X-ray studies of RE NbO₄* compounds.

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A complete series of RE NbO₄ compounds (RE = rare earth) has been prepared and characterized by X-ray powder diffraction. The compounds have the monoclinic fergusonite structure, a distorted form of the scheelite structure. Variation of the monoclinic cell parameters with the atomic numbers of the rare earth are compared with a recent set of the ionic radii of eight-coordinated trivalent rare earths in oxides.

As part of a spectroscopic study of ABO_4 compounds in our laboratory (Holt & White), it was necessary to prepare and identify by X-ray diffraction a number of rare earth niobates of the stoichiometry RE NbO₄. All but five of these compounds had been prepared in an earlier study by Komkov (1959*a*). Since there were several cases of small, but significant, discrepancies in the cell parameters reported by Komkov and those from this study, it was decided to determine precision cell parameters on fifteen rare earth niobates (including YNbO₄ but not PmNbO₄).

Komkov prepared his compounds by melting the end-member oxides in an oxyhydrogen flame and then cooling. The compounds were prepared in the present study by lengthy heatings to achieve steady-state conditions and with atmospheric control in the case of CeNbO₄, PrNbO₄, and TbNbO₄. Equimolar quantities of high-purity RE₂O₃† and Nb₂O₅ were mixed, pelletized, and heated at 1300°C for 36 hours, followed by regrinding and reheating at 1200°C for a further 24 hours in air and slow cooling to room temperature. In the case of PrNbO₄ and TbNbO₄ the reactions were carried out in a purified argon atmosphere to prevent any substitution of the tetravalent for trivalent rare earth. For CeNbO₄, CeO₂ was used instead of the highly unstable Ce₂O₃, and the reactions were performed in air, argon, and hydrogen atmosphere. Each experiment yielded pure CeNbO₄ with the same cell parameter, but the argon run yielded the best crystallized product and was used in the refinement.

X-ray powder measurements were performed on a Siemens diffractometer calibrated with high-purity silicon ($a = 5\cdot4301$ Å) and gold ($a = 4\cdot0786$ Å). Nickel-filtered Cu $K\alpha$ radiation ($\lambda = 1\cdot54178$ Å) was used throughout. Intensities were measured from relative peak heights. From 15 to 25 unambiguously indexed reflexions were used to calculate precision cell parameters using the least-squares refinement computer program of Appleman, Handwerker & Evans (1963).

The structure of the low-temperature form of RE NbO₄ compounds has been described by Komkov (1959*b*). It is a monoclinic modification (space group *I*2) of the tetragonal mineral fergusonite (space group *I*4₁/*a*). Both are related to the scheelite structure. The RE atoms are irregularly surrounded by eight oxygen atoms, while the Nb atoms are approximately tetrahedrally coordinated by oxygen atoms. The tetragonal/monoclinic phase transition occurs in the approximate range 500 to 800°C depending on the size of the rare earth, and is completely reversible (Stubican, 1964). The tetragonal modification could not be preserved at room temperature with water quenching from 1200°C.

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* RE = rare earth
† Tb₂O₃ and Pr₂O₃ were prepared from commercial Tb₄O₇ and Pr₆O₁₁ by heating in hydrogen for 12 hours at 1200°C.

Refined cell parameters are listed in Table 1. Parameters for the compounds prepared by Komkov are listed for comparison. Also listed are the parameters measured by Belyaev, Dmitrieva, Melankholin, Popova & Soboleva (1969) on single crystals of LaNbO₄ and YNbO₄. These are in very good agreement with those of the present study. A typical powder pattern, that of TmNbO₄, is given in Table 2.

Table 1. *Refined cell parameters of* RE NbO₄ *compounds*

	a	b	c	β
LaNbO₄	5·567 (3) Å	11·525 (4) Å	5·205 (2) Å	94°03 (4)′
LaNbO₄*	5·575	11·511	5·206	94 30
LaNbO₄†	5·567 (5)	11·522 (5)	5·204 (5)	94 06 (10)
CeNbO₄	5·539 (1)	11·410 (2)	5·162 (1)	94 30 (1)
CeNbO₄*	5·534	11·423	5·168	94 30
PrNbO₄	5·492 (1)	11·327 (2)	5·153 (1)	94 31 (1)
PrNbO₄*	5·517	11·347	5·163	94 30
NdNbO₄	5·468 (3)	11·283 (5)	5·147 (3)	94 35 (2)
NdNbO₄*	5·482	11·289	5·150	94 30
SmNbO₄	5·421 (1)	11·174 (2)	5·120 (1)	94 42 (1)
SmNbO₄*	5·441	11·202	5·121	94 40
EuNbO₄	5·393 (4)	11·129 (4)	5·112 (3)	94 40
GdNbO₄	5·369 (2)	11·093 (2)	5·105 (1)	94 35 (2)
GdNbO₄*	5·386	11·092	5·104	94 24
TbNbO₄	5·344 (1)	11·033 (1)	5·084 (1)	94 37 (1)
DyNbO₄	5·323 (2)	10·996 (3)	5·081 (2)	94 36 (3)
DyNbO₄*	5·321	10·986	5·090	94 30
HoNbO₄	5·291 (1)	10·937 (1)	5·068 (1)	94 34 (1)
ErNbO₄	5·279 (2)	10·915 (3)	5·064 (1)	94 32 (2)
ErNbO₄*	5·277	10·915	5·055	94 30
TmNbO₄	5·258 (1)	10·872 (1)	5·044 (1)	94 34 (1)
YbNbO₄	5·231 (2)	10·829 (3)	5·038 (1)	94 27 (2)
YbNbO₄*	5·247	10·819	5·040	94 30
LuNbO₄	5·223 (1)	10·814 (1)	5·038 (1)	94 26 (1)
YNbO₄	5·292 (1)	10·937 (1)	5·069 (1)	94 35 (1)
YNbO₄†	5·29 (2)	10·95 (4)	5·07 (2)	94 30 (10)

* After Komkov (1959*a*).
† After Belyaev *et al.* (1969).

The variation of these cell parameters with the atomic number of the rare earth is shown in Fig. 1. Cell edges *a*, *b*, and *c* gradually decrease as the size of the rare earth decreases. The variation of the interaxial angle β is similar, except for a sharp decrease with the light rare earths. Also plotted in Fig. 1 are Shannon & Prewitt's (1969, 1970) effective ionic radii of the rare earths in 8-fold coordination
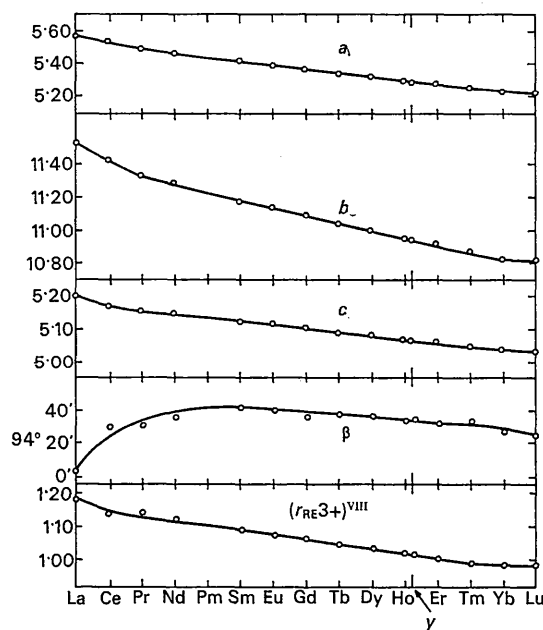
Fig. 1. Monoclinic cell parameters (Å) of RE NbO₄ and ionic radii of the corresponding eight-coordinated trivalent rare earth (after Shannon & Prewitt, 1969, 1970).

Table 2. X-ray powder pattern of $TmNbO_4$

d_{obs}	d_{calc}	I/I_0	hkl
5·44	5·44	2	020
4·718	4·720	2	110
4·562	4·563	9	011
3·106	3·105	100	$\bar{1}21$
2·981	2·980	10	130
2·939	2·939	90	031, 121
2·718	2·717	20	040
2·620	2·621	20	200
2·514	2·513	25	002
2·285	2·286	2	$\bar{1}12$, 022
2·206	2·205	7	$\bar{1}41$, 211
2·145	2·144	7	141
2·005	2·006	2	150, $\bar{2}31$
1·996	1·996	9	051
1·966	1·966	3	$\bar{1}32$
1·891	1·891	3	$\bar{2}02$
1·8865	1·8867	40	240
1·8455	1·8458	30	042
1·7457	1·7460	12	202
1·6564	1·6562	2	013
1·6344	1·6343	16	$\bar{1}03$, $\bar{1}61$
1·6161	1·6163	14	$\bar{3}21$
1·6083	1·6086	24	161
1·5737	1·5735	2	330
1·5654	1·5657	13	$\bar{1}23$
1·5524	1·5526	9	$\bar{2}42$
1·5444	1·5441	13	152, 321
1·4999	1·5000	11	123

in oxides. The contraction of the rare earths' radii is essentially linear, except for positive deviations at La and Lu. This deviation from linearity is reflected in the cell parameters of the RE NbO₄ compounds.

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Note on the space group of potassium hydrogeniodate(V), KIO₃.HIO₃. A correction.

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Contrary to the conclusion given in an earlier note, we have adopted the space group $P2_1/c$ for KIO₃.HIO₃, as the observed piezoelectric effect appeared to be caused by a thin layer of KIO₃ present on the surface of the crystal of KIO₃.HIO₃ used for the piezoelectricity measurement.

The difficulties concerning the space group of KIO₃.HIO₃ reported in an earlier note (Kemper & Vos, 1970) have now been solved. It appeared that the piezoelectric effect which had been measured for a large crystal of KIO₃.HIO₃ having a volume of approximately 0·25 mm³, is caused by a thin layer of KIO₃ deposited on the surface of the crystal. The presence of the KIO₃ layer was found by a careful study of a zero level Weissenberg photograph about the b axis of the large crystal, taken with Ni-filtered Cu radiation. This photograph showed 13 weak streaks which were identified as KIO₃ reflexions by their good fit to the pattern of a zero-layer Weissenberg photograph of the room temperature modification of KIO₃ at present being studied by F. van Bolhuis in our laboratory. We have therefore adopted $P2_1/c$ as the correct space group for KIO₃.HIO₃ in agreement with the results of the X-ray refinement reported in the earlier note (Kemper & Vos, 1970). In the mean time a neutron powder-diffraction study of KIO₃.HIO₃ and of KIO₃.DIO₃