominal thickness from the PLD growth.

The determined dielectric function of the BFCO is plotted in Figure 1 as a function of energy. The energy position of the Gaussian oscillators obtained from the fit at 2.27, 3.69, and 5.25 eV are marked in the same figure by arrows. It should be mentioned that also a 4th peak located at 9.6 eV, i.e., outside the measured range, had to be considered. In the same figure the energy position of the laser lines used as excitation for the Raman spectroscopy measurements are also indicated by dotted vertical lines.

![Figure 1](image-url)

**Figure 1.** Real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) part of BiFe$_{0.5}$Cr$_{0.5}$O$_3$ dielectric function. The dotted vertical lines indicate the energy position of the laser lines used for Raman spectroscopy, while the vertical grey arrows show the energy position of the absorption peaks. The inset show the linear extrapolation of $(\alpha E)^2$ to zero absorption which give the value of the optical band gap.

From the real $\varepsilon_1$ and imaginary $\varepsilon_2$ part of the dielectric function, the complex refractive index $n + ik$ is calculated. The absorption coefficient $\alpha$ can be derived from the extinction coefficient $k$ as: $\alpha = 4\pi k/\lambda$. The absorption coefficient of BFCO is plotted in Figure 2 in comparison to the absorption coefficient of BiFeO$_3$ and BiCrO$_3$ films. It is very clear from the figure (especially from the zoom in the inset of Figure 2) that the BFCO films start to absorb at lower energies than its parent materials BiFeO$_3$ and BiCrO$_3$. The arrow at 2.27 eV indicates the position of the first absorption peak as determined from ellipsometry. These results corroborate that BFCO is promising material in the field of photovoltaic applications due to its extended absorption of the solar spectrum when compared with BiFeO$_3$ or BiCrO$_3$.
In order to gain a better look on the onset of the absorption, this region was analysed in detail. The optical gap of the BFCO films was determined by using the procedure for bandgap determination proposed by Tauc et al. [22] that was already successfully applied to BiFeO$_3$ and BiCrO$_3$ films [23–25].

Using the proportionality $(\alpha E)^2 \sim E - E_g$ and extrapolating to zero absorption, a value of the energy gap $E_g$ of 2.07 eV was obtained, as can be seen in the inset of Figure 1. This value is well below the values of the direct optical gaps of 2.8 eV or 2.95 eV reported for BiFeO$_3$ [23,24] and BiCrO$_3$ [25], respectively. The bandgap value obtained is, however, in good agreement with the values determined for Bi$_2$FeCrO$_6$ films which were found to be strongly influenced by the deposition conditions, cation ordering, domain size, or film thickness [9,10,12,13,26–28].

Considering the first peak determined in the imaginary part of the dielectric function, $\varepsilon_2$, of BFCO at ~2.27 eV, its position is very close to the first absorption peaks observed in stoichiometrically similar Bi$_2$FeCrO$_6$ films [11] or in LaFe$_{0.5}$Cr$_{0.5}$O$_3$ [29,30]. Its origin was attributed to a charge transfer excitation between Cr and Fe, being only present in the Fe/Cr mixed systems [11,29–31]. The lowest transition in Bi$_2$FeCrO$_6$ was also predicted to be between the Fe3d and Cr3d states using ab initio calculations in the pioneering work of Baettig et al. [1]. The appearance of this charge transfer band plays a crucial role in understanding the Raman spectra of BFCO that will be presented in the next section.

3.2. Raman Spectroscopy

The structure of BiFe$_{0.5}$Cr$_{0.5}$O$_3$ is composed of alternating ABO$_3$-AB’O$_3$ perovskite cells (also called as double-perovskite structure $A_2BB’O_6$). Structural studies using XRD and neutron diffraction showed that at room temperature BiFe$_{0.5}$Cr$_{0.5}$O$_3$ has a trigonal lattice of the space group R3c (No. 161) very similar to that of the BiFeO$_3$ [32,33]. In the case of BiFeO$_3$, for this space group, group theory predicts 4A$_1$ and 9E polar Raman modes [34–36]. The Raman spectrum of a 200 nm thick BiFe$_{0.5}$Cr$_{0.5}$O$_3$ film deposited on the SrTiO$_3$ substrate measured with an excitation of 633 nm is shown by the continuous line in the upper part of Figure 3. The Raman signal is dominated by the broad peaks of the
substrate. In order to extract the BiFe$_{0.5}$Cr$_{0.5}$O$_3$ signal, the substrate spectrum (dotted line in Figure 3) was measured by focusing the laser at a depth of about 30 µm below the film surface, and subsequently subtracted from the film/substrate spectrum. The difference spectrum is shown by the red line in the upper part of Figure 3. As can be seen, besides some weak peaks below 600 cm$^{-1}$, there is a prominent peak at 670 cm$^{-1}$. This peak was attributed in a previous Raman study of BiFe$_{0.5}$Cr$_{0.5}$O$_3$ films to the SrTiO$_3$ substrate due to its proximity to the substrate peak [18]. As can be seen in the lower panel of Figure 3, the 670 cm$^{-1}$ peak is also present in the difference spectrum obtained with the 532 nm and nearly absent in the case of 442 nm excitation line, using the same procedure of subtraction for these excitations. Such a strong intensity dependence on the excitation wavelength is a clear indication of coupling phenomena.

Figure 3. Raman spectra of a 200 nm BiFe$_{0.5}$Cr$_{0.5}$O$_3$ thin film on SrTiO$_3$ substrate and of the substrate normalised at the same intensity in the 200–400 cm$^{-1}$ region, measured with an excitation of 633 nm. The corresponding film signal was calculated as a difference spectrum of the two (upper panel). The difference spectra of the thin film obtained with different excitations lines (633 nm, 532 nm, and 442 nm) and the as measured spectrum with the 325 nm excitation (lower panel).

Its origin will be discussed in the following part using also the ellipsometry data. The penetration depth $d$ of light in a material can be calculated from the absorption coefficient $\alpha$ or from the extinction coefficient $k$ as: $d = 1/\alpha = \lambda/4\pi k$. Considering the determined absorption coefficient (Figure 2) the penetration depths of the 633, 532, and 442 nm light are 750, 248, and 115 nm, respectively. This of course means that the laser light penetrates through the film and that also a substrate signal is expected when measuring 100–200 nm thick films. On the other hand, when measuring the Raman spectra using 325 nm excitation, which has a penetration depth of only 25 nm in BiFe$_{0.5}$Cr$_{0.5}$O$_3$ the measured spectra correspond only to the film. As can be seen in Figure 3, the peak at 670 cm$^{-1}$ is also present in the spectra recorded with the 325 nm excitation. This clearly indicates that the 670 cm$^{-1}$ peak is intrinsic to BiFe$_{0.5}$Cr$_{0.5}$O$_3$ and not to the substrate. Its strong intensity dependence
on the excitation energy can be understood by the proximity of the energy of the excitation laser to the absorption peaks (see Figure 1). The 633 nm and 532 nm wavelengths are close to the first absorption peak, 325 nm is close to the second absorption peak, while 442 nm is far from such resonances and the Raman peak at 670 cm$^{-1}$ is hardly observable for this last excitation.

It should be also mentioned that the Raman spectra for Bi$_2$FeCrO$_6$ previously published in the literature [18] show a very strong peak at $\sim$830 cm$^{-1}$ which was also found in the case of Cr doping of BiFeO$_3$ or for BiFe$_x$Cr$_{1-x}$O$_3$ powder, and was attributed to Cr-O vibration [19,37]. In our films, as it can be seen in Figure 3, we do not observe such a peak. However, such peak was found previously in different species of chromium oxides species [38–41]. The presence of this peak in the studies [18,19] may indicate that, in those cases, BiFe$_x$Cr$_{1-x}$O$_3$ were not a pure phase and maybe contained species of chromium oxides.

In order to shed light on the origin of the 670 cm$^{-1}$ peak, we measured Raman spectra of bulk BiFe$_x$Cr$_{1-x}$O$_3$ ($x = 0.3, 0.4, 0.6, 0.7$) polycrystalline samples. The spectra measured with 633 nm excitation are shown in Figure 4 together with the difference spectra of the 200 nm BiFe$_0.5$Cr$_0.5$O$_3$ film, and of the parent compounds BiFeO$_3$ and BiCrO$_3$. As can be seen, a peak at 660–670 cm$^{-1}$ is present in all the spectra of Fe-Cr containing systems and absent for BiFeO$_3$ and BiCrO$_3$. On the other hand, no peak is measured between 800 and 900 cm$^{-1}$, which indicates the absence of secondary chromium oxides phases in our thin films and bulk samples.

Figure 4. The difference spectrum of the BiFe$_{0.5}$Cr$_{0.5}$O$_3$ thin film compared to the spectra of bulk BiFe$_x$Cr$_{1-x}$O$_3$, and of the parent compounds BiCrO$_3$ and BiFeO$_3$ measured with 633 nm excitation. Note the strong peak at 660–670 cm$^{-1}$ which is detected only for the samples with a Fe/Cr mixture.

For $x = 0.7, 0.6,$ and $0.5$ the Raman spectra are resembling more to those of BiFeO$_3$, indicating the expected $R\bar{3}c$ space group. On the other hand, for $x = 0.3$ and $0.4$ the spectra are more BiCrO$_3$-like (C2/c space group) [25]. The relative intensity of the 660–670 cm$^{-1}$ mode in respect to the polar mode ($A_{1LO}-E_{LO}$) at 172 cm$^{-1}$ (BiFeO$_3$-like) [36] or to the $A_g$ mode at 185 cm$^{-1}$ (BiCrO$_3$-like) [42] is strongest for the highest Fe-Cr mixture ($x = 0.4, 0.5,$ and $0.6$). This fact corroborated to the absence of the peak in the case of BiFeO$_3$ and BiCrO$_3$ indicate that the origin of the peak is related to the simultaneous presence of Fe and Cr in the structure. A very similar peak, at similar positions, has been measured also
for other perovskite systems with Fe/Cr intermixing. For example, for HoFe$_{1-x}$Cr$_x$O$_3$ a peak at 670 cm$^{-1}$ was attributed to oxygen breathing mode ($A_g$-like) and was found to be activated due to the charge transfer between Fe$^{3+}$ and Cr$^{3+}$ ions (mediated by O$^{2-}$) playing a role in electron–phonon coupling [31]. As for our system, the mode was absent or having a very low intensity for the stoichiometry with only Fe or only Cr. Fe-Cr charge transfer effects activated a similar oxygen vibration mode related to the octahedron breathing in the case of LaFe$_{0.5}$Cr$_{0.5}$O$_3$ [30] or LaFe$_x$Cr$_{1-x}$O$_3$ systems [29,43] where the mode again vanished in the case of the parent compounds. All these aspects also indicate that in the case of BiFe$_{1-x}$Cr$_x$O$_3$ the 670 cm$^{-1}$ mode is an oxygen-related mode activated by the charge transfer between the Fe and Cr ion, mediated by the excitation light and is strongest when the energy of the incident photons is close to the first absorption peak at 2.27 eV (corresponding to charge transfer excitation between Cr and Fe). This was observed in case of our BiFe$_{0.3}$Cr$_{0.7}$O$_3$ films, where the intensity of the 670 cm$^{-1}$ peak was higher for 633 nm and 532 nm than for 442 nm excitation. Raman spectra for the BiFe$_{0.3}$Cr$_{0.7}$O$_3$ polycrystalline sample measured with the same excitation lines are shown in Figure 5. Additionally, in this case the strongest peak at 667 cm$^{-1}$ is measured when exciting with 633 nm and 532 nm. Moreover, the second order of this peak at 1325 cm$^{-1}$ and even the third order at ~1995 cm$^{-1}$ are observable for these two excitations (the third order peak for 532 nm is not shown due to the coincidence with some CCD artefacts), while for 442 nm even the first order is very low in intensity. A very similar behaviour was also observed for the other stoichiometries of the polycrystalline BiFe$_x$Cr$_{1-x}$O$_3$ samples.

The multiple-order Raman scattering and the resonance effects were explained in the frame of the Franck–Condon type mechanism for rare-earth manganite systems [44–46]. The same Franck–Condon picture was also used to explain the Fe-Cr charge transfer which resonantly activates the oxygen breathing mode and its higher-orders. [31,43].

The temperature dependent Raman spectra of BiFe$_{0.3}$Cr$_{0.7}$O$_3$ polycrystalline sample in the 90–700 K temperature range are shown in Figure 6. With increasing the temperature up to 450 K the Raman peaks below 600 cm$^{-1}$ are decreasing in intensity, shifting to lower wavenumbers and become broader, which is a characteristic thermal behaviour related to anharmonicity of the phonon vibrations. However, the position and the broadening of the mode at 670 cm$^{-1}$ are much less affected by the temperature. This fact could be
another indication that the activation of the mode is related to the Fe-Cr charge transfer. Starting with 475 K some new peaks are developing as indicated by the arrows in Figure 6, while peaks corresponding to the lower temperatures (vertical lines) are disappearing. Such a behaviour points to a structural phase transition. The new peaks which develop above 475 K are also present in the spectra measured at 700 K. After subsequent cooling at room temperature the same spectrum as before heating is obtained, indicating that the phase transition is reversible. In the case of BiCrO$_3$, Raman spectroscopy revealed a reversible phase transition from $C2/c$ monoclinic phase to a $pnma$ orthorhombic phase above 400 K [25]. For BiFe$_{0.3}$Cr$_{0.7}$O$_3$ the transition temperature increases. Synchrotron X-ray powder diffraction (SXRD) data indicates a $pbam$ symmetry (PbZrO$_3$-type) at room temperature while at 600 K the structure changes to $pnma$ symmetry of GdFeO$_3$-type (see Figure S2 in Supplementary Materials). The refined lattice parameters obtained from the Rietveld analysis method of the SXRD data by means of RIETAN-2000 program [47], indicate that the phase transition is accompanied by a reduction in the volume of the unit cell by a factor of two.

Figure 6. Temperature dependence (90–700 K) of the Raman spectra for bulk BiFe$_{0.3}$Cr$_{0.7}$O$_3$ showing a reversible phase transition above 475 K.

4. Conclusions

In conclusion, in BiFe$_{0.5}$Cr$_{0.5}$O$_3$ thin films and BiFe$_x$Cr$_{1-x}$O$_3$ bulk appearance of a new Raman mode at ~670 cm$^{-1}$ which is absent in the BiFeO$_3$ and BiCrO$_3$ parent compounds was evidenced by Raman spectroscopy. The mode was attributed to an oxygen (octahedral) breathing vibration which is mediated by the charge transfer between the Fe and Cr ions. This charge transfer corresponds to an optical absorption peak at ~2.27 eV for BiFe$_{0.5}$Cr$_{0.5}$O$_3$ which lowers the bandgap of the material compared to the parent compound as was found by spectroscopic ellipsometry. On the other hand, Franck–Condon mechanism is manifested by a strong dependence of the intensity of the 670 cm$^{-1}$ Raman peak on the excitation wavelength, and resonant activation of its higher scattering orders. For BiFe$_{0.3}$Cr$_{0.7}$O$_3$ Raman spectroscopy revealed a reversible temperature induce structural phase transition.
Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12091607/s1, Figure S1: X-Ray diffraction 2θ-ω scan comprising (001) and (002) peaks of STO substrate and 200 nm BFCO thin film (left panel). Topography scan (5 × 5 μm2) acquired by atomic force microscopy (contact mode) of the same BFCO thin film (right panel); Figure S2: High-temperature synchrotron powder X-ray diffraction measurements of the BiFe0.3Cr0.7O3 sample confirmed the existence of a reversible high-temperature structural phase transition from the PbZrO3-type structure (at room temperature) to the GdFeO3-type structure (at 600 K) [47,48].

Author Contributions: C.H. proposed the study, performed, and analysed the ellipsometric measurements and part of the Raman measurements and wrote the manuscript with contributions from all other authors; E.D. performed and analysed the Raman measurements; A.B. and D.S.W. grown the thin films; A.A.B. prepared the polycrystalline samples and performed and analysed the X-Ray diffraction measurements; J.K. reviewed the manuscript with ideas on data interpretation. All authors have read and agreed to the published version of the manuscript.

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