Topotaxial formation of Mg$_4$Ta$_2$O$_9$ and MgTa$_2$O$_6$ thin films by vapour-solid reactions on MgO (001) crystals

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Abstract

Thin-film solid state reactions in the system MgO–Ta$_2$O$_5$ were experimentally studied, subjecting MgO (001) substrates to Ta–O vapours at different temperatures in a high vacuum system. Thin films mainly containing the phases MgTa$_2$O$_6$ and Mg$_4$Ta$_2$O$_9$ formed by reactions between the Ta–O vapours and the magnesium oxide. The crystallographic orientations of these phases were studied by X-ray diffractometry including pole figure analysis. Mg$_4$Ta$_2$O$_9$ was observed to grow (11.4)-, (11.6)- and (11.9)-oriented, while MgTa$_2$O$_6$ had two preferential orientations, viz. (430) and (214). The crystallographic relationships between the reaction products and the MgO substrate and their possible origins are discussed.

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1. Introduction

Investigations of solid state reactions are significant under both fundamental and applied aspects.$^{1-3}$ Reactions between different components frequently occur in heterogeneous thin films or bulk ceramics provided they are subject to high temperatures during production or in practical use. When these reactions occur on the nanometer scale, they are of interface-controlled rather than diffusion-controlled type. In these cases the structure of the involved interfaces, i.e. of the moving reaction fronts, plays an essential role in determining reaction kinetics.$^{4-6}$ Topotaxial reactions, for which there is a certain orientation relationship between the initial and product phases, are good models to study reaction mechanisms and interface structures. Reactions in oxide systems are most interesting in view of the actual significance of complex oxides as functional materials as, e.g., ferroelectrics, superconductors, solid electrolytes or mixed electron-ion conductors. Spinel-forming reactions are the prototype of those solid-state reactions where a ternary oxide forms. Using a series of six different spinel-forming reactions, the important influence of the atomic-scale structure of the reaction front onto reaction mechanisms and kinetics was demonstrated.$^{6-10}$ In particular, misfit dislocations may play a most important role both in spinel-forming and pyrochlore-forming solid-state reactions.$^{7,11}$ In the present paper we aim to extend our study to a new complex oxide system, viz. the Ta$_2$O$_5$–MgO system, which involves more than one reaction product.

Tantalum pentoxide (Ta$_2$O$_5$) has been extensively studied both experimentally and theoretically over the past three decades, because of its wide field of applications in semiconductor devices. There has been an increasing demand for high-dielectric constant insulators to replace SiO$_2$ for high-density dynamic random access memory (DRAM) applications, such as Si$_3$N$_4$, Y$_2$O$_3$ and Ta$_2$O$_5$. Among these, Ta$_2$O$_5$ is the most promising candidate as illustrated by the success of 256 Mb DRAM demonstration.$^{12,13}$ Meanwhile, there is also a great interest in using high-dielectric constant insulators for submicron metal-oxide-semiconductor field effect transistor (MOSFET).$^{14,15}$ Recently, the dielectric constant of Ta$_2$O$_5$ films was reported to vary from around 22 to 110$^{16}$ depending on the deposition method.
Additionally, Ta$_2$O$_5$ films can also be used as thin film electroluminescent devices, hydrogen ion sensing membranes, and biological sensors etc.

Magnesium oxide single crystals are widely used as substrates for epitaxial growth of various oxide thin films. Since MgO has a cubic NaCl-type structure, epitaxial oxide films grown on MgO frequently have the cube-on-cube orientation. MgTa$_2$O$_6$ single crystals can serve as polarizing devices. MgTa$_2$O$_6$ is one of the double oxides with a trirutile structure. Its refractive indices for ordinary and extraordinary rays are 2.07 and 2.18 respectively under white light while the birefringence is 0.11. Accordingly, MgTa$_2$O$_6$ single crystals can serve as polarizing devices.

In this paper, phase formation sequences during topotaxial reactions in the MgO–Ta$_2$O$_5$ system and corresponding orientation relationships of the growing phases are studied. The primary aims of this study were (1) to investigate topotaxial solid-state reactions involving non-cubic phases, (2) to try to reproduce some unexpected orientation relationships found in the system MgO–Nb$_2$O$_5$, and (3) to obtain information required for the high-resolution transmission electron microscopy (HRTEM) investigations on interface structure and reaction mechanisms. The latter are currently under way; as an example, a corresponding HRTEM micrograph is included into the present paper.

In previous studies of spinel-forming reactions in the MgO–Ta$_2$O$_5$ system, three compounds are reported by Baskin et al. The powder diffraction pattern of Mg$_3$Ta$_2$O$_8$ appears to be stable from low temperatures up to their melting points whereas Mg$_4$Ta$_2$O$_9$ was stable only between 1475 °C and 1675 °C. X-ray diffraction data of Mg$_3$Ta$_2$O$_8$ correspond to Mg$_5$Ta$_4$O$_15$, which has the crystal structure of the mineral Fe$_2$TiO$_5$, as later clarified by Kasper. The powder diffraction pattern of Mg$_3$Ta$_2$O$_8$ is indexed assuming an ordering of Mg and Ta cations making necessary the tripling of the lattice parameter to obtain the so-called “tripeudo-brookite” structure type.

In recent years, materials of rutile (TiO$_2$) structure with large refractive indices and birefringence attract intensive attention as most promising candidates for polarizers in optical communications and other optical devices. MgTa$_2$O$_6$ is one of the double oxides with a trirutile structure. Its refractive indices for ordinary and extraordinary rays are 2.07 and 2.18 respectively under white light while the birefringence is 0.11. Accordingly, MgTa$_2$O$_6$ single crystals can serve as polarizing devices.

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### 2. Experimental

In the reaction experiments, polished (001) surfaces of MgO single crystals 10×10×1 mm$^2$ in size (from Crystec GmbH, Berlin, Germany) were subjected to a Ta–O vapour. The latter was produced by electron-beam evaporation of a Ta$_2$O$_5$ powder target in a high-vacuum system. To fabricate the target, Ta$_2$O$_5$ powder of 99.9985% purity (from Johnson Matthey GmbH) was cold pressed under 35 kN and sintered at 1200 °C for 1 h. Prior to the reaction experiment the MgO substrates were heated in air at 1200 °C for 1 h.

The base pressure of the vacuum system was $1 \times 10^{-3}$ Pa. During deposition, 99.999% pure oxygen was introduced to establish a pressure of $1.0 \times 10^{-2}$ Pa. The deposition rate and the overall amount of Ta$_2$O$_5$ deposited were monitored in situ by a quartz microbalance. An amount of Ta$_2$O$_5$ equivalent to a nominal thickness of 100 nm was deposited for all samples. The nominal deposition rate was typically 0.03 nm/s. A complete deposition/reaction experiment required about 55 min. The substrate temperature was varied from 500 to 1100 °C, determined by a Pt/PtRh10 thermocouple. After deposition the samples were kept in the chamber and cooling down to room temperature while the oxygen partial pressure was held to avoid an additional oxygen deficiency.

The phases present in the samples after reaction and their orientation relationships were investigated by X-ray diffraction (XRD) (Philips X'pert MRD) with CuK$_\alpha$ radiation. The 2θ angle was scanned at a speed of 0.18°/min, and pole figures were taken with 2θ step of 0.1° and at a speed of 6°/min. Structural and morphological investigations by atomic force microscopy (AFM) and transmission electron microscopy (TEM) are in progress. An example of a TEM image, taken in a JEOL 4010 high-resolution electron microscope at a primary electron energy of 400 keV, has already been included into the present paper.

### 3. Results

#### 3.1. Phase formation

As mentioned above, there are three known phases in the Ta$_2$O$_5$–MgO binary system. Mg$_4$Ta$_2$O$_9$ is hexagonal (space group P3$_1$) with the lattice parameters $a = 0.51611$ nm and $c = 1.40435$ nm, and with a unit cell volume of 0.32396 nm$^3$. MgTa$_2$O$_6$ is tetragonal (space group P42/mnm) with the lattice parameters $a = 0.4718$ nm, $c = 0.9204$ nm and a unit cell volume of 0.20488 nm$^3$. Mg$_3$Ta$_4$O$_{15}$ is orthorhombic (space group Cmcm) with the lattice parameters $a = 1.1456$ nm, $b = 1.0058$ nm, $c = 1.0238$ nm and a unit cell volume of 1.17967 nm$^3$. Mg$_4$Ta$_2$O$_9$ is indexed assuming an ordering of Mg and Ta cations making necessary the tripling of the lattice parameter to obtain the so-called “tripeudo-brookite” structure type.
nm$^3$. MgO is cubic (space group Fm$ar{3}$m) with the lattice parameter $a=0.42112$ nm and a unit cell volume of 0.07468 nm$^3$.

The formation of Mg$_4$Ta$_2$O$_9$ and MgTa$_2$O$_6$ phases depending on temperature was systematically investigated by XRD. Table 1 presents some typical samples in terms of their deposition temperature and identified phases. At 500 °C, no diffraction could be observed from the film; the non-reacted Ta$_2$O$_5$ oxide seems to be amorphous at this temperature. Fig. 1(a)–(f) show $\theta$–$2\theta$ scans of the films grown on the MgO (001) substrates. The scans were taken after optimizing the deposition temperature and identified phases. At 500 °C, no diffraction could be observed from the film; the non-reacted Ta$_2$O$_5$ oxide seems to be amorphous at this temperature. Fig. 1(a)–(f) show $\theta$–$2\theta$ scans of the films grown on the MgO (001) substrates. The scans were taken after optimizing $\phi$ and $\psi$ for the MgO (202) plane ($\psi=0^\circ$ corresponds to the substrate surface being perpendicular to the plane defined by the incident and reflected X-ray beams). In Fig. 1(a), the peak at 28.4° shows that at 600 °C Ta$_2$O$_5$ starts to crystallize. The non-reacted Ta$_2$O$_5$, detected in the samples made from 600–900 °C, was identified by pole figure analysis; most of the peaks in the pole figures can be explained by a Ta$_2$O$_5$ phase (JCPDS18-1304).

For the samples made at temperatures below 700 °C, there is no peak from any product phase in the XRD scans. However, at 600 °C, the MgTa$_2$O$_6$ phase was clearly detected in XRD pole figures for 2$\theta$ values of 26.7, 34.8 and 21.1°, corresponding to MgTa$_2$O$_6$ {110}, {103} and {101}, respectively. In addition, at 700 °C weak peaks from the Mg$_4$Ta$_2$O$_9$ phase were detected in pole figures for 2$\theta$ values of 32.4, 19.85, and 34.7°, corresponding to Mg$_4$Ta$_2$O$_9$ {10.4}, {10.0} and {11.0}, respectively. At substrate temperatures between 700 and 950 °C, we also found some weak peaks in other pole figures, which we also attribute to this phase.

### 3.2. Orientations of Mg$_4$Ta$_2$O$_9$

Similar to the Nb$_2$O$_5$–MgO system investigated earlier (see 24), we found three orientation relationships at different deposition temperatures. Fig. 1(c)–(f) indicate that Mg$_4$Ta$_2$O$_9$ (10.0) // MgO (001). From other $\theta$–$2\theta$ scans, taken at some definite sample tilt, it was found that Mg$_4$Ta$_2$O$_9$ (00.1) // MgO (111), which is consistent with the first finding.

As an independent method to analyze the orientation relationship, a number of pole figures were recorded at different 2$\theta$ values. From a series of pole figures one can deduce that the (11.4) plane of the Mg$_4$Ta$_2$O$_9$ phase is parallel to the substrate surface. Noticeably the (11.4) (2$\theta=43.5^\circ$) reflection could not be detected in XRD $\theta$–$2\theta$ scans containing the MgO (002) peak because it is completely hidden behind the strong MgO (002) peak. Therefore, pole figures are more suitable to detect this phase and to analyze its crystallographic orientation. The in-plane orientation was determined by pole figures and $\phi$ scans (cf. 24 and further below.) The following orientation relationship was derived:

\[
\begin{align*}
\text{Mg}_4\text{Ta}_2\text{O}_9(11.4)/&\text{MgO}(001); \\
\text{Mg}_4\text{Ta}_2\text{O}_9{}^{11.0}/&\text{MgO}{}^{110}
\end{align*}
\]

This relationship is in good agreement with that reported by Manabe et al. 25 Such an orientation relationship is
observed for samples made at temperatures from 780 to 1100 °C.

Fig. 1(g) shows a HRTEM cross section image of the Mg$_4$Ta$_2$O$_9$/MgO interface region of a sample made at 1100 °C. This image is from a series of HRTEM investigations of the crystallography of different reactive interfaces involved in the reactive formation of Mg$_4$Ta$_2$O$_9$, MgTa$_2$O$_6$, Mg$_4$Nb$_2$O$_9$ and MgNb$_2$O$_6$, respectively. In Fig. 1(g), the orientation relationship (1)

The interface is not plane, it rather consists of ledges (steps) of different height. These ledges are formed by Mg$_4$Ta$_2$O$_9$ lamellae of a width of 1.4 nm that advance into the MgO substrate during the reaction. Their width corresponds to the (00.1) lattice plane distance of Mg$_4$Ta$_2$O$_9$ of 1.404 nm. Thus one lamella is exactly one unit cell wide. The different lamellae advancing not in one line, ledges are formed at the interface. Clearly visible strain contrasts point to the strained condition of the interface region due to the lattice misfit, which has a nominal value of 3.8% comparing the value of 6.75(111) = 1.4592 nm of MgO to 6(00.1) = 1.4043 nm of Mg$_4$Ta$_2$O$_9$. This misfit strain may be the reason why different lamellae advance with different rates. More investigations of this type are in progress.

Samples made at temperatures from 850 to 1000 °C showed a second orientation relationship for this phase. At 850 °C the second orientation relationship starts to appear, and its volume proportion increases with increasing temperature. Finally at 1000 °C it becomes the dominant one. Fig. 2 shows a pole figure taken at 2θ = 19.85° corresponding to Mg$_4$Ta$_2$O$_9$ (10.0) for the sample prepared at 1000 °C. While the peaks at ψ = 45° are due to (11.4) // MgO (001), those at ψ = 54° are due to (11.6) // MgO (001). Each peak at ψ = 54° is split into two sub-peaks with an interval of Δφ = 14°.

To determine the in-plane orientation relationship, ϕ scans with the {00.4} (2θ = 25.36°) reflections at ψ = 53.6° and 42.2° were performed, corresponding to the (11.4) and (11.6) orientations, respectively, as shown in Fig. 3. The Mg$_4$Ta$_2$O$_9$ {00.4} peaks are at the same ϕ positions as those of MgO [111]. In this way the second crystallographic relationship was derived as follows:
The orientation relationship according to Eq. (1) deviates from that of Eq. (3) by a tilt of 22.5° around the MgO [110]/Mg₄Ta₂O₉ [11.0] common axis.

The orientation relationship according to Eq. (2) deviates from that of Eq. (1) by a tilt of 11.4° around the MgO [110]/Mg₄Ta₂O₉ [11.0] common axis.

From samples made at temperatures from 950 to 1000 °C, a third orientation relationship for this phase was found. The peak intensities from this orientation are much weaker compared to the other two, see Fig. 2. The peaks at Ψ = 63° are arising from the orientation Mg₄Ta₂O₉ (11.9)//MgO (001). Each of them are split into two sub-peaks with an interval of Δφ = 22°.

Fig. 3(c) shows the Ψ scans with the Mg₄Ta₂O₉ {00.4} reflections from the sample made at 1000 °C. (a) Ψ = 53.6°, (b) Ψ = 42.2°, (c) Ψ = 31.1°. The Mg (222) Ψ scan taken at Ψ = 54.7° is presented as the reference. The peak intensity of the substrate is drawn with a logarithmic scale instead of linear ones in the other cases.

The orientation relationship according to Eq. (2) deviates from that of Eq. (1) by a tilt of 11.4° around the MgO [110]/Mg₄Ta₂O₉ [11.0] common axis.

The orientation relationship according to Eq. (3) deviates from that of Eq. (1) by a tilt of 22.5° around the MgO [110]/Mg₄Ta₂O₉ [11.0] common axis. From
Eqs. (1)–(3) we may generalize that the primary motif of the topotaxial reaction for this phase is the relation \( \text{Mg}_4\text{Ta}_2\text{O}_9 \{110\} \// \text{MgO} \{100\}\). The misfit values at room temperature along the mutually perpendicular directions in the \( \text{Mg}_4\text{Ta}_2\text{O}_9/\text{MgO} \) interface are shown in Table 2.

Similar to the present results, the (11.4), (11.6) and (11.9) orientations of \( \text{Mg}_4\text{Nb}_2\text{O}_9 \) start to appear at 800, 900 and 1000 °C, respectively, in the \( \text{Nb}_2\text{O}_5/\text{MgO} \) system.24 This strong similarity between phase formation temperatures and crystal orientations of \( \text{Mg}_4\text{Nb}_2\text{O}_9 \) and \( \text{Mg}_4\text{Ta}_2\text{O}_9 \) is certainly due to the well-known close chemical similarity of Nb and Ta, but certainly also due to the two phases having the same crystal structure and similar lattice parameters.

3.3. Orientations of \( \text{MgTa}_2\text{O}_6 \)

As mentioned above, in pole figures it was found that \( \text{MgTa}_2\text{O}_6 \) formed in large amounts by a reaction at temperatures from 600 °C upwards and was present over a large span of temperatures until 1000 °C. There are two kinds of orientation relationships for this phase. The intensity evolution of the \( \text{MgTa}_2\text{O}_6 \) (110) peak (2\( \theta = 26.7^\circ \)) vs. the deposition temperature is shown in Fig. 4. The two curves in the figure, i.e. \( \psi = 8^\circ \) and \( \psi = 46^\circ \), represent two different orientations, respectively, as explained in the following.

3.3.1. Main orientation

The intensity of the \( \psi = 8^\circ \) curve in Fig. 4 sharply increases at 700 °C, reaches a maximum at 800 °C, and then gradually decreases until zero at 1100 °C. Pole figures taken at 2\( \theta \) values of 26.7 and 21.1° for the sample made at 800 °C are given in Fig. 5(a) and (b), respectively. In Fig. 5(a), the peaks at \( \psi = 8 \) and \( 82^\circ \) are from the \( \text{MgTa}_2\text{O}_6 \{110\} \) family, while in Fig. 5(b) the peaks at \( \psi = 45 \) and \( 58^\circ \) come from the \{101\} family. Thus the orientation is deduced as \( \text{MgTa}_2\text{O}_6 \) (430) // \( \text{MgO} \) (001). Four-fold symmetry domains are observed. For the \{101\} family, each of the peaks is split into two subpeaks. The in-plane orientation relationship was determined by \( \phi \) scans. Fig. 6 shows the \( \phi \) scans taken from

Fig. 4. The intensity evolution of the \( \text{MgTa}_2\text{O}_6 \) (110) peaks versus temperature. (a) \( \psi = 8^\circ \) due to \( \text{MgTa}_2\text{O}_6 \) (430) // \( \text{MgO} \) (001), (b) \( \psi = 46^\circ \) due to \( \text{MgTa}_2\text{O}_6 \) (214) // \( \text{MgO} \) (001).

Fig. 5. X-ray pole figures measured with (a) 2\( \theta = 26.7^\circ \), i.e. \( \text{MgTa}_2\text{O}_6 \) 110 family, with peaks situated at \( \psi = 8 \) and \( 82^\circ \); (b) 2\( \theta = 21.1^\circ \), i.e. \( \text{MgTa}_2\text{O}_6 \) 101 family, with peaks situated at \( \psi = 45 \) and \( 58^\circ \). Sample made at 800 °C.
3.3.2. Second orientation

The intensity of the $\psi = 46^\circ$ curve in Fig. 4 is always weak and does not change much with the deposition temperature. Above $\sim 800^\circ$ C, the peak disappears, showing that there is no longer a second orientation present. A pole figure taken at $2\theta = 26.7^\circ$ for the sample made at $600^\circ$ C is given in Fig. 7. The peaks at $\psi = 8$ and $82^\circ$ are due to MgTa$_2$O$_6$ (430) // MgO (001), while the peaks at $\psi = 46$ and $77^\circ$ are due to MgTa$_2$O$_6$ (214) // MgO (001). They agree well with the theoretical values, i.e. the (430) plane makes angles of 8.1 and 81.9$^\circ$ with the {110} planes, while the (214) plane makes angles of 46 and 76$^\circ$, respectively, with the {110} planes. Each of the {110} peaks is split into two subpeaks in this case.

In pole figures taken at $2\theta = 34.8^\circ$ (MgTa$_2$O$_6$ (103)), in addition to the peaks at $\psi = 64$ and $71^\circ$ due to MgTa$_2$O$_6$ (430) // MgO (001), peaks at $\psi = 22$, 40, and 67$^\circ$ due to MgTa$_2$O$_6$ (214) // MgO (001) appear. They agree well with the theoretical values, i.e. the {103} planes make angles of 22.2, 41.7, and 67$^\circ$ with the (214) plane.

Thus the following relationship is deduced:

$$\text{MgTa}_2\text{O}_6(214) // \text{MgO}(001);$$

$$\text{MgTa}_2\text{O}_6[\overline{4}41] // \text{MgO}[010]$$

(5)

The misfit values at room temperature along mutually perpendicular directions in the MgTa$_2$O$_6$/MgO interface are:

$$\left(4d_{[12\bar{4}]} - 3d_{\text{MgO}(020)}\right)/3d_{\text{MgO}(020)} = -1.5\%,$$

and

$$\left(2d_{[1\overline{1}0]} - 3d_{\text{MgO}(020)}\right)/3d_{\text{MgO}(020)} = -0.7\%.$$

The columbite (214) plane makes an angle of 91.3$^\circ$ with the (12$\overline{4}$) plane, while the (T11) plane makes angles of 89.3 and 90.7$^\circ$ with the (214) and (12$\overline{4}$) plane, respectively.

The columbite planes (001), (430) and (340) are at angles of 90$^\circ$ to each other, as are the MgO counterparts (1T0), (001) and (110).
Table 2 summarizes the orientation relationships and corresponding misfit values. Comparing this table with Table 2 of Sun et al., the similarities and differences between the MgO-Ta2O5 and MgO-Nb2O5 systems become obvious: whereas phase formation and crystal orientations of Mg2Nb2O7 and Mg5Ta3O15 are most similar, as noticed before, the orientation relationship of MgTa2O6 is clearly different from that of MgNb2O6, due to the difference in crystal structure between the two phases (MgTa2O6—tetragonal, space group No. 136; MgNb2O6—orthorhombic, space group No. 60).

4. Discussion

4.1. Phase sequence

In the bulk phase diagram of the Ta2O5–MgO binary system, the compounds MgTa2O6 and Mg4Ta2O9 coexist between about 900 and 1580 °C. MgTa2O6 and Mg4Ta2O9 appeared to be stable up to their melting points, i.e. 1770 °C and 1830 °C, respectively, whereas Mg5Ta4O15 is stable only between 1475 and 1675 °C.21

Usually, the phase sequence may be quite different in thin films from that in the bulk case. However, very little work has been devoted to the Ta2O5–MgO thin film system. Manabe et al. reported that Mg4Ta2O9 forms in Mg 4Ta2O9 (00.1) plane being parallel to the MgO (111) plane. This relationship is identical (with a small tolerance) to Mg4Ta2O9 (11.4) // MgO (001).

Fig. 8(a) and (b) show a schematic view down on the MgO (111) plane, sharing the pseudo right-angled isosceles triangles. For the sake of simplicity, without losing universality, we illustrate our experimental relationship with the Mg4Ta2O9 (00.1) plane being parallel to the MgO (111) plane. This kind of arrangement is also not preferential.

In the case of orientation (1), the Mg4Ta2O9 (11.4) plane is parallel to the MgO (001) plane, sharing the pseudo right-angled isosceles triangles. For the sake of simplicity, without losing universality, we illustrate our experimental relationship with the Mg4Ta2O9 (00.1) plane being parallel to the MgO (111) plane. This relationship is identical (with a small tolerance) to Mg4Ta2O9 (11.4) // MgO (001).

There are two kinds of metal-oxygen distances in each octahedron, which reflect deviation of the metal site from the center of the octahedron. The deviation is due to the repulsion between cations through the face-sharing octahedra. Mg1–O bond lengths are 0.209 and 0.214 nm, Mg2–O bond lengths are 0.202 and 0.217 nm, while Ta–O bond lengths are 0.191 and 0.212 nm, respectively.

In the case of orientation (1), the Mg4Ta2O9 (11.4) plane is parallel to the MgO (001) plane, sharing the pseudo right-angled isosceles triangles. For the sake of simplicity, without losing universality, we illustrate our experimental relationship with the Mg4Ta2O9 (00.1) plane being parallel to the MgO (111) plane. This relationship is identical (with a small tolerance) to Mg4Ta2O9 (11.4) // MgO (001).

Fig. 8(a) and (b) show a schematic view down on the MgO (111) plane, sharing the pseudo right-angled isosceles triangles. For the sake of simplicity, without losing universality, we illustrate our experimental relationship with the Mg4Ta2O9 (00.1) plane being parallel to the MgO (111) plane. This relationship is identical (with a small tolerance) to Mg4Ta2O9 (11.4) // MgO (001).

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In the case of orientation (2), instead of Mg4Ta2O9 (10.0) // MgO (T01) and Mg4Ta2O9 (00.1) // MgO (111) as in the first case, there is no low index Mg4Ta2O9 plane parallel to the substrate (111) plane. Obviously, this kind of arrangement is not preferential.

In the case of orientation (3), Mg4Ta2O9 (11.0) // MgO (T11) and Mg4Ta2O9 (10.1) // MgO (T01). The Mg4Ta2O9 (11.0) plane makes an angle of 58.9° with the (11.9) plane, while (101) makes an angle of 46.7° with the (11.9) plane. There are only small deviations of 4.2° and 1.7°, respectively, compared with the corresponding angles in the substrate. This interesting result is confirmed by φ scans with Mg4Ta2O9 (11.0) and MgO (T11).

The similarity between the projection of Mg4Ta2O9 (10.1) and MgO (T01) planes is not so obvious. The corresponding atomic distances are 0.421 and 0.297 nm for atoms in the MgO (T01) plane, while they are 0.319 and 0.259 nm for atoms in the Mg4Ta2O9 (10.1) plane. Thus during the solid-state reaction, the lattice of the MgO crystal has to be adjusted by a relatively large movement of the oxygen cations, requiring additional energy. Hence this kind of arrangement is also not the most preferential one.

In brief, all the three cases have some features in common. The Mg4Ta2O9 (1T.0) // MgO (1T0) orientation is always observed under different temperatures no matter how other orientations change. This means that the Mg4Ta2O9 (1T.0) plane is always parallel to the MgO (T10) plane. At different temperatures, the alignments of the other Mg4Ta2O9 planes change, rotating around the [1T.0] axis.
The rotation of the Mg₄Ta₂O₉ lattice around this axis at high temperatures may be caused by thermal expansion differences between Mg₄Ta₂O₉ and MgO, which may result in lower overall misfit values in the rotated orientations. By lack of Mg₄Ta₂O₉ thermal expansion data we are unable to evaluate quantitatively this effect. However, we can still apply the principle in understanding our experimental results. As mentioned above, in the (11.4) case the mismatch between the Mg₄Ta₂O₉ and MgO is positive, which means at room temperature...
the corresponding interplanar spacings of the film are larger than those of the substrate. Accordingly, the lattice of Mg₄Ta₂O₉ will be compressed by the mismatch stress.

### 4.3. Orientation of MgTa₂O₆

MgTa₂O₆ is of trirutile structure, corresponding to a tetragonal unit cell.²⁷ Like other oxides of the trirutile orientation relationship MgTa₂O₆ [001] // MgO [101], that along MgO [101] is 0.3067 nm, while the atomic distance along MgTa₂O₆ [001] is 0.297 nm. Considering the orientation relationship MgTa₂O₆ [001] // MgO [101], the difference along MgTa₂O₆ [001] and MgO [101] is 3.2%.

In both Nb₂O₅–MgO and Ta₂O₅–MgO systems, the same three orientations for Mg₄Nb₂O₉ and Mg₄Ta₂O₉ were obtained, cf. ²⁴ However, two orientations were found for MgTa₂O₆, instead of only one orientation for MgNb₂O₆, which is MgNb₂O₆ (241) // MgO (001).²⁴ It is likely that this difference is due to the different crystal structures of MgTa₂O₆ (trirutile) and MgNb₂O₆ (columbite), cf.²⁸

### 5. Conclusion

The formation of the phases Mg₄Ta₂O₉ and MgTa₂O₆ by a solid state reaction between Ta–O vapours and the (001) surface of MgO single crystals has been studied experimentally. The solid state reaction starts at 600 °C with MgTa₂O₆ as the only product phase. Both phases have been observed to form at reaction temperatures between 700 and 1000 °C, whereas at 1100 °C only Mg₄Ta₂O₉ is formed. Definite orientation relationships occur between these phases and the MgO substrate, indicating the presence of topotaxial reaction mechanisms.

Three different orientation relationships have been found for Mg₄Ta₂O₉, depending on the formation temperatures, all of which imply, however, a common plane Mg₄Ta₂O₉ (11T.0) being parallel to the MgO (T10) plane. Out of these three orientation relationships, the one mainly observed is identical to the one described previously,²⁵ while the two relationships observed at high temperatures (between 850 and 1000 °C) have not been observed before. MgTa₂O₆, too, was observed to form with two kinds of crystallographic orientations.

Most of the orientations observed can be explained in terms of a good lattice fit, in spite of cubic, hexagonal and tetragonal phases being involved. A more detailed discussion of the crystallographic details of these reactions, as well as related TEM and AFM investigations are in progress.

### References

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