# On the Structure of Tapiolite Formed by Solid State Reactions

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The structure of tapiolite formed by the solid state reactions of tantalum pentoxide with iron oxides is discussed. Reactions were carried out in the following systems. (1) In the $FeO-Ta_2O_5$ system, ordered tapiolite was formed on heating in vacuum at 1050°C for 10 hr. It has a trirutile structure and is isomorphous with $ZnSb_2O_6$. (2) In the $Fe_3O_4-Ta_2O_5$ system, a disordered tapiolite produced under the same condition as mentioned above is isomorphous with $SnO_2$. (3) In the $Fe_2O_3-Ta_2O_5$ system, a disordered tapiolite was also formed on heating in air at 1200°C for 24 hr.

The lattice constants of the three synthetic tapiolites are as follows : (1) $a_0=4.750$ (Å), $c_0=9.205$ (Å) ; (2) $a_0=4.708$ (Å), $c_0=3.075$ (Å) ; (3) $a_0=4.681$ (Å), $c_0=3.051$ (Å).

The above facts suggest that the interplanar spacings of the three synthetic tapiolites decreased in proportion as the iron valency increased, and that the composition and structure of tapiolite depend closely on the size of the iron ion.
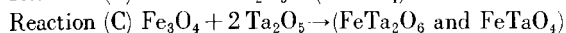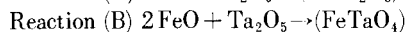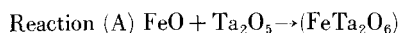
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## I. Introduction

The crystallographic relation of tapiolite to rutile and other oxides of $AX_2$ type has been discussed by Schaller[1] and the structural similarity of tapiolite and rutile by Goldschmidt[2]. Besides, the structure of tapiolite has so far been studied by Byström, Hök and Mason[3], Brandt[4], Tavora and Peixoto[5], Hutton[6], and Nakayama and Osaka[7]. Especially, Byström et al. have computed diffracted intensities in the structure determination of tapiolite. A natural mineral tapiolite, however, has served as an object of the studies.

In the present investigation an attempt was made to examine the structure of tapiolite formed by the solid state reactions of tantalum pentoxide with iron oxides, using a simplified method to measure diffracted intensities of X-ray powder patterns.

## II. Experimental

Starting materials for the preparation of mixtures consisted of tantalum pentoxide and three kinds of iron oxides (wüstite, magnetite and hematite). These oxides, except wüstite produced by the oxidation of pure iron in air, were obtained commercially and had the purity better than 99.5%. Mixtures of tantalum pentoxide and respective iron oxides were prepared in proportions indicated as follows :

Reaction (A) $FeO + Ta_2O_5 \rightarrow (FeTa_2O_6)$

Reaction (B) $2FeO + Ta_2O_5 \rightarrow (FeTaO_4)$

Reaction (C) $Fe_3O_4 + 2Ta_2O_5 \rightarrow (FeTa_2O_6$ and $FeTaO_4)$

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( 2 ) V. M. Goldschmidt : Vidensk.-Akad. i. Oslo I, Mat.-Nat. Kl., Skr. 1, paper 1, (1926), 5.
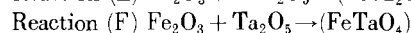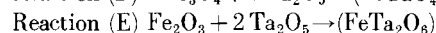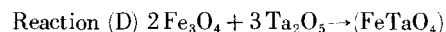( 3 ) A. Byström, B. Hök and B. Mason : Arkiv för kemi, min. o. geol., 15, **4** (1941), 1.
( 4 ) K. Brandt : Arkiv för kemi, min. o. geol., 17, **15** (1943), 8.
( 5 ) E. Tavora and F. Peixoto : Anais da Acad. Brazil de Ciênc., 23, **4** (1951), 449.
( 6 ) C. O. Hutton : Am. Mineral, **43** (1958), 112.
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Reaction (D) $2Fe_3O_4 + 3Ta_2O_5 \rightarrow (FeTaO_4)$

Reaction (E) $Fe_2O_3 + 2Ta_2O_5 \rightarrow (FeTa_2O_6)$

Reaction (F) $Fe_2O_3 + Ta_2O_5 \rightarrow (FeTaO_4)$

The compounds in parentheses are multiple oxides to be expected from the above reactions. $FeTa_2O_6$ and $FeTaO_4$ represent an ordered tapiolite and a disordered one, respectively. $FeO-$ and $Fe_3O_4-Ta_2O_5$ mixtures were heated in a stainless steel boat in vacuum ($3 \times 10^{-4}$ mmHg) at 1050°C for 10 hr, and $Fe_2O_3-Ta_2O_5$ mixtures in an alumina boat in air at 1200°C for 24 hr. A product in the first system was bright orange, that of the second was brown, and the third was ochre. Each of them was stable in air room temperature. The respective samples were examined by X-ray diffraction powder techniques (Ni-filtered Cu radiation) using a Geiger-counter diffractometer.

## III. Results and Discussion

(1) $FeO-Ta_2O_5$ system: A diffraction pattern obtained from the bright orange compound by reaction (A) indicated apparently the presence of a trirutile structure. On the other hand, the pattern from the product in reaction (B) contained diffraction lines from magnetite, which was considered to result from the oxidation of wüstite, besides those from the same rutile structure as formed in (A). Under the experimental conditions adopted in the present investigation, it was found that tantalum pentoxide was stable but wüstite was transformed into magnetite and iron. In comparing this result ($FeO-Ta_2O_5$ system) with that stated later ($Fe_3O_4-Ta_2O_5$ system), however, it seemed that the rate of the reaction of wüstite with tantalum pentoxide was greater than that of the transition from wüstite to magnetite. In addition, a diffractogram from the product in (A) was in agreement with that in (B) with respect to both the observed intensities and the interplanar spacings. From the above facts, the following conclusion was obtained ; in the $FeO-Ta_2O_5$ system, if iron ions are bivalent, an ordered tapiolite will be formed, and not a disordered tapiolite.

The lattice constants of tapiolite formed by reaction (A), determined from the quartz-calibrated diffractogram, are $a_0=4.750$ (A), $c_0=9.205$ (A), and $c_0/a_0=1.938$.

Both the observed intensities and the interplanar spacings are listed in Table 1.

Table 1 X-ray diffraction data for tapiolite in the FeO-Ta$_2$O$_5$ system
Radiation : CuK$\alpha$ ($\lambda=1.5418$ Å)

| h k l | d$_{obs}$.(Å) | d$_{calc}$.(Å) | I$_{obs}$. | h k l | d$_{obs}$.(Å) | d$_{calc}$.(Å) | I$_{obs}$. |
|---|---|---|---|---|---|---|---|
| 002 | 4.599 | 4.603 | 12 | 206 | 1.288 | 1.289 | 11 |
| 101 | 4.223 | 4.222 | 30 | 107 | 1.264 | 1.263 | <1 |
| 110 | 3.360 | 3.359 | 100 | 314 | 1.258 | 1.258 | 2 |
| 112 | 2.713 | 2.713 | 13 | 323 | 1.211 | 1.211 | 16 |
| 103 | 2.576 | 2.577 | 91 | 400 | 1.188 | 1.188 | 5 |
| 200 | 2.375 | 2.375 | 31 | 410 | 1.152 | 1.152 | 1 |
| 004 | 2.299 | 2.301 | 1 | 411 | 1.144 | 1.143 | <1 |
| 113 | 2.264 | 2.266 | 5 | 226 | 1.132 | 1.133 | 10 |
| 210 | 2.126 | 2.124 | 2 | 330 | 1.120 | 1.120 | 4 |
| 202 | 2.110 | 2.111 | 6 | 217 | 1.118 | 1.118 | 2 |
| 211 | 2.070 | 2.071 | 10 | 118 / 332 | 1.087 | 1.089 | 2 |
| 212 | 1.933 | 1.928 | <1 | 413 | 1.079 | 1.079 | 11 |
| 114 | 1.897 | 1.900 | 3 | 316 | 1.073 | 1.073 | 11 |
| 213 | 1.746 | 1.747 | 71 | 420 | 1.063 | 1.062 | 6 |
| 105 | 1.715 | 1.717 | 4 | 208 / 422 | 1.036 | 1.036 | 2 |
| 220 | 1.680 | 1.680 | 24 | 109 | 0.999 | 1.000 | 6 |
| 204 | 1.653 | 1.654 | 5 | 415 | 0.978 | 0.977 | 2 |
| 222 | 1.578 | 1.578 | 4 | 424 | 0.965 | 0.964 | 1 |
| 301 | 1.561 | 1.561 | 2 | 431 / 501 | 0.946 | 0.945 | 2 |
| 006 | 1.533 | 1.534 | 9 | 406 | 0.939 | 0.939 | 6 |
| 310 | 1.502 | 1.502 | 22 | 327 / 510 | 0.932 | 0.932 | 6 |
| 312 | 1.428 | 1.428 | 4 | 416 / 219 | 0.921 | 0.921 | 12 |
| 303 | 1.407 | 1.407 | 23 | 318 / 512 | 0.913 | 0.913 | 3 |
| 116 | 1.395 | 1.396 | 21 | 433 / 503 | 0.908 | 0.908 | 18 |
| 321 | 1.304 | 1.304 | 1 | 336 | 0.906 | 0.904 | 8 |

(2) Fe$_3$O$_4$–Ta$_2$O$_5$ system: At first, a new brown phase produced by reaction (C) was expected to be mixtures composed of an ordered tapiolite and a disordered one. A diffractogram of the product in (C), however, showed the presence of the rutile type structure and an unreacted tantalum pentoxide, and the product in (D) gave only a diffraction pattern corresponding to the rutile type structure. A difference between the diffractograms from the two tapiolites in (C) and (D) was little. In addition, no diffraction lines arising from a superstructure were detected. Accordingly, it was evident that in the Fe$_3$O$_4$–Ta$_2$O$_5$ system a disordered tapiolite was formed, and not an ordered tapiolite. This is probably related to the fact that the size of ferrous ions (in wüstite) is obviously greater than that of ferric mixed ions (in magnetite). Because, in comparing the interplanar spacings listed in Table 1 with those in Table 2, it is suggested that the lattice constants of tapiolite formed by reaction (C) or (D) are evidently smaller than those of tapiolite in reaction (A) or (B).

The lattice constants of tapiolite in reaction (D) were calculated from the powder data and found to be $a_0 = 4.708$ (Å), $c_0 = 3.075$ (Å), and $c_0/a_0 = 0.654$.

(3) Fe$_2$O$_3$–Ta$_2$O$_5$ system : An attempt to prepare an ordered tapiolite by reaction (E) was also unsuccessful. The presence of the rutile type compound and an unreacted tantalum pentoxide was clarified by X-ray diffraction data obtained after the reaction (E). Further, a diffractogram of the ochre compound produced by reaction (F) indicated the presence of only a disordered tapiolite. No diffraction effects indicating a superlattice formation

or a lower symmetry than the tetragonal one were visible in the powder pattern.

Table 2 X-ray deffraction data for tapiolites in the Fe$_3$O$_4$- and Fe$_2$O$_3$-Ta$_2$O$_5$ systems
Radiatidn : CuK$\alpha$($\lambda=1.5418$ Å)

| h k l | Fe$_3$O$_4$-Ta$_2$O$_5$ system | | | Fe$_2$O$_3$-Ta$_2$O$_5$ system | | |
|---|---|---|---|---|---|---|
| | d$_{obs}$.(Å) | d$_{calc}$.(Å) | I$_{obs}$. | d$_{obs}$.(Å) | d$_{calc}$.(Å) | I$_{obs}$. |
| 110 | 3.326 | 3.329 | 100 | 3.311 | 3.310 | 100 |
| 101 | 2.562 | 2.576 | 79 | 2.555 | 2.566 | 80 |
| 200 | 2.352 | 2.354 | 26 | 2.341 | 2.340 | 24 |
| 111 | 2.251 | 2.260 | 5 | 2.242 | 2.257 | 5 |
| 210 | 2.103 | 2.105 | 2 | 2.094 | 2.093 | 2 |
| 211 | 1.734 | 1.734 | 65 | 1.726 | 1.742 | 65 |
| 220 | 1.664 | 1.664 | 19 | 1.655 | 1.658 | 19 |
| 002 | 1.530 | 1.539 | 8 | 1.524 | 1.526 | 7 |
| 310 | 1.488 | 1.489 | 17 | 1.480 | 1.480 | 16 |
| 301 | 1.395 | 1.398 | 21 | 1.389 | 1.394 | 20 |
| 112 | 1.389 | 1.397 | 17 | 1.385 | 1.389 | 22 |
| 202 | 1.283 | 1.288 | 8 | 1.277 | 1.283 | 9 |
| 321 | 1.201 | 1.202 | 13 | 1.194 | 1.208 | 14 |
| 400 | 1.177 | 1.177 | 4 | 1.171 | 1.170 | 5 |
| 222 | 1.126 | 1.130 | 9 | 1.122 | 1.129 | 9 |
| 330 | 1.111 | 1.110 | 5 | 1.104 | 1.103 | 5 |
| 411 | 1.070 | 1.071 | 12 | 1.064 | 1.077 | 13 |
| 312 | 1.068 | 1.070 | 14 | 1.059 | 1.069 | 14 |
| 420 | 1.054 | 1.053 | 6 | 1.045 | 1.047 | 6 |
| 103 | 0.998 | 1.002 | 5 | 0.993 | 0.994 | 7 |
| 402 | 0.934 | 0.935 | 6 | 0.929 | 0.931 | 6 |
| 510 | 0.924 | 0.923 | 5 | 0.918 | 0.918 | 5 |
| 412 / 213 | 0.919 | 0.922 | 12 | 0.915 | 0.917 | 13 |
| 431 / 501 | 0.901 | 0.9005 | 14 | 0.895 | 0.899 | 14 |
| 332 | — | 0.9000 | — | 0.893 | 0.896 | 7 |

The lattice constants calculated are $a_0 = 4.681$ (Å), $c_0 = 3.051$ (Å), and $c_0/a_0 = 0.652$. It was also found that in the Fe$_2$O$_3$–Ta$_2$O$_5$ system the interplanar spacings of tapiolite in reaction (E) or (F) decreased in proportion as the iron valency increased.

It is suggested from the results of the present study that the size of iron ions plays an important role in the composition and structure of the synthetic tapiolite. It should be noted that there is a remarkable difference between the interplanar spacings of the mineral tapiolite reported by Hutton [6] and those obtained from the present study. In this experimental, however, all the reactions from (A) to (F) will not be true and the homogeneity of the product is doubtful, but without direct information about the exact composition of the phases analyzed by X-ray methods, anything better than the present qualitative observation can hardly be made.

## IV. Summary

Two phases have been found to exist in the solid state reactions of tantalum pentoxide with iron oxides. A bright orange phase in the FeO–Ta$_2$O$_5$ system has the trirutile-type structure. A brown or ochre phase in the system Fe$_3$O$_4$– or Fe$_2$O$_3$–Ta$_2$O$_5$ has only the rutile-type structure.

Moreover, it was found that the interplanar spacings of three kinds of synthetic tapiolite decreased in proportion as the iron valency increased.