

## Crystal chemistry of samarskite

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### ABSTRACT

Samarskite is a complex niobium tantalum titanium oxide that has been difficult to characterize because of its complex chemistry, metamictization, and pervasive alteration. Although X-ray diffraction (XRD) results show that the atomic arrangement of annealed samarskite is based on the  $\alpha$ - $\text{PbO}_2$  structure with a structural formula of  $\text{ABO}_4$ , previous chemical analyses supported other structural formulae ( $\text{AB}_2\text{O}_6$ ,  $\text{A}_3\text{B}_5\text{O}_{16}$ ). Results of electron microprobe analysis (EMPA) performed on 19 alteration-free samarskite samples show that the  $\text{ABO}_4$  structural formula is correct, if the B site contains Nb, Ta, and sometimes Ti and the A site contains all other cations. Analysis of average site charges and cation radii indicate that the structural formula is  $\text{A}^{3+}\text{B}^{5+}\text{O}_4$  with both A and B sites having octahedral coordination. A high-temperature form with a doubled  $a$  cell dimension may result from A-site ordering ( $\text{AA}'\text{B}_2\text{O}_8$ ).

### INTRODUCTION AND PREVIOUS WORK

Samarskite-(Y), most recently described as  $(\text{Y,Ce,U,Fe}^{3+})_3(\text{Nb,Ta,Ti})_5\text{O}_{16}$  (Fleischer, 1991), has always been found to be completely metamict (aperiodic). Efforts to determine the structure and crystal chemistry of samarskite have been complicated by three factors. First, because samarskite is metamict (Ewing et al., 1987), samples must be annealed prior to X-ray diffraction (XRD) analysis. Because both reduced and oxidized Fe are present, the annealing environment (oxidized vs. reduced) is important (Sugitani et al., 1984). Second, the chemical complexity of samarskite makes analysis difficult by any method. And finally, samarskite samples are often pervasively altered (Nilssen, 1970). With bulk analysis techniques such as wet-chemical methods and X-ray fluorescence, fine-grained alteration products are likely to be included in analyses. Thus, there is considerable disagreement about the formula and therefore the structure of samarskite.

Early morphological studies (Brögger, 1906) indicated that samarskite had cell dimensions similar to that of columbite ( $\text{AB}_2\text{O}_6$ ), although XRD results of annealed samples (Komkov, 1965) indicated a structure with cell dimensions similar to that of wolframite ( $\text{ABO}_4$ ).

Sugitani et al. (1985) synthesized samarskite in a reducing atmosphere with two starting material systems (Ca-U-Y-Nb-Fe-O and Y-Fe-Nb). Electron microprobe analysis (EMPA) of the synthesized material of both systems fit the structural formula  $\text{A}_3\text{B}_5\text{O}_{16}$ . Both Nilssen (1970) and Sugitani et al. (1985) grouped cations into A and B sites by ionic radius, with larger cations ( $>0.08$  nm) assigned to the A site and smaller cations assigned to the B site. The work of Sugitani et al. (1985) led to a redefinition of samarskite by the International Mineralogical As-

sociation Commission on New Minerals and Mineral Names.

Sugitani et al. (1984, 1985) also found both low-temperature and high-temperature phases corresponding to samarskite through annealing and synthesis. The low-temperature form has cell dimensions similar to those found by Komkov (1965) if the  $a$  and  $b$  cell dimensions are interchanged. The monoclinic high-temperature form requires a doubling of the  $a$  cell dimension, possibly due to cation ordering (Sugitani et al., 1984). This apparent reduction in symmetry at higher temperatures contradicts known models and will be discussed later. The  $a$  and  $b$  cell dimensions of Sugitani et al. (1984) are exchanged in this discussion to facilitate comparison with the Komkov model.

It is difficult to correlate the structure of samarskite with the formula  $\text{A}_3\text{B}_5\text{O}_{16}$  because the X-ray diffraction parameters determined by Komkov (1965) and Sugitani (1984, 1985) are more consistent with the  $\text{ABO}_4$  model. Sugitani et al. (1985) therefore proposed that samarskite might be only partially ordered or completely disordered ( $\text{MO}_2$ ). They also proposed that samarskite could be related to wolframite or  $M'$ -fergusonite, although the exact nature of the relationship was not known.

Graham and Thornber (1974) proposed a classification scheme for niobium oxide and tantalum oxide minerals based on the A-site radius and ordering type (Table 1). Schematic representations of the  $\alpha$ - $\text{PbO}_2$  and derivative structure types (i.e., wolframite, columbite) and the mixed coordination structures (i.e., fergusonite, aeschynite) are presented in Figures 1 and 2.

In summary, the three most important undisputed relations concerning the crystal chemistry of samarskite are (1) samarskite has a cation to O ratio of 1:2 (e.g.,  $\text{MO}_2$ ,  $\text{ABO}_4$ ,  $\text{AB}_2\text{O}_6$  or  $\text{A}_3\text{B}_5\text{O}_{16}$ ); (2) the samarskite structure is

**TABLE 1.** Classification scheme of common Nb-Ta minerals based on A-site radius and ordering scheme after Graham and Thornber (1974)

| Structure type                                    | A-site radius (nm) | MO <sub>2</sub>  | ABO <sub>4</sub>   | AB <sub>2</sub> O <sub>6</sub>   |
|---|--------------------|--|--|--|
| Rutile derivatives                                | > 0.067            | ilmenorutile: (Ti,Nb,Fe <sup>3+</sup> ) <sub>2</sub> O <sub>6</sub><br>struverite: (Ti,Ta,Fe <sup>3+</sup> ) <sub>3</sub> O <sub>6</sub> | none   | tapiolite: Fe <sup>2+</sup> (Ta,Nb) <sub>2</sub> O <sub>6</sub>  |
| α-PbO <sub>2</sub> derivatives                    | 0.067 – 0.080      | ixiolite: (Ta,Nb,Sn,Fe,Mn) <sub>4</sub> O <sub>6</sub>   | wolframite: (Fe,Mn)WO <sub>4</sub><br>samarskite: (?)      | columbite-tantalite:<br>(Fe,Mn)(Nb,Ta) <sub>2</sub> O <sub>6</sub>                                       |
| α-PbO <sub>2</sub> + eightfold-coordinated A site | > 0.080            | none   | fergusonite:<br>(Y,REE)(Nb,Ta) <sub>2</sub> O <sub>4</sub> | aeschynite: Ce(Ti,Nb) <sub>2</sub> O <sub>6</sub><br>euxenite: (Y,Ce)(Ti,Nb) <sub>2</sub> O <sub>6</sub> |

based on one of the α-PbO<sub>2</sub> structure types (i.e., octahedral A, B, or M sites); and (3) the cell dimensions of heated samples are consistent with either the disordered MO<sub>2</sub> or the ordered ABO<sub>4</sub> (wolframite) structure type. A clear definition of the role of site occupancies, however, does not exist. Chemical data from the literature support the AB<sub>2</sub>O<sub>6</sub> or A<sub>3</sub>B<sub>5</sub>O<sub>16</sub> ordering schemes, in contradiction to XRD results. In this study, detailed electron microprobe analyses of fresh, unaltered samarskite samples are described in order to resolve these inconsistencies.

#### EMPA OF UNALTERED SAMARSKITE AND RELATED PHASES

Electron microprobe analyses (EMPA) were performed on over 1200 points on 35 samples of samarskite and related minerals. A listing of all samples and localities is included in Table 2.<sup>1</sup> Samples typically consist of dark to opaque cores surrounded by lighter altered material as observed in thin sections. Additional alteration was found along fractures and in veins. Points for EMPA were chosen from the unaltered cores so that alteration effects could be avoided. Analyses with low totals were discarded, as were those that clearly corresponded to a mineral other than samarskite.

An automated Jeol 733 SuperProbe with five crystal spectrometers was used for the analyses. Weight percents obtained from the microprobe were corrected for overlapping X-ray lines (especially a problem for REE) after the procedure of Amlı and Griffin (1975). This procedure involves the application of an overlap correction factor to observed counts from EMPA. In the present study, the overlap correction was applied to both observed K ratios and to Bence-Albee-corrected weight percents (the Bence-Albee routine was applied to the K ratios after the overlap correction was completed). The corrected K ratios and the corrected weight percents produced similar results; the differences in analytical sums for both procedures was <0.30 wt% for all samarskite samples. Therefore, the latter method was used. Sugitani et al. (1985)

performed a crosscheck of the ZAF data reduction procedure against the Bence-Albee procedure for analyzing samarskite and concluded that the Bence-Albee routine produced comparable results.

Standards used for EMPA are listed in Table 3.<sup>1</sup> Points were analyzed using an electron beam 1 μm in diameter to help ensure that the analyses were of homogenous regions of unaltered material. A beam current of 20 nA was used with an operating voltage of 15 kV. Because of the number of elements analyzed, each point required approximately 20 min of analysis time. Volatility was not a problem; one point was analyzed twice with no significant differences in results. Original EMPA data are recorded in Table 4<sup>1</sup> (refer to Warner, 1991, for more details).

All samples were metamict, except for columbite, as determined by X-ray diffraction analysis. Samples were annealed at 800 °C in an H<sub>2</sub>-reducing atmosphere for approximately 4 h preceding identification by XRD. Quenching was achieved by removing the samples from the heating coils to room temperature. Annealed samples were analyzed using an X-ray powder diffractometer. The annealed results were not completely crystalline, although all peaks were comparable to the Sugitani et al. (1984) annealing and (1985) synthesis results. Some of the samples had peaks attributable to columbite, in addition to the samarskite peaks. X-ray results were used for identification only; refer to Sugitani et al. (1985) for unit-cell parameters. The samples were grouped according to the X-ray powder diffraction patterns of annealed samples. Nineteen samples were identified as samarskite, ten as fergusonite, five as aeschynite, and one as columbite. In addition, five of the samarskite samples also contained columbite. In three cases, a quantity of sample insufficient for annealing and XRD analysis remained after EMPA preparation. These samples were grouped according to similarity of EMPA results.

SamarSKite is known to contain both oxidized Fe (Fe<sup>3+</sup>) and reduced Fe (Fe<sup>2+</sup>) (Sugitani et al., 1984). Because of ionic radii considerations, Fe<sup>2+</sup> (0.077 nm) is usually assigned to the A site, whereas Fe<sup>3+</sup> (0.0645 nm; radii from Shannon and Prewitt, 1969) is normally assigned to the B site. Because EMPA cannot distinguish between oxidation states, the amount of oxidized Fe needed to fill the B site can be calculated, and the remainder of the Fe assumed to be reduced and included in the A site. The difficulty with this approach is that a structural formula

<sup>1</sup> A copy of Tables 2, 3, and 4 may be ordered as Document AM-93-523 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

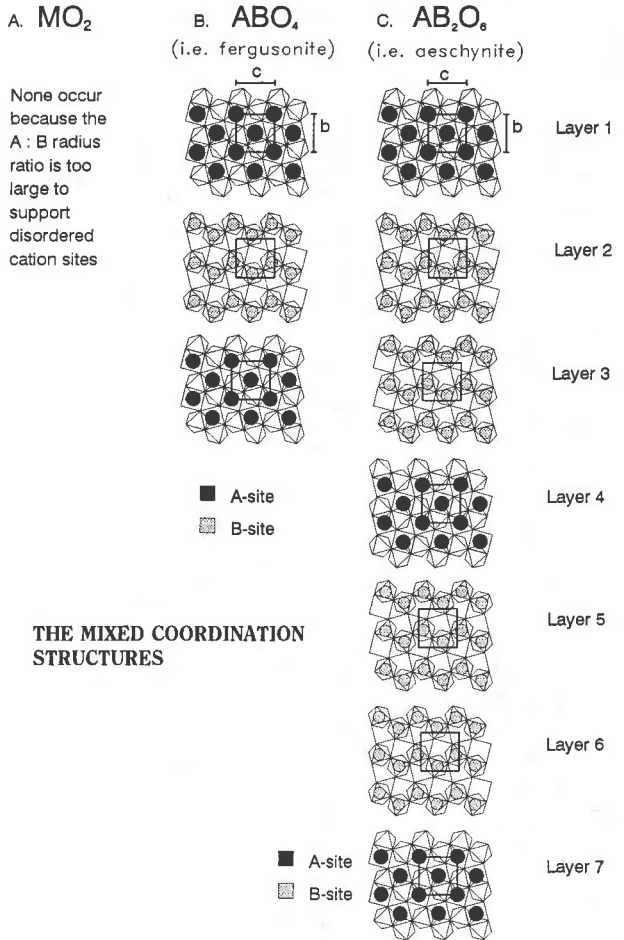
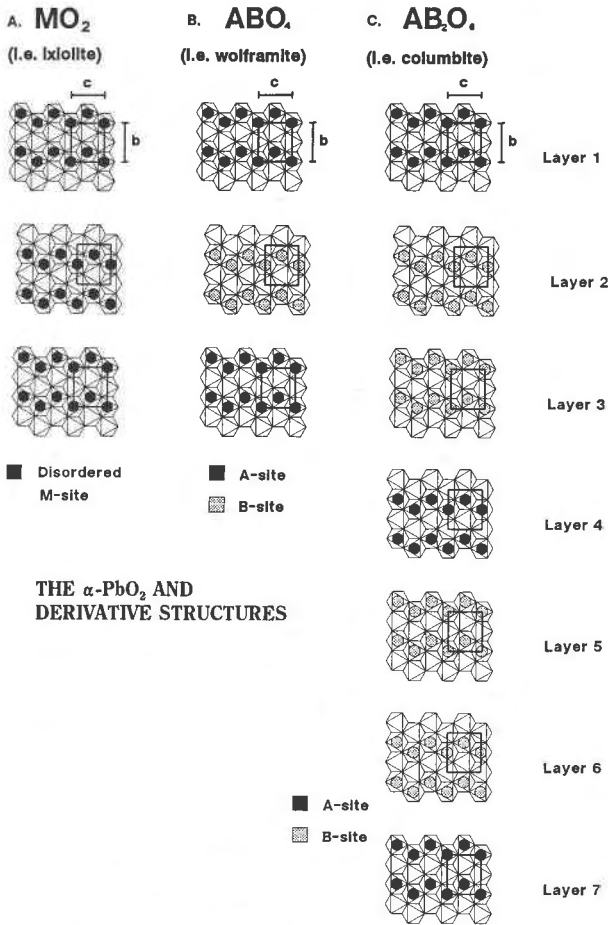


Fig. 1. The  $\alpha$ -PbO<sub>2</sub> and derivative structure types. The *a* dimension is tripled because of ordering in the AB<sub>2</sub>O<sub>6</sub> type structure (columbite). The cell dimensions in the ABO<sub>4</sub> type structure (wolframite) are similar to those of the disordered MO<sub>2</sub>-type structure. MO<sub>2</sub>- and AB<sub>2</sub>O<sub>6</sub>-type structures are orthorhombic; ABO<sub>4</sub>-type structures are monoclinic because of distortions caused by the ordering (Graham and Thornber, 1974).

Fig. 2. The mixed coordination structures have sheets of eightfold-coordinated sites alternating with sheets of zig-zag chains of octahedra. The *a* cell dimension is tripled in the AB<sub>2</sub>O<sub>6</sub>-type structure (aeschnynte) relative to the ABO<sub>4</sub>-type structure (fergusonite). The sheets are actually offset slightly from one another, causing the ABO<sub>4</sub>-type structure to be monoclinic. The AB<sub>2</sub>O<sub>6</sub>-type structure is orthorhombic because layer 7 is situated exactly above layer 1, whereas intervening sheets are slightly offset.

must be assumed in order to determine a ratio of A to B sites.

In this study, the ratio of reduced to oxidized Fe was calculated so that the metal to O ratio was 1:2. Although postmetamictization oxidation and hydration could pose a problem with this technique, only analyses from unaltered material (described above) were used. In this way, different structural formula models can be tested to determine which formula best fits the chemical data.

**CRYSTAL CHEMISTRY OF SAMARSKITE AND RELATED PHASES**

Most of the samarskite samples were Nb-rich (29.9–47.6 wt% Nb); however, one sample (from Ceara, Brazil) was found to be Ta-rich samarskite (53.7 wt% Ta) (analysis by G. R. Lumpkin, personal communication). Si was detected during analysis and has been included in the samarskite structure in previous references (see Nilssen,

1970). Si could be present as submicroscopic domains of quartz, possibly due to alteration. In most cases, however, the contribution from Si is minor.

Cations were assigned to the A and B sites according to the ionic radii criteria used by Nilssen (1970) and Sugitani et al. (1985). On the basis of 16 O atoms, in accordance with the A<sub>3</sub>B<sub>5</sub>O<sub>16</sub> formula of Sugitani et al. (1985), the mean A:B ratio was 2.64(0.22):5.34(0.20) for the 19 samarskite samples (standard deviations are included in parentheses). On the basis of six O atoms, in accordance with the AB<sub>2</sub>O<sub>6</sub> formula of Nilssen (1970), the mean A:B ratio was 0.99(0.08):2.00(0.08), clearly a better fit.

However, on the basis of four O atoms, in accordance with the ABO<sub>4</sub> formula of Komkov (1965), the mean A:B ratio was 1.01(0.02):0.99(0.03), if Nb and Ta were as-

TABLE 5. EMPA analytical sums recalculated into cation assignments based on 4 O atoms

|                  | 138  | 140  | 156  | 180  | 217  | 241  | 243  | 244  | 250  | 256  | 302  | 303  | 309  | 311  | 312  | 313  | 315  | 322  | 942  |
|------------------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|------|
| <b>A Site</b>    |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| Na               | 0.00 | 0.01 | 0.04 | 0.02 | 0.00 | 0.01 | 0.01 | 0.00 | 0.04 | 0.00 | 0.02 | 0.00 | 0.01 | 0.02 | 0.01 | 0.00 | 0.00 | 0.01 | 0.00 |
| Mg               | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Al               | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.02 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.02 | 0.01 | 0.01 |
| Si               | 0.04 | 0.03 | 0.00 | 0.00 | 0.00 | 0.00 | 0.08 | 0.01 | 0.01 | 0.21 | 0.00 | 0.00 | 0.03 | 0.00 | 0.00 | 0.01 | 0.22 | 0.00 | 0.00 |
| K                | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Ca               | 0.05 | 0.15 | 0.01 | 0.01 | 0.01 | 0.02 | 0.22 | 0.03 | 0.14 | 0.12 | 0.01 | 0.02 | 0.21 | 0.02 | 0.01 | 0.12 | 0.15 | 0.07 | 0.00 |
| Ti               | 0.04 | 0.11 | 0.05 | 0.06 | 0.09 | 0.05 | —    | 0.07 | —    | 0.04 | 0.02 | 0.11 | 0.11 | 0.06 | 0.06 | 0.16 | 0.01 | 0.05 | 0.07 |
| Mn               | 0.00 | 0.06 | 0.01 | 0.03 | 0.04 | 0.02 | 0.02 | 0.02 | 0.03 | 0.04 | 0.02 | 0.04 | 0.04 | 0.00 | 0.02 | 0.01 | 0.06 | 0.01 | 0.12 |
| Fe <sup>2+</sup> | 0.25 | 0.07 | 0.12 | 0.11 | 0.26 | 0.19 | 0.04 | 0.18 | 0.00 | 0.02 | 0.22 | 0.29 | 0.03 | 0.17 | 0.15 | 0.07 | 0.15 | 0.15 | 0.01 |
| Fe <sup>3+</sup> | 0.19 | 0.15 | 0.30 | 0.32 | 0.14 | 0.24 | 0.16 | 0.23 | 0.33 | 0.00 | 0.15 | 0.06 | 0.17 | 0.25 | 0.31 | 0.22 | 0.10 | 0.22 | 0.23 |
| Y                | 0.18 | 0.12 | 0.18 | 0.21 | 0.17 | 0.17 | 0.16 | 0.18 | 0.10 | 0.03 | 0.15 | 0.18 | 0.10 | 0.21 | 0.22 | 0.22 | 0.03 | 0.21 | 0.37 |
| Zr               | 0.00 | 0.01 | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 | 0.00 | 0.03 | 0.03 | 0.00 | 0.01 | 0.00 | 0.00 | 0.01 | 0.04 | 0.01 | 0.02 |
| Sn               | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.02 | 0.05 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 | 0.00 | 0.09 |
| REE              | 0.09 | 0.16 | 0.13 | 0.11 | 0.11 | 0.10 | 0.07 | 0.09 | 0.13 | 0.13 | 0.20 | 0.07 | 0.16 | 0.12 | 0.07 | 0.08 | 0.07 | 0.08 | 0.08 |
| W                | 0.05 | 0.01 | 0.00 | 0.00 | 0.06 | 0.00 | 0.04 | 0.00 | 0.02 | 0.02 | 0.07 | 0.02 | 0.01 | 0.00 | 0.00 | 0.00 | 0.02 | 0.02 | 0.00 |
| Pb               | 0.00 | 0.00 | 0.00 | 0.00 | 0.02 | 0.00 | 0.01 | 0.01 | 0.02 | 0.01 | 0.01 | 0.00 | 0.00 | 0.00 | 0.02 | 0.01 | 0.02 | 0.01 | 0.01 |
| Th               | 0.02 | 0.01 | 0.01 | 0.01 | 0.03 | 0.00 | 0.04 | 0.00 | 0.02 | 0.09 | 0.04 | 0.03 | 0.02 | 0.01 | 0.00 | 0.03 | 0.05 | 0.03 | 0.00 |
| U                | 0.11 | 0.10 | 0.12 | 0.11 | 0.12 | 0.16 | 0.11 | 0.15 | 0.15 | 0.09 | 0.06 | 0.15 | 0.11 | 0.11 | 0.12 | 0.08 | 0.08 | 0.12 | 0.02 |
| □                | —    | —    | —    | —    | —    | —    | —    | —    | —    | 0.14 | —    | —    | —    | —    | —    | —    | —    | —    | —    |
| TOTAL            | 1.02 | 0.99 | 0.98 | 0.99 | 1.07 | 0.96 | 0.99 | 0.97 | 0.99 | 1.00 | 1.02 | 1.03 | 1.02 | 0.97 | 0.99 | 1.03 | 1.03 | 1.00 | 1.03 |
| <b>B Site</b>    |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |      |
| Nb               | 0.92 | 0.90 | 0.88 | 0.82 | 0.94 | 0.81 | 0.82 | 0.83 | 0.82 | 0.87 | 0.68 | 0.89 | 0.88 | 0.70 | 0.94 | 0.87 | 0.91 | 0.90 | 0.21 |
| Ta               | 0.06 | 0.11 | 0.14 | 0.19 | 0.01 | 0.21 | 0.10 | 0.18 | 0.07 | 0.14 | 0.29 | 0.09 | 0.10 | 0.31 | 0.07 | 0.08 | 0.05 | 0.10 | 0.77 |
| Ti               | —    | —    | —    | —    | —    | —    | 0.09 | —    | 0.15 | —    | —    | —    | —    | —    | —    | —    | —    | —    | —    |
| TOTAL            | 0.98 | 1.01 | 1.02 | 1.01 | 0.95 | 1.02 | 1.01 | 1.01 | 1.04 | 1.01 | 0.97 | 0.98 | 0.98 | 1.01 | 1.01 | 0.95 | 0.96 | 1.00 | 0.98 |

Note: Fe<sup>2+</sup>/Fe<sup>3+</sup> ratios calculated by the method outlined in text.

signed to the B site and all remaining cations to the A site, instead of assignment by radii criteria (Table 5). Cation assignments in three of the 19 samples required minor modifications to fit the ABO<sub>4</sub> formula. In two of the three, the ratio of A to B sites equals 1 if all Ti is assigned to the B site with Nb and Ta, and, for the remaining sample, if a 12% cation vacancy in the A site is assumed. Reasons for this are discussed below.

With this model, Ti is assumed to occupy the A site, although Ti is ordinarily considered a B-site cation. This occupancy is possible, however, because both the A and B sites are octahedrally coordinated. Komkov (1965) alluded to the fact that Ti could occupy the A site of samarskite, but did not include any supporting data. In the two cases where Ti occurred in the B site, all of the Ti was found in the B site and none at the A site. In these two samples, Ti represented 9 and 14% of the total cations in the B site, respectively.

Although this cation assignment scheme is novel, three major inconsistencies related to the AB<sub>2</sub>O<sub>6</sub> model are resolved. First, the cell dimensions are consistent with the ordering scheme; the *a* cell dimension of the ABO<sub>4</sub> structure corresponds to two layers, whereas the *a* cell dimension of the AB<sub>2</sub>O<sub>6</sub> structure corresponds to six layers (refer to Fig. 1). Observed cell dimensions of samarskite (Komkov, 1965; Sugitani et al., 1985) are consistent with an *a* cell dimension corresponding to two layers, supporting the ABO<sub>4</sub> formula. Second, the calculated average A-site radius fits the proposed structure type. Komkov (1965) determined that the samarskite structure is similar to that of wolframite, in which both A and B are octahedrally coordinated. When the ABO<sub>4</sub> formula is used, the average radius of the A-site occupants ranges from

0.077 to 0.083 nm, in the proper range for octahedral coordination (Fig. 3). The average radius of the A-site cations for the AB<sub>2</sub>O<sub>6</sub> formula ranges from 0.082 to 0.117 nm, clearly too large for octahedral coordination. Samarskite, therefore, is an ABO<sub>4</sub> analogue of columbite. Finally, the average A-site charge is consistent with the ide-

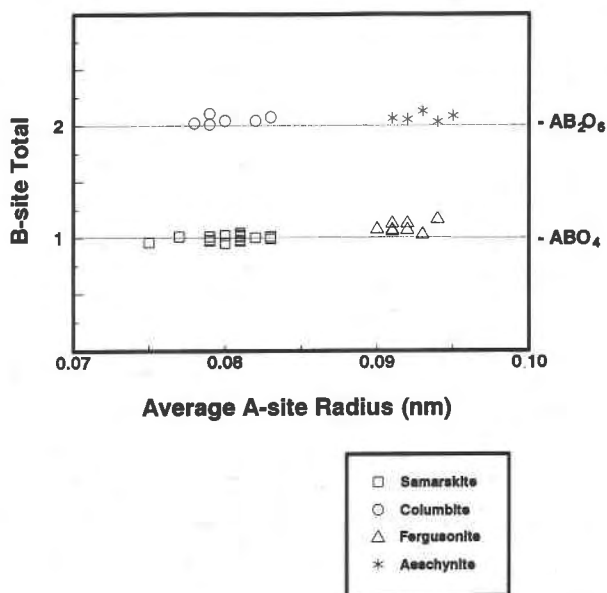


Fig. 3. Average A-site radius of samarskite based on the formula ABO<sub>4</sub> plotted against the number of cations in the B site. The samples of this study define a field that is an ABO<sub>4</sub> analogue of columbite, where the average A-site radius is in the range of octahedral coordination.

**TABLE 6.** Ideal structural formulae of samarskite and related minerals

| Mineral     | A site                   |              |                     | B site       |                     |
|-------------|--------------------------|--------------|---------------------|--------------|---------------------|
|             | Ideal structural formula | Ideal charge | Charge (this study) | Ideal charge | Charge (this study) |
| Columbite   | $A^{2+}B_5^{5+}O_6$      | 2+           | 2.06+               | 5+           | 4.93+               |
| Aeschnyite  | $A^{3+}B_5^{5+}O_6$      | 3+           | 2.96+               | 4.5+         | 4.39+               |
| Fergusonite | $A^{3+}B^{5+}O_4$        | 3+           | 2.99+               | 5+           | 4.87+               |
| Samarskite  | $A^{3+}B^{5+}O_4$        | 3+           | 3.02+               | 5+           | 4.99+               |

Note: Ideal formulae based on the formula  $ABO_4$ .

al structural formula. The calculated average site charges for the  $ABO_4$  formula are remarkably consistent. The average A-site charge is 3.02 (0.05) for the 19 samples, whereas the average B-site charge is 4.99 (0.04). Samarskite therefore, is based on the simple ideal structure of  $A^{3+}B^{5+}O_4$  (Table 6). An example of this type of structure is the ordered form of  $Fe^{3+}NbO_4$  which also has the wolframite structure (Roth and Waring, 1964). The average A- and B-site charges calculated for the  $AB_2O_6$  model are 2.80 (0.08) and 4.61 (0.10), respectively.

The three anomalous samples can be explained through charge-balancing considerations. Both the addition of Ti at the B site and the inclusion of vacancies at the A site in these three samples allows the average charge on the A site to approach 3.0. Preservation of the average site charge was not an expected result, when one considers that coupled substitutions commonly occur in other niobium tantalum oxide minerals (e.g.,  $Ca + Nb = Y + Ti$  in the fersmite-euxenite series). However, average site charges were preserved regardless of the substitution scheme for all of the four minerals analyzed in this study (refer to Table 6).

The high-temperature form of samarskite can be explained as a derivative of the  $ABO_4$  structure. The high-temperature phase involves an apparent doubling of the  $a$  cell dimension. This has been attributed to a possible ordering phenomenon (Sugitani et al., 1985), although the formation of an ordered superstructure at higher temperatures seems to contradict known relations (Muller and Roy, 1974, p. 113). However, the wide range of radii for cations found in substantial amounts in the A site (0.053 nm for Al to 0.100 nm for Ca and Th) would result in a more distorted, perhaps less stable, structure. Perhaps the high-temperature phase involves a partitioning of the A-site cations where site selection is based on ionic radii. This would result in the derivative formula of  $AA'B_2O_8$ , where smaller cations prefer one site (A), and larger cations prefer another (A'). Each site would then be less distorted, accommodating a smaller range of ionic radii. A structure with this type of formula ( $NaFeW_2O_8$ ) has the same space group and similar cell dimensions (Muller and Roy, 1974, p. 114) as the high-temperature form of samarskite.

A close relationship exists between samarskite and fer-

**TABLE 7.** The synthesis results of Sugitani et al. (1985) recalculated based on the formula  $ABO_4$ 

|                     | Sample 1                           |                   | Sample 2                 |                   |
|---------------------|------------------------------------|-------------------|--------------------------|-------------------|
|                     | Old*                               | New**             | Old*                     | New**             |
|                     | <b>A site</b>                      |                   |                          |                   |
| Ca                  | 0.24                               | 0.24              | —                        | —                 |
| Fe <sup>2+</sup>    | 1.56                               | 1.56              | 2.0                      | 2.0               |
| Y                   | 0.84                               | 0.84              | 1.0                      | 1.0               |
| U                   | 0.20                               | 0.20              | —                        | —                 |
| Nb                  | —                                  | 1.04              | —                        | 1.0               |
| □                   | —                                  | 0.12              | —                        | —                 |
| TOTAL               | 2.84                               | 4.00              | 3.0                      | 4.0               |
| Avg. charge         | 2.43+                              | 3.03+             | 2.33+                    | 3.00+             |
| Avg. radius         | 0.83 nm                            | 0.79 nm           | 0.81 nm                  | 0.77 nm           |
|                     | <b>B site</b>                      |                   |                          |                   |
| Nb                  | 5.04                               | 4.00              | 5.0                      | 4.0               |
| Avg. charge         | 5.00+                              | 5.00+             | 5.00+                    | 5.00+             |
| Avg. radius         | 0.64 nm                            | 0.64 nm           | 0.64 nm                  | 0.64 nm           |
| Structural formula: | $A_{2.84}^{2+}B_{5.04}^{5+}O_{16}$ | $A^{3+}B^{5+}O_4$ | $A_3^{3+}B_5^{5+}O_{16}$ | $A^{3+}B^{5+}O_4$ |

Note: An A:B ratio of 1:1 is achieved by assigning Nb to both the A and B sites. Some 3% A-site vacancies occur in Sample 1.

\* Old = data of Sugitani et al. (1985).

\*\* New = same data based upon model of the present study.

gusonite, also an  $ABO_4$ -type structure. One of 19 samarskite samples actually crystallized with the fergusonite structure upon annealing, although its chemical composition is consistent with the other samarskite samples. The fergusonite structure,  $[(Y,REE)(Nb,Ta)O_4]$ , differs from the  $ABO_4$  samarskite structure only in the coordination of the A site (eightfold-coordinated in fergusonite). The sample that crystallized with the fergusonite structure actually has the largest average A-site radius of the samarskite samples in the present study and the greatest concentration of REE and Y.

Finally, the synthesis results of Sugitani et al. (1985) that are in apparent contradiction of the  $ABO_4$  structure fit the  $A^{3+}B^{5+}O_4$  model, if the present site ordering scheme is used. The data of Sugitani et al. (1985) from two starting mixtures suggest that the A:B:O ratio is 3:5:16 if the cations are ordered according to ionic radius. However, the cations of both samples can be rearranged to give an A:B:O ratio of 4:4:16, consistent with the  $ABO_4$  model (Table 7). This is achieved if sufficient Nb is assigned to the B site so that the B-site total equals 4.0, and the remaining cations are assumed to occupy the A site. One sample would also have 3% vacancies in the A site. With the cations divided according to the new ordering scheme, the average radii and average charge for the A and B sites are similar to those calculated for the samarskite samples of this study (refer to Table 7). The vacancies included in the A site of sample 1 are apparently needed for charge balance.

## CONCLUSIONS

The compositional diversity of samarskite samples from a wide variety of geologic localities provides a basis for analysis of the samarskite structure. Analysis of A- and

B-site cations demonstrates that samarskite has a structural formula of  $A^{3+}B^{5+}O_4$  and possesses a structure based on the  $\alpha$ - $PbO_2$  atomic arrangement, with a 1:1 ordering of A- and B-site cations similar to that of wolframite. The A-site cations, with a radius range of 0.077–0.083 nm, include Ca, Ti,  $Fe^{2+}$ ,  $Fe^{3+}$ , Y, REE, U, and Th, with minor amounts of Na, Mg, Al, K, Mn, Zr, Sn, W, and Pb. The remainder of the cations (Nb and Ta) occupy the B site, although Ti can occupy either site. The high-temperature polymorph of samarskite has the possible structural formula of  $AA'B_2O_8$ .

Unfortunately, there is no samarskite sample with a simple end-member composition that is suitable for structure refinement. The A-site must always be occupied by a number of different cations because a single trivalent cation with a radius in the range required for the A site of samarskite (0.077–0.083 nm) does not exist.  $Fe^{3+}$  is too small and would result in the disordered ixiolite structure, whereas Y and REE are too large and would result in the fergusonite structure. Samarskite is a true complex oxide without a simple compositional analogue.

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