

SYNTHESIS AND STABILITY OF BISMUTOTANTALITE,
STIBIOTANTALITE AND CHEMICALLY SIMILAR
ABO₄ COMPOUNDS

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ABSTRACT

Bismutotantalite (BiTaO₄) and stibiotantalite (SbTaO₄) have been synthesized by appropriate heating of the mixed oxides in sealed Pt tubes. Bismuth trioxide and antimony trioxide have been mixed with niobium, tantalum and vanadium pentoxides and the resulting ABO₄ compounds are discussed with respect to structure type and stability of the various phases.

Dihlstrom (1938) has shown that the mineral stibiotantalite (SbTaO₄) has the same structure as antimony tetroxide (SbSbO₄). The mineral bismutotantalite (BiTaO₄) is also known to have the same or a similar structure type (Hurlbut, 1957). The mineral pucherite (BiVO₄) was also thought to be of similar structure (Ungemach, 1909), but it has been indicated by DeJong and DeLange (1936) and by Qurashi and Barnes (1952, 1953) that the structure of pucherite is considerably different from that described by Dihlstrom for stibiotantalite and Sb₂O₄.

Dihlstrom (1938) attempted to synthesize BiNbO₄, BiTaO₄ and BiVO₄ by sintering together the respective oxides. However he found that the x-ray powder patterns were very different from that of stibiotantalite. Aurivillius (1951) also prepared BiNbO₄ and BiTaO₄ by heating a mixture of the oxides in air and O₂ at 1100°–1200° C. but the samples were not isomorphous with stibiotantalite. Crystals picked from the melt of these compositions proved to be triclinic. Roth and Waring (1962) studied the phase equilibrium relations in the system Bi₂O₃—Nb₂O₅ and reported that BiNbO₄ transformed irreversibly (in laboratory time) from the orthorhombic bismutotantalite type structure to the triclinic form at about 1020°C. As a result of this study of BiNbO₄ it was thought advisable to attempt to synthesize the other compounds which might possibly have similar structure types, namely BiTaO₄, BiVO₄, SbNbO₄, SbTaO₄, and SbVO₄. The results of these experiments are described in this paper.

The experimental procedure for specimens involving Bi₂O₃ has been previously described (Roth and Waring, 1962). For specimens containing Sb₂O₃ the mixtures of oxides were dried in air at about 220° C. and then heated in sealed Pt tubes at higher temperatures so that oxidation of the antimony trioxide might be kept at a minimum.

BiNbO₄: Synthesis of BiNbO₄ has been previously described (Roth and Waring 1962). Below about 1020° C. the material has the orthorhombic

stibiotantalite-type structure with $a=4.980 \text{ \AA}$, $b=11.709 \text{ \AA}$, $c=5.675 \text{ \AA}$. Specimens which have been heated above $\approx 1020^\circ \text{ C}$. are triclinic with $a=7.61_1 \text{ \AA}$, $b=5.53_6 \text{ \AA}$, $c=7.91_9 \text{ \AA}$, $\alpha=89.88^\circ$, $\beta=77.43^\circ$, $\gamma=87.15^\circ$. Indexed x -ray diffraction powder patterns of both forms were listed (Roth and Waring, 1962). The phase transition could not be reversed by heating as long as 184 hours at 1008° C .

BiTaO₄: Specimens of BiTaO_4 were prepared in a manner analogous to that reported for BiNbO_4 . The mixture was calcined at 700° C . for 3 hours. The orthorhombic bismutotantalite structure was obtained as a single phase by heating the calcined mixture in a sealed Pt tube at 846° C . for 62 hours and quenching to room temperature. A specimen similarly treated at 900° C . for 18 hours showed mostly bismutotantalite, but also had a trace of a high temperature form. Heating at 995° C . for 19 hours as well as 1149° C . for 65 hours both resulted in single phase specimens of the high temperature, triclinic form previously reported by Aurivillius (1951). The unit cell dimensions found for synthetic orthorhombic bismutotantalite are $a=4.957 \text{ \AA}$, $b=11.76_3 \text{ \AA}$, $c=5.633 \text{ \AA}$; for the triclinic form $a=7.65_2 \text{ \AA}$, $b=5.58_4 \text{ \AA}$, $c=7.77_2 \text{ \AA}$, $\alpha=89.92^\circ$, $\beta=77.12^\circ$, $\gamma=86.45^\circ$. Indexed x -ray diffraction powder patterns are given in Tables 1 and 2.

SbNbO₄: The specimens were calcined at 220° C . for 2 hours. When heated in sealed Pt tubes at 995° C . for 16 hours, 1000° C . for one hour or 1103° C . for four hours the specimens were single-phase orthorhombic, isostructural with the mineral stibiotantalite, $a=4.929 \text{ \AA}$, $b=11.79_7 \text{ \AA}$, $c=5.559 \text{ \AA}$ (Table 1). Some decomposition of preformed SbNbO_4 was accomplished by heating at 1000° C . for one hour in air. When the calcined material was heated in air at 1000° C . for one hour it contained only an Sb_2O_4 solid solution plus a solid solution of the low temperature form of Nb_2O_5 . No other material is known to stabilize the low temperature form of Nb_2O_5 to temperatures as high as 1000° C . When SbNbO_4 was heated to 1200° C . for one hour it melted and leaked out of the Pt tube, the antimony oxide all volatilized and left only $\text{H-Nb}_2\text{O}_5$.

SbTaO₄: After calcining at 220° C . for 2 hours, single phase specimens of stibiotantalite structure were obtained by heating in sealed Pt tubes at 995° C . for 16 and 24 hours, 1000° C . for one hour and 1103° C . for one hour. After heating at 1199° C . for one hour there was a small amount of a second unidentified phase also present in the specimen. When the original mixture was heated for one hour at 1000° C . in air only Sb_2O_4 solid solution and Ta_2O_5 solid solution were present. However, the preformed SbTaO_4 decomposed very slowly at this temperature in air to

TABLE 1. X-RAY DIFFRACTION POWDER PATTERNS OF SYNTHETIC BISMUTOTANTALITE, STIBIOTANTALITE AND SbNbO_4 ($\text{CuK}\alpha$ radiation)

| hkl | BiTaO_4 Synthetic bismutotantalite 900° C.—18 hr; Q-sealed Pt tube | | SbTaO_4 Synthetic stibiotantalite 995° C.—16 hr; Q-sealed Pt tube | | SbNbO_4 Stibiotantalite-type structure 995° C.—16 hr; Q-sealed Pt tube | |
|--------------------|---|----------------|--|-----|---|-----|
| | dÅ | I | dÅ | I | dÅ | I |
| 020 | 5.88 | 3 | 5.90 | 30 | — | — |
| 110 | 4.56 | 18 | 4.53 | 28 | 4.54 | 33 |
| 101 | 3.717 | 18 | — | — | 3.682 | 11 |
| 111 | 3.543 | 124 | 3.506 | 174 | 3.517 | 75 |
| 121 | 3.144 | 506 | 3.121 | 464 | 3.125 | 408 |
| 130 | 3.072 | 16 | 3.070 | 23 | 3.072 | 23 |
| H-202 ¹ | 3.010 ¹ | 8 ¹ | — | — | — | — |
| 040 | 2.938 | 178 | 2.950 | 160 | 2.947 | 116 |
| 002 | 2.814 | 68 | 2.766 | 30 | 2.779 | 40 |
| 012 | 2.738 | 64 | 2.692 | 99 | 2.704 | 35 |
| 131 | 2.698 | 52 | 2.687 | 102 | 2.688 | 22 |
| 022 | 2.540 | 58 | 2.506 | 28 | 2.513 | 22 |
| 200 | 2.477 | 104 | 2.456 | 62 | 2.464 | 34 |
| 112 | 2.398 | 4 | 2.363 | 4 | 2.372 | 5 |
| 141 | 2.306 | 23 | — | — | 2.303 | 13 |
| 032 } 220 } | 2.287 | 27 | 2.265 | 37 | 2.271 | 12 |
| 122 | 2.261 | 11 | 2.232 | 9 | 2.240 | 11 |
| 211 | 2.227 | 11 | 2.205 | 12 | 2.122 | 17 |
| 150 | — | — | — | — | 2.129 | 3 |
| 221 | — | — | 2.098 | 5 | 2.105 | 5 |
| 132 | 2.076 | 7 | 2.056 | 7 | 2.061 | 7 |
| 042 | 2.034 | 72 | 2.019 | 25 | 2.023 | 39 |
| 151 | 1.989 | 29 | 1.987 | 40 | 1.987 | 15 |
| 231 | 1.963 | 15 | 1.950 ² | 14 | 1.955 ² | 19 |
| 060 | 1.960 | 8 | 1.968 | 5 | 1.965 | 4 |
| 240 | 1.895 | 124 | 1.888 | 79 | 1.891 | 49 |
| 202 | 1.861 | 52 | 1.837 | 13 | 1.843 | 15 |
| 212 | 1.837 | 63 | 1.815 | 66 | 1.822 | 28 |
| 052 | 1.805 | 29 | 1.797 | 28 | 1.799 | 14 |
| 222 | 1.774 | 44 | 1.754 | 16 | 1.760 | 14 |

¹ A trace of the high temperature form of BiTaO_4 is present in this material² These peaks represent reversals in the order of hkl values of the various compounds.

TABLE 1—(continued)

| hkl | BiTaO ₄ Synthetic bismutotantalite 900° C.-18 hr.; Q-sealed Pt tube | | SbTaO ₄ Synthetic stibiotantalite 995° C.-16 hr.; Q-sealed Pt tube | | SbNbO ₄ Stibiotantalite-type structure 995° C.-16 hr.; Q-sealed Pt tube | |
|-----|--|-----|---|----|---|----|
| | dÅ | I | dÅ | I | dÅ | I |
| 103 | 1.756 | 70 | 1.728 ² | 48 | 1.735 | 85 |
| 161 | 1.734 | 150 | 1.735 | 90 | | |
| 113 | — | — | 1.709 | 30 | 1.716 | 21 |
| 152 | 1.696 | 6 | 1.687 | 4 | 1.690 | 5 |
| 232 | 1.681 | 57 | 1.664 | 52 | 1.669 | 27 |
| 123 | | | — | — | 1.664 | 10 |
| 310 | 1.636 | 10 | 1.622 ² | 11 | 1.628 | 15 |
| 251 | 1.633 | 12 | 1.627 | 9 | | |
| 062 | 1.609 | 20 | 1.604 | 10 | 1.606 | 10 |
| 133 | 1.603 | 28 | 1.581 | 20 | 1.587 | 12 |
| 242 | 1.572 | 53 | 1.559 | 15 | 1.563 | 18 |
| 311 | — | — | 1.557 | 17 | | |
| 260 | — | — | 1.536 | 9 | — | — |
| 171 | — | — | 1.533 | 19 | 1.533 | 7 |
| 321 | 1.531 | 98 | 1.517 | 39 | 1.522 | 29 |
| 143 | 1.508 | 63 | 1.4910 | 31 | 1.496 | 17 |
| 213 | 1.4847 | 8 | 1.4638 ² | 7 | — | — |
| 080 | 1.4704 | 36 | 1.4767 | 18 | 1.475 | 11 |
| 331 | — | — | 1.4586 | 17 | 1.463 | 5 |
| 252 | 1.4596 | 23 | 1.4505 | 19 | 1.454 | 9 |
| 072 | 1.4431 | 15 | 1.4411 | 16 | 1.441 | 9 |
| 312 | 1.4154 | 8 | 1.3992 | 7 | 1.404 | 6 |
| 153 | 1.4076 | 15 | 1.3946 | 15 | 1.398 | 8 |
| 004 | | | 1.3834 | 7 | — | — |
| 172 | 1.3855 | 3 | — | — | — | — |
| 233 | — | — | 1.3814 | 6 | 1.386 | 3 |
| 024 | 1.3700 | 40 | | | 1.353 | 10 |
| 350 | 1.3520 | 8 | 1.3473 | 22 | 1.349 | 11 |
| 271 | 1.3498 | 17 | — | — | | |
| 262 | | | | | | |
| 332 | 1.3395 | 6 | 1.3264 | 4 | | |
| 034 | 1.3256 | 3 | 1.3054 ² | 7 | | |
| 351 | 1.3148 | 7 | 1.3076 | 9 | | |
| 163 | 1.3080 | 6 | — | — | | |
| 082 | 1.3035 | 11 | 1.3029 | 6 | | |
| 124 | — | — | 1.2992 | 5 | | |
| 134 | 1.2802 | 4 | — | — | | |
| 280 | 1.2648 | 36 | 1.2658 | 18 | | |
| 272 | 1.2473 | 12 | 1.2431 | 11 | | |

TABLE 1—(continued)

| (correlation of hkl beyond this point is virtually impossible) | | | | | |
|--|--------|----|--------|----|-------------|
| hkl | dÅ | I | dÅ | I | hkl |
| 303 | 1.2406 | 16 | 1.2362 | 6 | 191 |
| 400 | 1.2395 | 15 | 1.2276 | 16 | 400/361 |
| 281/313 | 1.2333 | 42 | 1.2247 | 15 | 303 |
| 191/361 | | | 1.2176 | 5 | 313 |
| 352 | 1.2192 | 5 | 1.2103 | 4 | 352 |
| 173/323 | 1.2141 | 12 | 1.2073 | 8 | 173 |
| 411 | 1.2042 | 8 | 1.1936 | 4 | 054/411 |
| 224 | 1.1993 | 40 | 1.1860 | 5 | 092 |
| 092/421 | 1.1855 | 6 | 1.1814 | 15 | 0·10·0/224 |
| 333 | 1.1829 | 9 | 1.1694 | 6 | 333 |
| 431 | 1.1565 | 6 | 1.1506 | 5 | 282 |
| 282 | 1.1538 | 20 | 1.1495 | 5 | 371 |
| 064 | 1.1438 | 30 | 1.1331 | 14 | 291 |
| 343 | 1.1429 | 33 | 1.1319 | 18 | 064 |
| 440 | 1.1423 | 27 | 1.1310 | 16 | 343 |
| 402 | 1.1345 | 6 | 1.1249 | 12 | 1·10·1 |
| 183 | 1.1275 | 22 | 1.1226 | 17 | 183/402 |
| 1·10·1 | 1.1218 | 28 | 1.1174 | 8 | 412 |
| 164/422 | 1.1140 | 5 | 1.0872 | 6 | 353 |
| 105 | 1.0989 | 18 | 1.0795 | 10 | 105/432 |
| 353 | 1.0975 | 9 | 1.0691 | 5 | 451 |
| 432 | 1.0899 | 8 | 1.0679 | 7 | 292 |
| 372/254 | 1.0865 | 5 | 1.0451 | 6 | {174/2·10·1 |
| 0·10·2 | | | | | 193 |
| 451 | 1.0764 | 4 | 1.0421 | 6 | 460 |
| 292 | 1.0700 | 6 | 1.0310 | 5 | 1·11·1 |
| 442 | 1.0585 | 8 | 1.0283 | 10 | 264 |
| 283/193 | 1.0485 | 6 | 1.0145 | 12 | 145 |
| 363 | | | 1.0073 | 5 | 423/391 |
| 264 | 1.0388 | 23 | | | |
| 413 | 1.0304 | 9 | | | |
| 461/145 | 1.0294 | 25 | | | |
| 452/215 | 1.0220 | 6 | | | |

SbTaO₄-Sb₂O₄ solid solution. The unit cell dimensions of synthetic orthorhombic stibiotantalite were found to be $a = 4.911 \text{ \AA}$, $b = 11.81_4 \text{ \AA}$, $c = 5.535 \text{ \AA}$. The x -ray diffraction powder pattern is listed in Table 1.

TABLE 2. X-RAY DIFFRACTION POWDER PATTERNS OF SOME ABO₄ COMPOUNDS (CuK_α RADIATION)

| BiTaO ₄ | | | | SbVO ₄ | | | | BiVO ₄ | | | | BiVO ₄ | | | |
|---|-------|-----|-----|--|----|-----|--------|--|---------|--------|----|---|-------|-----|--|
| High Temperature Triclinic Form 1149° C-65 hr; Q-sealed Pt tube | | | | Rutile type structure + High temperature form 800° C-16 hr; Q-sealed Pt tube | | | | Zircon-type structure ppt, washed and dried at 110° C. | | | | Fergusonite-type structure 895° C-16 hr; Q-sealed Pt tube | | | |
| hkl | d Å | I | hkl | d Å | I | hkl | d Å | I | hkl | d Å | I | hkl | d Å | I | |
| 100 | 7.43 | 12 | | 1.867 | 37 | a | 4.45 | 4 | 101 | 4.82 | 62 | 020 | 5.82 | 9 | |
| 101 | 6.02 | 4 | | 1.862 | 59 | 110 | 3.245 | 180 | 200 | 3.641 | 40 | 110 | 4.73 | 67 | |
| 011 | 4.51 | 7 | | 1.844 | 26 | a | 2.908 | 5 | 211 | 2.908 | 40 | 011 | 4.65 | 80 | |
| 002 | 3.787 | 41 | | 1.834 | 14 | a | 2.869 | 12 | 112 | 2.735 | 80 | 130 | 3.110 | 73 | |
| 200 | 3.723 | 30 | | 1.802 | 26 | a | 2.629 | 5 | 220 | 2.576 | 36 | 031/121 | 3.089 | 260 | |
| 210 | 3.191 | 98 | | 1.776 | 58 | 101 | 2.555 | 112 | 202 | 2.419 | 5 | 121 | 3.074 | 240 | |
| 012 | 3.155 | 100 | | 1.746 | 32 | a | 2.414 | 5 | 301 | 2.274 | 38 | 040 | 2.921 | 112 | |
| 112 | 3.123 | 48 | | 1.734 | 22 | 200 | 2.297 | 33 | 103 | 2.062 | 19 | 200 | 2.593 | 48 | |
| 012 | 3.111 | 104 | | 1.722 | 10 | 111 | 2.233 | 17 | 321 | 1.929 | 26 | 002 | 2.542 | 55 | |
| 201 | 3.079 | 72 | | 1.706 | 29 | 210 | 2.055 | 6 | 312 | 1.875 | 82 | 220 | 2.370 | 6 | |
| 202/210 | 3.010 | 139 | | 1.698 | 10 | a | 1.858 | 6 | 400 | 1.823 | 28 | 141 | 2.279 | 25 | |
| 020 | 2.786 | 84 | | 1.680 | 32 | a | 1.812 | 6 | 213 | 1.796 | 14 | 141/211 | 2.275 | 31 | |
| 211 | 2.765 | 11 | | 1.675 | 26 | a | 1.780 | 5 | 411 | 1.705 | 12 | 211 | 2.261 | 45 | |
| 112 | 2.761 | 9 | | 1.659 | 28 | 211 | 1.710 | 94 | 420 | 1.631 | 22 | 112 | 2.246 | 38 | |
| 212 | 2.696 | 33 | | 1.653 | 31 | a | 1.676 | 5 | 004 | 1.611 | 11 | 112 | 2.236 | 17 | |
| 212 | 2.610 | 32 | | 1.643 | 23 | 220 | 1.626 | 33 | 332 | 1.517 | 18 | 150 | 2.130 | 22 | |
| 121 | 2.567 | 7 | | 1.623 | 42 | 002 | 1.539 | 12 | 204 | 1.4752 | 19 | 051 | 2.123 | 51 | |
| 120 | 2.556 | 8 | | 1.615 | 19 | 310 | 1.4537 | 20 | 501/431 | 1.4227 | 10 | 231 | 1.992 | 22 | |
| 121 | 2.494 | 6 | | 1.611 | 17 | 112 | 1.3911 | 18 | 224 | 1.3674 | 16 | 231 | 1.984 | 14 | |
| 121 | 2.464 | 4 | | 1.595 | 33 | 301 | 1.3720 | 25 | 512 | 1.3073 | 17 | 132 | 1.975 | 24 | |
| 202 | 2.400 | 68 | | 1.578 | 12 | 202 | 1.2792 | 9 | 600 | 1.2160 | 5 | 132 | 1.966 | 34 | |
| 113 | 2.332 | 23 | | 1.564 | 9 | 321 | 1.1782 | 14 | 404 | 1.2081 | 10 | 060 | 1.948 | 15 | |
| 220 | 2.303 | 19 | | 1.556 | 12 | 400 | 1.4931 | 7 | | | | 240 | 1.940 | 79 | |
| | 2.260 | 7 | | 1.541 | 5 | 222 | 1.1175 | 9 | | | | 042 | 1.918 | 87 | |

^a These peaks apparently belong to a high temperature polymorph of SbVO₄.

TABLE 2. X-RAY DIFFRACTION POWDER PATTERNS OF SOME ABO_4 COMPOUNDS (CuK_α RADIATION)

| BiTaO ₄ | | | | SbVO ₄ | | | | BiVO ₄ | | | | BiVO ₄ | | | |
|---|-------|----|-----|---|----|-----|-----|--|-----|-----|---|--|---------|-------|----|
| High Temperature Triclinic Form 1149° C-65 hr; Q-sealed Pt tube | | | | Rutile type structure+ High temperature form 800° C-16 hr; Q-sealed Pt tube | | | | Zircon-type structure ppt, washed and dried at 110° C. | | | | Fergusonite-type structure 895° C.-16 hr; Q-sealed Pt tube | | | |
| hkl | d Å | I | hkl | d Å | I | hkl | d Å | I | hkl | d Å | I | hkl | d Å | I | |
| | 2.230 | 7 | | 1.529 | 4 | | 330 | 1.0838 | 6 | | | | 202 | 1.822 | 41 |
| | 2.217 | 12 | | 1.513 | 7 | | 312 | 1.0568 | 8 | | | | 202 | 1.810 | 38 |
| | 2.167 | 30 | | 1.506 | 18 | | 411 | 1.0487 | 11 | | | | 161 | 1.718 | 90 |
| | 2.129 | 19 | | 1.496 | 6 | | 420 | 1.0283 | 7 | | | | 161 | 1.715 | 84 |
| | 2.117 | 22 | | 1.482 | 9 | | | | | | | | 310 | 1.708 | 10 |
| | 2.089 | 32 | | 1.472 | 6 | | | | | | | | 013 | 1.678 | 11 |
| | 2.036 | 10 | | 1.463 | 30 | | | | | | | | 251 | 1.645 | 12 |
| | 2.010 | 21 | | 1.445 | 16 | | | | | | | | 251 | 1.642 | 14 |
| | 1.944 | 60 | | 1.434 | 12 | | | | | | | | 152 | 1.637 | 8 |
| | 1.916 | 7 | | 1.420 | 5 | | | | | | | | 152 | 1.632 | 7 |
| | 1.912 | 12 | | 1.405 | 5 | | | | | | | | 170 | 1.590 | 20 |
| | 1.896 | 9 | | 1.394 | 15 | | | | | | | | 071 | 1.586 | 14 |
| | | | | | | | | | | | | | 330/321 | 1.580 | 47 |
| | | | | | | | | | | | | | 321 | 1.574 | 39 |
| | | | | | | | | | | | | | 260 | 1.558 | 28 |
| | | | | | | | | | | | | | 123 | 1.556 | 35 |
| | | | | | | | | | | | | | 033 | 1.554 | 26 |
| | | | | | | | | | | | | | 123 | 1.551 | 49 |
| | | | | | | | | | | | | | 062/242 | 1.549 | 50 |
| | | | | | | | | | | | | | 242 | 1.539 | 37 |
| | | | | | | | | | | | | | 080 | 1.462 | 20 |

SbVO₄: The mixture was calcined at 220° C. for 2 hours and a small portion was quenched in a sealed Pt tube after 16 hours at 700° C. The specimen showed an *x*-ray diffraction powder pattern which could be indexed on the basis of a rutile type structure (Table 2). The unit cell dimensions of this phase were found to be $a = 4.598 \text{ \AA}$, $c = 3.078 \text{ \AA}$ as compared with the values given by Vernon and Milligan (1951) of $a = 4.58 \text{ \AA}$, $c = 3.06 \text{ \AA}$. Specimens which were heated at 700° C. or higher, when cooled to room temperature without quenching, all showed only the rutile type phase. However, when the specimens were quenched from a temperature between 800° C. and the melting point (about 865° C.) the rutile phase appeared, together with a second phase which can only be interpreted as the remnants of a high temperature polymorph. All attempts to "quench in" the high temperature form were unsuccessful. When quenched from above 865° C. the specimen contained only glass. High temperature *x*-ray diffraction patterns revealed no change in the rutile structure at 750° C. after 24 hours; however, at about 825° C. the new phase began to form at the expense of the rutile type structure. However, at this temperature volatility was excessive and the specimen completely volatilized before a complete *x*-ray pattern could be obtained. The *d*-values of the *x*-ray diffraction peaks identified as belonging to the high temperature phase are also given in Table 2; however, the structure type is unknown.

It is worth noting that (together with all the peaks in the rutile pattern) the small peaks at 4.45 Å and 2.629 Å can be indexed respectively, as (101) and (211) of a zircon structure type with $a = 6.503 \text{ \AA}$, $c = 6.157 \text{ \AA}$. However, the high temperature *x*-ray patterns indicate that these peaks actually belong to the high temperature phase rather than to the low temperature form.

BiVO₄: Due to the low melting point of V₂O₅, the specimen of Bi₂O₃:V₂O₅ was only calcined at 220° C. After being heated at 500° C. for 16 hours and 600° C. for 1½ hours, the patterns showed only partial reaction; however, specimens heated at 700° C. for 16 hours, 800° C. for one hour and 900° C. for one hour all showed only a single phase. This phase did not have the same structure as the mineral pucherite (DeJong and DeLange, 1936; Qurashi and Barnes, 1952, 1953). Instead, a monoclinic form, isostructural with fergusonite (Ferguson, 1957), or a monoclinic distortion of the scheelite structure type, was identified in the *x*-ray diffraction patterns (see Table 2). The unit cell dimensions were found to be $a = 5.186 \text{ \AA}$, $b = 11.692 \text{ \AA}$, $c = 5.084 \text{ \AA}$, $\beta = 89.61^\circ$. A specimen quenched from 1000° C. was completely melted but showed only the fergusonite structure type. Differential thermal analysis showed no sign of a phase transition and indicated the melting point to be about 940° C.

A specimen of BiVO₄ was precipitated from solution of Na₃VO₄ and

$\text{Bi}(\text{NO}_3)_3$ (Swanson *et al.*, 1962) and proved to have a tetragonal zircon type structure. Table 2 lists the *x*-ray diffraction powder pattern observed in this study which was indexed on the basis of $a = 7.290 \text{ \AA}$, $c = 6.444 \text{ \AA}$. This zircon type structure transformed irreversibly to the fergusonite type between about $400^\circ\text{--}500^\circ \text{ C}$. When the precipitate was made in boiling water it contained mostly the fergusonite type structure with only a small amount of zircon type. The (*x*-ray) density of the zircon type is about 6.25 g/cm^3 and that of the fergusonite type is 6.98 g/cm^3 . The density of a natural specimen of pucherite was calculated as 6.63 g/cm^3 from the unit cell dimensions. As this is intermediate between the two synthetic forms it was thought possible that pucherite might represent a low temperature, intermediate pressure form. However, the unreacted mixture of oxides heated at $\approx 450^\circ \text{ C}$. and $30,000 \text{ lbs/in}^2$ for eight days as well as the zircon type material heated at 250° C . and $10,000 \text{ lbs/in}^2$ for one week both yielded only the fergusonite type structure.

A natural specimen of pucherite, from the original locality of Pucher Mine, Schneeberg, Saxony, was obtained from Dr. G. Switzer of the Smithsonian Museum, Washington, D. C. When heated at 500° C . for 64 hours in a sealed Pt tube the pucherite structure was completely destroyed and the pattern showed mostly the monoclinic fergusonite type plus a few small unidentified peaks. It should also be noted that the only synthetic compound known to form a pucherite type structure is CrUO_4 (Felton *et al.*, 1962), and that the state of oxidation of this phase may not be completely known (Smith *et al.*, 1961). It is suggested that that perhaps pucherite is not a stable phase in the system $\text{Bi}_2\text{O}_3\text{--V}_2\text{O}_5$, but is stabilized in nature either by the presence of slightly reducing conditions, minor amounts of impurities or a combination of these and other factors commonly occurring in nature.

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