Flux growth of YNbO_4 . YOSHINORI SUGITANI and KOZO NAGASHIMA,
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Natural fergusonite is nominally expressed as $(\text{Y, RE, U})(\text{Nb, Ta, Ti,} \dots)\text{O}_4$, where RE means rare-earth elements, and it is in most cases metamict due to its radioactivity, giving very weak peaks of X-ray powder diffraction. In the textbooks by "Dana" (1952) and by Strunz (1970), fergusonite is described as tetragonal in the first place, as seems based mainly on the works by Barth (1926) and by Komkov (1957, 1959a).

Berman (1955) was the first who suggested the necessity of more detailed work before a definite decision can be reached as to the original fergusonite structure. Ferguson (1957) pointed out from the study on a synthetic YTaNbO_4 that original fergusonite is not tetragonal but monoclinic and pseudo-tetragonal. Further, Gorshevskaya *et al.* (1961) reported a natural β -fergusonite which belongs to monoclinic system. Many of the synthetic fergusonites including various rare-earth niobates and tantalates, mostly prepared by sintering method, have been reported as isomorphous with the monoclinic form of heat-treated natural fergusonites (Komkov, 1959b; Keller, 1962; Rooksby and White, 1963; Stubican, 1964; Wolten and Chase, 1967).

The present work reports the single crystal growth of YNbO_4 by flux method, and the direct measurement of its 2V angle, as well as presenting a short comment in favor of the suggestion by Ferguson (1957) on the original fergusonite structure.

Experimental, results and discussion

Equi-molar Nb_2O_5 (purity, 3N) and $\text{Y}_2\text{O}_3(\text{Tb}_2\text{O}_3, \text{Dy}_2\text{O}_3)(4\text{N})$ were

mixed in a platinum-crucible together with a flux material (PbF_2 : PbO =80:20 or Bi_2O_3 : V_2O_5 =120:8) of about ten times amount in molar ratio. The crucible was covered by a larger alumina-crucible filled with alumina powder, and this system was put in an electric muffle furnace kept at 1350°C . After about ten hours hold it was cooled down to 900°C in the rate of $1\sim 3^\circ\text{C/h}$ by a programmed controller. At the temperature, the system was taken out of the furnace and allowed to cool down to room temperature. The products in the platinum-crucible were taken out and washed with hot 6N- HNO_3 for several hours. The crystals thus obtained are shown in Fig. 1.

Fig. 1. Crystals of (a) YNbO_4 ,
(b) DyNbO_4 , and (c) TbNbO_4 .
(1 division=1 mm)

They are mostly shaped of slightly elongated octahedron, and their sizes range from 0.2 mm to 3 mm in the longest directions. The color of YNbO_4 grown from PbF_2 - PbO flux is pale yellow with a tint of brown, while that grown from Bi_2O_3 - V_2O_5 flux has yellow color. Chemical analysis data for YNbO_4 from PbF_2 - PbO flux are: $\text{Nb}_2\text{O}_5=52.22\%$, $\text{Y}_2\text{O}_3=43.9\%$, $\text{PbO}=3.84\%$, and this gives the composition very close to YNbO_4 . The presence of a small amount of the flux material seems to be responsible for the color of the crystal. When the crystal is heated the color at first deepens and then fades away, but recovers to the original color when cooled. This process can be repeated.

The X-ray powder data agree well with those for natural fergusonite $(\text{Y}, \text{Er})(\text{Nb}, \text{Ta}, \text{Ti})\text{O}_4$ heated over 400°C (Barth, 1962), and those for synthetic YTaO_4 by Ferguson (1957) as seen in Table 1. The indices for monoclinic system are after Ferguson (1957). This result indicates that the YNbO_4 grown in this study is monoclinic. Cell parameters were obtained as shown in Table 2, where results for TbNbO_4 (brownish orange) and for DyNbO_4 (yellow) are also included.

Optical observation by transmitted light reveals that YNbO_4 is optically biaxial positive with $2V=40^\circ\pm 8^\circ$, which also shows that the synthetic YNbO_4 is monoclinic rather than tetragonal. The large error in $2V$ is due to vague extinctions because of the high refractive indices of fergusonites.

If the X-ray powder peaks of the grown YNbO_4 are tentatively indexed as tetragonal, then the cell parameters are obtained as $a=7.74\pm 0.04\text{ \AA}$, and $c=11.31\pm 0.06\text{ \AA}$, which are naturally very close to Barth's data: $a=7.74\text{ \AA}$, $c=11.34\text{ \AA}$. This result for the synthetic YNbO_4 is apparently correct, but is not consistent with the optical data showing that the crystal is biaxial. Further, the standard deviations are about one order larger than those calculated as monoclinic (Table 2).

Stubican (1964) reported that the monoclinic form of rare-earth

Table 1. *d*-spacings and peak intensities of synthetic and natural fergusonites.

YNbO ₄ (Syn.) this work		(Y, Er)(Nb, Ta, Ti) O ₄ *		YTbO ₄ (Syn.)**		
<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>	<i>hkl</i>
5.45	10	5.47	4	5.47	10	020
				4.79	40	110
		4.58	4			
		4.02	4			
3.32	5	3.29	4			
3.12	100	3.12	100	3.14	100	$\bar{1}21$
		3.10	20	3.02	5	130
2.96	80	2.96	90	2.94	100	031, 121
2.73	90	2.74	40	2.74	40	040
2.64	30	2.64	20	2.64	40	200
		2.59B	4			
2.53	20	2.53B	10	2.52	30	002
		2.52	10			
				2.38	5	220, $\bar{2}11$
				2.30	5	$\bar{1}12, 022$
2.22	3	2.22	4			
2.16	10	2.16	6	2.15	30	112, 141
2.01	5	2.01	6	2.02	20	$\bar{2}31, 150, 051$
				1.921	30	231, $\bar{2}02$
1.90	50	1.901	50	1.901	50	240
1.86	30	1.855B	30	1.846	60	042
1.76	20	1.754	10			
1.64	20	1.646	10			
1.63	10	1.643B	10			

* after Barth (1926). Indices for tetragonal system are not quoted in this Table.

** after Ferguson (1957).

niobates approaches by a gradual change to tetragonal form on heating LaNbO₄ up to 500°C, and YbNbO₄ up to 825°C. The corresponding temperature for YNbO₄ can be interpolated to about 800°C,

Table 2. Main powder X-ray peaks and cell parameters.

YNbO_4			DyNbO_4			TbNbO_4		
2θ		$d(\text{\AA})$	2θ		$d(\text{\AA})$	2θ		$d(\text{\AA})$
28.59	S	3.122	28.59	S	3.122	28.39	S	3.144
30.20	S	2.959	30.08	S	2.971	29.86	S	2.992
32.75	M	2.734	32.58	S	2.748	32.31	S	2.770
33.95	M	2.640	33.96	S	2.640	33.68	S	2.661
35.49	M	2.529	35.44	M	2.533	35.31	M	2.542
47.81	M	1.902	47.86	S	1.901	47.48	S	1.915
49.03	M	1.858	48.91	S	1.862	48.63	S	1.872
$a=5.30\pm0.009\text{ \AA}$			$a=5.29\pm0.01\text{ \AA}$			$a=5.33\pm0.006\text{ \AA}$		
$b=10.96\pm0.01$			$b=10.99\pm0.02$			$b=11.07\pm0.01$		
$c=5.07\pm0.007$			$c=5.07\pm0.009$			$c=5.10\pm0.005$		
$\beta=94.6^\circ\pm0.1^\circ$			$\beta=94.0^\circ\pm0.2^\circ$			$\beta=94.0^\circ\pm0.1^\circ$		

while Rooksby and White (1963) report the temperature as about 700°C .* Wolten and Chase (1967) reported the presence of two monoclinic phases, M- and M'-phases, in the case of YTbO_4 at room temperature. According to their study the M-phase transforms reversibly and continuously at 1325°C to tetragonal T-phase, while the M'-phase undergoes sluggish, irreversible M'-T transformation between 1400°C and 1800°C .

Supposing that YNbO_4 behaves in a similar way to YTbO_4 , the reversible monoclinic-tetragonal change in YNbO_4 around $700\text{--}800^\circ\text{C}$ (Rooksby and White, 1963; Stubican, 1964) seems to correspond to the M-T transformation in YTbO_4 . On the other hand, the phase of YNbO_4 which seems to correspond to the M'-phase of YTbO_4 has not been reported so far, except a phase reported by Berman (1955) which was, however, indexed with a tetragonal unit cell ($a=5.18$, $c=5.48\text{ \AA}$) for a sample heated between 400°C and 800°C . Our attempts to grow a phase corresponding to the M'-phase or that having

* According to ASTM data (McCarthy, 1971), monoclinic YNbO_4 transforms to tetragonal form at $\sim 810^\circ\text{C}$.

tetragonal system have not been successful.

Considering these facts along with the many experimental results on synthetic fergusonites appeared after Ferguson (1957), the possibility that the original fergusonite belongs to tetragonal symmetry is very small, but on the contrary it is monoclinic and pseudo-tetragonal, with probably a distorted scheelite type structure (Komkov, 1959 a, b).

REFERENCES

- BARTH, T. (1926) *Norsk. Geol. Tidsskr.*, **9**, 23.
BERMAN, J. (1955) *Amer. Miner.*, **40**, 805.
BLASSE, G. & BRIL, A. (1968) *Zeits Phys. Chem. N.F.*, **57**, 187.
DANA, J.D. & E.S. *The System of Mineralogy*, 7th ed. by C. PALACHE, H. BERMAN & C. FRONDEL (1952) John Wiley and Sons, Inc. London.
FERGUSON, R.B. (1957) *Can. Miner.*, **6**, 72.
GINGERICH, K.A. & BAIR, H.E. (1964) *Adv. X-Ray Anal.*, **7**, 22.
GORSHEVSKAYA, S.A., SIDORENKO, G.A. & SMORCHKOV, J.E. (1961) *Geol. Mestor. Red. Elementov*, **9**, 28.
KELLER, C. (1962) *Zeits anorg. allg. Chem.*, **318**, 89.
KOMKOV, A.I. (1957) *Mem. All-Union Miner. Soc.*, **86**, 432.
KOMKOV, A.I. (1959a) *Kristallografiya (USSR)*, **4**, 836; *Sov. Phys. Cryst.*, **4**, 796.
KOMKOV, A.I. (1959b) *Doklady Akad. Nauk SSSR*, **126**, 853.
ROOKSBY, H.P. & WHITE, E.A.D. (1963) *Acta Cryst.*, **16**, 888.
STRUNZ, H. (1970) *Mineralogische Tabellen*, 5th ed. Akad. Verlag, Leipzig.
STUBICAN, V.S. (1964) *Journ. Amer. Ceram. Soc.*, **47**, 55.
WOLTEN, G.M. (1967) *Acta Cryst.*, **23**, 939.
WOLTEN, G.M. & CHASE, A.B. (1967) *Amer. Miner.*, **52**, 1536.

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