

IXIOLITE AND OTHER POLYMORPHIC TYPES OF  $\text{FeNbO}_4$ 

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## ABSTRACT

$\text{FeNbO}_4$  was found to be trimorphic. The low temperature (ordered?) polymorph, stable from room temperature to about  $1085^\circ\text{C}$ . is monoclinic, space group  $P2_1/a(C^6_{2h}\text{-No. 14})$   $a=5.001\text{ \AA}$ ,  $b=5.620\text{ \AA}$ ,  $c=4.653\text{ \AA}$ ,  $\beta=89.84^\circ$  ( $90.16^\circ$ ). An orthorhombic ixiolite type structure is stable from about  $1085^\circ\text{C}$ . to about  $1380^\circ\text{C}$ . and a rutile type polymorph is stable from about  $1380^\circ\text{C}$ . to the melting point at about  $1475^\circ\text{C}$ . The unit cell dimensions as well as the stoichiometry of the latter two polymorphs are dependent upon the heat treatment of the specimen. Other synthetic compounds which apparently have the ixiolite structure type are listed.

The compound  $\text{FeNbO}_4$  was originally reported to have the rutile structure type by Brandt (1943). However, it was noted by Brandt that a large amount of "columbite- $\text{FeNb}_2\text{O}_6$ " was always present at temperatures as low as  $1200^\circ\text{C}$ . and this phenomenon was explained as reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . In a study of phase equilibrium relations in the quaternary system  $\text{BaO-Nb}_2\text{O}_5\text{-Gd}_2\text{O}_3\text{-Fe}_2\text{O}_3$  (Roth, 1960) the 1:1 compound ( $\text{Fe}_2\text{O}_3\cdot\text{Nb}_2\text{O}_5$ ) was always observed to crystallize in the "columbite" structure type (in binary, ternary or quaternary systems) even though little or no reduction was observed. No rutile type structure was ever noted, although temperatures in this study were in the range  $1000^\circ\text{C}$  to  $1350^\circ\text{C}$ . and exceeded those reported by Brandt to form a rutile type phase.

Goldschmidt (1960a, b) was the first to report that the system  $\text{Fe}_2\text{O}_3\text{-Nb}_2\text{O}_5$  contained both a rutile and a "columbite-type" phase. He indicated that the "columbite-type" was the low temperature phase and could be formed by annealing the rutile-type phase at low temperatures. The "columbite $\leftrightarrow$ rutile"-type transition was also reported by Goldschmidt (1960a, b) to occur in systems of  $\text{Nb}_2\text{O}_5$  with  $\text{Co}_3\text{O}_4$ ,  $\text{NiO}$ , and  $\text{MgO}$ . As the rutile-type phase was formed by arc melting in argon and the "columbite-type" by annealing in air at  $800^\circ\text{C}$ ., it is obvious that the rutile-type phase in the  $\text{Fe}_2\text{O}_3\text{-Nb}_2\text{O}_5$  system actually represents a greater amount of reduction than does the "columbite-type" phase.

Nickel and Rowland (1962) proposed that an  $(A, B)_2\text{O}_4$  composition could have an  $x$ -ray diffraction pattern which could be completely indexed on the basis of an orthorhombic unit cell, related to that of columbite by having the  $c$  axis (space group  $Pnab$ ) equal to  $\frac{1}{3}$  of the corresponding axis of the columbite structure. The term "ixiolite" was redefined as the mineral which resulted in this type of an  $x$ -ray pattern (Nickel, *et al.*, 1963). The present authors were kindly supplied with a preprint of this

ixiolite paper and the results of the experimental investigation of polymorphism in  $\text{FeNbO}_4$  is interpreted in the present note on the basis of this previous study of ixiolite.

A specimen of  $\text{FeNbO}_4$  was prepared by weighing the appropriate amounts of  $\text{Fe}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$ , mixing and firing to  $1000^\circ\text{C}$  for 2 hours. The resultant material, as well as small portions refired at  $1200^\circ\text{C}$ . and  $1350^\circ\text{C}$ . and slowly cooled, showed an  $x$ -ray diffraction powder pattern which greatly resembled the columbite structure type. However, when some of the  $1000^\circ\text{C}$ . calcine material was heated (and quenched) in sealed Pt tubes at temperatures below about  $1085^\circ\text{C}$ ., for long periods of time, the resultant  $x$ -ray powder diffraction pattern could only be indexed as monoclinic with  $a=5.001\text{ \AA}$ ,  $b=5.620\text{ \AA}$ ,  $c=4.653\text{ \AA}$ ,  $\beta=89.84^\circ$  ( $90.16^\circ$ ) (Table 1). (All  $x$ -ray diffraction data were taken at room temperature. and the unit cell dimensions reported can be considered accurate to about  $\pm 2$  in the last decimal place listed.)

Specimens which were quenched from temperatures between about  $1085^\circ\text{C}$ . and  $1380^\circ\text{C}$ . were orthorhombic (Table 1) and apparently isostructural with the mineral ixiolite. The unit cell dimensions of the ixiolite-structure type in this composition depend upon the temperature from which the specimen has been quenched and vary from  $a=5.005\text{ \AA}$ ,  $b=5.613\text{ \AA}$ ,  $c=4.647\text{ \AA}$  to  $a=5.015\text{ \AA}$ ,  $b=5.627\text{ \AA}$ ,  $c=4.654\text{ \AA}$ . This phenomenon is due to either a change in the Fe:Nb ratio of the phase with temperature, or to a reduction of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  (and corresponding oxygen loss), as the temperature is increased. Actually, although both factors may be involved, the reduction phenomenon undoubtedly plays a large role. A specimen previously quenched from  $1350^\circ\text{C}$ . after 70 hrs. was reheated in a sealed Pt tube, to minimize reoxidation, at  $1040^\circ\text{C}$ . for 144 hrs. It showed a monoclinic  $x$ -ray diffraction powder pattern with  $a$  and  $b$  dimensions ( $a=5.007\text{ \AA}$ ,  $b=5.625\text{ \AA}$ ,  $c=4.653\text{ \AA}$ ,  $\beta=89.84^\circ$ ) slightly larger than those observed in specimens in which the phase transition had not been reversed.

Specimens which were quenched from about  $1380^\circ\text{C}$  to  $1500^\circ\text{C}$ . showed the rutile-structure type (Table 1) with unit cell dimensions varying with temperature from  $a=4.694\text{ \AA}$ ,  $c=3.043\text{ \AA}$ , to  $a=4.717\text{ \AA}$ ,  $c=3.052\text{ \AA}$ . The solidus temperature appeared to be about  $1410^\circ\text{C}$ . and the specimen was completely melted at about  $1475^\circ\text{C}$ . However, the solid in equilibrium with the liquid between  $1410^\circ$  and the melting point was definitely the rutile-type phase. It is evident, that, at these temperatures, either the phase is not exactly 1:1 (as suggested by Goldschmidt, 1960a) or else the Fe:Nb ratio of the as-prepared specimen was slightly off composition.

Nickel and Rowland (1962) proposed the space group  $Pnab$  for the

ixiolite structure type, but later revised this to *Pcan* (Nickel *et al.*, 1963) to conform with the corresponding setting for columbite-tantalite. However, the original space group of *Pnab* is preferred for  $\text{FeNbO}_4$  of the ixiolite-type, so that the convention of *b* as the unique axis in the monoclinic system may be maintained for the low-temperature ordered form. Two weak diffraction peaks in the powder pattern of the low temperature

TABLE 1. X-RAY DIFFRACTION POWDER PATTERNS AT ROOM TEMPERATURE OF THE POLYMORPHS OF  $\text{FeNbO}_4$ . ( $\text{CuK}\alpha$  RADIATION)

Monoclinic Ordered (?) Form 1037°C.—115 hrs Quenched sealed Pt tube			Orthorhombic Ixiolite-type 1114° C.—16 hrs Quenched sealed Pt tube			Tetragonal Rutile-type 1420°C.—85 hrs Quenched sealed Pt tube		
hkl	d Å	I	hkl	d Å	I	hkl	d Å	I
001	4.65	17	—	—	—	110	3.234	320
110	3.737	19	—	—	—	101	2.554	184
011	3.586	125	011	3.581	130	200	2.348	50
111/11 $\bar{1}$	2.903	280	111	2.912	390	111	2.249	35
020	2.810	48	020	2.807	38	210	2.101	12
200	2.501	61	200	2.502	55	211	1.730	178
120	2.450	66	120	2.449	58	220	1.661	85
002	2.326	28	002	2.325	22	002	1.523	12
201/20 $\bar{1}$	2.200	26	201	2.204	19	310	1.4860	21
121/12 $\bar{1}$	2.168	38	121	2.167	38	301	1.3930	38
211/21 $\bar{1}$	2.050	31	211	2.051	36	112	1.3848	32
112/11 $\bar{2}$	1.976	9	—	—	—	311	1.3359	7
220	1.868	34	220	1.868	28	202	1.2792	18
022	1.792	28	022	1.791	27	321	1.1982	15
031	1.737	62	031	1.737	46	400	1.1751	12
202	1.705	47	202	1.704	70	222	1.1225	16
20 $\bar{2}$	1.700	51	—	—	—	330	1.1081	8
122/12 $\bar{2}$	1.686	76	122	1.686	73	411	1.0675	16
131/13 $\bar{1}$	1.641	9	131	1.641	8	312	1.0638	15
311	1.512	36	311	1.512	47	420	1.0511	9
31 $\bar{1}$	1.510	39	—	—	—			
013	1.4951	10	013	1.4949	7			
222	1.4576	15	222	1.4568	16			
22 $\bar{2}$	1.4541	19	—	—	—			
320	1.4324	56	320	1.4341	37			
113/11 $\bar{3}$			113	1.4318	47			
231/23 $\bar{1}$	1.4267	48	231	1.4271	45			
040	1.4044	10	040	1.4041	5			
—	—	—	132	1.4000	5			
140	1.3522	25	140	1.3519	18			

monoclinic form, at  $d=4.65 \text{ \AA}$  and  $3.737 \text{ \AA}$ , are indexed as (001) and (110). Starting from the ixiolite space group ( $Pnab$ ), the presence of the (001) and (110) peaks, together with monoclinic splitting of other peaks, indicate that the most likely space group is  $P2_1/a-C^5_{2h}$  (No. 14).<sup>1</sup>

It may be concluded that  $\text{FeNbO}_4$  is trimorphic, although as in all systems containing  $\text{Fe}_2\text{O}_3$  there is some deviation from stoichiometry.

The polymorphism of  $\text{FeNbO}_4$  can be summarized as follows:

	Monoclinic	Ixiolite	Rutile	Rutile + Liquid
R.T.	← 1085°	← 1380°	← 1410°	← 1475°
	$a=5.001 \text{ \AA}$	$a=5.005 \text{ \AA}$	$a=4.700 \text{ \AA}$	
	$b=5.620 \text{ \AA}$	$b=5.613 \text{ \AA}$	$c=3.046 \text{ \AA}$	
	$c=4.653 \text{ \AA}$	$c=4.647 \text{ \AA}$		
	$\beta=89.84^\circ (90.16^\circ)$			

(Unit cell dimensions are those derived from data listed in table 1).

The low temperature, probably stoichiometric, form has a very slight monoclinic distortion of the ixiolite structure type. A reversible phase transition occurs at about  $1085^\circ \text{ C.}$  to a true orthorhombic ixiolite-type structure. This phase transition probably represents an order-disorder transition. The ixiolite-type phase then transforms reversibly to a rutile-type structure at about  $1380^\circ \text{ C.}$  In both of the latter structure-types non-stoichiometry due to reduction of iron may be at least partially cancelled out by an increase in the Nb:Fe ratio, so that the total cation:anion ratio is maintained at close to 1:2.

It was noted by Nickel, *et al.* (1963), that the ixiolite-type structure had been reported for several synthetic phases. They mentioned the orthorhombic form of  $\text{ReO}_2$  (Magneli, 1956)  $\alpha\text{-PbO}_2$  (Zaslavskij and Tolkacev, 1952) and  $\text{GaTaO}_4$  (Bayer, 1962).  $\text{FeNbO}_4$  can now definitely be added to this list.  $\text{ZrTiO}_4$  (Coughanour *et al.* 1954) and possibly  $6\text{ZrO}_2 \cdot \text{Nb}_2\text{O}_5$  and  $6\text{ZrO}_2 \cdot \text{Ta}_2\text{O}_5$  (Roth and Coughanour, 1955), can also be added to the list of ixiolite structure types. It should be noted that two orthorhombic forms of  $\text{ZrTiO}_4$  exist and that they probably also represent an order-disorder transformation. It should also be mentioned that the compound  $\text{SnZrO}_4$  has been prepared (as a metastable phase) and was described as having a structure similar to  $\text{ZrTiO}_4$  (Stocker and Collonques, 1957a, b). The high pressure form of  $\text{FeVO}_4$  recently reported by Young and Schwartz (1962) is a still further example of the

<sup>1</sup> It should be noted that this monoclinic phase is apparently isostructural with the wolframite-type structure ( $\text{MgWO}_4\text{-FeWO}_4$ ) except for the absence in the powder pattern of the (010). As this is a very weak peak in most wolframite type structures, it is possible that the true space group of the monoclinic polymorph of  $\text{FeNbO}_4$  is actually  $Pa/a-C^4_{2h}$  (No. 13).

ixiolite structure type. Apparently the ixiolite-type structure is a much more common (A, B)<sub>2</sub>O<sub>4</sub> structure type than has previously been realized.

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