

The Structures of 1:1 Compounds of Rare Earth Oxides with Niobia and Tantalum

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The crystal structures of various synthetic ABO_4 compounds, in which A is one of the rare earths La, Ce, Nd, Sm, Gd, Dy, Y or Sc, and B is either Nb or Ta, have been examined. Most of the compounds are isotypic with the monoclinically distorted scheelite-like structure, identified by Ferguson for a high-temperature-fired specimen of $YTaO_4$. The lattice parameters are recorded.

High-temperature X-ray study of niobium compounds with this structure proves that the monoclinic distortion is progressively reduced with increasing temperature, and a reversible transition to a tetragonal structure occurs below 800 °C. With tantalum compounds, no structure transition takes place up to 1300 °C, though at 1300 °C a marked reduction of the monoclinic distortion is evident.

The two scandium compounds are exceptional and have a monoclinic wolframite-like crystal structure. This difference in structure appears to be dictated by the relatively small radius of the scandium cation. With the largest rare-earth cation, La^{3+} , the niobium compound has the monoclinically distorted scheelite-like structure, but the tantalum compound has a different and unidentified structure.

1. Introduction

In the course of a broad survey of phases formed by combining various rare earth oxides with niobia or tantalum, several compounds were prepared with the molar ratio 1:1. X-ray studies of these 1:1 compounds revealed that the majority are isostructural with the monoclinic form of synthetic yttrium tantalate, $YTaO_4$, described by Ferguson (1957). This structure was also found by Komkov (1957) for a specimen of the mineral fergusonite, $Y(Nb,Ta)O_4$, which had been heated to 900 °C. Some notable exceptions to this monoclinic structure were observed, in particular for the scandium compounds. In the present paper the results of the X-ray studies are reported and the measured structure data are recorded.

During the investigations it became clear that the monoclinic structure, which it will be convenient to describe as fergusonite-type, was probably derived in a relatively simple way from a higher symmetry form. A tetragonal structure for natural fergusonite and for $YNbO_4$ and $YTaO_4$ was reported by Barth (1926). Komkov (1957) has more recently shown that this structure is of the scheelite type, but, as mentioned above, he found, for a mineral specimen, that it changed to the monoclinic structure on firing to 900 °C. High-temperature X-ray examinations were therefore carried out to examine the possible structural relationship and these are briefly described below.

Whilst the work was in progress, a second paper by Komkov (1959) was published which described the preparation and examination of the structures of a series of rare-earth niobates of the 1:1 composition.

The results in some measure anticipated our conclusions. In particular Komkov confirmed that the monoclinic fergusonite-type structure is in fact a slightly distorted version of the tetragonal scheelite type, and that at some temperature above room temperature there is a reversible transition between the two structures.

2. Raw materials and preparation

The rare-earth oxides, which were mostly approximately 99% pure, and the niobium and tantalum pentoxides, which were better than 99.5% pure, were supplied by Johnson Matthey & Co. The scandium oxide was of somewhat lower purity, *ca.* 95%.

Most of the compounds were made by conventional ceramic processes. These included mixing and milling the constituent oxides, pressing discs of the milled mixtures and firing them at 1000 °C for 2 hours, and after further milling, pressing discs to fire finally at *ca.* 1400 °C for 2 hours in air. A few powder mixtures, ground with an agate pestle and mortar, were fired at 1000 °C without pressing, and then, after further grinding, at 1400 °C in a small tubular laboratory furnace. Substantially similar products were obtained by both methods, except that it appeared more difficult to carry reactions to completion in the small-scale laboratory method.

3. Results of X-ray examinations

The synthesized compounds were examined by conventional X-ray powder diffraction techniques, 11.46 and 19 cm diameter cameras being used with either

Table I. *Structures and ionic radii*

| Compound | Structure* | Structure-cell dimensions | | | | Radius of rare earth ion |
|--------------------|------------|---------------------------|---------|--------|---------|--------------------------|
| | | a_0 | b_0 | c_0 | β | |
| LaNbO ₄ | <i>F</i> | 5.56 Å | 11.54 Å | 5.20 Å | 94.0° | 1.22 Å |
| LaTaO ₄ | <i>U</i> | — | — | — | — | 1.22 |
| CeNbO ₄ | <i>F</i> | 5.48 | 11.30 | 5.13 | 94.5 | 1.18 |
| NdNbO ₄ | <i>F</i> | 5.45 | 11.24 | 5.13 | 94.5 | 1.15 |
| NdTaO ₄ | <i>F</i> | 5.52 | 11.27 | 5.12 | 95.6 | 1.15 |
| SmNbO ₄ | <i>F</i> | 5.41 | 11.15 | 5.12 | 94.7 | 1.13 |
| SmTaO ₄ | <i>F</i> | 5.46 | 11.13 | 5.08 | 95.6 | 1.13 |
| GdNbO ₄ | <i>F</i> | 5.37 | 11.09 | 5.11 | 94.7 | 1.11 |
| GdTaO ₄ | <i>F</i> | 5.40 | 11.04 | 5.07 | 95.7 | 1.11 |
| DyNbO ₄ | <i>F</i> | 5.23 | 11.02 | 5.10 | 94.5 | 1.07 |
| DyTaO ₄ | <i>F</i> | 5.30 | 10.89 | 5.03 | 95.1 | 1.07 |
| YNbO ₄ | <i>F</i> | 5.30 | 10.96 | 5.08 | 94.6 | 0.93 |
| YTaO ₄ | <i>F</i> | 5.34 | 10.94 | 5.07 | 95.3 | 0.93 |
| ScNbO ₄ | <i>W</i> | 4.80 | 5.65 | 5.09 | 88.3 | 0.78 |
| ScTaO ₄ | <i>W</i> | 4.80 | 5.65 | 5.10 | 88.5 | 0.78 |

* *F* = Monoclinic fergusonite-type. *W* = Monoclinic wolframite-type. *U* = unknown structure.

Cu $K\alpha$ or Co $K\alpha$ radiation. All the structures except one were readily identified: indexing of the principal powder lines was therefore possible, and lattice parameters were determined. The results are summarized in Table I.

It will be seen that most of the compounds have the monoclinic structure established by Ferguson (1957) for synthetic YTaO₄. The exceptions are the lanthanum-tantalum oxide, LaTaO₄, and the two scandium compounds.

The X-ray powder patterns of the two scandium compounds were very similar to one another, and resembled those given by tungstates and molybdates of the wolframite family. By analogy with patterns of known members of this family, for example MgWO₄ and MnWO₄, the principal lines of the patterns of ScNbO₄ and ScTaO₄ were indexed, and the cell dimensions determined.

No satisfactory solution to the structure of LaTaO₄ was found.

4. Changes of structure at elevated temperatures

The β angle of the monoclinic cell of the family of compounds typified by YTaO₄ is only a little above 90°. Moreover the a and c parameters are not widely different in value. It is therefore possible that the monoclinic distortion might disappear on thermal expansion, and the structure become orthorhombic, or tetragonal if a_0 became equal to c_0 .

Examinations of representative members of the family were made in a high-temperature powder camera, capable of covering the temperature range up to 1300 °C. Three niobates were chosen, namely those of lanthanum, samarium, and yttrium. X-ray patterns, taken at successively increasing temperatures, showed that for each substance there was a progressive reduction of the monoclinic distortion which resulted finally in a transition to a tetragonal

structure. The elimination of the monoclinic distortion was most rapid near the transition temperature, which was for all three compounds below 800 °C. The tetragonal cell dimensions measured just above the respective transition temperatures are given below:

| Compound | Structure transition temperature | Tetragonal cell dimensions | |
|--------------------|----------------------------------|----------------------------|---------|
| | | a_0 | c_0 |
| LaNbO ₄ | 450–500 °C | 5.40 Å | 11.66 Å |
| SmNbO ₄ | 700–750 | 5.28 | 11.30 |
| YNbO ₄ | c. 700 | 5.21 | 11.05 |

Apart from the increase in cell dimensions to be expected on thermal expansion, no further changes were observed up to 1300 °C.

To represent the monoclinic tantalates, SmTaO₄ and YTaO₄ were chosen for investigation. Their behaviour on thermal expansion was in marked contrast to that of the niobates. Whilst, accompanying expansion, there appeared to be a gradual reduction of the monoclinic distortion no actual structure transition took place up to 1300 °C. As an example, in the case of YTaO₄ it was found that the monoclinic β angle of 95.3° at room temperature had decreased to 91.7° at 1300 °C. From the magnitude of the reduction of the structure distortion up to 1300 °C, and, assuming that the reduction continued with further increase of temperature, a transition to the tetragonal form might be expected to occur by about 1600 °C. Further investigation is required to test this prediction.

5. Discussion

The results show that the majority of the 1:1 compounds of rare earth oxides with niobia or tantalum, prepared by firing at high temperatures, have a characteristic monoclinic crystal structure at room temperature. This is the structure established by Ferguson (1957) for YTaO₄. Komkov's (1957) struc-

ture for YNbO_4 is similar, except that he describes the monoclinic cell by lattice parameters of which the β angle is the supplement of that adopted by Ferguson and used in the data presented here.

The high-temperature X-ray studies of LaNbO_4 , SmNbO_4 , and YNbO_4 show that they undergo a reversible transition below 800 °C to a closely related tetragonal structure, which appears to be isomorphous with scheelite, CaWO_4 . By comparing the values of the lattice parameters of the two structures, of SmNbO_4 for example, the transition is seen to be equivalent to a removal of a monoclinic distortion of the tetragonal scheelite-type structure. At the transition point, the monoclinic β angle is decreased to 90°, the monoclinic a and c parameters reach equality to give the tetragonal a parameter, and the monoclinic b parameter becomes the c parameter of the tetragonal cell.

It appears reasonable to conclude that the remaining rare earth niobates, with the room-temperature monoclinic fergusonite-type structure, go through analogous structure transitions at temperatures in the 20 to 800 °C range. The results of the high-temperature studies of samarium and yttrium tantalates, however, reveal a conspicuous difference in the behaviour of the tantalum oxide compounds. Up to 1300 °C thermal expansion is not accompanied by any structure transition, although there is evidence that at some considerably higher temperature a monoclinic-tetragonal transition might occur. This difference in behaviour between a rare earth tantalate and the corresponding rare earth niobate suggests that the monoclinic deformation of the scheelite-like structure is linked with the oxygen-tantalum and oxygen-niobium interatomic bonding forces, these forces being appreciably stronger for tantalum. It appears likely that the cation-oxygen tetrahedra, which are comparatively symmetrically arranged in a tetragonal scheelite-like structure, are deformed and puckered in the monoclinic form. Such distortions in the atomic arrangement would be more difficult to eliminate by thermal expansion when the combining cation is tantalum than when it is niobium because of the assumed greater strength of the tantalum-oxygen bonding forces.

The early identification of tetragonal structures for synthetic YTaO_4 and YNbO_4 by Barth (1926) is a little difficult to explain entirely satisfactorily. Barth's structure appears to be similar to the scheelite type which Komkov (1957) found for a specimen of natural fergusonite before ignition at high temperature, although Barth chose a differently oriented cell with an a value multiplied by the factor $\sqrt{2}$. The pos-

sibility arises that, in certain circumstances, the high-temperature scheelite-like structure can be retained at room temperature, for example by rapid quenching, or in mineral specimens because of irradiation damage. No experiments were carried out, however, during the present investigations to test this supposition.

An explanation of the failure of ScNbO_4 and ScTaO_4 to crystallize in the same monoclinic structure as the remainder of the compounds except LaTaO_4 emerges if the radii of the combining rare earth cations are considered. Values of the radii are listed in the last column of Table I. It is apparent that the scandium ion is by far the smallest. Evidently the atomic packing characterizing the monoclinic fergusonite-type structure becomes impossible with the small scandium ion, and both scandium compounds assume the wolframite-type of structure. Since the monoclinic structure is only a distortion of the tetragonal scheelite-type, this different structure for the scandium compounds is consistent with what is known about the incidence of scheelite and wolframite structures amongst tungstates and molybdates. The tungstates and molybdates of the relatively large cations calcium, strontium, and barium, have tetragonal scheelite-type structures. With smaller cations, including magnesium, zinc and cadmium, atomic packing in the scheelite arrangement becomes impossible, and the monoclinic wolframite-type tungstates and molybdates are formed.

Concerning LaTaO_4 , the structure of which has not been solved, the combining rare earth cation is the largest of the series. The size may in fact be near the upper limit for accommodation in the monoclinic scheelite-like arrangement. Whilst this size is just tolerated in the niobium compound, an alteration to a new structure for the tantalum compound is possibly associated with the more complex electron orbital structure of tantalum compared with niobium.

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