

Polymorphism of samarskite and its relationship to other structurally related Nb–Ta oxides with the α -PbO₂ structure

YOSHINORI SUGITANI, YOSHIHISA SUZUKI AND KOZO NAGASHIMA

Institute of Chemistry

University of Tsukuba

Sakura-mura, Ibaraki 305, Japan

Abstract

Samarskite, synthesized in a reducing atmosphere using starting materials in the Ca–U–Y–Nb–Fe–O system and analyzed by EPMA, has an empirical formula of:



The ratios between the number of total metal atoms and oxygen atoms were found to be close to 1:2 for the several synthetic samarskites having various relative amounts of metal atoms. Samarskite was also synthesized using starting materials in the ternary Y–Fe–Nb–O system. Analysis of this material gave a formula: $\text{YFe}_2\text{Nb}_5\text{O}_{16}$, which was the same bulk composition as that of the starting reagents. The synthesized and recrystallized natural samarskites changed into mixtures of mostly three to four compounds when heated in air. They changed into the high temperature structural form of samarskite when heated at 950–1200°C in a reducing atmosphere. Refinement of cell parameters for the high temperature form of a samarskite from Kawabe, Japan yielded: $a = 5.642(7)\text{\AA}$, $b = 9.914(8)\text{\AA}$, $c = 5.229(3)\text{\AA}$, and $\beta = 93.8(7)^\circ$.

On the basis of the experimental results obtained in the present and previous studies, samarskite is proposed to be a mineral with α -PbO₂ structure, covering a wide range of chemical compositions and occurring as either partially disordered $\text{A}_3\text{B}_5\text{O}_{16}$ or completely disordered M_8O_{16} . A diagram showing the structural relation to related minerals columbite, ixiolite, wolframite, and others is presented.

Introduction

Since samarskite was first described by Ross (1847), it has been known as one of the multiple Nb–Ta–Ti–REE oxides containing iron, uranium and other elements (Palache et al. 1944; Strunz, 1970). Samarskite has always been found in the metamict state due to the presence of radioactive uranium and thorium (Lima de Faria, 1964), and a number of the studies on this mineral have been carried out on samples heat-treated in order to restore the original lattice structure (Berman, 1955; Komkov, 1965; Nilssen, 1970; Nudel'man and Sidorenko, 1963; Mitchell, 1970; Sugitani et al., 1980; Van Wambeke, 1960). However, the chemical formula and crystal structure of samarskite have not been fully elucidated in the same way as other related metamict minerals such as euxenite, fergusonite, and others. A variety of chemical formulas for samarskite have been proposed:

- (1) AB_2O_6 (Palache et al., 1944; Fleischer, 1983),
- (2) $(\text{Y, Er})_4[(\text{Nb, Ta})_2\text{O}_7]_3$ (Strunz, 1957),
- (3) $\text{AB}_{2+x}[\text{O, (OH)}]_{6+2.5x} \cdot n\text{H}_2\text{O}$: altered samarskite (Van Wambeke, 1960).
- (4) ABO_4 (Komkov, 1965),
- (5) $(\text{Fe, REE, U})_2(\text{Nb, Ta, Ti})_2\text{O}_7$ (Vlasov, 1966),

- (6) $\text{A}_{1+x}\text{B}_{2+x}\text{O}_6$: $0 \leq x \leq 0.2$ (Nilssen, 1970),
 where $\text{A} = \text{Y, Er, Ce, La, U, Ca, Pb, Th, Fe}$,
 $\text{B} = \text{Nb, Ta, Ti, Sn, W, Zr, Fe}$,
 and $\text{REE} = \text{Rare earth elements}$.

Some samarskites have been reported to occur as euhedral crystals, mostly found adjacent to columbite crystals. Orthorhombic symmetry, with the axial ratio, for example, 0.5456:1:0.5173 has been determined from morphological measurements (Palache et al., 1944), suggesting a close relationship to columbite.

Nilssen (1970) showed from a precise chemical analysis study of a variety of samarskite samples that the approximate metal to oxygen ratio (atomic) is 1:2. He also reported that the chemical formula should be somewhere between AB_2O_6 and ABO_4 , where A represents metal atoms with large ionic radii and B those with small radii. He interpreted the X-ray powder diffraction pattern of a sample heated to 1000°C in air as a superposed pattern of three phases, one of which was orthorhombic with axial ratios close to that of samarskite.

Komkov (1965) reported, on the other hand, that a samarskite sample, which was heated to 660°C in air and then cooled immediately down to room temperature, was suspected to have the original, pre-metamict structure of the

mineral, which was of the wolframite type, with $\beta = 90^\circ$ having the probable formula ABO_4 .

Weitzel and Schröcke (1980) pointed out the similarity between the wolframite and the M' -fergusonite structure and proposed that samarskite has the M' -fergusonite structure.

Graham and Thornber (1974) reported on an intensive crystallochemical study of niobium and tantalum oxides including samarskite. One of their important findings is that the complex oxides of tantalum and niobium can be classified according to the size of the A cation and the linking of coordination polyhedra, despite complications due to isomorphous substitution, polymorphism and metamictization. On the basis of α - PbO_2 packing structure they presented a structural classification of MO_2 type phases. Another important point that they correctly made is that it is not certain whether heating in air restores the original crystal structure, but that it may produce a new nonequilibrium variety. They did not, however, indicate anything about heating in a reducing atmosphere. According to Tokonami (1980), EPMA line analysis of a samarskite showed fluctuations in element content over distances of several μm in the specimen, suggesting that the mineral was inhomogeneous before heat treatment.

Samarskite is still considered to be an incompletely understood and characterized mineral because previous investigations, in most cases, have not involved primary and non-metamict samarskite. This is due to the fact that no definitive structure of samarskite (natural and synthetic) has been presented, and because of the lack of knowledge about how to restore the original structure.

Recently, Sugitani et al. (1984) have found that the original pre-metamict samarskite structure can be restored by heating metamict material at high temperature ($1200^\circ C$) in a reducing (H_2) gas flow. This suggests that some of the iron and/or uranium in samarskite was present in lower oxidation states e.g., Fe(II), U(IV) etc. at the time of its formation. A new definition of samarskite is proposed on the basis of the experiments on synthetic and recrystallized natural samarskites, as well as on some related compounds. The redefinition of samarskite in the present article has been approved by the International Mineralogical Association Commission on New Minerals and Mineral Names.

Experimental

Commercially available oxides of various metals: CaO , Fe_2O_3 , Y_2O_3 , Nb_2O_5 , and TiO_2 (reagent grade, Rare Metallic Co., Ltd.) were used as starting materials for the synthesis of samarskite and related compounds. Since the valence states of iron and uranium in the starting materials were suspected to be of critical importance in the synthesis of samarskite, Fe_2O_3 and U_3O_8 were used in experiments utilizing an oxidizing atmosphere, while FeO and UO_2 were used in those requiring a reducing atmosphere. U_3O_8 was prepared by heating $UO_2(NO_3)_2 \cdot 6H_2O$ at $700^\circ C$ in air, while UO_2 was prepared by heating U_3O_8 at $1200^\circ C$ in an H_2 gas flow.

An oxidizing or reducing atmosphere was produced by the controlled flow of air or hydrogen (plus nitrogen) gas, respectively. Starting materials were mixed in the desired ratios, stirred and

finely ground in an agate mortar under acetone, and dried and pressed into pellets for the sintering experiment.

In the sintering method, mixtures of the starting materials were pressed into disk pellets at 200 kg/cm^2 and heated in an electric furnace with SiC heater rods in the temperature range 700 – $1400^\circ C$ for 1–30 hrs. The cooling rate was approximately $20^\circ C/\text{min}$. The flow rate of hydrogen gas was 10–20 ml/min for synthesis in a reducing atmosphere.

In the melt method, mixtures of the starting materials were loaded into platinum tubes, sealed and heated in an electric furnace with $LaCrO_4$ heater rods at 1 atm for 1–2 hrs at temperatures (1400 – $1600^\circ C$) above the melting point, and then cooled down to room temperature at the approximate rate of $1^\circ C/\text{min}$.

In Table 1, the mixing ratio of the starting materials, the type of atmosphere and the synthesis temperature are listed together with the run products obtained. The six elements listed under the heading of mixing ratios are representative component elements of samarskite determined on the basis of chemical analysis data of natural samarskites. Minor component elements such as divalent Mn and trivalent Er are considered to be represented by Ca and Y, respectively.

Analyses

The run products were examined by X-ray powder diffraction or by Gandolfi camera methods. EPMA analyses of the products were conducted only when precise chemical compositions were needed. The EPMA apparatus used was a JEOL JXA 50A combined with an Erionix ACPS XR controlling system. Since the sintered materials were found mostly in the form of recrystallized grains, only several μm in diameter (Fig. 1), the electron beam was focused to as small as $2 \mu m$ in diameter. Operating conditions were: 15 kV accelerating voltage, $0.015 \mu A$ on the Faraday cage, $2 \mu m$ beam diameter. Standards used were: Y: Y_2O_3 ; U: KUO_2VO_4 ; Ca: $CaSiO_3$; Nb: Nb_2O_5 ; Ti: TiO_2 ; Fe: Fe_2O_3 . The procedure of the EPMA analysis was as follows: a mapping photograph was taken of the surface of the sample; several grains which appeared to be single and uniform phases, were marked in the mapping photograph; intensity measurements were conducted for each of the marked grains; and corrections were made by the Bence-Albee method (Bence and Albee, 1968). Since this method has been widely used only for silicate samples, its applicability to oxide minerals was crosschecked by analyzing the same multi-component oxides with the ICP emission spectroscopic method and with the EPMA method utilizing Bence-Albee correction procedures. The results were found to be satisfactory. Results of a total ICP analysis of a samarskite sample from Kawabe, Fukushima pref., Japan, is given in Table 2 (Nagashima et al., 1981). For the ICP analysis, several milligrams of the sample immersed in $HF + H_2SO_4$ were heated on a sandbath until the H_2SO_4 fumed. After cooling, the dissolved material in solution was mixed in diluted (5%) H_2SO_4 containing a small amount of H_2O_2 .

Results and discussion

Samarskite

Low temperature form of samarskite. Prior to samarskite synthesis, details of the chemical composition of samarskite were obtained to place limits on the mixing ratios of the starting materials. Because the ideal chemical formula of samarskite is not established, a starting mixing ratio was tentatively chosen which took into account the chemical data for natural samarskites. Due to the number of ele-

Table 1. Mixing ratios of starting materials and products obtained

No.	Mixing ratios						Atmosphere	Method (#)	Temp.	Products
	Ca	U	Y	Nb	Fe	Ti				
1			1	1			air	S	1300	YNbO ₄
2				1	1		air	S + M	1150 - 1430 [#]	FeNbO ₄ (Ixiolite-like)
3				2	1		H ₂	S + M	950 - 1500 [#]	FeNb ₂ O ₆ (Columbite, Tapiolite)
4				2	1		air	S	1000 - 1150 [#]	FeNbO ₄ + α*
5	1			1			air	S	1300	CaNb ₂ O ₆
6		1				1	H ₂	S	1180 - 1320 [#]	UTi ₂ O ₆ + St*
7			2	3	1		air	S + M	930 - 1430 [#]	YNbO ₄ + FeNbO ₄ + St*
8			1	5	2		H ₂	S	1000 - 1200 [#]	Samarskite + α*
9			1	1		1	air	S	1150 - 1350 [#]	YTiNbO ₆ (Euxenite) + YNbO ₄ + St*
10	1			4	1		H ₂	S	1180	CaNb ₂ O ₆ + FeNb ₂ O ₆
11	1			4	1		air	S	1150	CaNb ₂ O ₆ + FeNbO ₄
12	1		1	2	2		H ₂	S	1150	YNbO ₄ + CaNb ₂ O ₆ + α*
13	1		1	2	2		air	S	1150	Pyrochlore + FeNbO ₄ + CaNb ₂ O ₆ + α*
14		1	2	4	2		air	S	1150	Fergusonite (*) + FeNbO ₄ + Nb ₃ UO ₁₀
15	2	2	5	21	6		air	S	900 - 1200 [#]	Fergusonite (*) + pyrochlore + FeNbO ₄ + Nb ₃ UO ₁₀
16	2	2	5	21	6		H ₂	S	700 - 1200 [#]	Samarskite + Fergusonite (*)

* St. = Starting materials. α = Unidentified phase. (*) M-fergusonite
A few to several runs of synthesis experiments were conducted in the temperature range indicated.
(#) S = sinter, M = melt.

ments found in natural samarskites, the elements were grouped into five major groups for simplicity in the synthesis experiments. Ca was chosen to represent most of the divalent elements, Y to represent the rare-earth elements, Ti to represent other minor elements such as Al and Zr which can substitute for Ti. Nb was chosen to represent Nb + Ta, and Fe with or without U to make an indepen-

dent group. These latter two elements are commonly found in natural samarskites and their oxidation states are considered to play an important role at the time of mineral formation.

With these in mind, a tentative mixing ratio

$$\text{Ca} : \text{U} : \text{Y} : \text{Fe} : \text{Nb} = 2 : 2 : 5 : 6 : 21$$

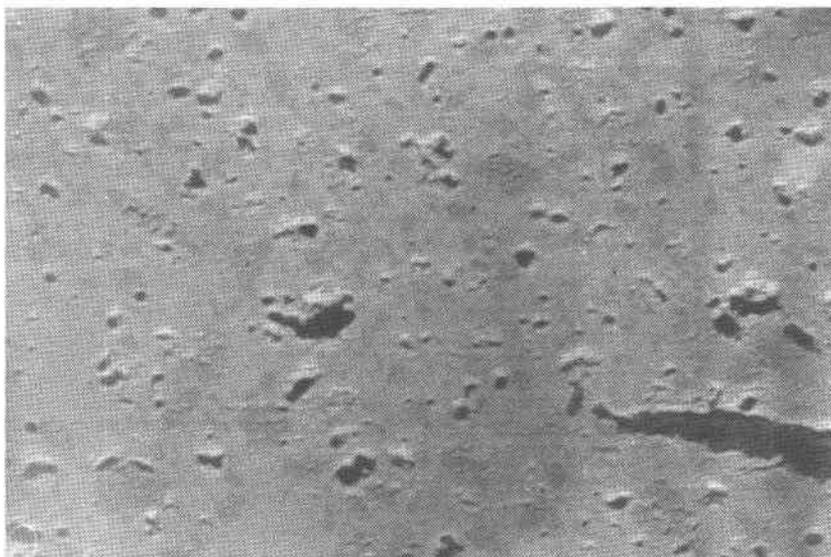


Fig. 1. Back scatter electron image (composition figure) of the material obtained by the sintering method from starting material of the Ca-Y-Nb-Fe-O system.

Table 2. ICP analysis of samarskite from Kawabe, Fukushima prefecture, Japan

	wt%	C.V. %		wt%	C.V. %
K ₂ O	0.1	—	U ₃ O ₈	29.6	1.2
Na ₂ O	0.1	—	PbO	0.0	
MgO	0.1	23	Al ₂ O ₃	0.3	16
ThO ₂	1.3	1.2	WO ₃	2.1	1.9
ZrO ₂	0.6	1.3	Sb ₂ O ₃	0.2	15
MnO	1.5	1.2	Nb ₂ O ₅	38.3	1.6
CaO	0.3	—	TiO ₂	0.2	1.0
FeO	10.0	0.9	Ta ₂ O ₅	10.2	0.5
Y ₂ O ₃	3.9	2.0	total	98.8	

A_{0.99}B_{1.01}O₄, Analysts : M.Hamada and K.Nagashima.
Coefficient of Variation(C.V.) were calculated from five runs of measurement.

was chosen, suspecting that it represents one of the several possible samarskite compositions. This ratio is given in lines 15 and 16 of Table 1. Other mixing ratios shown in Table 1 were all tentatively selected so as to conform to the guideline that the number of the metal ions is approximately half of the oxygen ions. It should be noted that some related compounds such as YTiNbO₆ (euxenite), YNbO₄ (fergusonite), CaNb₂O₇ (pyrochlore), CaNb₂O₆ (fermsite), and FeNb₂O₆ (columbite) were formed (Table 1) even though the ratios in Table 1 were selected to produce samarskite. X-ray diffraction data for a synthesized samarskite (No. 16 in Table 1) are shown in Table 3 together with those for the natural Kawabe samarskite which was recrystallized in a reducing atmosphere. In Table 3 only the peaks corresponding to the samarskite phase are shown, while those of an associated monoclinic fergusonite phase are omitted. Data for the recrystallized and synthesized samarskites are in good agreement within experimental error. The space group of the low temperature form of orthorhombic samarskite is probably *Pbcn*. However, a structure determination is needed to confirm this assignment. Table 4 shows the EPMA analysis data for the synthesized samarskites obtained by sintering at 1200°C for 30 hrs.

The synthesized samarskite was found to behave almost the same way as the natural samarskite when heated in an oxidizing atmosphere. If heated to 900–1200°C in air, the material obtained gave a complicated X-ray powder pattern which was very similar to that reported by Nilssen (1970). As reported by Sugitani et al. (1984), the complicated pattern was interpreted as the superposition of peaks corresponding to fergusonite, pyrochlore, and ixiolite-like FeNbO₄. EPMA analysis of the products obtained here showed that these three compounds were always present together, along with the additional compound Nb₃UO₁₀. Figure 2 schematically shows the phase changes found in the above heat treatment. Synthesis of samarskite starting with a reduced number of component elements was also conducted with successful results. The mixing ratio for this case was Y:Fe:Nb = 1:2:5 (No. 8 in Table 1) which was

tentatively derived on the basis of the experimental results of Table 4 by replacing Ca plus U by Y. Since the amount of the unidentified phase α in the products is negligibly small compared to that of the samarskite phase, the composition of the synthetic samarskite can be regarded as being close to that of the starting mixture which may be rewritten as YFe₂Nb₅O₁₆ (= Y₂O₃ · 4FeO · 5Nb₂O₅). EPMA analysis of a synthesized crystal gave exactly the same composition as the mixture. This result strongly supports the suggestion (Sugitani et al., 1984) that the chemical formula of samarskite should not be restricted to a simple formula but that it corresponds to a wide range of composition with a variation in the number of component elements and metal positions. Supposing that Ca and U atoms are not essential for the samarskite structure, the chemical formula of YFe₂Nb₅O₁₆ could be presented as a possible ideal end-member of the samarskite group.

High temperature form of samarskite. It was reported (Sugitani et al., 1984) that the inversion temperature from the low to high temperature form of a natural samarskite was about 650°C. Formation of the high temperature form was characteristically indicated by the splitting of the main peak (111) of the low temperature phase into a doublet, but the cause of this splitting was not determined.

Table 3. X-ray powder diffraction data for low temperature synthetic samarskite and recrystallized Kawabe samarskite

h k l	synthesized*			recrystallized**	
	d _{cal}	d _{obs}	I/I ₀	d _{obs}	I/I ₀
1 1 0	3.671	3.681	24	3.728	15
1 1 1	2.973	2.976	100	3.030	100
2 0 0	2.870	2.874	8	2.843	15
0 0 2	2.534	2.534	12	2.603	15
2 0 1	2.498	2.499	10	2.495	10
2 1 0				2.463	5
0 2 0	2.387	2.387	6	2.461	5
0 1 2	2.238	2.240	4		
2 1 1	2.213	2.216	4		
1 1 2	2.085	2.084	6	2.136	5
3 0 0	1.913	1.910	10		10
2 0 2	1.900	1.903	10	1.920	10
2 2 0	1.835	1.836	6	1.863	10
3 1 0	1.776	1.777	10	1.767	10
0 2 2	1.738	1.736	10		
2 2 1	1.726	1.725	14		
0 3 1				1.567	5
1 1 3, 1 3 0	1.533	1.534	10		
2 2 2	1.486	1.486	2		
2 0 3, 1 3 1	1.468	1.468	6	1.511	5
3 1 2	1.454	1.454	10	1.463	5
4 0 1	1.381	1.381	4		

* (Ca_{0.24}U_{0.20}Y_{0.84}Fe_{1.56}Nb_{5.04})_{Σ7.88}O₁₆.

Synthesized by heating in H₂ gas flow at 1000°C for 15 hours (No. 16 of Table 1). Data are for an orthorhombic cell with: a=5.740Å, b=4.774Å, and c=5.068Å.

** Samarskite; Kawabe, Fukushima Prefecture, Japan. Heated in H₂ gas flow at 550°C for 16 hours. Data for an orthorhombic cell with a=5.687Å, b=4.925Å, and c=5.210Å.

Table 4. Empirical formulas of synthetic orthorhombic samarskites

No.	Empirical formula (O = 16)*
1	(Ca _{0.24} U _{0.20} Y _{0.84} Fe _{1.56} Nb _{5.04}) Σ 7.88O ₁₆
2	(Ca _{0.20} U _{0.16} Y _{0.36} Fe _{2.24} Nb _{5.12}) Σ 8.08O ₁₆
3	(Ca _{0.28} U _{0.01} Y _{0.60} Fe _{1.88} Nb _{5.16}) Σ 7.93O ₁₆
4	(Ca _{0.44} U _{0.40} Y _{1.12} Fe _{1.28} Nb _{4.72}) Σ 7.96O ₁₆
5	(Ca _{0.16} U _{0.08} Y _{0.36} Fe _{2.24} Nb _{5.32}) Σ 7.96O ₁₆

* : analyses done by EPMA.

X-ray powder diffraction data for the samarskite, from Kawabe, Japan, recrystallized in a reducing atmosphere at 950°C for 15 hrs, are shown in Table 5 together with those for synthetic samarskite (No. 3 in Table 7). The similarities in I/I_0 and d -spacings between the two should be noted. Indexing was successfully accomplished by referring to the basic structure of ixiolite ($Pbcn$), but with the a and b axes exchanged and the b dimension of the low temperature form being doubled. The deviation of the β ($=94^\circ$) angle from 90° is considered as having nothing to do with the intrinsic monoclinic $P2/c$ wolframite structure, but having something to do with the transition from the low ($Pbcn$?) to high ($P2/c$) temperature phase. The cell parameters and axial ratios for the natural, recrystallized samarskites at high and low temperatures are shown in Table 6. In spite of the high (up to about 1200°C) temperatures to which synthetic samarskites were heated, the low temperature structure form was obtained in all cases. Based on the syntheses experiments with variable amounts of UO_2 in the starting materials, the high temperature monoclinic form was found to be stable when the content of UO_2 was as much as about 30 wt.%, which is very close to that of

Kawabe samarskite, 29.6% U_3O_8 (Table 2). When the amount of UO_2 exceeded 30 wt.%, the crystalline products obtained contained no samarskite but were only mixtures of fergusonite, tapiolite and uranium oxide (UO_2 or U_4O_9). Discussion of the low and high temperature structure phases from a crystal chemical viewpoint will be given in the next section.

Chemical and structural relation of samarskite with respect to its related oxide compounds—what is samarskite?

X-ray powder diffraction patterns of samarskite show much resemblance to those of ixiolite, columbite, and wolframite which $\beta = 90^\circ$. The structures of wolframite, columbite, tapiolite, ixiolite, ashanite, wodginite, and others are closely related to each other, all being derived from the α - PbO_2 structure (Laves et al., 1963; Gorzhevskaya et al., 1974; Graham and Thorner, 1974; Nickel et al., 1963; Foord, 1982). In the α - PbO_2 structure, layers of oxygen atoms occur in a hexagonal closest packed (hcp) array, while metal atoms (Pb) occupy half of the octahedral sites produced between the oxygen layers. The columbite structure is referred to as a "superstructure" of the α - PbO_2 structure since it has an a cell dimension three times that of a for α - PbO_2 .

A rough idea of the crystal structure of primary (nonmetamict) samarskite has been proposed (Sugitani et al., 1984) on the basis of various results from studies such as X-ray powder diffraction of recrystallized samarskites, chemical analyses of natural and synthesized samarskites, observations of modes of occurrence of samarskite and its structurally related minerals, and others. One of the most important aspect of samarskite structure is that it is fundamentally composed of the α - PbO_2 packing structure. Another, almost equally important point is that the metal atoms in samarskite do not necessarily have a fully ordered site occupancy, but instead have a partially or completely disor-

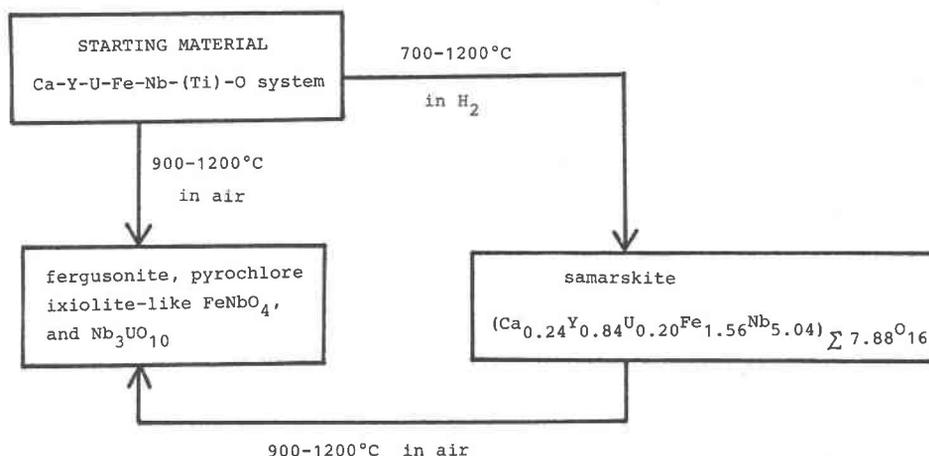


Fig. 2. Synthesis products obtained by heating under reducing and oxidizing conditions, and products obtained by heating synthesized samarskite in air.

Table 5. X-ray powder diffraction data for high temperature synthetic and natural samarskite

h k l	recrystallized*			synthesized**		
	d _{cal}	d _{obs}	I/I ₀	d _{cal}	d _{obs}	I/I ₀
0 1 0	9.914	9.927	15	9.897	9.872	10
1 2 0	3.720	3.719	20	3.715	3.712	15
		3.633	30			
0 3 0	3.305	3.291	10	3.299	3.288	20
$\bar{1}$ 2 1	3.094	3.098	100	3.092	3.092	100
1 2 1	2.968	2.961	100	2.965	2.966	100
2 0 0	2.815	2.815	20	2.811	2.808	25
2 1 0	2.708	2.715	5	2.704	2.703	35
0 0 2	2.609	2.611	25	2.609	2.615	15
$\bar{2}$ 0 1	2.549	2.511	5			
0 4 0	2.479	2.478	20	2.474	2.476	10
2 2 0	2.448	2.44(B)	10	2.444	2.443	10
1 1 2	2.248	2.249	5			
$\bar{1}$ 2 2	2.182	2.189	10			
2 3 0	2.143	2.141	10			
		2.114	10			
1 2 2	2.093	2.089	10	2.092	2.093	15
0 3 2	2.048	2.050	5			
$\bar{2}$ 0 2	1.980	1.98(B)	5			
		1.914	20			
2 0 2, 0 5 1	1.853	1.853	25	1.851	1.853	30
$\bar{2}$ 4 1, $\bar{3}$ 1 1	1.780	1.78(B)	5	1.775	1.775	15
3 2 0	1.755	1.754	10			
2 2 2, $\bar{1}$ 4 2	1.735	1.735	10	1.734	1.735	25
2 4 1	1.728	1.723	5			
0 6 0	1.652	1.654	10	1.649	1.651	30
$\bar{1}$ 2 3	1.603	1.603	15			
1 2 3	1.549	1.547	15			
2 4 2	1.484	1.484	10			
2 0 3	1.437	1.439	5			

* Samarskite; Kawabe, Fukushima Prefecture, Japan. Heated in H₂ gas flow at 950°C for 15 hours. Data for a monoclinic cell with a=5.642Å, b=9.914Å, c=5.229Å, and β=93.84°.

** (Y_{1.0}U_{1.5}Fe_{1.5}Nb_{4.0})₈O₁₆. Mixing ratio for the synthesis by heating in H₂ gas flow at 1200°C for 12 hours. Data for a monoclinic cell with a=5.638Å, b=9.90Å, c=5.230Å, and β=93.88°.

dered distribution. In the completely disordered case, each metal site in samarskite may be occupied by a complete variety of metal atoms. A limiting case of such disorder is

Table 6. Lattice parameters for natural samarskites recrystallized in H₂ gas flow at low (550–600°C) and high (950°C) temperatures

	Temp.	a/Å	b	c	β/°	a : b : c
Kawabe	550°C	5.687 (4)	4.925 (2)	5.210 (4)	90.02 (8)	1.155 : 1 : 1.058
	950	5.642 (7)	9.914 (8)	5.229 (3)	93.84 (7)	0.569 : 1 : 0.527
Ishikawa	550	5.664 (6)	4.940 (3)	5.173 (7)	90.0 (2)	1.147 : 1 : 1.047
	950	5.654 (6)	9.900 (4)	5.222 (4)	93.77 (8)	0.571 : 1 : 0.527
Utsumine	600	5.64 (2)	4.98 (4)	5.18 (2)	90.0 (4)	1.133 : 1 : 1.040
	950	5.68 (2)	9.98 (4)	5.21 (1)	93.5 (4)	0.569 : 1 : 0.522
Samekawa	600	5.71 (3)	9.80 (3)	5.20 (1)	90.5 (3)	0.583 : 1 : 0.531
		(1.165 : 1 : 1.061)				

low-temperature phase : Space group Pbcn(?) .

high-temperature phase : Space group P2/c.

found in ixiolite where all of the metal ions are randomly distributed (disordered arrangement) among the metal sites (Nickel et al., 1963). This is also true for ashanite, the Nb-dominant equivalent of ixiolite (Foord et al., 1984).

Table 8 shows the X-ray powder diffraction data for synthetic samarskite (low temperature phase) compared with those of columbite, ixiolite, and ixiolite-like FeNbO₄. Indexing of the peaks of samarskite has been based on those of the related minerals, especially that of ixiolite which belongs to the space group *Pbcn*. It should be noted that the *a* and *b* axes of samarskite in Table 8 are interchanged compared to the data shown in Table 3 so as to conform to the cell orientation of the other structurally related minerals. Peak positions of samarskite are similar to those of columbite (FeNb₂O₆), except for the absence of 200, 400 and some other reflections for *hkl* with *h* ≠ 3*n*. The *a* cell dimension of samarskite is one-third that of columbite, and equal to that of ixiolite, suggesting that samarskite is closely structurally related to ixiolite or ashanite (Zang et al., 1980) which is the completely disordered subcell form of columbite which also has the α-PbO₂ type packing structure. Samarskite is also closely related to wolframite which is, however, monoclinic, as previously suggested by Komkov (1965). It is also structurally related to wadginitite which may exist in an ordered form, *C2/c*, A₄C₄B₈O₃₂, or a disordered form, M₁₆O₃₂. The high temperature form of FeNbO₄, having the ixiolite structure, has the packing structure of α-PbO₂, but it has smaller cell dimensions compared to those of samarskite and this is primarily a function of the chemical composition.

The structural relationship of samarskite to related phases is schematically shown in Figure 3 which has been constructed on the basis of all the available reports on samarskite and the experimental results obtained in our previous (Sugitani et al., 1980, 1984) and present study. This can be regarded as a revised figure of what was shown in Figure 3 of Sugitani et al. (1980). The two horizontal planes represent domains of orthorhombic (upper) and monoclinic (lower) minerals composed of the α-PbO₂ pack-

Table 7. Synthetic run products obtained during synthesis of the high temperature form of samarskite

No.	chemical composition	1100°C	1200°C
1.	'samarskite' composition**	Sl***, F	Sl, F
2.	(Y ₃ U _{0.5} Fe _{0.5} Nb ₄) ₂₈ O ₁₆	F, U	F, U
3.	(Y ₁ U _{1.5} Fe _{1.5} Nb ₄) ₂₈ O ₁₆	Sh, F	Sh, F
4.	(Y _{0.5} U _{1.75} Fe _{1.75} Nb ₄) ₂₈ O ₁₆	T, U, F	T, U, F

* calculated on the basis of the starting composition.

** (Ca_{0.24}U_{0.20}Y_{0.84}Fe_{1.56}Nb_{5.04})_{27.88}O₁₆

*** Sl: samarskite low temp. phase,
Sh: samarskite high temp. phase,
F: fergusonite, U: UO₂ or U₄O₉,
T: tapiolite.

ing structure. Samarskite should be located somewhere between ixiolite (disordered M₄O₈ structure) and columbite (ordered AB₂O₆ structure) which has an *a* parameter three times that of ixiolite (or samarskite). Samarskite, which is shown in the orthorhombic plane also projects to the lower monoclinic plane, where it should be regarded structurally as a mineral closely related to wolframite, but having a β angle of 90°. The space group of the monoclinic samarskite may be considered to be *P2/c*, as given by Komkov (1965). Wolframite, on the other hand, is related to M'-fergusonite and to M-fergusonite in the monoclinic plane. It might be said that Komkov (1965) was fortunate to have worked on a very fresh samarskite sample which was free from oxidation or weathering and consequently contained mostly ferrous ions. Additionally, he was right in recrystallizing the sample at a low (660°C) temperature with a very short time. Otherwise, oxidation of ferrous to ferric iron would have resulted in a decomposition of the sample into a mixture including FeNbO₄.

The high temperature form of samarskite is located at a position displaced to the right with respect to the low temperature form. It is monoclinic but its *c* axis slants not towards the *a* axis as in wolframite but towards the *b* axis so that the *a* and *b* axes of the high temperature phase are interchanged as shown in the figure. In addition, the new *b* cell dimension is $2 \times a$ of the low temperature phase. The high temperature samarskite phase can be regarded as an ordered phase of the low temperature form of samarskite, similar in the manner that columbite may be regarded as another ordered superstructure of low temperature samarskite. In the present study, all of the samarskite synthesized was found to change into the high temperature form of samarskite or into a phase with the trirutile structure upon heating, and none of the synthetic samarskite changed into the columbite phase. We believe that some samarskites, presumably those containing a limited number of metal ions could be transformed into the columbite structure.

Related minerals

Fergusonite type. Fergusonite is known to have three different structural forms, identified as M, M', and T (Van Wambeke, 1960). The M' phase is considered as being closely related to samarskite (Komkov, 1965). The M phase fergusonite has the space group C2 (or I2 according to Wolten, 1967), and its chemical formula is generally expressed as ABO₄, where the A atom is surrounded by 8 oxygens. Although the A and B atoms are ideally tri- and penta-valent ions, respectively, substitution of atom(s) with other valences may occur provided that a total charge balance of the atoms exists. In the present study, only the M phase fergusonite was obtained from the starting materials of Nos. 14, 15, and 16 in Table 1. Products synthesized in a reducing atmosphere with the starting materials of the Ca-Y-U-Nb-Fe-O system (No. 16 of Table 1), showed that a considerable number of Y sites, up to about 50%, were replaced by Ca + U as seen in Table 9. Since the ionic radii of Ca²⁺, Y³⁺, and U⁴⁺ are 1.12Å, 1.015Å, and 1.00Å, respectively, the substitution of 2Y³⁺ \rightleftharpoons Ca²⁺ + U⁴⁺ seems very likely to occur. It was also found that Fe atoms, though added in the starting material, were not incorpor-

Table 8. X-ray powder diffraction data for the synthetic low-temperature form of samarskite compared with columbite, ixiolite, and orthorhombic FeNbO₄

columbite		ixiolite		samarskite [#]		FeNbO ₄	
d	h k l	d	h k l	d _{obs}	h k l	d	h k l
	Pbcn [*]		Pbcn [*]		Pbcn(?)		Pbcn ^{**}
a	14.28Å	a	4.76Å	a	4.774Å	a	4.65
b	5.728	b	5.74	b	5.740	b	5.614
c	5.06	c	5.14	c	5.068	c	5.00
7.14	200						
5.30	110						
3.66	310, 111	3.65	110	3.681	110	3.58	110
3.57	400						
2.96	311	2.98	111	2.976	111	2.912	111
2.86	020	2.87	020	2.874	020	2.807	020
2.53	002	2.57	002	2.534	002	2.502	002
2.49	021	2.51	021	2.499	021	2.499	021
2.38	600	2.37	200	2.387	200	2.325	200
2.279	511						
2.236	302	2.265	102	2.238	102	2.204	102
2.207	321	2.213	121	2.216	121	2.167	121
2.084	312	2.104	112	2.084	112	2.051	112
2.043	421	2.017	211	1.910	003		
1.898	022	1.915	022	1.903	022	1.868	022
1.831	620	1.826	220	1.836	220	1.791	220
1.796	512, 711						
1.772	330	1.772	130	1.777	130	1.737	130
1.735	602	1.746	202	1.736	202	1.704	202
1.721	621	1.722	221	1.725	221	1.686	221
1.672	331					1.641	131
1.608	-						
1.534	313	1.554	113	1.534	113, 310	1.512	113
1.516	910	1.521	310			1.495	310
1.484	622	1.490	222	1.486	222	1.457	222
1.465	023					1.434	023
1.454	911, 332	1.459	023, 311	1.468	023, 311	1.432	311
				1.454	132	1.427	132
1.432	040					1.404	040
1.393	-					1.400	231
1.380	041	1.380	041	1.381	041	1.352	041

* ASTM CARD: 15-733

** ASTM CARD: 16-358

This work

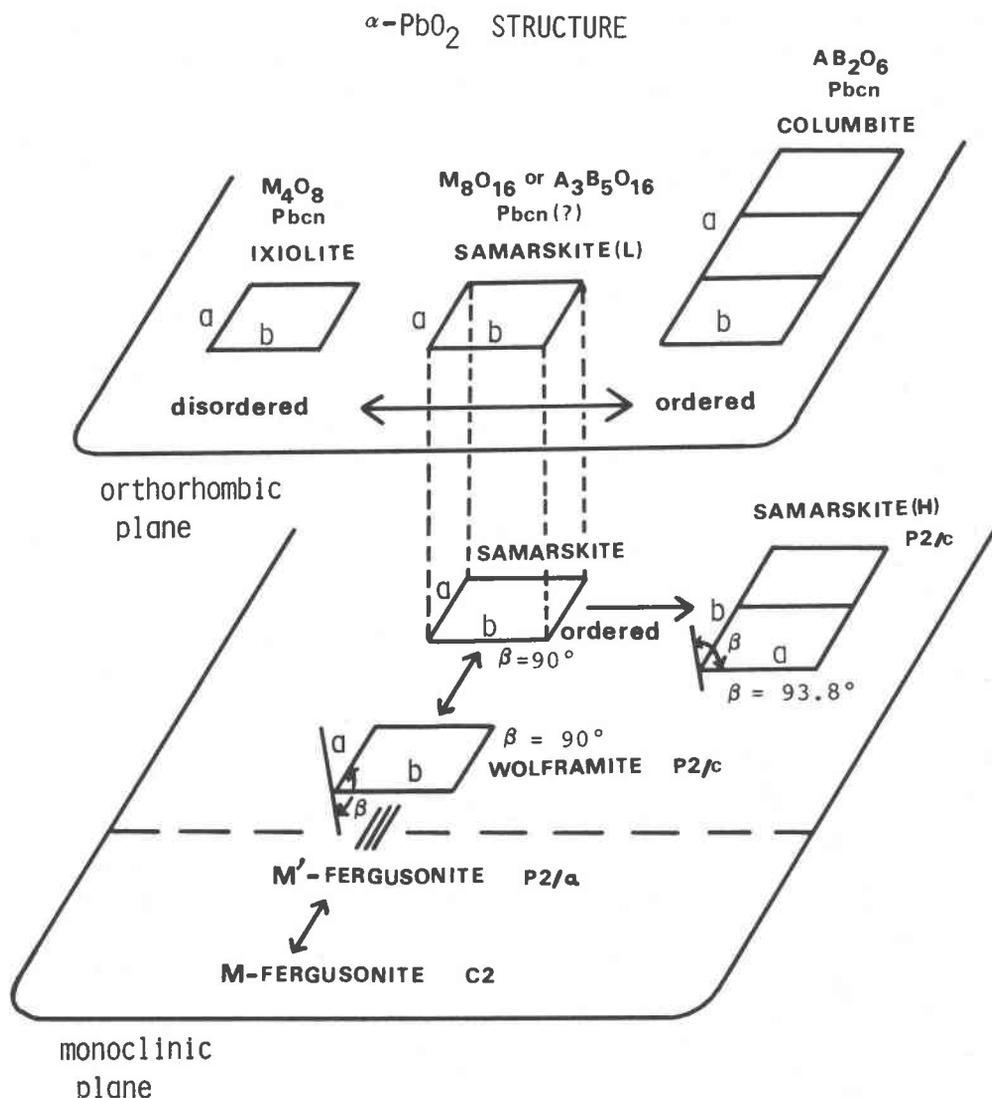


Fig. 3. Diagram showing the structural relationships between samarskite and related minerals.

ated in synthetic fergusonites in either oxidizing or reducing atmospheres.

$FeNb_2O_6$ (columbite), $FeNbO_4$ (ixiolite-type structure) and $YTiNbO_6$ (euxenite). According to the phase diagram for the system $FeNb_2O_6$ - $FeNbO_4$ given by Schröcke (1967) $FeNbO_4$ and $FeNb_2O_6$ show partial solution toward each other, but there is a wide immiscibility gap where $FeNb_2O_6$ and $FeNbO_4$ do not form any solid-solution phase even though they are composed of the same α -PbO₂ packing structure. The results of the present study, however, are somewhat contrary to those obtained by Schröcke in the sense that $FeNb_2O_6$ and $FeNbO_4$ were never found at the same time in the products of each run of the syntheses experiments (e.g., see Table 1). $FeNb_2O_6$ was always a synthesis product in a reducing atmosphere, while

$FeNbO_4$ was formed in an oxidizing atmosphere. The identifications of the phases were made by X-ray powder diffraction. There is a possibility that the synthesized $FeNb_2O_6$ may contain a small amount of Fe^{3+} , and similarly that the $FeNbO_4$ may contain a small amount of

Table 9. Empirical formulas for synthetic fergusonites analyzed by EPMA method

No.	Empirical formula (O = 4)
1	$(Y_{0.68}Ca_{0.13}U_{0.14})\Sigma_{0.95}Nb_{1.03}O_4$
2	$(Y_{0.70}Ca_{0.12}U_{0.12})\Sigma_{0.94}Nb_{1.03}O_4$
3	$(Y_{0.45}Ca_{0.23}U_{0.28})\Sigma_{0.96}Nb_{1.02}O_4$
4	$(Y_{0.73}Ca_{0.10}U_{0.10})\Sigma_{0.93}Nb_{1.05}O_4$

Table 10. X-ray powder diffraction data and lattice parameters for synthetic FeNb_2O_6 with the tapiolite structure

h k l	d_{cal}	d_{obs}	I/I ₀
110	3.379	3.379	100
103	2.574	2.575	82
200	2.389	2.390	18
113	2.266	2.267	12
213	1.751	1.751	66
220	1.687	1.689	16
006	1.527	1.528	8
310	1.511	1.511	14
303	1.412	1.413	18
116	1.392	1.392	11
215	1.391	1.388	6
206	1.287	1.287	4
323	1.216	1.216	8
400	1.194	1.194	4
226	1.133	1.133	4

Tetragonal, Space Group P4₂m (unpublished data).
 $a = 4.7270$ (5)
 $c = 9.2160$ (17)

Fe^{2+} . In these cases FeNb_2O_6 should be written as $(\text{Fe}^{2+}, \text{Fe}^{3+})\text{Nb}_2\text{O}_6$, and FeNbO_4 should be written as $(\text{Fe}^{3+}, \text{Fe}^{2+})\text{NbO}_4$. It was found that FeNb_2O_6 changed into FeNbO_4 , when heated in air, in the same way that samarskite decomposed into a mixture of oxides including FeNbO_4 with the ixiolite-type structure. This shows that samarskite is chemically and structurally closer to columbite which contains dominant Fe^{2+} , than to FeNbO_4 with the ixiolite-type structure which contains dominant Fe^{3+} .

It is known that FeNb_2O_6 also has an ordered high temperature trirutile-type structure (Banas and Kucha, 1975; Dunn et al., 1979), equivalent to that of ordered tapiolite, which develops from the columbite type at about 1250°C (Schröcke, 1967). Our FeNb_2O_6 which was synthesized in H_2 gas flow was found to change into the ordered or disordered form of tapiolite type even below 1000°C when kept in the same H_2 gas flow for more than 10 hrs. When kept at an elevated temperature of 1020°C only a columbite-type phase was obtained, while only a tapiolite-type phase was obtained at 1080°C. When kept at temperatures between 1020 and 1080°C, mixtures of both phases resulted. On the other hand, when FeNb_2O_6 was synthesized under less reducing conditions, at 700–800°C for two hours in H_2 gas flow, followed by keeping it in an N_2 gas flow at 1000–1300°C for 10 hours, only columbite-type phases were formed. The ionic radius of the A atom in $\text{A}(\text{Nb}, \text{Ta})_2\text{O}_6$ is one of several factors influencing the structure-type developed. Figure 4 shows the structural phases at room temperature for ANb_2O_6 – ATa_2O_6 solid-solution series obtained by the flux method (Kawajiri et al., 1978; Yamasaki, 1980). According to the figure, FeNb_2O_6 could form with either the columbite or the tapiolite structure.

The development of FeNb_2O_6 in either the columbite or tapiolite structure depends on the oxidation level ($f\text{O}_2$) of FeNb_2O_6 at the time of crystallization. A phase with the columbite-structure would appear if formed (and kept) in a less reducing (moderate $f\text{O}_2$) atmosphere, while a tapiolite-type phase would appear if formed (and kept) in relatively more reducing (low $f\text{O}_2$) atmosphere. A small amount of Fe^{3+} in FeNb_2O_6 which was synthesized in a relatively less reducing atmosphere, would make the average radius of the divalent Fe-cation site somewhat smaller, thus favoring formation of the columbite phase. However, if the effect of a reducing atmosphere acts to reduce Nb(V) to Nb(IV), the conditions would favor formation of tapiolite having the rutile-type structure. It is not known whether the reducing procedure in the present experiment works to make the relative ratio $\text{Fe}^{2+}/\text{Fe}^{3+}$ ($\text{Fe}^{2+} \gg \text{Fe}^{3+}$) higher, or $\text{Nb}^{5+}/\text{Nb}^{4+}$ ($\text{Nb}^{5+} \gg \text{Nb}^{4+}$) lower, or results in the formation of oxygen vacancies in FeNb_2O_6 . Further detailed experiments under controlled atmospheric conditions will be needed in order to fully solve the problem of the relative stabilities of the columbite and tapiolite structures in terms of physico-chemical factors such as ionic radii and redox potentials of the metal atoms contained.

Euxenite has been considered as having a close structural relationship to samarskite. In this study, however, it was found only as a product of synthesis in an oxidizing atmosphere (e.g. No. 9 in Table 1). This result is consistent with the phase diagram of YTiNbO_6 – FeNb_2O_6 system (Schröcke, 1967) where they do not form any continuous solid-solution series. This is also consistent with the data of Tokonami (1980) indicating no evidence for solid-solution between samarskite and euxenite.

Pyrochlore type. Pyrochlore is generally expressed as $\text{A}_{2-m}\text{B}_2\text{O}_6(\text{O}, \text{OH}, \text{F})_{1-n} \cdot p\text{H}_2\text{O}$, in which some vacancies are found at the A metal sites and the oxygen sites (Ho-

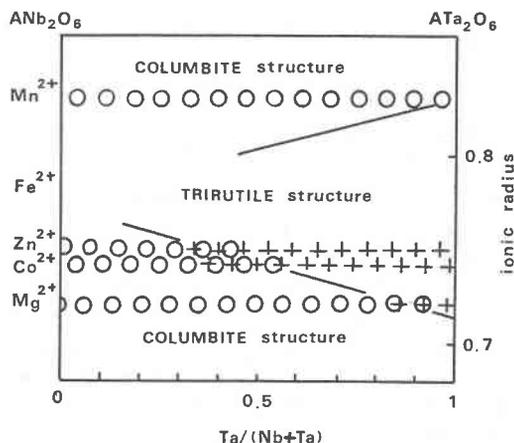


Fig. 4. Results showing the phase types which appeared in the synthetic experiments on the ANb_2O_6 – ATa_2O_6 system, where A represents various divalent cations. O: columbite type, +: trirutile type.

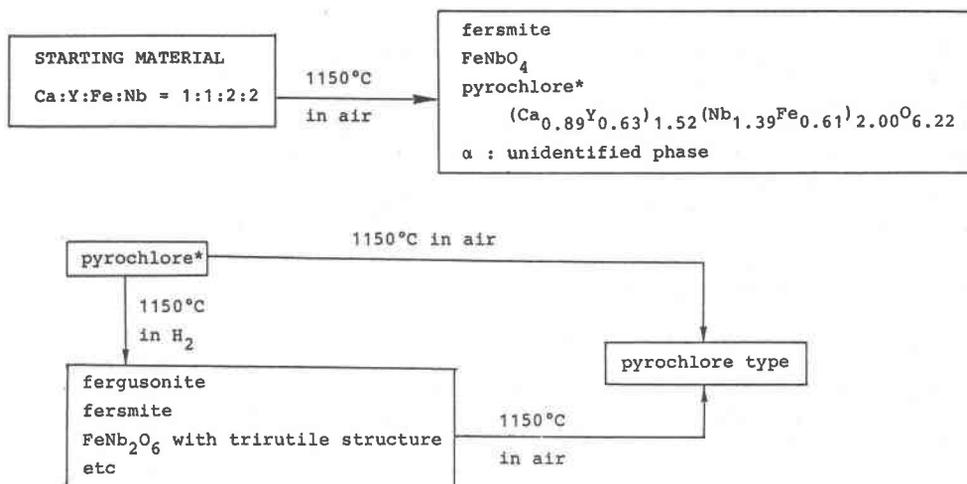


Fig. 5. Synthesis of pyrochlore and associated phases in air and products obtained by heating of pyrochlore in reducing and oxidizing atmospheres.

garth, 1977). It was found that pyrochlore could be synthesized from various combinations of the starting materials (e.g. No. 13 and 15 in Table 1), but only in air. When the pyrochlore, synthesized from Ca–Y–Fe–Nb–O system, was heated again in an H₂ gas flow, it decomposed into a mixture of phases, mostly YNbO₄, CaNb₂O₆, and FeNb₂O₆ (Fig. 5). This shows that Fe³⁺ is stably incorporated into pyrochlore, while Fe²⁺ is not.

Pyrochlore synthesized from the Ca–U–Y–Nb–Yi–Fe–O system was determined to have the chemical composition,



which can be expressed by taking O = 4,



This latter formulation is very similar to that of samarskite with a metal-to-oxygen ratio of approximately 1:2. Synthetic experiments, using the same starting materials as above, showed that a single samarskite phase was obtained in a reducing atmosphere, while a pure pyrochlore phase was obtained in an oxidizing atmosphere. It should be noted that the ionic radius of the A atom in AB₂O₆ would also influence the formation of structural variants of the compound.

Conclusion

Samarskite has been synthesized by heating appropriate mixtures of starting materials in the Ca–Y–U–Fe–Nb–(Ti)–O system, in a reducing atmosphere (e.g., in H₂ gas flow). The X-ray powder diffraction pattern of the synthetic material agrees with that of natural samarskite recrystallized in a reducing atmosphere. Both the synthetic and the recrystallized samarskite decompose into a mixture of compounds; mostly fergusonite, pyrochlore, ixiolite-like FeNbO₄, and Nb₃UO₁₀, when heated in an oxidizing atmosphere (e.g., in air). Samarskite has also been synthesized

from a mixture of starting materials having a reduced number of component elements such as those in the Y–Fe–Nb–O system. The chemical formula of samarskite for the system can be expressed as YFe(II)₂Nb₅O₁₆. It must be noted, however, that samarskite cannot be uniquely formulated, but should be expressed, for instance, as A₃B₅O₁₆ or M₈O₁₆ which may include a wide range of chemical compositions, degree of structural order and crystal symmetry.

At high temperatures, about 950°C, the orthorhombic low temperature form of samarskite changes into the high temperature monoclinic structural modification having a doubled *b* unit cell dimension, probably due to formation of a superstructure of the low temperature orthorhombic phase. The *b*-axis actually corresponds to the *a*-axis of the low temperature phase because the *a*- and *b*-axes are interchanged in the low and high temperature phases.

Ferrous iron can be incorporated as a major component into samarskite, tapiolite or columbite, while ferric ion cannot be incorporated but is only found in ixiolite-like FeNbO₄.

Euxenite and pyrochlore have been synthesized only in an oxidizing atmosphere.

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