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SYNTHETIC FERGUSONITES AND A NEW POLYMORPH OF YTTRIUM TANTALATE

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Introduction, Review of Previous Work

Fergusonite[1] is nominally yttrium orthoniobate, $YNbO_4$, or yttrium-lanthanon niobate-tantalate, (Y, Ln) (Nb, Ta)O_4. The mineral is very impure (Dana, 1944), often radioactive and, in most cases, metamict (Barth, 1926). The metamict form becomes tetragonal when heated for prolonged periods of time between 400 and 800° (Barth, 1926). When heated to 1000° and cooled it is monoclinic (Komkov, 1959).

Using a single crystal chip of the tetragonal form found in fergusonite from the Urals, Komkov (1959) determined that its structure was that of scheelite, space group $I4_1/a$. He then prepared the monoclinic form by heating and found its structure to be a distorted scheelite, space group $I2$.

Synthetic $YNbO_4$, $YTaO_4$, all lanthanon niobates $LnNbO_4$ and those $LnTaO_4$ with Ln between Nd and Lu are isomorphous with the monoclinic form of fergusonite (Komkov, 1959; Ferguson, 1957; Keller, 1962). However, Keller (1962), who also published the most precise lattice parameters, had some reservations about $TmTaO_4$, $YbTaO_4$, and $LuTaO_4$. The niobates and some of the tantalates were found to undergo a reversible and seemingly continuous phase transformation to the tetragonal form on heating (Komkov, 1959; Rooksby and White, 1963; Stubican, 1964). For the niobates this phenomenon was investigated in detail by Gingerich and Bair (1964). They found that on heating the monoclinic phase, the a and c lattice parameters approach each other smoothly while at the same time β tends toward 90° until the symmetry is tetragonal. No discontinuities were observed. Thus, in the thermodynamic sense, the transformation is of the second order, and the so-called transformation temperature is more properly termed a critical endpoint. Because of common even though imprecise usage, we will continue to speak of a transformation temperature and define it as the lowest temperature at which a monoclinic distortion of the tetragonal cell is not present.

Gingerich and Bair (1964) found the transformation temperatures to range from 500° for $LaNbO_4$ to 825°C for $YbNbO_4$. Stubiçan (1964) found transformation temperatures for the tantalates from 1325° for $NdTaO_4$

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[1] When the mineral contains more tantalum than niobium, it is called formanite; the term fergusonite used here is a crystallographic structure type.

to 1410°C for $HoTaO_4$. He did not observe any transformation for tantalates with rare earth ions smaller than Ho.

Brixner (1964) found that replacement of the pentavalent ion with equimolar mixtures of tetra- and hexavalent ions results in fergusonite structures in which the transformation temperatures are lowered to the extent that some compounds are tetragonal at room temperature.

AIM OF PRESENT INVESTIGATION AND SUMMARY OF FINDINGS

The original purpose of this investigation was the growth of single crystals having the noncentrosymmetric structure proposed by Komkov (1959) for the monoclinic form of fergusonite, and the examination of various properties of the crystals. The initial results changed the course of this investigation, and our findings can be summarized as follows:

The monoclinic form described by Komkov (1959), hereafter designated the *M*-phase, results only if the material is prepared at temperatures within the stability range of the tetragonal form (*T*-phase) or, if prepared at lower temperatures, is held for some time well above the transformation temperature. The compounds then form with the tetragonal structure, which on cooling undergoes the reversible second-order transformation to the *M*-phase.

If the material is crystallized below the transformation temperature, a new monoclinic structure, called the *M′*-phase, results. The *b*-axis of its unit cell is only half as long as that of the *M*-phase, its *a*, *c*, and β parameters are about 1 percent larger, and the space group is $P2/a$ instead of $I2$. If the *M′*-phase is held for some time at a high temperature, it will transform sluggishly, by a first-order phase change, to the *T*-phase which on cooling will go to *M* in the manner already described.

A structure determination of *M′*, using three-dimensional data from a single crystal of $YTaO_4$, is now in the process of refinement and will be reported in an appropriate medium.

If the material is quenched from its solution in a high-temperature solvent rather than allowed to crystallize, a nearly amorphous powder results. This behaves in a manner analogous to that of the metamict mineral. When held for several days at 500°, it becomes tetragonal, with broad and diffuse reflections, indicating considerable disorder. This disorder is probably responsible for stabilization of the tetragonal structure. If held for some time at a high temperature, the peaks sharpen and a good tetragonal (scheelite) diffraction pattern develops. On cooling, the *M*-phase is obtained.

EXPERIMENTAL

Synthesis. All crystallizations were performed from a KF solvent. Equimolecular mixtures of Ln_2O_3 and Ta_2O, (or Nb_2O), were dissolved at 1250° in KF to the extent of 10 to 20 mole percent oxide mixture, in covered platinum crucibles. One of the following three procedures was always used:

1) The melt was held at 1250° for 1–2 hours and then program-cooled to 850° at the rate of 4.2°/h. Crystallization occurred by a combination of solvent evaporation and lowered solubility due to the dropping temperature.
2) Starting as in 1) above, mixture was air-quenched (by removal from furnace) when large amounts of solvent were still present, and few crystals had formed.
3) Mixture was held for 2–3 days at 1250° until all solvent had evaporated isothermally.

The solution temperature of 1250° is well above the transformation temperature of the niobates, but since the presence of the solvent does not seem to depress the transformation temperatures drastically, it is below that of the tantalates.

Procedure 1 was used preferentially since it resulted in complete crystallization of the M'-phase, generally free of other products, for $YTaO_4$ and all $LnTaO_4$ with Ln from Sm through Yb. It was also used for $LaNbO_4$ doped with BaO and for pure $YbNbO_4$. With $LaNbO_4$, large water-clear crystals in the form of highly distorted octahedra were obtained. These were polycrystalline pseudomorphs which, on crushing, yielded a few single-crystal fragments of the M-phase. $YbNbO_4$ gave small octahedra which were also pseudomorphs and on washing disintegrated to a polycrystalline mass of M-phase.

Procedure 3 was tried only with $YTaO_4$. The results were similar to those of procedure 1, but the twinning (see below) was on an even finer scale, and a few percent of another product, a pyrochlore structure $(Y,K)_2Ta_2(O,F)_7$ accompanied the M' crystals. The pyrochlore crystals were octahedra with an average size of 0.1 mm.

Procedure 2 was used for $YTaO_4$ and $SmTaO_4$. The few crystals of the M'-phase obtained here were similar to but less perfect than those obtained by the other procedures. Many gave weak extra X-ray reflcetions which indicated the presence of oriented inclusions or nuclei of another phase which could not be identified. The bulk of the material precipitated in the form of an amorphous powder as indicated above.

EXPERIMENTAL

High-Temperature X-Ray Diffraction. High-temperature X-ray diffraction distinguishes clearly and easily between the second-order $M-T$ transformation and the sluggish, first-order $M'-T$ transformation. In the case of the former, the $\bar{1}21$ and 121 reflections (which are the two strongest peaks in the pattern) move together on heating and merge to form the tetragonal 112 reflection. In the case of the latter, the same two reflections, now indexed $\bar{1}11$ and 111, remain apart but diminish in intensity while the tetragonal 112 rises midway between them and grows more intense.

The M'-phase of $YTaO_4$ begins to transform rather slowly above 1400° and is nearly completely transformed after 20 minutes at 1800°. Complete elimination of all traces of M' required several cycles, however. Once the tetragonal phase is well crystallized, it will transform reversibly and continuously, without delay, at 1325° between M and T. M' cannot be recovered.

$YbTaO_4$, starting also in the M'-phase, became tetragonal in a few minutes between 1900 and 2000°. This was observed in two separate experiments, but each time the material melted a few minutes later, destroying the heating element, so that it was not possible to observe the $T-M$ transition on cooling.

It will be recalled that Stubiçan (1964) did not find a phase transition for $YbTaO_4$ and that Keller (1962) thought that it might not have the fergusonite structure. Since all previous investigators prepared the tantalates at quite high temperatures by sintering or fusion they would generally have obtained the M-phase, with the possible exception of the small-ion tantalates which have the highest transformation temperatures. These may have been obtained in the M'-phase described in this work. This would account for the slight difference in the diffraction pattern noticed by Keller (1962) and for Stubiçan's (1964) failure to find the transformation, since the $M'-T$ transition does not take place with reasonable speed except at temperatures considerably higher than the $M-T$ transition.

The amorphous powder behaved quite similarly to the M' crystals, except that the transition was from a defective, poorly crystallized T-phase, rather than from a crystalline M'-phase, to a well crystallized T-phase. It took several cycles to 1800° to effect complete conversion of the defect T-phase to the M-phase via the high-temperature T-phase.

The BaO-doped $LaNbO_4$, starting out in the M-phase, showed only the rapid $M-T$ transformation near 500°, as described by Gingerich and Bair (1964).

X-ray Discrimination Between M and M′ Phases. Appropriate single-crystal measurements or photographs will reveal the different length of the b-axis and the different extinction rules quite clearly. Note however that the two kinds of metal ions (*i.e.*, Y and Ta) alternate parallel to the c-axis, hence $YNbO_4$ and $YbTaO_4$ will show additional extinctions in the M'-phase which are not space-group extinctions but are due to the near equality of the scattering factors for the combinations, Y—Nb and Yb—Ta.

On the other hand, it is quite difficult to distinguish between the M and M' phases in powder patterns. The following list, which includes only reflections at 2θ less than 50° for Cu radiation will help. The M'-structure (short b-axis) gives rise to the following reflections, visible in a good powder pattern, which do not occur in the M-structure. In the body-centered M-structure, these reflections (with a doubled k) have odd index sums and are extinct: 001, 110, 011, $\bar{2}01$, 120, 211, 112, $\bar{1}22$.

The M-structure (long b-axis) has the following reflections which do not occur in the M'-structure because they would have fractional k indices. 110, (130), $\bar{1}31$, 131, 150, $\bar{1}51$, 151. The 130 reflection is set apart because it should not be used as a criterion although its conspicuous location between the two strongest reflections of the pattern makes it especially tempting to use. Its position nearly overlaps that of the tetragonal 112, and polycrystalline samples of monoclinic fergusonite often contain traces of (defect) tetragonal phase, giving rise to the presence of the tetragonal 112 reflection which is the strongest one in the tetragonal pattern. The true *M*-130 is a very weak reflection and is rarely seen. We observed it at high temperatures, where the material crystallizes well, as a small hump on the high-angle shoulder of *T*-112. This incidentally suggests that *M* may be an intermediate in the transformation from *M′* to *T*.

STRUCTURAL RELATIONSHIPS BETWEEN T, M, AND M′

All three structures have 8—4 oxygen coordination about the metals. A qualitative picture of the relationships can be had in terms of the metal ions alone. These form nets normal to the unique crystal axis. In the *T*-structure (scheelite), the nets are square and flat. In *M*, they are somewhat puckered and distorted. In addition, in *M′* the third and fourth nets are translated parallel to themselves through 1/2, 1/2 with respect to the first and second net.

Thus, the relationship between *M* and *T* imposes no restraints upon the possible nature of the phase transformation and, in effect, permits it to be what it is found to be. On the other hand, the reconstructive nature of any transformation from *M′* to either of the other two would compel it to be a first-order and diffusional (nucleation and growth) phase transformation. Since many strong bonds need to be broken and reformed, the reaction may also be expected to be sluggish. These expectations are in complete accord with the experimental findings.

HABIT AND TWINNING OF THE M′-PHASE

Crystals of the *M′*-phase of $YTaO_4$ and all $LnTaO_4$ isomorphous with it grow in clumps of blades or acicular parallelepipeds. They are twinned frequently on (110) and occasionally on (210), resulting in angles between the joined blades that are close to but not equal to 90° and 60°, respectively. The crystals part easily on these twin planes, and the remaining pieces are still twinned polysynthetically on a fine scale on (001). This type of twinning results in striations on the large faces of the blades or two opposing sides of the parallelepipeds, which are composite (001) faces. The smooth and shiny long edges of the blades are (010) faces, the elongation of the crystals is parallel to *a*. The crystals do not part on the (001) twin planes, attempts to separate them result either in fracturing the crystal roughly parallel to (100) or in crushing it altogether. Crushing a large number of crystals does however lead to a few twins of only two individuals or pieces of one orientation traversed by several extremely narrow bands of the opposite orientation, and with persistance, to an occasional single crystal. A single crystal is always a (010) lath, elongated parallel to *a*. Typical dimensions are 0.3 mm along *a*, 0.1 mm along *c**, and 0.02 mm along *b*. The faces, in order of size are {010} (flat faces), {012} (long edges), {110} and {100} (terminations).

The single crystal fragments of $LaNbO_4$ found in this work, *M*-phase rather than *M′*, were also (010) flakes but gave no indication of twinning. According to Wolten and Chase (1964), twinning should be uncommon in this noncentrosymmetric structure.

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A sample of fergusonite from Murchison Township, Ontario, Canada, was obtained through commercial channels. It was black, featureless, and radioactive. The activity, mostly gamma, measured 10 mr/h on the surface of the specimen. The material gave a weak powder pattern of monoclinic fergusonite. The pattern was not good enough to tell the *M* from the *M′*-phase. After heating to 1000°, it was *M*. The black fergusonite was embedded in a matrix of large crystals that appeared to be reddingite or phosphoferrite but were not identified with certainty.

SUMMARY

Attempts to grow single crystals of rare earth niobates and tantalates with the noncentrosymmetric monoclinic structure described by Komkov (1959) led to the discovery that the fergusonite structure can exist in a third, also monoclinic, polymorphic modification. The transformations between the various forms and their structural relationships have been described. If the phase of the mineral (fergusonite) could be determined, additional light would be shed on its thermal history. The discovery that a synthetic, nonradioactive product can be made that resembles the metamict form of the mineral is noteworthy. Clarification of the phase relationships and the morphology of synthetic fergusonites offered here will aid future attempts to grow single crystals in this system.

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