

Chromium oxides mixtures in PLD films investigated by Raman spectroscopy

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The composition of Pulsed Laser Deposited thin films from Cr₈O₂₁ targets has been investigated by Raman spectroscopy. To this purpose we have prepared the chromium oxides Cr₈O₂₁, Cr₂O₅, CrO₂ and Cr₂O₃ in bulk form to provide standard Raman spectra for characterisation of the samples. The range of oxides has been prepared by thermal decomposition of CrO₃ following the thermo-gravimetric analysis. CrO₂ was obtained by two other specific ways, i.e. hot pressing of Cr₈O₂₁ and hydrothermal synthesis. Structural characterization was performed by X-ray diffraction, SEM, IR and Raman spectroscopy. Raman investigation is demonstrated to have the capacity to identify CrO₂ as well as trace concentrations of secondary phases in the PLD thin films. The Raman measurements have led us also to the conclusion that PLD of Cr₈O₂₁ targets yields in thin films containing either mixtures of (Cr₂O₅, CrO₂ and Cr₂O₃) or, under particular conditions of oxygen pressure and substrate temperature, of (CrO₂ and Cr₂O₃) only.

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1. Introduction

As a new trend for a better use of the electron (both the charge and the spin), “spintronics” is evolving along with specific material systems such as the half metals (HM) [1, 2]. The most popular HM systems to date can be divided into two major groups: a) the half- and full-Heusler alloys [2] and b) various ferromagnetic oxides [3], with CrO₂ predicted to be one of the most promising, showing fully spin polarized conductivity even at ambient temperature [4]. However, chromium forms many competing sub-oxides from which chromium dioxide is metastable [5] at atmospheric pressure, decomposing into Cr₂O₃ when heated [6,7]. Therefore, it is necessary to find reliable characterisation protocols for these films, capable of establishing the presence of even trace densities of secondary Cr oxide phases. In this paper we examine the capacity of Raman spectroscopy to provide such an analysis and specifically apply it to an investigation of pulsed laser deposition of Cr oxide films.

Although thin films of CrO₂ have been successfully prepared by chemical vapour deposition (CVD) [8] or molecular beam epitaxy (MBE) [9-12] the route to film growth by pulsed laser deposition (PLD) is not straightforward, and requires that the starting material is either CrO₃ or Cr₈O₂₁ [12]. We thus review experimental work that we have carried out on the range of chromium

oxides CrO₃ to Cr₂O₃ with the aim to investigate PLD as a potential technique for preparing thin films with a high content of CrO₂. In this investigation we have made several attempts [13, 14] with Cr₈O₂₁ targets, which led to PLD films consisting of mixtures of CrO₂ and other chromium oxides, such as Cr₈O₂₁, Cr₂O₅ and Cr₂O₃. Characterization of both the films and the ablated targets have aimed to identify the components of those mixtures and consequently understand the processes that develop in the Cr_xO_y systems through the pulsed laser action [13]. X-ray diffraction, SEM, IR and Raman spectroscopy have contributed to this effort. XRD can give information about fully crystalline phases with concentrations of over 1%wt., but when samples consist of mixtures with low-concentration or amorphous secondary phases the sensitivity of this technique is inadequate. Raman spectroscopy offers an attractive alternative, which furthermore has the potential to identify characteristic bonding structures even in amorphous material [15]. It can be further enhanced with the use of a range of excitation wavelengths, which alters the balance between majority and secondary spectra.

There are many reports in the literature of Raman [16-21] and IR spectra [21-24], of the various Cr oxides and several reports also of its use in identifying various phases in composite Cr oxide material [25-27]. However, there is insufficient data available on well-characterised single-

phase materials to understand all of the Raman signals we have observed in our PLD films. With the exceptions of CrO_2 and Cr_2O_3 the spectra are still incompletely characterized, in part because the compositions other than Cr_2O_3 are unstable against loss of oxygen [28] and thus difficult to prepare as pure single phase. It has thus been necessary as part of this study to perform measurements on large crystallites within samples of several Cr oxides, and much of this paper is concerned with exactly that background study.

2. Experimental

As outlined above this work concerns both preparation of various materials and their Raman/IR investigation. This section is arranged to describe the preparation of Cr oxides by careful thermal decomposition of CrO_3 (section 2.1) and of CrO_2 by two specific ways (section 2.2). Section 2.3 describes the PLD targets and thin-film growth. The Raman and IR spectroscopy is covered in Section 2.4.

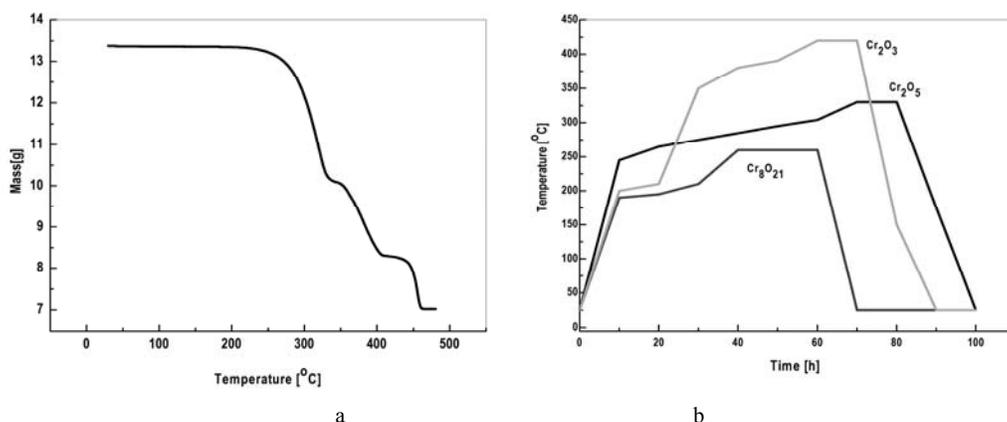


Fig. 1. a) thermo-gravimetric analysis of the controlled thermal decomposition of CrO_3 in air b) thermal regimes used to obtain Cr_2O_3 (a), Cr_2O_5 (b) and Cr_8O_{21} (c) from melted CrO_3 .

2.2 Synthesis of CrO_2

Synthesis of CrO_2 occurred by two specific ways: i) hydrothermal and ii) hot-press;

i) the hydrothermal synthesis of chromium dioxide powders is widely described in literature [29]. The CrO_3 precursors in contact with water (providing both pressure and a reaction environment) produce a partial dissolution of the material forming chromium acid under ambient conditions. This mixture was sealed in a gold container placed in an autoclave under 500 bar external water pressure. The process leading to CrO_2 developed between 430°C and 480°C. We obtained black whisker-like grains, with strong metallic reflections. Small but varying amounts of Cr_2O_3 were found in the final product.

ii) a CrO_2 target has been obtained by annealing powder of Cr_8O_{21} under a pressure of 0.074GPa. The process developed 8h at 245°C. The pellet contained traces of Cr_2O_5 .

2.1 Preparation of Cr_xO_y ($x=2,8;y=3,5,21$) as pure phases

We have prepared polycrystalline samples of the different Cr_xO_y phases starting from CrO_3 (a commercial powder of CrO_3 -ACROS ORGANICS, Chromium (VI) oxide 99.9%, ref: 214100010). These phases were obtained on the basis of the thermo-gravimetric analysis (TGA) of the controlled thermal decomposition of CrO_3 in air (Fig. 1a). Powder of CrO_3 is placed in an alumina crucible set in a furnace and heated in air up to about 180°C. A low heating rate (1°C/h) is employed to achieve the melting of CrO_3 ($T_m = 196^\circ\text{C}$). Then, a second slow variation is performed around the temperature of formation of the chromium oxide phase we are looking for (260°C for Cr_8O_{21} , 330°C for Cr_2O_5 and 420°C for Cr_2O_3) (Fig. 1b). The relative mass losses $\Delta m/m$ starting from CrO_3 correspond to the expected values for Cr_8O_{21} , Cr_2O_3 , and Cr_2O_5 .

We have obtained sheet-like crystals of about 20 μm width.

2.3 PLD targets and corresponding thin films

The detailed preparation of the Cr_8O_{21} PLD targets as well as of the corresponding PLD films are reported elsewhere [13, 14, 30]. Briefly, pellets (about 1.5 mm thick) are prepared in a 13 mm diameter steel die, under a 0.3 GPa pressure during 15 minutes and then annealed 16 hours at $T = 245^\circ\text{C}$. The targets were ablated with a pulsed laser to deposit thin films onto various substrates, such as single-crystalline sapphire and quartz, held at temperatures between 300K and 600K in the different experiments. The PLD runs were performed with an UV KrF*excimer laser ($\tau_{\text{FWHM}} \geq 20\text{ns}$, $\lambda = 248\text{nm}$), with fluences of 1-2 J/cm^2 and under a dynamical pressure of oxygen within the range 1-20 Pa. A total of 64 PLD films have been produced and investigated.

2.4 Raman and infrared measurements

The Raman spectra of crystalline Cr_xO_y powders as well as of the Cr_8O_{21} PLD targets and corresponding films

were taken with a Renishaw RM2000 micro-Raman instrument, in the back-scattering geometry. All measurements have been carried out at room temperature, with a 633 nm laser source, delivering 0.5mW on the sample's surface. Our work showed that a higher incident laser power modifies the surface of the films and possibly the composition too. The calibration was monitored using the silicon signal and peak positions were determined with the conventional Lorentz function provided in GRAMS/32 (Galactic Industries) software. The spectral resolution at the spectrograph is better than 2 cm^{-1} with 50x objective. IR transmission of the bulk samples was measured using a Brücker Equinox 55 spectrometer. The samples were pressed within KBr pellets (99%wt of KBr). The crystalline chromium oxides show IR activity in the range $350\text{--}1100\text{ cm}^{-1}$.

3. Results and discussion

Although the purity of Cr_2O_3 samples was not in doubt and their characterization went smoothly, the tendency of Cr_8O_{21} [30] - to come out mixed with Cr_2O_5 [16, 22] raised a few difficulties in our attempts to produce these materials as pure phases. Nonetheless the XRD patterns (Fig. 2) taken on powders of our crystalline Cr_8O_{21} (47-1312), Cr_2O_5 (36-1329) and Cr_2O_3 (38-1479) samples are in a very good agreement with the standard diffractogrammes. However, XRD on CrO_2 (43 - 1040) hot pressed pellet show clearly the presence of Cr_2O_5 . The IR spectra of our chromium oxides samples shown in the Fig. 3 are in a good agreement with already published data [22-25]. Obviously, if traces of Cr_2O_3 had occurred in the samples, they would have shown up in the IR spectra. It is significant that the Cr_2O_5 from this work shows no trace of Cr_8O_{21} in comparison with previously reported data [16].

This may be due mainly to the fact that our samples are large enough platelet-like crystallites (see SEM images

in Fig. 4) while the ones reported in ref. [16] were ceramic pellets where phases intergrowth had most likely occurred.

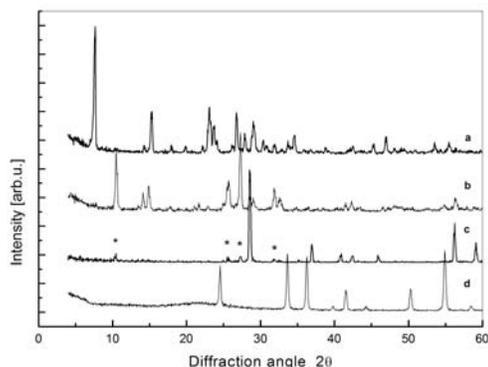


Fig. 2. XRD patterns of powder samples from crystalline: a) Cr_8O_{21} , b) Cr_2O_5 , c) CrO_2 and d) Cr_2O_3 . The symbol * in the spectrum c) signifies Cr_2O_5 .

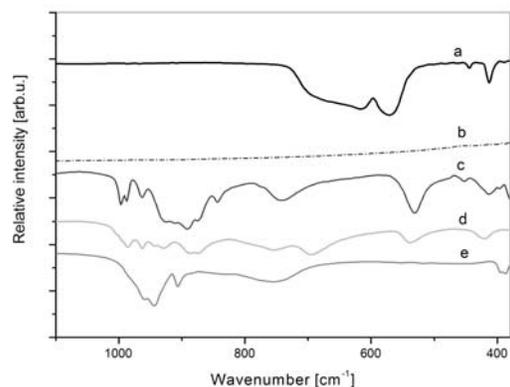


Fig. 3. The IR spectra of the chromium oxides samples: a) Cr_2O_3 , b) CrO_2 , c) Cr_2O_5 , d) Cr_8O_{21} , e) CrO_3

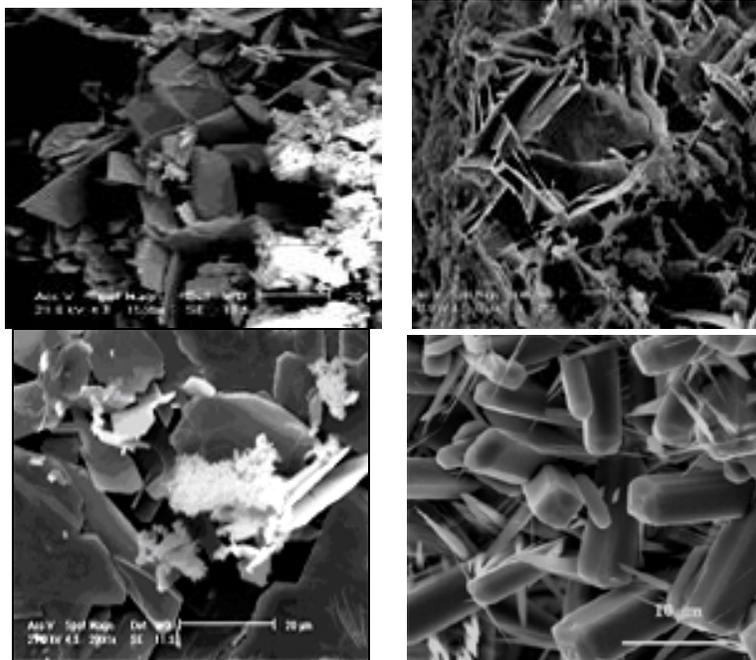


Fig. 4. SEM images of platelet-like crystallites a) Cr_8O_{21} , b) Cr_2O_5 , c) CrO_2 , d) Cr_2O_3

CrO_2 has been predicted to have 4 IR active modes [33], and Iliev [17] cites unpublished results of optical conductivity measurements in the IR range showing 3 peaks. However, IR transmission measurements on our CrO_2 samples show no evidence of those modes, being in agreement with earlier publications [24]. A possible explanation of this result may be that the high absorbance of CrO_2 dominates the spectrum, masking features from the other chromium oxides. Therefore, it is impossible to see contributions from secondary phases in the IR spectra of this compound. In all of these materials the secondary phase content is small, but it is essential that its influence on the Raman or IR spectra be monitored. It is particularly important to monitor the presence of any features that might result from a small density of Cr_2O_3 crystallites or intergrowths, for this is the most stable of all Cr oxides, and it is known to form in any case when these materials are exposed to air for an extended period [33].

The Raman spectra of the crystalline Cr_8O_{21} , Cr_2O_5 and Cr_2O_3 are displayed in Fig.5 (a, b, and c) and the main peak frequencies resulted from curve fitting are listed in the table I. Their strongest features are consistent with data published earlier [16,19, 27]. In view of the potential for Cr_2O_3 intergrowths in any of these materials we choose to discuss first the data from that sample. These are

Table 1. Main Raman frequencies resulted from curve fitting.

Cr_2O_3 Raman freq. [cm^{-1}]	Cr_2O_5 Raman freq. [cm^{-1}]	Cr_8O_{21} Raman freq. [cm^{-1}]
305, 348, 397, 524, 550, 610, 826	188, 214, 253, 269, 312, 327, 353, 387, 421, 446, 477, 629, 741, 838, 865, 880, 996	246, 308, 344, 368, 397, 487, 549, 732, 878, 899, 1001

Neither the 397 [20], nor the 826 cm^{-1} lines seem to be issued from the Cr_2O_3 structure. Whereas the 397 cm^{-1} feature is presumed to be responsible for the one-magnon scattering [20], 826 has yet to be assigned [27]). However, it is the pair of strong doublets that will signal the presence of Cr_2O_3 in any multiphase film. Turning next to the Raman features exhibited by Cr_8O_{21} and Cr_2O_5 there are strongly dominant lines at 899 cm^{-1} and 880 cm^{-1} respectively, corresponding satisfactorily to the 904 cm^{-1} and 884 cm^{-1} in the work [16]. There are in addition weaker lines spread across the spectra, such as those in the 400-500 cm^{-1} range, that again correspond with earlier data in reference [16], and in agreement with that report these are seen at nearly two orders of magnitude lower level than the dominant lines near 900 cm^{-1} . Cr^{III} oxides ($\text{Cr}^{\text{III}}\text{-O}_6$) exhibit peaks in the range 303-609 cm^{-1} [19], which again agree with the values of the Raman and IR wavenumbers (see Fig. 3) we have obtained for our samples. Thus it is clear that these phases should be associated with strong lines at 900 cm^{-1} (Cr_8O_{21}) and 880 cm^{-1} (Cr_2O_5) at least under 633 nm excitation.

All Raman spectra of CrO_2 given in literature were taken on epitaxial films [18] to our knowledge. The main Raman modes of CrO_2 (458 and 570 cm^{-1}) [17] are present

particularly clear, with the phase identified by strong doublets at 550/610 cm^{-1} and 305/348 cm^{-1} . In addition these show weaker satellites at 524 and 397 cm^{-1} and a weak line at 826 cm^{-1} .

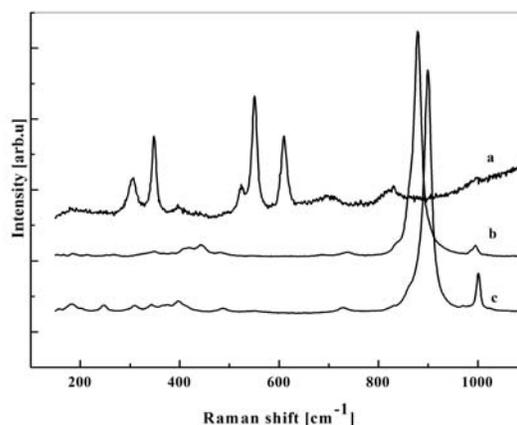


Fig. 5. Raman spectra of a) Cr_2O_3 , b) Cr_2O_5 , c) Cr_8O_{21} single phase samples.

in the spectra of the two CrO_2 samples (hot-pressed pellet and whiskers from hydrothermal synthesis), which are compared in the Fig.6.

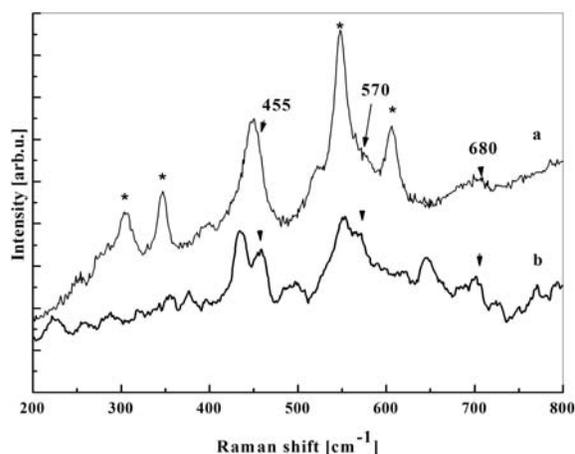


Fig. 6. Raman spectra of CrO_2 . The main Raman modes of CrO_2 (458 and 570 cm^{-1}) are present in the spectra of: a) hot-pressed pellet and b) whiskers from hydrothermal synthesis. The symbol * corresponds to Cr_2O_3 .

However, the Raman spectrum of the hydrothermally produced powders shows some additional peaks, which correspond to Cr_2O_3 . The explanation is straightforward through the preparation process (see section 2.2.) on one hand, and through the loss of oxygen from the powders in contact with atmospheric air, on the other hand.

This second reason can also explain the observation of Cr_2O_3 peaks in the Raman spectrum of the hot-pressed pellet. Raman scattering is a most surface sensitive technique in comparison with XRD and IR measurements.

Before attempting to interpret the Raman spectra taken on PLD films it is important to discuss the influence that a disordered or nanocrystalline structure might have on the spectra. Firstly small crystals of diameter d permit the Raman activity of non-zone-centre modes, out to wave vectors of about π/d . That will lead to both broadening of the lines and either up or down shifts, depending on the sense of the phonon dispersion [28]. In the absence of any vibration mode calculations it is impossible to predict in which sense the shift will occur, but it can be expected that the magnitudes of broadening and shifts will be similar. In addition there can be expected to be defect lines originating from intergrain regions or even within strongly defected crystals. One obvious source is the $\text{Cr}^{\text{VI}}\text{-O}$ terminating structures that occur also in some of the ordered oxides and lead to the strong lines in the 800-1000 cm^{-1} region [16].

Armed with Cr_xO_y spectra as described above we have attempted interpretations of the Raman measurements of PLD films (Fig. 7) deposited from Cr_8O_{21} targets onto sapphire substrates held at T_s 300 (a), 450 (b) and 600K(c).

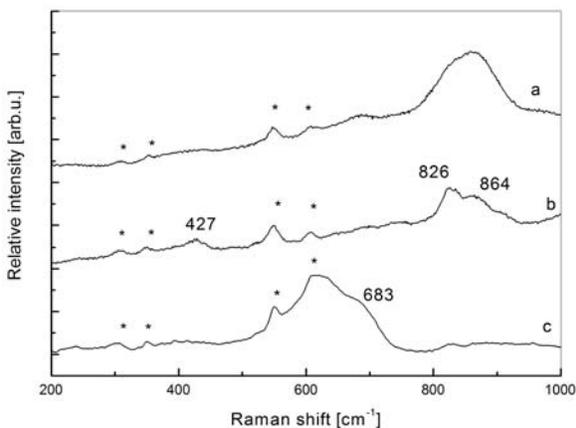


Fig. 7. Raman spectra of PLD thin films deposited at $T_s = 300\text{K}$ (a), 450K , (b) and 600K , (c) The * correspond to Cr_2O_3 .

It is seen immediately that all three spectra have the pair of doublets associated with Cr_2O_3 , so the films all contain a low concentration of that phase. It is notable that none of the PLD spectra shows any weight at 900 cm^{-1} suggesting that there is no measurable level of Cr_8O_{21} in the films. It is likely that the line at 864 cm^{-1} , which does indeed carry substantial weight at 880 cm^{-1} , signals the presence of nanocrystalline Cr_2O_3 , but its partner at 826

cm^{-1} is not identifiable as originating from any of the phases we have prepared in bulk. We speculate that it is associated with terminating $\text{Cr}^{\text{VI}}\text{-O}$ structures mentioned by Maslar [27], in intergrain regions. It is interesting to note that it appears also as a minor peak in our spectra from bulk Cr_2O_3 samples, but the feature in these PLD films is much too strong in relation to the pair of doublets to assign it to that phase. Thus, the two films grown at the corresponding substrate temperatures of 300K and 450K are mixtures of Cr_2O_5 and Cr_2O_3 .

The 600 K film consists of a mixture of CrO_2 and Cr_2O_3 , with CrO_2 leading to the prominence of the B_{2g} mode at 682 cm^{-1} and the large broad feature lying across 580-150 cm^{-1} [17, 28]. The CrO_2 in the film is in high concentration but clearly nanocrystalline [28], as signaled by the fact that these lines are prominent but much broader than in single crystals. The second compound in the film is Cr_2O_3 , probably at a small concentration but well crystallised once it is only this one coming out in the XRD spectrum [13]. Magnetic measurements confirmed CrO_2 in this film.

4. Conclusions

The nearly single phase Cr_8O_{21} , Cr_2O_5 , CrO_2 and Cr_2O_3 have been prepared in bulk form and used as standard samples to establish the Raman spectra to be expected from various phases within Cr_xO_y PLD films. Clear Raman signatures of the various oxides have been identified and used to investigate the phases present in PLD films. From the point of view of PLD, the laser interaction with the Cr_8O_{21} targets seems to produce the lower chromium oxides (see Fig. 1a), which are then deposited or even formed on the substrate under the specific conditions of the PLD run, such as oxygen pressure, substrate temperature, fluence. Raman spectroscopy and its sensitivity to some minority phases have been demonstrated as particularly useful as an aid to characterisation of PLD films. However, a particular difficulty can arise when the material being sought in a mixture is a reasonable conductor (CrO_2) and the other phases are insulators (Cr_2O_3 , for example), as it is the case in our PLD films.

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