Control of phase formation and film orientation by molar volume stress during MgO–GeO$_2$ thin-film solid–solid reactions

W. Blum, D. Hesse

Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle/Saale, Germany
Sonderforschungsbereich 345, Georg-August-Universität Göttingen, Bunsenstr. 9, D-37073 Göttingen, Germany

Abstract

Experimental investigations were performed on the role molar volume stresses play during thin-film solid–solid reactions and phase transformations. Reactions and transformations in the thin-film system MgO–GeO$_2$ were studied under two different conditions, viz. a planar thin-film geometry on a rigid substrate involving stress, and a microbeam geometry ensuring the immediate relaxation of any stresses via microbeam bending. Induced by reactions or transformations, respectively, the formation of the different phases (MgGeO$_3$, Mg$_2$GeO$_4$, Mg$_n$Ge$_m$O$_{3n}$) and their polymorphs (clino- and orthopyroxene, spinel and olivine) was investigated by RBS, XRD, TEM/SAED and EDX as well as by in situ-TEM-observations applying a double-tilt heating holder. The results show that phase formation under thin-film conditions involving stress indeed differs from that under stress-free conditions. Stability ranges and transformation temperatures were distinctly shifted under conditions involving stress. Moreover, the crystallographic orientation of the olivine phase was stress-dependent. The observations are discussed in terms of different phase transformation mechanisms and a contribution of the stress enthalpy to the Gibbs free energy.

Keywords: Phase formation; Thin film; Stress

1. Introduction

Thin-film solid–solid reactions differ from solid state reactions in the bulk by, e.g., reaction kinetics or phase formation sequence [1–3]. The factors responsible for that imply nucleation phenomena [4], interfacial reaction barriers [5] and stress [6]. Corresponding mechanisms have been described theoretically, mostly on a phenomenological basis. The influence of elastic stress on the kind and sequence of the phases forming has been pointed out by W.C. Johnson et al. [6–8]. Experimental evidence, however, is rather rare and, moreover, focused on non-planar, i.e. spherical or cylindrical geometries [8,9]. In view of this situation, experimental studies of the influence of stress on phase formation during planar thin-film solid solid reactions or phase transformations are necessary. A convenient way of generating stress is to use molar volume stresses involved in solid state reactions and transformations.

We have chosen a reaction system that fulfils two conditions: First, the chemical driving force of the reaction is low, and second, the elastic effects during the reaction are high. Only under these conditions the elastic enthalpy term may be expected to enter the free energy balance with significant weight. The first condition is fulfilled by reaction systems that have several intermediate phases, because here the
difference in the free energy between the individual intermediate phases is generally lower than that between an initial phase and a single final phase. The second condition is satisfied by a system that involves at least two polymorphs of the product phase, which are characterized by a large molar volume difference $\Delta V_m$. Systems of this kind can be expected to distinctly reply to an elastic stress by a corresponding shift of the temperature ranges characterizing the stability ranges of the various polymorphs.

The system MgO–GeO$_2$ fulfills the above conditions. It comprises the intermediate phases MgGeO$_3$, Mg$_2$GeO$_4$ and Mg$_{28}$Ge$_{10}$O$_{48}$, two of which imply two polymorphs, viz. MgGeO$_3$ (clinopyroxene CPX and orthopyroxene OPX, $\Delta V_m = 3\%$) and particularly Mg$_2$GeO$_4$ (spinel and olivine, $\Delta V_m = 8\%$). The corresponding pressure-induced phase transitions in the bulk are well-established [10–13].

The present paper describes the experiments in detail, with the results, however, being presented in rather a concise way. A detailed report is in progress [14].

2. Experimental

Thin-film reactions and phase transformations in the system MgO–GeO$_2$ were studied under two different geometrical conditions differing in the state of stress: (i) a planar thin-film geometry on a rigid substrate (involving stress), and (ii) a microbeam geometry ensuring the immediate relaxation of any stress owing to, for instance, the small dimensions via sample bending.

In either case, first an amorphous GeO$_2$ film was grown under high vacuum (HV) conditions (background pressure $< 5 \times 10^{-6}$ mbar) on an epi-type polished, commercial MgO(100) single crystal substrate of $10 \times 10 \times 0.5$ mm in size. After thermal pre-treatment (60 min at 1100°C in HV) the substrate was heated to 600°C in an e–beam-type substrate heater. The temperature was controlled by a PtRh/Pt thermocouple attached to the heater and carefully calibrated by a micropyrometer focused on a molybdenum film deposited on the back of the MgO substrate. The substrate was then subjected to a Ge–O vapour beam, generated by electron-beam evaporation (6 kV, 50–100 mA) of a pressed and sintered powder target made of 99.998% germanium(IV)oxide. The evaporation/deposition rate ranging between 0.05 and 0.1 nm/s was controlled by a quartz microbalance. The deposited film thickness was between 50 and 150 nm. Owing to the high vapour pressure and incongruent evaporation of GeO$_2$ [15] during deposition an oxygen background pressure had to be applied in order to obtain stoichiometric GeO$_2$ films. The deposition conditions optimum with respect to the stoichiometry of the GeO$_2$ films grown were found by applying Rutherford backscattering spectrometry (RBS) to GeO$_2$ films grown onto glassy carbon substrates. Films of an oxygen content corresponding to the stoichiometry of GeO$_2$ formed at an oxygen pressure of $2 \times 10^{-2}$ Pa.

After deposition on MgO, the GeO$_2$ films were heat-treated in a laboratory furnace for 4 h at 750°C in air, with the films crystallizing into the trigonal phase of GeO$_2$. This phase appeared, though at this temperature the tetragonal phase is the equilibrium phase [16]. The absence of solid–solid reactions at the GeO$_2$/MgO interface after this heat treatment was carefully checked by RBS.

While the different heat treatment experiments in planar reaction geometry started with these plane crystalline GeO$_2$ films on thick rigid MgO substrates (Fig. 1a), ‘microbeam’ samples (Fig. 1b) had to be prepared in order to attain the microbeam reaction geometry. This preparation procedure comprised sawing, mechanical grinding and polishing, and ion

![Fig. 1. Schematic view of the two different reaction geometries used during the heat treatments, (a) planar reaction geometry, (b) 'microbeam' reaction geometry.](image-url)
beam thinning. The standard equipment of preparing cross section samples for transmission electron microscopy (TEM) was used, viz. a diamond wire saw, a micropolishing machine, a dimple grinder, and an ion beam thinner run at an acceleration voltage of 5 kV and an ion beam current of 0.5 mA. Microbeam samples of dimensions as shown in Fig. 1b were obtained by applying the standard procedures as described, e.g., in Ref. [17]. These samples were then exposed to the same heat treatments as the planar samples were.

The heat treatments were performed at temperatures between 800 and 1300°C for different times in either a laboratory furnace in air ('ex situ experiments'), or in a double-tilt heating holder in the TEM thus enabling the direct observation of the processes going on in the samples during heating ('in situ' experiments). The in situ experiments were limited to temperatures up to 1100°C. Three types of experiments were carried out, viz. (a) ex situ planar, (b) in situ planar, and (c) in situ microbeam experiments. In order not to damage the moisture-sensitive GeO₂ films during the extensive mechanical treatments of the preparation procedure, most of the in situ microbeam experiments were carried out on samples that had been shaped into the microbeam after the GeO₂ film had been turned into a MgGeO₃ film before.

Before and after the heating experiments the phases grown, their composition, structure, morphology, and crystallographic orientation as well as the crystal defects grown were analysed by RBS, X-ray diffractometry and texture analysis (XRD), scanning electron microscopy (SEM), TEM, selected area electron diffraction (SAED), and energy-dispersive analysis of X-ray spectra generated by the electron beam in TEM (EDX). Part of these analyses were also performed on the in situ samples after the in situ experiment had been finished. For the TEM/SAED investigations, the planar samples were thinned to electron transparency using the same standard methods as for the shaping of the microbeam samples. TEM, SAED and EDX were used in the TEM Philips CM20T at 200 kV, while the Jeol JSM 6300F was used for SEM. XRD was performed in the Philips X'Pert MPD system. RBS was carried out with ⁴He⁺ ions applying primary energies between 1.0 and 1.4 MeV.

3. Results

3.1. The observed phases, their morphologies and orientations

Figs. 2–4 outline the ex situ planar (Fig. 2), in situ planar (Fig. 3), and in situ microbeam experiments (Fig. 4). With increasing temperature the following thin-film solid–solid reactions occurred:

\[
\begin{align*}
\text{GeO}_2 + \text{MgO} & \rightarrow \text{MgGeO}_3, \\
\text{MgGeO}_3 + \text{MgO} & \rightarrow \text{Mg}_2\text{GeO}_4, \\
10 \text{Mg}_2\text{GeO}_4 + 8 \text{MgO} & \rightarrow \text{Mg}_{28}\text{Ge}_{10}\text{O}_{48}.
\end{align*}
\]

In the following, the phases (polymorphs) observed and their crystallographic orientations and morphologies are listed as they arose from detailed evaluations of the XRD, EDX and TEM/SAED investigations. Furthermore, from the literature the unit cell parameters \(a, b, c, \alpha, \beta, \gamma\) are given [21,31–34] as well as the number of formula units \(Z\) per unit cell, the volume \(V_{\text{FU}}\) of a formula unit (FU), and the molar volume \(V_{\text{m}}\).

3.1.1. \(\text{GeO}_2\) films

Only the trigonal phase (trigonal space group \(P3_211\); \(a = 4.8772(2)\) Å, \(c = 5.5930(1)\) Å, \(\gamma = 120°\), \(Z = 3\); \(V_{\text{FU}} = 40.5\) Å³/FU; \(V_{\text{m}} = 24.44\) cm³/mole) occurred, growing as a polycrystalline film with random grain orientation.

3.1.2. \(\text{MgGeO}_3\) films (CPX)

Clinopyroxene films (CPX; monoclinic space group \(C2/c\); \(a = 9.601(0)\) Å, \(b = 8.932(3)\) Å, \(c = 5.159(2)\) Å, \(\beta = 101.03°\), \(Z = 8\); \(V_{\text{FU}} = 54.8\) Å³/FU; \(V_{\text{m}} = 32.70\) cm³/mole) were observed to grow with different orientations. At 850°C, polycrystalline films were detected showing random grain orientations, but tending towards orientation relationship (1). At 1000°C, films of this very orientation (1) have been obtained. The latter consists of four positions as follows:

Position 1:

\[103] \text{MgGeO}_3 || [001] \text{MgO}; \]

\[(010) \text{MgGeO}_3 || (110) \text{MgO}.\]
T = 700°C: GeO₂

T = 850°C: MgGeO₃ (CPX) + Mg₂GeO₄ (Sp)

T = 1000°C: MgGeO₃(CpX)

T = 1100°C: Mg₂GeO₄ (Sp)

T = 1200°C: Mg₂GeO₄ (Ol)

T = 1300°C: Mg₂Ge₄O₄₈

Fig. 2. Survey of the ex situ heat treatments over the temperature range T = 700°C to 1300°C. TEM bright-field micrographs and SAED patterns of the observed phases formed under conditions involving stress (planar reaction geometry). Note that the low-temperature modification of Mg₂GeO₄ (spinel) is metastable up to 1100°C.

Position 2:

[103]MgGeO₃ || [001]MgO

(301)MgGeO₃ || (110)MgO.

Position 3:

[103]MgGeO₃ || [001]MgO;

(010)MgGeO₃ || (110)MgO.

Position 4:

[105]MgGeO₃ || [001]MgO;

(301)MgGeO₃ || (110)MgO.

3.1.3. MgGeO₃ films (OPX)

Orthopyroxene films (OPX; orthorhombic space group Pbc a; a = 18.8099(1) Å, b = 8.9484(8) Å, c = 5.3451(4) Å, Z = 16; V_M = 56.2 Å³/FU; V_M = 33.80 cm³/mole) showed the following fourfold orientation:

Position 1:

[105]MgGeO₃ || [001]MgO

(010)MgGeO₃ || (110)MgO.

Position 2:

[105]MgGeO₃ || [001]MgO

(501)MgGeO₃ || (110)MgO.

Position 3:

[105]MgGeO₃ || [001]MgO;

(501)MgGeO₃ || (110)MgO.

Position 4:

[105]MgGeO₃ || [001]MgO;

(501)MgGeO₃ || (110)MgO.
Fig. 3. Survey of the in situ planar heat treatments over the temperature range $T=700^\circ\text{C}$ to $1100^\circ\text{C}$. TEM bright-field micrographs and SAED patterns of the observed phases formed during in situ experiments under conditions involving stress (planar reaction geometry). The low-temperature modification of Mg$_2$GeO$_4$ (spinel) is again metastable up to $1100^\circ\text{C}$ (cf. Fig. 2).

3.1.4. Mg$_2$GeO$_4$ films (spinel)

Spinel films (cubic space group $Fd\bar{3}m$; $a=8.246(2)$ Å, $Z=8$, $V_F=70.17$ Å$^3$/FU; $V_M=42.21$ cm$^3$/mole) were well-oriented with the following orientation:

$$[001]\text{Mg}_2\text{GeO}_4 \parallel [001]\text{MgO};$$
$$[100]\text{Mg}_2\text{GeO}_4 \parallel [100]\text{MgO}. \quad (3)$$

3.1.5. Mg$_2$GeO$_4$ films (olivine)

Olivine films (orthorhombic space group $Pnma$; $a=10.2417(6)$ Å, $b=6.0234(5)$ Å, $c=4.9059(2)$ Å, $Z=4$, $V_F=76.02$ Å$^3$/FU; $V_M=45.97$ cm$^3$/mole) were found to be polycrystalline of random grain orientation under microbeam conditions (Fig. 5a). However, under planar conditions the olivine films were well oriented as it was shown by XRD (Fig. 5b). The orientation followed the relationship:

$$[110]\text{Mg}_2\text{GeO}_4 \parallel [101]\text{MgO};$$
$$[001]\text{Mg}_2\text{GeO}_4 \parallel (11\bar{1})\text{MgO}. \quad (4)$$

3.1.6. Mg$_{28}$Ge$_{10}$O$_{48}$ films

These films (orthorhombic space group $Pbam$; $a=14.512(2)$ Å, $b=10.219(2)$ Å, $c=5.944(1)$ Å, $Z=1$, $V_F=881$ Å$^3$/FU; $V_M=55.0$ cm$^3$/mol) were epitaxial showing the orientation

$$[120]\text{Mg}_{28}\text{Ge}_{10}\text{O}_{48} \parallel [001]\text{MgO};$$
$$[001]\text{Mg}_{28}\text{Ge}_{10}\text{O}_{48} \parallel (110)\text{MgO}. \quad (5)$$

The crystallographic orientations of the different phases are not arbitrary or accidental. As a detailed comparison shows, they are mutually aligned in a definite way, determined by the nearly parallel arrangement of the dense-packed oxygen planes and
Fig. 4. Partial survey of the in situ microbeam heat treatments over the temperature range $T=700^\circ\text{C}$ to $1100^\circ\text{C}$. TEM bright-field micrographs and SAED patterns of the observed phases formed during in situ experiments under stress-free conditions (’microbeam’ reaction geometry, cross section sample). The spinel phase ($\text{Mg}_2\text{GeO}_4$) is stable only up to $810^\circ\text{C}$. From $810^\circ\text{C}$ on solely the equilibrium phase, i.e. olivine is observed.

Fig. 5. Stress-dependent crystallographic orientation of olivine ($\text{Mg}_2\text{GeO}_4$) on MgO(100). (a) SAED pattern of a polycrystalline olivine film with random grain orientation grown in the stress-free microbeam geometry. (b) XRD pole figure ($\Phi$--$\Psi$ scan) in the $\{200\}$ reflection of well-oriented olivine grown under planar reaction conditions, with stress involved. Directions [14,18,19]. The oxygen sublattices of all these phases are of either (more or less distorted) c.c.p. or h.c.p. type.

3.2. The transformation temperatures and stability ranges observed

Table 1 shows the transformation temperatures and stability ranges observed (cf. also Figs. 2–4). A discussion of the CPX/OPX transition and of the smaller temperature differences observed between ex situ and in situ experiments, for instance, is beyond the scope of the present paper. The latter are mainly due to the influence of the electron beam during the in situ experiments. The present paper will focus on the striking difference in the spinel–olivine transformation temperature (spinel stability range) under planar and microbeam conditions, respectively.
Table 1
The transformation temperatures and stability ranges observed during experiments of different type

<table>
<thead>
<tr>
<th>Phases grown</th>
<th>Type of experiment</th>
<th>Ex situ planar</th>
<th>In situ planar</th>
<th>In situ microbeam</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgGeO$_3$ (CPX/OPX)</td>
<td></td>
<td>850–1000°C</td>
<td>850–950°C</td>
<td>below 800°C</td>
</tr>
<tr>
<td>Mg$_2$GeO$_4$ (spinel)</td>
<td></td>
<td>850–1100°C</td>
<td>750–1100°C</td>
<td>700–800°C</td>
</tr>
<tr>
<td>Mg$<em>5$Ge$</em>{22}$O$_{48}$ (olivine)</td>
<td></td>
<td>1100–1250°C</td>
<td>--</td>
<td>810–900°C</td>
</tr>
<tr>
<td>Mg$<em>{1+}$<em>Ge$</em>{10}$O$</em>{48}$</td>
<td></td>
<td>above 1250°C</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

While in planar samples the spinel is stable up to 1100°C, under microbeam conditions it is converted into olivine at already 810°C. This has reproducibly been revealed by many experiments both under ex situ and in situ conditions and can thus be considered well-established.

4. Discussion

Owing to extensive experimental and theoretical work the bulk transformation temperatures and stability ranges in the MgO–GeO$_2$ system are well known [12,16,20–22]. The main reason for this is the model character of the MgO–GeO$_2$ bulk system, which is being used to understand deep earthquakes by help of laboratory experiments. The earthquakes are believed to originate from sudden olivine-to-spinel transitions in the (Mg,Fe)$_2$SiO$_4$ layers of the deep earth mantle proceeding at high temperatures and high pressures [23–25]. To simulate the behaviour of (Mg,Fe)$_2$SiO$_4$ in the laboratory, Mg$_2$GeO$_4$ is frequently used in view of its considerably lower transition pressures.

The bulk spinel/olivine transition at atmospheric pressure is at 825°C [22]. As Table 1 shows, the thin-film spinel/olivine transition temperature we observed is at about 1100°C under planar conditions, but under microbeam conditions it is at about 800°C. The difference of 300 K between planar and microbeam temperatures is too vast to explain it by experimental uncertainties or by an influence of the electron beam during the in situ experiments. We thus conclude that under planar reaction conditions the stability range of the spinel is extended by 300 K.

Fig. 6 schematically shows what we believe explains this behaviour. As it is known from literature [26–28], the olivine formation in bulk samples begins at internal grain boundaries of the spinel. We have observed that it starts at the internal MgO/Mg$_2$GeO$_4$ phase boundary. Accordingly, it can be assumed that an olivine nucleus which tries to form at the MgO/Mg$_2$GeO$_4$ interface in a 'rigid' planar sample will immediately feel a large compressive stress exerted by the surrounding spinel matrix (Fig. 6a). This stress is the result of the molar volume difference of 8% between olivine and spinel. On the other hand, under microbeam conditions (Fig. 6b) no stresses arise, because the molar volume difference can easily be accommodated by the deformation of the thin microbeam. As a consequence, the transition
temperature under microbeam conditions corresponds to the equilibrium value for bulk samples. It is thus assumed that the extension of the spinel stability range observed under planar conditions is caused by the molar volume stresses.

The orientation difference observed of the olivine phase strongly supports this conclusion: While under microbeam conditions the olivine grains are randomly oriented, there is a strong epitaxial olivine/spinel relation in the olivine films grown under planar conditions. This orientation difference indicates a different transition mechanism: While the random orientation hints at a nucleation-growth mechanism, the epitaxial relationship indicates a coordinated shear mechanism. Corresponding observations of the Mg$_2$GeO$_4$ spinel/olivine transition in bulk samples under pressure revealed a shear mechanism, while without stress a nucleation mechanism was operative [28].

Let us qualitatively estimate the orders of magnitude of stress and elastic enthalpy arising from the molar volume difference of 8%, if the stress involved is completely unrelaxed. The elastic enthalpy of an isotropic material can be expressed as a function of the relative volume increase $\Delta V/V$:

$$\Delta H = \frac{1}{2} K (\Delta V/V)^2,$$

where $K$ is the bulk compression modulus. For $K \approx 150$ GPa [22] and for the increase of the molar volume by $\Delta V/V = 0.08$, it follows that the elastic enthalpy may reach values of

$$\Delta H = 0.5 \text{ GPa} = 0.5 \text{ kJ/cm}^3 \quad (7)$$

or, for the Mg$_2$GeO$_4$ (olivine) molar volume of 46 cm$^3$, $\Delta H \approx 23$ kJ/mole.

This estimate is, of course, only valid, if the film can stand the high stresses involved. In bulk spinels, the elastic enthalpy corresponding to the yield stress is of the order of 0.1 kJ/mole. However, in thin films much higher stresses are stable, because first, the processes of generation and extension of dislocation loops need a minimum size and second, because the film defects of high density act as pinning sites for moving dislocations. With the linear strain $\epsilon = \frac{1}{2} \Delta V = 0.03$, it follows that the elastic stress which the film should stand in the above case is $\sigma = E \cdot \epsilon = K(3 - 6\nu) \cdot \epsilon = 2.5$ GPa, where $E$ is Young's modulus and $\nu \approx 0.4$ is Poisson's modulus. This value of $\sigma$, though rather high, is still below the highest stress values reported for thin films, ranging between several and up to 10 GPa [29,30].

The above elastic enthalpy of 23 kJ/mole has to be compared to the Gibbs free transition energy of the spinel–olivine transition, which is $\Delta G_T \approx 1$ kJ/mole. Even if a great part of the stress was relaxed by plastic processes, it can be concluded that under favourable conditions the elastic enthalpy owing to the molar volume stress may indeed overcome the transition energy and thus suppress the transition. At higher temperatures the transition will be induced by either the higher transformation energy at higher temperatures, or by plastic processes owing to stress relaxation at high temperatures.

5. Conclusions

It has experimentally been shown that stresses exert a strong influence on phase formation, phase stability and crystallographic orientations during planar solid–solid reactions and phase transformations in MgO–GeO$_2$ thin film systems. Exerted via different transformation mechanisms and/or a large contribution of the elastic enthalpy to the overall reaction or transformation energy balance, this influence results in different crystallographic orientations and in severe changes of the transformation temperatures and stability ranges of the phases involved.

Acknowledgments

This work benefitted from fruitful discussions with W.C. Johnson and J.Y. Huh. The encouragement by J. Heydenreich and U. Gösele is gratefully acknowledged. The authors appreciate the invaluable experimental assistance by W. Bolse (RBS), J. Fritzsch (in situ TEM), R. Gaebel (target sintering), G. Geyer (XRD), R. Mattheis (RBS), and St. Senz (XRD). This work was supported by the DFG via Sonderforschungsbereich 345 at the Georg-August-Universität Göttingen.
References