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ABSTRACT

Oriented phase transformations are considered to be cases of topotaxy. The anatase-rutile transformation has been shown to result in preferred orientation of the product and is, therefore, classified as a case of intermediate topotaxy.

Single crystals of anatase were transformed to rutile at temperatures of 900°-950°C. The resulting rutile crystallites were found to exhibit preferred orientation which was studied by means of oscillation photographs. Interpretation of the resultant pole figures led to a mechanism of transformation which was similar to that of the brookite-rutile transformation. The mechanism involves retention of the $\{112\}$ pseudo-close-packed planes in anatase and rearrangement of the titanium and oxygen ions within the plane. A cooperative movement of the titanium and oxygen ions is proposed in which the majority of the titanium ions, in order to reach their new sites, break two of their original six Ti-O bonds.

INTRODUCTION

It is frequently possible to determine the mechanism of crystallographic phase transformations by studying the orientation of the product phase with respect to that of the reactant. If the transformation occurs so that the orientation of the product phase is correlated with the orientation of the reactant phase, then a topotactical relation is said to exist* (Lotgering, 1959; Shannon and Rossi, 1963). The degree of correlation determines the degree of topotaxy. If the atoms undergo only a change in secondary coordination and no primary bonds are broken, such as in displacive phase transformations, then a high degree of topotaxy results. A crystal undergoing such a reaction results in a single-crystal diffraction pattern before and after the transformation. If, however, the atoms must undergo extensive rearrangement, little accord exists between the original and final structures and the transformation is weakly topotactical or reconstructive. The dehydroxylation of $\gamma\text{-FeOOH}$ to form $\gamma\text{-Fe}_2\text{O}_3$ (Mackay, 1960) and the $\alpha\text{-}\beta$ quartz transformation are two examples of strong topotaxy. Cases of intermediate and weak topotaxy occur respectively in the dehydration of $\text{Mg}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ (West, 1934), while the quartz-cristobalite transformation is reconstructive (Chaklader, 1963), and is thus not expected to exhibit topotaxy.

*Bernal (1960) and Mackay (1960) use more restricted criteria of (a) the retention of at least one axis of symmetry, or (b) a three-dimensional accord between the structures and preservation of the majority of the atomic positions. Taylor et al. (1962) assume Gorter's definition, as stated by Lotgering, with the added restriction that three-dimensional accord between the initial and final structures is present.

A study of the brookite-rutile transformation (Barblan et al., 1958) revealed a moderately topotactical transformation and allowed the investigators to postulate a mechanism involving small atomic rearrangements. The brookite [100] was found to remain coincident with the rutile [100]. In the brookite (100) plane, the rutile assumed three different orientations: (1) at 700°C, rutile [001] || brookite [001]; (2) at 800°C, rutile [001] || brookite [010]; and (3) at 800°C, rutile [001] || brookite [027] or [023]. In a [100] projection of the brookite structure, zig-zag chains of TiO_6 octahedra running along the c-axis are evident so that formation of the chains of octahedra in rutile in case (1) is not unexpected and involves only a straightening of the chains and breaking up of every other octahedron by a shift of the Ti atom from its octahedral site to a new one. In cases (2) and (3), the movement required of the oxygen atoms is less than that in case (1), but the movement of the Ti atoms is greater. Barblan et al. suggested that the mobility of the oxygen atoms relative to that of the Ti atoms is greater at lower temperatures, making case (1) reasonable. As the temperature increases, the mobility of the Ti atoms becomes greater and case (2) becomes predominant. The same authors made an attempt to find similar behavior in the anatase-rutile transformation but failed to discover any preferred orientation of the rutile crystals. From Table I, it can be seen that the volume change in the brookite-rutile transition is $\sim 3\%$, while that in the anatase-rutile transition is $\sim 8\%$; thus, in the latter case a more random distribution of the rutile crystals can be expected from the distortion alone.

Our experiments have shown, however, that large octahedral single crystals of anatase could be transformed without loss of their

external shape even though severe cracks had developed. The fact that the crystals were still bipyramidal in shape and had not disintegrated allowed the determination of the orientation of the product phase by X-ray diffraction methods. It was hoped that a study of this orientation would provide some information concerning movements of the atoms during the transformation.

EXPERIMENTAL PROCEDURE AND RESULTS

Three crystals were chosen for a detailed orientation study. The first crystal, G-2*, from Disentis, Graubünden, Switzerland, was a bipyramid 0.5 mm x 0.2 mm, the long dimensions being along the c-axis. The other two crystals, V-2 and V-4**, from the area of Val Vals, Graubünden, Sw. were large bipyramidal crystals, one 4 mm x 2 mm, and the other, 1-1/2 mm x 1 mm. Crystal G-2 was heated at 850°C for 28 hours, 900° for 66 hours, 925° for 25 hours, and at 950° for 10 hours. Crystal V-2 was heated for 3 hours at 850°, 3 hours at 900° and 1 hour at 950°C. Crystal V-4 was heated for 48 hours at 900° after which it developed severe cracks throughout as seen in Fig. 1. The transformation was found to proceed from the surface of the crystal toward the center. This behavior, combined with the large shrinkage, necessitated the formation of these cracks. Crystal G-2 was transparent and tan in color before the transformation and brilliant orange afterward; the other two crystals, being less pure, were translucent and dark green in color.

* Obtained from Minerals Unlimited, Berkeley, California

** Obtained from Scott Williams Mineral Co., Inc., Scottsdale, Arizona.

Rotation patterns resulted in discontinuous rutile powder rings, indicating polycrystalline specimens exhibiting preferred orientation. Determination of the orientation of the rutile crystallites was made in a manner similar to that used in the study of preferred orientation in metal wires and sheets (Henry, Lipson and Wooster, 1960). When a polycrystalline specimen exhibiting preferred orientation is irradiated with monochromatic X-rays, discontinuous powder rings result. If the crystallite size is large, oscillation patterns, rather than stationary patterns, must be used. Oscillation patterns provide the angle ρ which the normals to the reflecting planes make with the axis of oscillation. The intersection of the cone of angle 2ρ with the cone of angle $(180^\circ - 2\theta)$, whose axis is the incident X-ray beam, gives the position of the pole. These poles can then be plotted on a stereogram. A series of oscillation patterns made with the incident X-ray beam oriented in different positions with respect to the original anatase crystals provide the complete pole figure.

Each heat-treated crystal was mounted in an oscillation camera so that the c-axis of the original anatase crystal was perpendicular to the X-ray beam. Ten-degree oscillation patterns using filtered Cu radiation were made at appropriate intervals around the [001] axis for crystals V-2 and V-4 and around the [001] and [100] axes for crystal G-2. The rutile (110), rather than the (100) poles, were chosen because of their relatively high intensity. A typical pattern showing rutile preferred orientation in crystal G-2 is seen in Fig. 2. The diffraction rings were analyzed to provide the rutile (110) and (001) pole figures shown in Fig. 3a. Composite diagrams for both the [001] and [100] orientations of the original anatase,

in which the pole figures for the three crystals were superimposed, were also constructed. Fig. 3b shows the composite diagram for the anatase [100] orientation.

The regions of intensity within the diffraction rings were sometimes discontinuous because of the large size of the crystallites. The large degree of scatter in the positions of the poles was evidently caused by the distortion resulting from the shrinkage and cracking accompanying the transformation. Despite these difficulties regions of concentration of the rutile (110) and (001) poles are evident in the pole figures. It can be seen that clustering of the (110) poles occurs around the equator and around the anatase [001] and that the (001) poles are situated at a latitude of about 45°.

MECHANISM OF TRANSFORMATION

From a study of the kinetics of the reaction (Shannon, 1964), it was apparent that the mechanism cannot be a mere change of bond angles and/or bond lengths which result in a slight shift or retention of major crystallographic axes. The activation energy was found to vary among different samples, depending upon the impurity content, from 100 to 180 kcal/mole. These values suggest that the process involves the rupture of bonds and a major rearrangement of atoms. In addition, an examination of the anatase and rutile structures did not reveal any close similarity of structures, thus indicating the necessity of a rearrangement of atoms.

The anatase and rutile structures can be represented as sodium chloride structures with half the cations removed and the anions slightly offset from their normal positions. Then, it is possible to consider the two structures to be made up of pseudo-close-packed oxygen layers with

different arrangements of the Ti atoms (see Figs. 4a, 4b, and 4c).

In anatase the close-packed plane is the (112) plane with the Ti atoms arranged in zig-zag chains running along $[221]$ as indicated in Fig. 4a.

For the sake of clarity only one oxygen plane with its associated titanium ions is shown. Actually, four of these planes are necessary to cover the repeat distance. In the next layer of oxygen atoms the zig-zag chains of titanium ions are displaced along $[110]$ by half the distance between chains and along $[221]$ by $0.6 \text{ \AA}$. Fig. 4b shows part of the second oxygen layer.

In rutile the close-packed plane is (100) and the Ti atoms lie in rows along $[001]$ as indicated in Fig. 4c. The rutile structure may also be pictured as a series of chains of TiO_6 octahedra parallel to the c-axis, where each octahedron shares two of its opposite edges with two other octahedra. The Ti atoms in the $[001]$ rows form the centers of these octahedra, some of which are shown in Fig. 4c.

The anion framework is expected to remain intact if the least spatial disturbance of the structure is to take place. Since the interplanar spacing of the close-packed planes in anatase and rutile are nearly identical ($d_{112}^{\text{anat}} = 2.336$; $d_{200}^{\text{rut}} = 2.297$), it was assumed that most of the atomic movement occurred within the planes themselves. Since the Ti atoms lie in rows in the rutile structure, one looks for similar rows in the anatase (112) plane. The possible directions for the resultant rutile c-axis are indicated in Fig. 4a. Directions "a", "b", and "c" do not result in the experimentally observed distribution of (110) and (001) planes. The line of atoms along "d" is clearly the direction in which most of the $[001]$ poles were found. Figure 5a is a stereogram showing the trace of one of the (112) planes containing two directions which the c-axes

of rutile may assume after the transformation. Figure 5b shows the orientation of four of the eight possible equivalent rutile unit cells and the complete pole figure which would be anticipated if the resultant rutile crystals grew in all possible orientations. Although the positions of the calculated poles (Fig. 5b) do not lie exactly at the center of the experimental intensity distribution (Fig. 3b), the agreement is considered satisfactory in light of the large amount of shrinkage and distortion which takes place during the transformation.

The mechanism of the transformation appears to be similar to that of brookite in the sense that the close-packed planes in the reactant remain as close-packed planes in the product with almost the same spacing while the major rearrangement occurs within these planes. Figure 4b shows the atoms of the rutile TiO_6 octahedral structure as they are arranged in anatase before the transformation. In achieving the rutile configuration shown in Fig. 4c, considerable distortion occurs, as may be seen from the relative positions of the atoms shown in the figures. In the lower layer, half the titanium atoms undergo no change in nearest neighbors while the other half break two Ti-O bonds and acquire two new nearest neighbors. In the upper layer all the cations must break two bonds in achieving their new position. It is clear from the positions of the cations in Figs. 4b and 4c that a shrinkage of approximately 20% occurs in the new [001] direction and an expansion of approximately 10% in the new [100] direction.

Figure 6 shows two adjacent cations and the surrounding oxygen configuration (a) before and (b) after the transformation. Figure 6a corresponds to Fig. 4b and shows octahedra a and b in anatase while

Fig. 6b shows the rutile octahedra a and b indicated in Fig. 4c. The dimensional changes noted above allow a closing of the oxygen configuration on the right and a relaxation of the configuration on the left, allowing the shifts of the titanium atoms to their new octahedral sites between 3 "a" atoms and 3 "b" atoms as a consequence of the anion movement. These shifts occur by the cation breaking two bonds indicated by dashed lines in the diagram and result in the cations having four nearest neighbors and two more distant neighbors at the midpoint of the movement. The apparent movement of the cations into tetrahedral sites does not actually occur because what were previously tetrahedral sites have become octahedral sites as a consequence of the indicated oxygen movements and the associated rearrangement. This mechanism is best described as a cooperative movement of the titanium and oxygen atoms and is in contrast to a diffusion mechanism in which the anion structure remains essentially fixed.

The question then remains as to the reason for the failure of the rutile c-axes to lie in the "a", "b" or "c" directions as indicated in Fig. 4a. A careful consideration of the movements that would be necessary for alignment of the titanium atoms in the "b" direction indicates that a similar type of cooperative movement of the atoms would be necessary as that for the "d" direction. Rearrangement in this direction, however, would involve greater distortion of the oxygen configuration and would require an expansion along this direction. Consideration of the movements that would be necessary for alignment of the titanium atoms in the "a" or "c" direction show that the distortion of the oxygen atom configuration is not great. However, a diffusion type of movement of half

the cations in an anion structure that remains essentially fixed would be necessary. Such a movement would have required that only two original neighbors be retained, thus breaking four Ti-O bonds.

DISCUSSION

Oriented transformations have been assumed to occur with the least spatial disturbance (Glasser and Glasser, 1961). This follows since it implies that the minimum degree of movement and rearrangement of atoms results in the path of minimum energy. However, spatial disturbance must refer to: (1) changes in position of the largest structure-determining ions and (2) the change in distribution of the remaining ions. Thus, it appears from the above that the transformation is controlled by two factors: (1) not only must the principle of the least spatial disturbance of oxygen ions be obeyed but also (2) the minimum number of bonds must be broken. The activation energy should therefore be made up of two terms: (1) the strain energy which must be overcome for the oxygen atoms in the close-packed planes to reach their new configuration and (2) the energy necessary to break the Ti-O bonds as the titanium atoms redistribute themselves.

Strong topotaxy implies similarity of the initial and final structures and the preservation of at least one of the axes of symmetry. The anatase-rutile transformation should not, therefore, be highly topotactical because the structures are dissimilar and none of the major axes of symmetry of the product correspond to those of the reactant. However, neither is the reaction reconstructive or heteromorphous, i.e., with no dimensional accord between reactant and product because this type of reaction is characterized by random orientation of the product. Since the product

exhibits preferred orientation, it could be classified as an intermediate case of topotaxy. Intermediate cases of topotaxy should occur when only some of the structural elements are preserved. Such cases would include the anatase and brookite transformations and reactions involving substances with layer structures in which the layers are retained with reconstruction within the layers. In the TiO_2 transitions, retention of the anatase (112) and the brookite (100) planes accompanied by considerable rearrangement of both the cation and anion configurations within the planes results in intermediate cases of topotaxy. The higher degree of topotaxy exhibited by brookite is a result of the smaller dimensional change.

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Table I. Properties of TiO_2

Form	Symmetry	Space group	Unit cell Dimensions, Å	Calculated Density, gm/cm^3
Brookite	Orthorhombic	D_{2h}^{15} Pbca	$a = 9.18^a$ $b = 5.45$ $c = 5.14$	4.126
Anatase	Tetragonal	D_{4h}^{19} $I \frac{4}{a}$ md	$a = 3.785^b$ $c = 9.514$	3.892
Rutile	Tetragonal	D_{4h}^{14} $P \frac{4}{m}$ nm	$a = 4.593^c$ $c = 2.959$	4.249

^a Pauling, L., and Sturdivant, J. H., Zeits. Krist. 68, 239-56 (1928).

^{b, c} Cromer, D. T., and Herrington, K., J. Am. Chem. Soc. 77[18],
4708-09 (1955).

FIGURE CAPTIONS

Fig. 1. Section through crystal V-4 1 [100]

Fig. 2. Ten-degree oscillation pattern of crystal G-2 showing discontinuous rutile diffraction rings.

Fig. 3. a. Pole figure showing rutile (110) and (001) poles superimposed on a [100] anatase projection, crystal G-2.

(110) pole, high intensity reflection

(110) pole, low intensity reflection

(001) pole, high intensity reflection

(001) pole, low intensity reflection

b. Composite pole figure showing rutile (110) and (001) poles on a [100] projection of crystals V-2, V-4, and G-2.

Fig. 4. a. Projection perpendicular to the (112) pseudo-close-packed plane in anatase showing possible directions of the rutile c-axes.

oxygen ions

titanium ions

b. The (112) plane in anatase showing the rutile octahedral structure.

oxygen ions in the upper plane

titanium ions below the upper plane of oxygen ions

oxygen ions in the lower plane

titanium ions below the lower plane of oxygen ions

c. Projection perpendicular to the (100) pseudo-close-packed plane in rutile showing the rutile octahedral structure.

Fig. 5. a. An anatase [100] stereogram showing the orientation of two rutile crystals whose c-axes lie in an anatase (112) plane.

- rutile (110)
- rutile (001)
- rutile (100)

b. Anatase [100] stereogram showing rutile (110) and (001) poles and the orientation of four equivalent rutile crystals.

Fig. 6. a. The configuration of the octahedral structure in anatase before the transformation, showing the same group of atoms indicated in Fig. 4b, i.e., a projection perpendicular to the anatase (112) plane. The dashed lines represent Ti-O bonds that are broken as a consequence of the movement of the titanium ions.

b. The octahedral structure of rutile, perpendicular to the rutile (100) plane as in Fig. 4c.

ZN-4151

Fig. 1.

ZN-4152

Fig. 2.

Fig. 3 a.

Fig. 3 b.

MU-33142

Fig. 4 a.

MU-33143

Fig. 4 b.

MU-33144

Fig. 4 c.

MU-33145

Fig. 5 a.

MU-33146

Fig. 5 b.

(a)

(b)

MU-33147

Fig. 6.

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