Chapter 6

TbMnO$_3$ films grown on SrRuO$_3$-buffered (001)-DyScO$_3$ substrates

6.1 Abstract

In this chapter, we present the structure and properties of TbMnO$_3$ perovskite thin films on single crystals of (001)-oriented DyScO$_3$. (001)-DyScO$_3$ was chosen because it has the same space group and similar lattice parameters as TbMnO$_3$, it is commercially available and it can be prepared to have atomically flat surfaces. Because this substrate’s orientation has been used in this thesis for the first time, we dedicate a section to explain the treatment procedure to lead to atomically-flat surfaces. The TbMnO$_3$ films were grown with a buffer layer of SrRuO$_3$ in order to perform the dielectric characterization of the films. By using different growth conditions and thicknesses of the buffer layer, the relaxation of SrRuO$_3$ could not be prevented, and the TbMnO$_3$ films were found to be under compressive strain determined by the SrRuO$_3$ layer. Under these conditions, epitaxial TbMnO$_3$ films were successfully deposited with the (001)-orientation with different buffer layers grown under different conditions and with different morphology. Unlike for the growth on SrTiO$_3$ substrates, the films follow a typical strain relaxation characterized by the gradual evolution of the out-of-plane lattice parameter toward the bulk value. The dielectric characterization of the films shows no clear influence of the relaxation mechanisms associated to the domain walls that were so prevalent in the case of the films grown on SrTiO$_3$ sub-
6.2 Introduction

The structure and properties of orthorhombic TbMnO$_3$ films grown on SrTiO$_3$ were studied in the previous chapters. We have found that the orthorhombicity of the TbMnO$_3$ films can be tuned by changing the thickness of the layers. The films contain four domain variants with the same out-of-plane (001)-orientation. The strain relaxes suddenly at a thickness that depends on the oxygen pressure during deposition. The films show predominant antiferromagnetic interactions, but a net magnetic moment arises below the antiferromagnetic transition temperature, which is observed as a split between the field-cooled (FC) and zero-field-cooled (ZFC) magnetization versus temperature curves. Other recent works in antiferromagnetic manganite thin films have also reported ZFC-FC splitting in the magnetization curves, but the origin is still unknown. Motivated by the possibility of a general mechanism for the observed ferromagnetism in antiferromagnetic thin films, we have dedicated considerable effort to elucidate the origin of the ferromagnetism in our TbMnO$_3$ films.

In bulk samples, there is an anomaly in the dielectric constant related to the onset of ferroelectricity, which is in turn related to the transition from the sinusoidal to the spiral spin state. In the fully strained TbMnO$_3$ films grown on SrTiO$_3$, no anomaly in the dielectric constant was found. This points to the disappearance of the macroscopic ferroelectric order and the long range spiral ordering, and may be explained by the small size of the crystallographic domains present in the films. Since we have observed a change in the slope of the temperature dependence of the relaxation time at the bulk ferroelectric temperature, $T_C \approx 27$K, we postulate that short-range order, with similar local structure to the one of the bulk structure, is present.

Despite the interest of the previously studied films, it would also be desirable to obtain domain-free films with macroscopic properties resembling those of multiferroic
TbMnO$_3$ single crystals. Thus, in order to have a better control on the orthorhombic structure of TbMnO$_3$, and to investigate its intrinsic properties, a different substrate was chosen: Orthorhombic (001)-oriented DyScO$_3$. This material has been recently synthesized in single crystal form and its (110)-orientation has already been used for thin film growth of ferroelectric materials because it provides a pseudo-cubic lattice with lattice parameter of 3.95 Å. In our case, the motivation for choosing (001)-DyScO$_3$, among all commercially available substrates, is different and three-fold: First, the lattice parameters of DyScO$_3$ are close to those of TbMnO$_3$, as shown in figure 6.1 (a)-(b); second, because film and substrate are both orthorhombic, the presence of crystallographic domains is not foreseen; and third, atomically flat surfaces with terrace-step morphology can also be obtained, as in the case of SrTiO$_3$, leading to a high quality interface and a better control of the growth. This makes the (001)-oriented DyScO$_3$ a very interesting substrate for epitaxial stabilization of TbMnO$_3$ and a promising candidate for the manipulation of the spiral state of TbMnO$_3$.

From the lattice parameters of both DyScO$_3$ and TbMnO$_3$, the mismatch strain along the [100]$_o$ direction, given by $u_m = (a_{\text{substrate}} - a_{\text{bulk}})/a_{\text{substrate}}$, is around 2.9%, compared to 4% along the same direction, [110]$_c$, of SrTiO$_3$. The mismatch in the [010]$_o$ direction is -1.9% in the case of TbMnO$_3$ on DyScO$_3$, compared to -5.7% in the case of TbMnO$_3$ on SrTiO$_3$. This means that in both cases, the a-direction of TbMnO$_3$ is under tensile strain whereas the b-direction of TbMnO$_3$ is under compressive strain, although the epitaxial strain is substantially smaller in the case of DyScO$_3$ substrates. Looking at the overall epitaxial strain, TbMnO$_3$ should be under overall tensile strain on DyScO$_3$ and under overall compressive strain on SrTiO$_3$.

In this final chapter, we will describe the first attempts to growth TbMnO$_3$ films on (001)-DyScO$_3$. We will describe the growth and the structure of the films and their dielectric behavior. Although sample optimization is still needed, the results show that the microstructure of the film and the associated properties, which highly determine the dielectric relaxation processes, can be controlled to a very high extent by the choice of substrate.
6.3 Growth and structural characterization

6.3.1 Substrate treatment

There are, as far as we know, no previous reports using this orientation of DyScO$_3$ substrates for thin film deposition. Therefore, we will report the substrate treatment in detail.

The (001)-oriented DyScO$_3$ substrates were provided by CrysTec GmbH (Berlin, Germany). Prior to deposition, they were thermally treated after cleaning with acetone and ethanol. The optimized thermal treatment consisted of heating the substrates to 1020°C with a rate of around 20°C/min for 12.5h under and oxygen flow of around 300mm$^3$/min. The duration of the thermal treatment is a crucial parameter. Figure 6.2 shows AFM images of 3 different DyScO$_3$ substrates which were heated during 11h.

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**Figure 6.1:** Sketch of one unit cell of DyScO$_3$, TbMnO$_3$, and SrRuO$_3$ (a), along with their lattice parameters and atomic positions.
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Figure 6.2: AFM images of (001)-oriented DyScO$_3$ substrates treated for 11h (a), 12h (b) and 12.5h (c). In order to better appreciate the morphology, a 3D view of the measured AFM images, using the WSXM software [155], is presented. The 2D images corresponding to a) and c) are shown in figures 6.3(a) and (b), respectively.

(a), 12h (b) and 12.5h (c). Figure 6.2 (a) shows terraces with a specific pattern: only one step out of two shows a straight edge. However, substrates treated during 12h and 12.5h show straight steps. A more careful look reveals that the steps for the substrates treated for 12.5h are more regularly spaced than the steps of the substrates treated for 12h.

By taking a line profile, as shown in figure 6.3 (c), it becomes clear that the substrate showing the irregular terraces (a), has alternating steps of $\sim 4\AA$ and $\sim 8\AA$, corresponding to a half unit cell and a full unit cell of DyScO$_3$, respectively. However, for the substrate treated for 12.5h and showing terraces with parallel edges (figure 6.3 (b) and (d)), only steps of 1/2 unit cell are observed. This shows that, indeed, the (0 0 1) and (0 0 2) planes of DyScO$_3$ are not structurally identical and that diffusion is somewhat easier for one of them. However, because the two planes have the same chemical composition (they correspond to the (0 0 1) planes of a simple perovskite unit cell), a longer thermal treatment is likely to provide steps having equally a height of one unit cell.

It is important to note that this optimized time is only valid for DyScO$_3$ substrates having a similar miscut to the one used in this thesis ($\sim 0.1^\circ$), which corresponds to a terrace length of about 200nm. The effect of the miscut on the heat treatment of the
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Figure 6.3: (a) AFM image of a (001)-oriented DyScO₃ substrate treated for 11h. (b) Profile along a line taken perpendicular to the steps of (a). (c) AFM image of a (001)-oriented DyScO₃ substrate treated for 12.5h. (d) Profile along a line taken perpendicular to the steps of (b).

substrate is not the scope of this thesis and will not be discussed here.

6.3.2 Growth conditions

In this section, the growth of TbMnO₃ films on (001)-oriented DyScO₃ substrates will be shortly described. Prior to the deposition of TbMnO₃, a buffer layer of SrRuO₃ was grown to be used as a bottom electrode for the dielectric characterization. The SrRuO₃ thin films were grown at two different temperatures, 600°C and 700°C, under an oxygen pressure of 0.13mbar. The frequency of the laser pulses was set to 1Hz with a laser energy density at the target of 2Jcm⁻² per pulse. The distance between target and substrate was 58mm. TbMnO₃ was subsequently deposited under the same conditions as those used for the films on SrTiO₃: At a temperature of 750°C, under an oxygen pressure of 0.9mbar, with a laser frequency and energy density of 1 Hz and 2J.cm⁻², respectively, and a target-substrate distance of 55mm. The deposition was stopped after one hour of growth, aiming to a TbMnO₃ film thickness of ~40nm, estimated from the growth rate of the samples on SrTiO₃. After the growth of TbMnO₃, 100mbar of oxygen was inserted in the deposition chamber and the sample was then cooled.
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down to room temperature at a rate of $3^\circ \text{C}. \text{min}^{-1}$.

6.3.3 SrRuO$_3$ growth

Figure 6.4 (a) shows the RHEED image of a (001)-oriented DyScO$_3$ substrate, showing the excellent quality of the surface of the substrate. By using a deposition temperature of 700°C, atomically flat SrRuO$_3$ with a thickness of around 6nm was deposited, as shown in figure 6.4(b), where the RHEED pattern exactly resembles that of the substrate, indicating that 2D growth takes place at this temperature. This thickness of 6 nm is thick enough to be above the metal-insulator transition observed for SrRuO$_3$ films of about 6 monolayers (slightly thinner than 5nm) and thin enough to display a decreased magnetic moment, which saturates at 15 monolayers (around 11nm) [156].

For a growth temperature of 600°C, the growth of SrRuO$_3$ on (001)-oriented DyScO$_3$ is similar to that reported for the growth of SrRuO$_3$ on (111)-SrTiO$_3$ [157]: The initial stage of growth is 3D (island-like) and the films flatten after a certain thickness of the SrRuO$_3$ layer of about 30 nm. Under these growth conditions, the deposition was stopped at the beginning of the 3D-to-2D transition, in order to have a SrRuO$_3$ layer as thin as possible. The deposition was stopped after a time estimated to give a thickness of around 30nm. After the growth of such layer, the RHEED pattern consists of a mixed pattern of weak streaks at the positions of the substrate spots, indicating a 2D morphology with certain disorder, along with extra spots, characteristics of 3D islands, as shown in figure 6.4 (c).

The growth of TbMnO$_3$ at an oxygen pressure of 0.9mbar after the SrRuO$_3$ growth cannot be followed by RHEED due to a very low signal-to-noise ratio, but the effect of the electrode layer on the morphology of the TbMnO$_3$ films will be discussed in the next section.
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Figure 6.4: RHEED images of a treated (001)-oriented DyScO$_3$ substrate before deposition (a), after the deposition of SrRuO$_3$ with an initial 2D growth (b), and after the deposition of SrRuO$_3$ with an initial 3D growth (c).

6.3.4 Morphology and structure of the films

Figure 6.5 (a) shows an AFM image for the sample grown on a 6nm 2D SrRuO$_3$ layer. The image shows deep ridges between groups of columns or grains. This could be a consequence of the morphology of the underlying SrRuO$_3$, which most likely has a mound-like (or wedding-cake-like) morphology [158]. The total RMS roughness of the image in 6.5(a) is 3.5nm, but the roughness of an area without ridges is $\sim$1nm, close to 1 unit cell. Figures 6.5 (b) and (c) show the profiles along a line that does not cross a ridge and a line that crosses a ridge, respectively. Figure 6.5 (c) shows that the ridges can be as wide as 100nm at the surface. However, the ridge depth is not comparable to the thickness of the film, so the ridges do not seem to reach the SrRuO$_3$ layer, which would create a conduction path. As displayed in figure 6.5(d)-(e), the sample in which the SrRuO$_3$ electrode is thicker and had an initial 3D growth (from now on called 3D SrRuO$_3$) shows a more uniform morphology at the surface but still a high RMS roughness of 3.9nm.

The lattice parameters of a bulk SrRuO$_3$ are shown in figure 6.1. The mismatch strain with the substrates along [100] is 1.5% compressive, while along [010] it is 3.3% tensile. It is reasonable to assume that the 30nm 3D-SrRuO$_3$ layers are completely relaxed. On such template, the TbMnO$_3$ films would grow under compressive strain (see figure 6.1) and the out-of-plane lattice parameter of a fully strained TbMnO$_3$ film is estimated to be around 7.44Å (simply using volume conservation considerations). This value agrees very well with the one we find for a 10nm thin film of TbMnO$_3$ grown
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Figure 6.5: (a) AFM image of the TbMnO$_3$ sample with a 6nm buffer layer of SrRuO$_3$. (b) Profile along a line in (a) that does not cross a ridge. (c) Profile along a line in (a) that crosses a ridge. (d) AFM image of the TbMnO$_3$ sample with a 30nm buffer SrRuO$_3$ layer. (e) Profile along a line randomly chosen in (d).

on the 30nm 3D-SrRuO$_3$ layer, as shown by the (002) diffraction peaks of figure 6.6. A 40nm thick film grown on a similar SrRuO$_3$ layer is also plotted in the same graph. The slightly smaller lattice parameter of the 40nm film (c = 7.42 Å) indicates that strain relaxation of the film has began at this thickness and that, indeed, the strain is compressive. In order to confirm this, a reciprocal space map around the (116) reflection of DyScO$_3$ is shown in figure 6.7. It is evidenced that the 40nm film is not fully coherent with the substrate since they do not share the parallel component of the scattering vector ($K_{par}$), confirming the relaxing character of this TbMnO$_3$ layer.

Thus, our results are consistent with the TbMnO$_3$ films growing compressively strained on a relaxed SrRuO$_3$ layer. In order to confirm this possibility, reciprocal space mapping was used to detect the SrRuO$_3$ layer, which is difficult to observe in the $2\theta$-$\omega$ scans due to its proximity with the substrate peak. A reciprocal space map around the (002) of DyScO$_3$ is shown in figure 6.8 for a 40nm TbMnO$_3$ film grown on a 30nm 3D-SrRuO$_3$ layer. The peak associated with the SrRuO$_3$ layer can now clearly be seen thanks to
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**Figure 6.6:** X-ray diffraction $2\theta$-$\omega$ scans around the (002) reflections of a 10nm (a) and a 40nm (b) $\text{TbMnO}_3$ film. Both films were grown with a 30nm $\text{SrRuO}_3$ layer that initially grew in 3D mode and flattened during the growth.

**Figure 6.7:** Reciprocal space map taken around the (116) Bragg peak of $\text{DyScO}_3$. The film’s peak corresponds to the peak at larger $K_{\text{perp}}$ in the map, whereas the substrate’s peak corresponds to the spot at smaller $K_{\text{perp}}$. The $\text{SrRuO}_3$ peak is too weak to be observed in this map. From its position, an out-of-plane lattice parameter of around 7.84 Å was found, consistent with a relaxed $\text{SrRuO}_3$ layer at this thickness.

X-ray diffraction $2\theta$-$\omega$ scans around the (002) and (004) reflections are shown in figure 6.9 for the $\text{TbMnO}_3$ film grown with a thin 2D $\text{SrRuO}_3$ buffer layer. Although the quality of the patterns is not as good as those of the samples grown on $\text{SrTiO}_3$ (and without buffer layer) in chapter 3, Laue fringes are also present, indicating relatively good interfaces, better than those of the samples grown with 3D $\text{SrRuO}_3$ layers, as
expected. The thickness of the TbMnO$_3$ film could be measured from the oscillations of the reflectivity curve (not shown here), and it was found to be 40nm, as expected from the growth time.

From the fit of the (002) reflection shown in 6.9(a), the substrate and the SrRuO$_3$ could be well matched (see black stars) but the fit deviates from the data on the right-hand side of the TbMnO$_3$ peak. This is probably due to some strain relaxation, not taken into account in the model. An out-of-plane lattice parameter of $\sim 7.42\AA$ was used for fitting the position of the TbMnO$_3$ peak. This value is not consistent with the smaller out-of-plane lattice parameter, compared with the bulk $\sim 7.40\AA$, expected for a film under overall tensile strain, but it is the same value found for a film of the same
thickness (40nm) grown on the 3D-SrRuO$_3$ buffer layer, as previously discussed. We therefore postulate that, unexpectedly, the 2D SrRuO$_3$ buffer layer is relaxed already at this very low thickness of 6nm.

Thus, although we have successfully stabilized TbMnO$_3$ on SrRuO$_3$ buffered (001)-oriented DyScO$_3$, we believe that the electrode layer does not grow coherent with the substrate and, therefore, the epitaxial strain could not be transferred from the substrate to the TbMnO$_3$ film, even in the films with a very thin and flat electrode layer.

### 6.4 Physical properties

#### 6.4.1 Magnetic behaviour

The paramagnetic contribution of the DyScO$_3$ substrate dominates the signal and clear magnetic information cannot be obtained from the films. However, the inverse susceptibility of the ZFC curve seems to indicate different magnetic transitions reflected by the change of slope. The measure of the magnetic moment, under zero-field-cooled conditions, for a 40nm TbMnO$_3$ film grown on a 30nm SrRuO$_3$ (with an initial 3D growth) is shown in figure 6.10.

Looking at the low temperature region, as shown in figure 6.10, the data does not seem to depart from this linear behavior for this range of temperatures. This reflects the possible absence of magnetic transition (or too weak to be observed) in the film or the possibility that the transition has been shifted to higher temperatures. As shown in the inset of figure 6.10, where the inverse susceptibility for the full range of temperatures, from 5K to 300K, is shown for a 40nm thick film grown on a 3D SrRuO$_3$ layer, a change of slope of the inverse susceptibility ($\chi^{-1}$ ) with respect to the high temperature linear fit can be seen for a temperature around 150K. This seems to indicate the onset of the ferromagnetic transition of SrRuO$_3$, which occurs at 150K with a magnetic moment of $\sim 1.5\mu_B$/Ru atom [159, 160]. However, the inverse susceptibility should evolve below the paramagnetic line, in the case of a ferromagnetic transition, instead
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Figure 6.10: Inverse magnetic susceptibility as a function of temperature, ranging from 5K to 70K, for a 40nm TbMnO$_3$ thin film grown on a DyScO$_3$ substrate buffered with a SrRuO$_3$ layer initially grown in 3D mode. The line is a guide to the eyes. The inset shows the full range of temperatures from 5K to 300K. The line shows a linear fit to the data in the high temperature range.

of above the paramagnetic line, as observed in the inset. This suggests that the transition observed is antiferromagnetic-like and might be associated with the manganese ordering of TbMnO$_3$. However, the Curie-Weiss fit gives a positive Curie-Weiss temperature, suggesting dominant ferromagnetic interactions. Further experiments are required to clarify these observations.

6.4.2 Dielectric behaviour

The dielectric behaviour of the 40nm films grown on DyScO$_3$ with buffer layers of SrRuO$_3$ has been characterized. Figure 6.11 shows the frequency dependence of the capacitance for both 40nm thin samples grown with a 3D SrRuO$_3$ layer (a) and a 2D-SrRuO$_3$ layer (b), at different temperatures. The behavior is very different in both cases: A temperature-dependent dielectric relaxation, in the range of frequencies from $10^2$-$10^5$ Hz occurs in the sample grown on 3D SrRuO$_3$, whereas a relaxation at lower frequencies about 10-100 Hz, which is independent of temperature, occurs in the film...
grown on a 2D SrRuO$_3$ layer. Moreover, the film grown on 2D SrRuO$_3$ shows a very large low-frequency capacitance. This could be explained by an interface contribution at the sample ridges.

As explained in the previous chapter for the films on Nb-SrTiO$_3$, according to the universal dielectric response (UDR), localized charge carrier hopping not only contributes to the conductivity but also to the polarizability [152]. According to that model,
the real part of the dielectric constant can be calculated as 
\[ \varepsilon' = \tan\left(\frac{s\pi}{2}\right)\sigma_o f^{s-1}/\varepsilon_o, \]
where \( \sigma_o \) (dc conductivity) and \( s \) are temperature dependent and \( \varepsilon_o \) is the permittivity of free space. This can be rewritten as 
\[ f \varepsilon' = A(T)f^s, \]
where \( A(T) = \tan\left(\frac{s\pi}{2}\right)\sigma_o/\varepsilon_o \) [152]. Consequently, a plot of \( \log(f\varepsilon') \) versus \( \log f \), at a given temperature, is expected to give a linear behaviour if the material follows the UDR law. Such a plot is shown in figure 6.12 for three samples discussed in this and previous chapter.

We note that a nearly perfect linear dependence can be obtained for the sample on DyScO$_3$ at all temperatures, while in the samples grown on Nb-SrTiO$_3$, the behavior departs from a linear dependence with \( s = 1 \) at the intermediate temperatures, where the contribution from domain wall starts appearing.

The s-exponent for the low frequency region is shown in figure 6.13. A clear de-
Figure 6.13: $s$-exponent as a function of temperature for three different TbMnO$_3$ films discussed in these thesis.

In the case of the samples on Nb-SrTiO$_3$ substrates, the conduction was assigned to polaron hopping and the data shown here and in the previous chapter for these films are indeed consistent with a thermally-activated process. The film grown on DyScO$_3$, shows a very different behaviour with an exponent $s$ equals to 1 (the conductivity is linearly dependent on the frequency), independent of temperature. Although the microstructure of the films on DyScO$_3$ has not been directly observed, the orthorhombic symmetry of the substrate, electrode and layer precludes the formation of domains and of a large numbers of domain walls, like those observed on the SrTiO$_3$ substrates. Therefore, the conduction processes associated to the domain walls that determined the dielectric properties of the films on Nb-SrTiO$_3$, are not expected in the films on
Figure 6.14: Magnetocapacitance (a) and magnetoresistance (b) as a function of applied magnetic field, ranging from -80kOe to 60kOe, at 15K under an applied frequency of 1MHz for a 40nm TbMnO$_3$ film grown on a 2D SrRuO$_3$ layer on a (001)-oriented DyScO$_3$ substrate.

We have also investigated the magnetocapacitance of the sample grown on DyScO$_3$ with a 2D SrRuO$_3$ layer. A frequency of 1MHz was applied to minimize the influence of the interface polarizability on the magnetoelectric properties of the films. Figure 6.14, shows the magnetocapacitance (left) and magnetoresistance (right), measured at 15K, as a function of applied magnetic field. A positive magnetoresistance associated with a negative magnetocapacitance effect have been observed, evidencing the small core-dominated magnetoresistance, similar to that observed for the films on Nb-SrTiO$_3$ below the domain wall relaxation frequency. Both magnetocapacitance and magnetoresistance are small, as already seen for the films on SrTiO$_3$.

### 6.4.3 Conclusions

We have grown single phase epitaxial films of TbMnO$_3$ on single crystals of (001)-oriented DyScO$_3$, used in this work for the first time, with SrRuO$_3$ electrode layers. However, contrary to our expectations, the SrRuO$_3$ layer is the one that determines the TbMnO$_3$ strain state. Because the substrate, the electrodes and the TbMnO$_3$ film belong to the same orthorhombic space group, domain formation is not expected. However, the high paramagnetic contribution from the substrate hides clear features
in the zero-field-cooled magnetic measurements, making difficult to observe transitions associated with small magnetic moment, as in the case of the antiferromagnetic TbMnO$_3$. This is confirmed by the dielectric measurements that, unlike those of the films on SrTiO$_3$, are not determined by the relaxation/conduction processes at the domain walls. Although thin films under tensile strain imposed by the DyScO$_3$ substrate have not been achieved yet and more work is needed. This study shows progress in that direction and clearly shows that microstructures and domain structures have tremendous effects in the physical properties of a material.