be less susceptible to anisotropy effects because of the presence of the same chalcogen ligand in all of the four compounds, and their validity is now supported by our results from studies on the analogous thio compounds of the type $(CH_3)_3SiSX(CH_3)_3$.

For the sequence with X = Si, Ge, Sn the proton signals of the $(CH_3)_3Si$– group are shifted to higher fields, whereas the $(CH_3)_3X$ signals appear at the low-field side with respect to the signals of the related $[(CH_3)_3X]_2S$ compounds.[2] Simultaneously, as in the case of the oxygen derivatives, the coupling constants $J(^1H-^{13}C)$, $J(^1H-^{29}Si)$, and $J(^1H-^{117,119}Sn)$, respectively, are increased in $(CH_3)_3X$ and decreased in $(CH_3)_3Si$, but obviously the effects for δ and J are in all cases smaller than in the $(CH_3)_3SiOX(CH_3)_3$ series, and are, as for $J(^1H-^{13}C)$ of $(CH_3)_3Si$, within the standard deviations of the experiment. The suggestion that these values (Table III) are reflecting the weaker π-interactions between sulfur and the group IVb elements rather than between oxygen and these elements (particularly with silicon) should remain open for discussion.

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Preparation and Properties of Some Novel Rare Earth Compounds of the Types $LnTi_{0.5}Mo_{0.5}O_4$ and $LnTi_{0.5}W_{0.5}O_4$

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In 1935 Beintema[1] presented evidence for a defect rare earth tungstate, $Ln_{2/3}\square_{1/3}WO_4$, of the scheelite type where $\square$ represents lattice defect sites. Later work by Sillén[2] failed to verify the structure. More recently, Nassau[3] described substituted tungstates of the type $(Ca_{1-x}Eu_x{}^{II})WO_4$, $(Ca_{1-3x}Nd_{2x}{}^{III})WO_4$, $(Ca_{1-2x}$-$Nd^{III}Na_x{}^{+})WO_4$, $(Ca_{1-3x}Y_{3x}{}^{III})(W_{1-x}Cr_x{}^{III}O_4)$, and $Ca(W_{1-x}Cr_x{}^{VI}O_4)$, where x was generally very small. Van Uitert[4] described molybdates of the type $M^A{}_{0.5}M^B{}_{0.5}MoO_4$, where M^A = Li, Na, and K; $M^B = Y^{+3}$ and the trivalent rare earth ions or combinations thereof. Van Uitert[5] has also published a summary of the alkaline earth, alkali metal rare earth tungstates and molybdates of the scheelite type.

In this note, compounds of the type $Ln^{III}Ti^{IV}{}_{0.5}$-$Mo^{IV}{}_{0.5}O_4$ and $Ln^{III}Ti^{IV}{}_{0.5}W^{IV}{}_{0.5}O_4$ are described and structural correlations are made. Although most of these compounds do crystallize in the "scheelite" structure, one can best consider them as IV/VI substituted niobates or tantalates of the types $Ln^{III}Nb^VO_4$ or $Ln^{III}Ta^VO_4$. Keller[6] has recently shown that most of these compounds crystallize in a monoclinic lattice of the "fergusonite" type. The compounds investigated in this study can be characterized as crystallizing in one of these two types. Extended solid solutions of scheelites and fergusonites are formed in the series $(LnM^AO_4)_x(LnM^BO_4)_{1-x}$ where $M^A = Nb^{+5}$ and Ta^{+5} and $M^B = Mo^{+6}$ and W^{+6}. The transition of one type into the other has been specifically investigated for the $EuNbO_4$–$CaWO_4$ and $YNbO_4$–$CaWO_4$ systems, to be reported in another paper.

Experimental

Tungsten oxide (99.9+%) was obtained from the Sylvania Chemical and Metallurgical Division, MoO_3 was Fisher certified reagent, and the rare earth oxides (99.9%) were obtained from the Lindsay Chemical Division. Scandium oxide was prepared from resublimed $ScCl_3$ which in turn was obtained by chlorination of thortveitite from Norsk Feldspat, Norway. High-purity TiO_2 was made from water-clear redistilled $TiCl_4$ by careful hydrolysis and subsequent sintering at 900–1000° under oxygen. The oxides of Ce, Pr, and Tb were obtained in a valence state higher than three and the true sesquioxides were prepared by hydrogen reduction at 1200°. All subsequent reactions with these three particular oxides were carried out under purified argon to prevent any reoxidation.

The component oxides were weighed to the nearest 0.1 mg. according to stoichiometry, and mixing was effected by ballmilling in a mechanical agate ballmill under acetone. In a first firing step, the dried mixture was heated to 700° for 10–14 hr. in the case of the molybdenum-containing compositions, and to 950° for the tungstates. These prereacted products were then homogenized by a second ballmilling under acetone, dried, and pressed into 1-in. diameter pellets under 20,000 to 40,000 p.s.i. In a second step, these pellets were fired at 1000–1200° for another 10–14 hr., which yielded completely reacted homogeneous preparations free of any component oxides as evidenced by the X-ray patterns. Outside of some spot analyses for Ti, Mo, or W, chemical analyses were generally not performed, since the constituent components were already of confirmed purity and weight losses during the different firing steps did not generally exceed 0.2% for 10.000-g. charges.

X-Ray Results.—All parameter determinations are based on powder patterns obtained with a 114.6-mm. Philips camera. The samples were ground to −325 mesh, sealed in 0.2-mm. Lindemann glass capillaries, and exposed to copper Kα radiation (λ = 1.5418 Å.) at 25° for 3–5 hr. The readings were taken visually at constant temperature with a Hilger and Watts film measuring rule with 0.05-mm. vernier divisions. All films were corrected for film shrinkage. The tetragonal patterns could be completely indexed on the basis of the reported $CaWO_4$ structure, ASTM file card 7-210. The a-parameter was generally derived from the (200), (220), (400), and (420) reflections and the c-parameter from (004), (327), (1.0.11.), (3.1.10), and (428). The other diagrams could be completely indexed based upon monoclinic symmetry isostructural with fergusonite, $YTaO_4$, ASTM file card 9-341. The extraction of the monoclinic lattic constants from powder data was generally based on the following six low-angle (*hkl*) reflections: (040), (200), (002), (204), (042), (202). Pycnometric densities were obtained by vacuum distilling CCl_4 onto the −200 mesh powders contained in a 5-ml. calibrated pycnometer. Lattice parameters together with the densities are summarized in Table I for the molybdates and in Table II for the tungstates.

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TABLE I

LATTICE PARAMETERS AND DENSITIES FOR THE $LnTi_{0.5}Mo_{0.5}O_4$ SERIES

Tetragonal Schellite Type Cell

Composition	a_t, Å.	c_t, Å.	c/a	V, Å.^{3}	g. ml.$^{-1}$ ρ x	g. ml.$^{-1}$ ρ pyc.
$ScTi_{0.5}Mo_{0.5}O_4$	...	...	...	...	...	...
$YTi_{0.5}Mo_{0.5}O_4$	5.083	11.060	2.17	285.75	5.22	5.09
$LaTi_{0.5}Mo_{0.5}O_4$	...	...	...	...	...	...
$CeTi_{0.5}Mo_{0.5}O_4$	5.238	11.585	2.11	317.85	5.76	5.71
$PrTi_{0.5}Mo_{0.5}O_4$	5.220	11.513	2.20	313.71	5.86	5.84
$NdTi_{0.5}Mo_{0.5}O_4$	5.201	11.457	2.20	309.91	6.00	5.97
$SmTi_{0.5}Mo_{0.5}O_4$	5.160	11.349	2.19	302.17	6.29	6.12
$EuTi_{0.5}Mo_{0.5}O_4$	5.145	11.288	2.19	298.80	6.39	6.24
$GdTi_{0.5}Mo_{0.5}O_4$	5.123	11.236	2.19	297.20	6.55	6.43
$TbTi_{0.5}Mo_{0.5}O_4$	5.114	11.170	2.18	292.12	6.70	6.51
$DyTi_{0.5}Mo_{0.5}O_4$	5.108	11.169	2.18	291.41	6.80	6.79
$HoTi_{0.5}Mo_{0.5}O_4$	5.085	11.094	2.18	286.86	6.96	6.94
$ErTi_{0.5}Mo_{0.5}O_4$	5.071	11.059	2.18	284.38	7.08	7.01
$TmTi_{0.5}Mo_{0.5}O_4$	5.060	11.011	2.17	281.92	7.18	6.98
$YbTi_{0.5}Mo_{0.5}O_4$	5.051	10.983	2.17	280.20	7.32	7.31
$LuTi_{0.5}Mo_{0.5}O_4$	5.039	10.955	2.17	278.16	7.42	7.33

TABLE II

LATTICE PARAMETERS AND DENSITIES FOR THE $LnTi_{0.5}W_{0.5}O_4$ SERIES

Composition	a_t, Å.	c_t, Å.	c/a	V, Å.^{3}	g. ml.$^{-1}$ ρ x	g. ml.$^{-1}$ ρ pycn.
		A. Tetragonal Scheelite Type Cell				
$ScTi_{0.5}W_{0.5}O_4$	...	...	...	...	...	
$LaTi_{0.5}W_{0.5}O_4$	...	...	...	...	...	...
$CeTi_{0.5}W_{0.5}O_4$	...	...	...	...	...	...
$PrTi_{0.5}W_{0.5}O_4$	...	...	...	...	...	...
$NdTi_{0.5}W_{0.5}O_4$	5.235	11.375	2.17	311.73	6.90	6.85
$SmTi_{0.5}W_{0.5}O_4$	5.199	11.256	2.16	304.24	7.20	6.99
$EuTi_{0.5}W_{0.5}O_4$	5.178	11.199	2.16	300.26	7.34	7.29
$GdTi_{0.5}W_{0.5}O_4$	5.163	11.124	2.15	296.53	7.55	7.51
$TbTi_{0.5}W_{0.5}O_4$	5.149	11.090	2.15	294.02	7.65	7.53
$DyTi_{0.5}W_{0.5}O_4$	5.142	11.077	2.15	292.88	7.76	7.67
$HoTi_{0.5}W_{0.5}O_4$	5.121	11.001	2.15	288.50	7.93	7.78
$ErTi_{0.5}W_{0.5}O_4$	5.106	10.959	2.15	285.71	8.06	7.94
		B. Monoclinic Fergusonite Cell				
$YTi_{0.5}W_{0.5}O_4$	5.22 $\beta = 93.6°$	5.00 $b = 10.97$	...	285.81	6.24	5.94
$TmTi_{0.5}W_{0.5}O_4$	5.245 $\beta = 93.82°$	4.95 $b = 10.86$	...	281.50	8.22	7.99
$YbTi_{0.5}W_{0.5}O_4$	5.22 $\beta = 93.79°$	4.96 $b = 10.84$	...	280.21	8.36	8.17
$LuTi_{0.5}W_{0.5}O_4$	5.21 $\beta = 94.48°$	4.99 $b = 10.90$	...	282.50	8.34	8.01

Discussion

The described compositions constitute novel substitutions in the B site of the ABO_4 composition, which crystallize either in the tetragonal scheelite or the monoclinic fergusonite type.

The fact that the yttrium compound of molybdenum crystallized in the tetragonal lattice, while the yttrium compound of tungsten is monoclinic, points out the very close structural relationship of these two structure types, since the difference, if any, in ionic radius of Mo^{+6} and W^{+6} is very small. While the molybdate represents the "scheelite" ($CaWO_4$) type (space group $I4_1/a$) the tungstate is of "fergusonite" ($YTaO_4$) type (space group I2/a). The monoclinic structure can simply be considered a distorted version of the tetragonal unit cell with the a-parameters nearly identical, b_m about double a_t, c_m about $^1/_2 c_t$, and the monoclinic angle near 90°. Both structures have four molecules per unit cell.

If one plots both a_t and c_t for either the molybdates or the tungstates as a function of the atomic numbers of the rare earths, the lanthanide contraction is reflected and relatively smooth curves of slight curvature are obtained.

In the tungstate series, the smaller rare earth cations with r_B/r_A ratios of 0.71 or larger tend to stabilize the monoclinic fergusonite type. Roth[7] has found that the monoclinic $GdNbO_4$ inverts reversibly into a tetragonal form at about 850°, and more recently Gingerich[8] has stated that all rare earth niobates transform into this tetragonal form which he identi-

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fied as the scheelite type. In some of the compositions investigated in this paper, we seem to have a similar fergusonite $\rightleftharpoons$ scheelite transition at much lower temperature. It appears to be in the vicinity of room temperature and therefore is very sluggish. In the case of $LnTi_{0.5}W_{0.5}O_4$ we could detect a small portion of scheelite type oxide with a_t = 5.10 Å. and c_t = 10.90 Å., indicating that part of the compound had not completely inverted to the lower symmetry upon cooling.

With $YTi_{0.5}W_{0.5}O_4$ we also obtained samples which were sometimes free of scheelite, sometimes contained small portions thereof. In general, a decrease in cation size causes an increase in the transformation temperature. An r_B/r_A ratio of 0.57 as for the La compound is obviously too small and the ratio of 0.80 for the Sc compound is too large to allow for either the fergusonite or the scheelite structure. This establishes a rough tolerance limit for r_B/r_A of 0.62–0.76 permitting either fergusonite or scheelite structure.

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Preparation and Properties of Crystalline Gold Trifluoride

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Auric trifluoride was first prepared by Moissan[3] by heating gold wire in fluorine at dull red heat. Treatment of gold powder with BrF_3 has been successfully employed to prepare essentially pure AuF_3 contaminated with a small amount of bromine.[4,5]

The only gold trihalide for which crystallographic data have been reported is $AuCl_3$. The crystal structure analysis[6] showed that auric trichloride is composed of Au_2Cl_6 dimers in square-planar configuration as predicted by Wells.[7] Extensive work has been done on the crystal structure of trifluorides of the transition elements preceding gold in the periodic table so that structural analogies can be drawn.[8]

In the present work the structural characterization carried out by X-ray powder methods at Newcastle has been confirmed and extended by single-crystal techniques and by density determination at Los Alamos. AuF_3 is hexagonal and is not isostructural with other known crystalline trifluorides.

Experimental

Synthesis of AuF_3.—Two general methods which yielded pure AuF_3 on the multigram scale were used.

(a) **BrF_3.**—Gold powder, produced by reduction of an aqueous solution of gold(I), was dissolved in excess BrF_3 upon gentle warming.[4] After evaporation of Br_2, the solution was lemon-yellow. Removal of the excess BrF_3 in an inert atmosphere or by vacuum distillation gave a yellow solid, presumably $AuBrF_6$. Further heating of this salt under vacuum at temperatures up to 300° yielded nearly pure AuF_3.[5] The purity was checked by optical and X-ray methods.

(b) **Fluorine.**—A number of Au(I) salts were treated with gaseous fluorine in an unsuccessful attempt to prepare pure AuF_3; AuCN, AuI, and AuCl all reacted violently, yielding mixtures of AuF_3, Au, and an unidentified dark brown or black material. However, $AuCl_3 \cdot xH_2O$ could be converted to pure AuF_3 by the slow addition of fluorine at 200°. The purity was checked by weight change and by optical and X-ray examination. AuF_3, contaminated by unreacted gold, can also be prepared by fluorination at 250° of powdered gold made by reduction of gold salts in solution.

Preparation of Single Crystals.—In the direct fluorination of gold salts, an orange-yellow sublimate was formed in the reactor at temperatures exceeding 300°. The crystals were preserved by immersion in Fluorolube oil.[9]

Density of AuF_3.—Densities were measured on two different preparations of AuF_3. The first sample (2 g.) resulted from the reaction of BrF_3 with gold powder. The second sample (7 g.) was made by reaction of gaseous fluorine with $AuCl_3$. In each case, the freshly prepared AuF_3 was transferred in a helium atmosphere to a 10-ml. pycnometer containing Fluorolube oil. The density of the oil was 1.941 g./cm.^{3} at 25°. The occluded gas was removed from the sample by evacuating the pycnometer and contents. The density was then measured. On standing for a day or more, gradual darkening of the orange-yellow AuF_3 was noticed, but no change in the density was observed. Protection from light slowed or prevented this effect. The densities of the two different preparations were 6.722 for the BrF_3 preparation and 6.714 for the F_2 preparation. The value chosen is 6.72 g./cm.^{3} at 25°.

X-Ray Methods.—X-Ray powder photographs were taken at 18 ± 2° using a 19-cm. diameter Unicam camera with crystal-reflected Fe $K\alpha$ radiation from a lithium fluoride monochromator.

Positions of the X-ray reflections were measured with a direct reading vernier scale[10] and accurate unit-cell dimensions were calculated using the standard extrapolation method of Nelson and Riley.[11] Values of wave lengths used in the calculations were: Fe $K\alpha_1$ = 1.93597 Å. and Fe $K\alpha_2$ = 1.93991 Å. Measurements of relative intensities are in arbitrary units and were made on at least two films for each specimen with a Dobson-type microphotometer constructed from a design by Taylor.[12]

For the single-crystal studies the bladed orange crystals were immediately immersed in dry Fluorolube oil when the fluorinator was opened. A crystal was selected under the binocular micro-

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(1) Work at Los Alamos was sponsored by the U. S. Atomic Energy Commission. Requests for reprints should be directed to Los Alamos.

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