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# Growth of Oxide Single Crystals by Topotactic Reaction

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Single crystals of MgO have been heated with crystals of $Al_2O_3$, $Fe_2O_3$ and $TiO_2$ on cut and polished faces, in known relative crystallographic orientations. The initial product in every case was a spinel phase with $a_0 = 8.38$ Å, oriented with its axes parallel to those of MgO. Crystals reacted in different orientations gave the same product, but kinetic rates appeared to differ. CaO and $TiO_2$ crystals, treated in the same way, gave an unoriented product.

## 1. Introduction

While most crystal growth methods depend basically on L→S or V→S phase transformations, there are essentially no methods at all based on a S→S reaction and there have been very few papers either from a theoretical or an experimental standpoint in this field. The strain-anneal technique is the obvious exception, but it has been limited so far to a few metallic elements. In order to generalise the problem one should investigate the possibility of the growth of a binary phase by the reaction $S + S' \rightarrow S''$ and the most favourable conditions under which this could perhaps be achieved would certainly be if S and S′ both started as single crystals. The "opposite" reaction, of the type $S' \rightarrow S'' + V$ where oriented single crystals of S″ are formed from single crystals of S′ has, in fact, received a great deal of attention in recent years, under the general subject area of "topotactic reactions." This study, therefore, was an attempt to design a reverse topotactic reaction of two oriented single crystal phases to yield a third or desired single crystal.

The recent emphasis in topotactic studies has been largely confined to studies of oriented products formed in solid state degradative and reconstructive reactions (Dent-Glasser, Glasser, and Taylor [1], Brindley [2], Deschanvres and Raveau [3]) and while these are of great significance in extending our understanding of the mechanisms of reactions occurring within an initially homogeneous system, they give no information about mechanisms obtaining when reaction occurs across an interface in an initially homogeneous system. The single exception, where this method has been applied before, is the paper by Rossi and Fulrath [4] who have used the proposed technique to synthesise spinel from single crystals of MgO and $Al_2O_3$ and have shown that reaction can occur across an interface in a topotactic manner in this case.

It was decided to extend this study of topotaxy into other, similar systems and to investigate, where possible, the effects of several other parameters on the quality and perfection of single crystals formed, and the rates of growth. Our present knowledge of topotactic mechanisms indicates that the course of the reaction is controlled by the structure of the starting material, in particular by the oxygen packing in the case of complex oxide phases, and by the relative sizes and ionic character of the cations. The products are formed in definite crystallographic orientations relative to the host material. It is, therefore, reasonable to expect that the course and kinetics of synthesis-growth reactions will be controlled by these factors also. Experiments were designed to study the effects on the reaction of changes in the structure type in one or both oxides, including the effects of using different faces of any phase, of changes in the relative crystallographic orientations for a given pair of faces, the perfection of the surfaces in contact,

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and the density of dislocations present. It is in the potential degree of control of these parameters in the reacting components that the method differs from those involving reaction between single crystals and powders. In the present exploratory study, attention has been concentrated on the structure, orientation and the surface perfection.

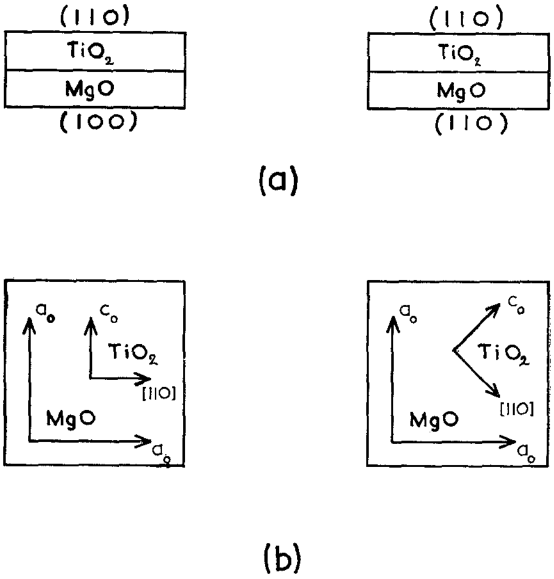

*Figure 1* Diagrammatic representation of (a) typical cross-section of reaction couples between MgO and $TiO_2$, showing two different pairs of faces in contact, and (*b*) plan views of two orientations of MgO and $TiO_2$ in contact on the same faces.

## 2. Experimental

Studies were made in the systems MgO–$Al_2O_3$, MgO–$Fe_2O_3$, CaO–$TiO_2$, and MgO–$TiO_2$, with the major emphasis on the last system mentioned. MgO, CaO and $Al_2O_3$ single crystals were obtained commercially and analysed semi-quantitatively, spectroscopically pure ($\sim 99.9\%$), and were not annealed before use. Single crystal plates of $Fe_2O_3$ with (0001) orientations were grown in this laboratory by R. Barks [5] using a flux method. Two different "habits" of $TiO_2$ were used; needles of known stoichiometry grown in this laboratory by J. Berkes [6], again by a flux method under a controlled oxygen pressure, and a boule from the Linde Corporation. The needles were about 10 mm × 1 mm, elongated parallel to the c-axis and showing well developed (110) faces. The compositions of the different preparations ranged from $TiO_{1.999}$, straw yellow, to $TiO_{1.993}$, deep blue, and all lay within the rutile field in the binary system Ti–O. The boule was straw yellow in colour, probably corresponding to a composition closely approaching $TiO_{1.999}$'.

MgO and CaO orientations, parallel to the (100) face, were readily obtained by cleaving the crystals, but all other orientations had to be prepared by cutting the various crystals. A special technique had been developed for this (Lange [7]). The crystal preparation was completed by hand-polishing the slices with, successively, 15, 6, 3, and 1 $\mu$m diamond pastes, until the faces were flat to within $\sim 10$ fringes. Ideally, of course, the faces should be atomically flat, but since this is unattainable, it was felt that this compromise was sufficient for a preliminary study. The slices were generally less than 1 mm thick.

The orientation of a principal crystallographic direction in the plane of the polished face was found using X-ray single crystal oscillation photographs, when this was not self-evident from the morphology, and the reaction couple prepared by placing the faces of the two reactant phases together with the required directions parallel, as shown schematically in fig. 1. Two types of furnace were used to heat the samples: a vertical tube, molybdenum-wound furnace in which the atmosphere could be controlled, and a horizontal iridium-strip furnace operated with a nitrogen atmosphere.The raection couples were suspended in a platinum tray at the hot spot of the vertical furnace and the strip acted as support in the horizontal. Temperatures were measured with a calibrated Leeds and Northrup optical pyrometer and are estimated to be correct to within $\pm 10°$ C in the vertical furnace. Accurate temperature estimation was more difficult on the strip, partly because black body conditions could not be assumed and partly because there was no way of measuring the temperature at the actual crystal interface where reaction was occurring. But temperature was regarded as relatively unimportant. Values given were obtained by reading the apparent temperature on the strip and applying the necessary correction, using the published emissivity for iridium. Calibration on the melting point of platinum showed that the temperature so measured was correct, again to within $\pm 10°$ C.

Analysis of the products of reaction was carried out by X-ray single crystal diffraction methods. A combination of 10° oscillation and Weissenberg photographs was used to characterise the phases formed and to describe their orientations relative to the original crystals. An ARL electron microprobe analyser was used to measure cation ratios, both in the reaction plane and perpendicular to it, and coloured products were further investigated by optical microscopy.

## 3. Results

An oriented "single crystal" product of some type was formed in each reaction couple, except CaO–$TiO_2$. The results of various runs are presented in table I, together with the relative orientations of the crystalline phases, where known. The results are summarised below for the different systems.

*MgO–$Al_2O_3$*. The results obtained agree with those of Rossi and Fulrath [4]. The reaction couple split apart after treatment and the oriented spinel phase adhered to the $Al_2O_3$, as reported by them. No observations were made on the relative orientations of spinel and $Al_2O_3$.

*MgO–$Fe_2O_3$*. The product, formed within the MgO crystal, was a spinel phase with $a_0 = 8.38$ Å. Its axes were oriented parallel to those of the MgO and it appears to represent a first stage in the reaction process.

*CaO–$TiO_2$*. Reaction occurred and the couple split apart after heating. The CaO was markedly more brittle than before and there was no evidence of orientation in the reaction product which adhered to the $TiO_2$.

*MgO–$TiO_2$*. The results differ slightly depending on whether the reaction was carried out in a reducing or an oxidising atmosphere, as might be expected. Under both conditions a spinel phase was formed in the MgO crystal and, when slices cut from the $TiO_2$ boule were used, the couples normally split after heating, the product adhering to the $TiO_2$ crystal. The cell size was again 8.38 Å and the axes were oriented parallel to the original MgO axial directions, as shown in fig. 2. Under reducing conditions the product was blue, and under oxidising conditions it was yellow.

Runs made using the $TiO_2$ needles were all carried out under reducing conditions in the horizontal furnace. As seen in table I, attempts were made to study the effect of different relative orientations on the reaction kinetics and it was

TABLE I Examples of results of heating oxide couples in contact on known crystallographic faces.

| Crystal number | Oxides and reaction faces | Relative orientations | Reaction conditions | Time | Products | Comments |
|---|---|---|---|---|---|---|
| MA 2 | MgO (1 0 0)<br>$Al_2O_3$ (0 0 0 1) | Unknown | 1850° C<br>Air | 6 h | Spinel | As in work of Rossi and Fulrath. |
| MF 1 | MgO (1 0 0)<br>$Fe_2O_3$ (0 0 0 1) | Unknown | 1250° C<br>Air | 4 h | Spinel | Reddish-brown in MgO. |
| CT 1 | CaO (1 0 0)<br>$TiO_2$ (1 1 0)<br>boule | [1 1 0] parallel to $c_0$ | 1600° C<br>Strip | 4 h | Unidentified phase | Unoriented product adheres to $TiO_2$. |
| MT 6 | MgO (1 0 0)<br>$TiO_2$ (1 1 0)<br>needles | $a_0$ at 45° to $c_0$ | 1580° C<br>Strip | 5 h | Spinel + unidentified phase | Blue MgO. Isotropic and anisotropic regions.<br>Spiky interface. |
| MT 9 | MgO (1 0 0)<br>$TiO_2$ (1 1 0)<br>boule | $a_0$ at 45° to $c_0$ | 1580° C<br>Strip | 4 h | As MT 6 | |
| MT 10 | MgO (1 0 0)<br>$TiO_2$ (1 1 0)<br>boule | $a_0$ parallel to $c_0$ | 1580° C<br>Strip | 4 h | As MT 6 | Melting of the $TiO_2$ has occurred. |
| MT 22 | MgO (1 1 0)<br>$TiO_2$ (1 1 0)<br>boule | $a_0$ parallel to [1 1 0] | 1550° C<br>Strip | 75 h | Tetragonal phase<br>No spinel | "Hill" grown from $TiO_2$ into MgO, $TiO_2$ brittle. |
| MT 23 | MgO (1 1 0)<br>$TiO_2$ (1 1 0)<br>boule | $a_0$ parallel to $c_0$ | 1550° C<br>Strip | 75 h | As MT 22 | No difference due to different relative orientations of MgO and $TiO_2$. |
| MT 26 | MgO (1 1 0)<br>$TiO_2$ (0 0 1) | $a_0$ parallel to [1 1 0] | 1550° C<br>Oxidising | 60 h | Spinel + unoriented pattern | MgO clear and yellow.<br>$TiO_2$ reddish-purple and brittle. |

Couples heated on the "strip" reacted in an atmosphere of $N_2$, i.e. under reducing conditions.
Temperatures recorded from the "strip" are only approximate.

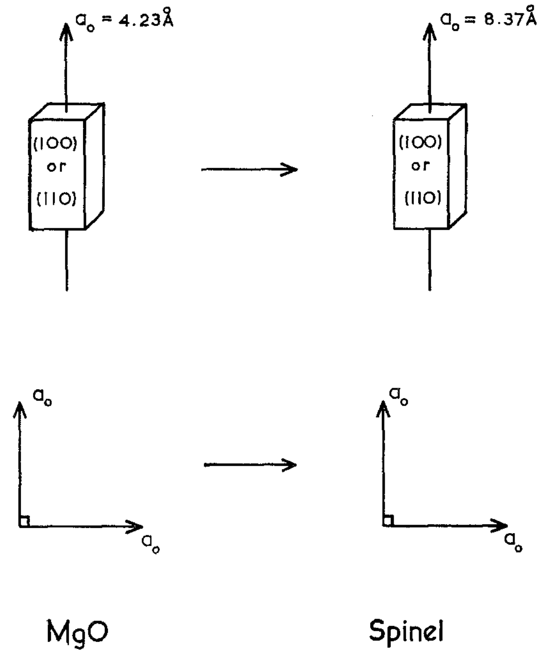

*Figure 2* Relative crystallographic orientations of MgO and the spinel-phase product found throughout this study.

noted that melting of $TiO_2$ had occurred, apparently with certain preferential orientations, suggesting that countermigration of ions is easier when the MgO (100) and $TiO_2$ (110) faces are in contact with the MgO a-axis at 45° to the $TiO_2$ c-axis, than when these axes are parallel. Uncertainties in estimating the temperature at the reaction interface, however, make it difficult to be sure that this effect is caused by solution of MgO in the $TiO_2$, with melting at sub-liquidus temperatures, and not simply by hot spots on the strip giving local temperatures in excess of the liquidus at the interface. When the crystals were examined under the optical microscope in the plane perpendicular to the reaction face a very uneven, rather spiky, blue interface was seen between the MgO and the, supposed, spinel phase, suggesting that migration was occurring preferentially down faults in the crystal, possibly screw dislocations. Measurements of the Mg/Ti ratio were, therefore, made on the reaction face itself with the electron microprobe in an attempt to relate these to dislocations and grain boundaries, but the results were inconclusive.

An interesting effect was seen in some of the runs, in which the $TiO_2$ penetrated locally into the MgO crystal and, on subsequent splitting apart, left a "hill" on the $TiO_2$ and a "hole" in the MgO. Fig. 3 shows one of these "hills", and also emphasises the brittleness of the $TiO_2$, in the raggedness of the edges of the specimen, which were originally smooth. The X-ray pattern from the "hill" showed a rather complex set of reflections which could be indexed on a primitive tetragonal cell with $a = 4.85$ Å and $c = 2.95$ Å.

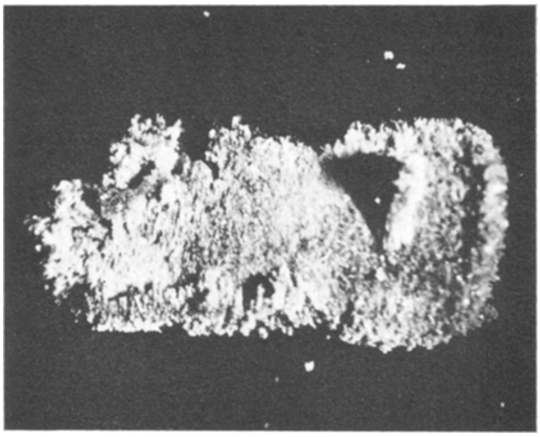

*Figure 3* Photomicrograph of "hill" formed on (110) face of $TiO_2$. Note the general roughness of the crystal and the raggedness of the edges, indicative of increased brittleness.

The evidence from runs made under oxidising conditions shows that the reaction follows a course very similar to that under reducing conditions, except that no blue colour was found associated with $TiO_2$.The penetration zone of the Ti-ions in the MgO was characterised by a light amber colour, and the MgO had again retained its strength. The $TiO_2$ was very brittle and had turned a reddish-purple hue. Under the binocular microscope some pieces of MgO were covered by a clear yellow fibrous overgrowth which was not identified and which did not occur on every piece. The presence of this overgrowth was thought to be due to vapour-phase transport of the titanium in certain cases, but no further work was done on this problem. The main product was again the spinel phase, but there also occurred an unoriented pattern which could not be accounted for in terms of any of the known compounds of MgO and $TiO_2$. The spinel layer again adhered to the $TiO_2$ on cooling.

## 4. Discussion

Results obtained from the systems studied so far indicate quite clearly that topotactic reactions can occur during the synthesis of complex oxide phases from single crystals of their constituent oxides. This appears to be particularly true of systems involving MgO, and, in every case investigated, it also appears that the MgO structure is the controlling factor in these topotactic syntheses, at least in the early stages of the reaction. The first easily identifiable phase to be formed in each case is a spinel, with an axial parameter slightly less than twice that of the MgO cell, and with its axes oriented parallel to those of the MgO. It is interesting to note, however, that in the systems $MgO$-$Al_2O_3$ and $MgO$–$TiO_2$ the spinel layer split away from the MgO on cooling, suggesting a considerable mismatch of the coefficients of thermal expansion between the MgO and the spinel phase.

Attempts to study the kinetics of the processes involved in terms of the relative orientations of the crystals in contact have been less definitive, mainly because the crystals separate after reaction, and it is well nigh impossible to measure sensible cation ratios at points across the interface. Qualitative indications are that reaction occurs more rapidly through the (100) face of the MgO than through the (110) faces, and the same relationship may possibly hold for the (001) and (110) faces of rutile. It is tempting to interpret these results in terms of the appearances of the structures when they are viewed in directions normal to these planes – and in fact both appear to be more "open" when viewed along the directions of faster rate. However, it is important to remember that our knowledge of the details of the reaction between the crystals is very scanty, and the observed differences in rate may be due to the different densities and mobilities of imperfections on the respective faces of the MgO and $TiO_2$.

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