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Refined Cell Parameters of the Ln_2WO_6-Type Rare Earth Tungstates

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Rare earth tungstates of the stoichiometry Ln_2WO_6 where Ln = Ce to Lu have been prepared and their lattice parameters were refined by a least-squares method. They have two structures: the *C2/c* symmetry for the compositions Ce_2WO_6 through Ho_2WO_6, and a monoclinic group from Er_2WO_6 to Lu_2WO_6 crystallizing most likely in the P2/*m* or *P*2$_1$/*m* structure. High pressure modifications are described for Dy_2WO_6 and Ho_2WO_6.

Introduction

Ln_2WO_6-type rare earth tungstates have been known in the literature since 1902 when Cleve (*1*) prepared and described Yb_2WO_6. More recently, Borchardt (*2*) studied these compounds comprehensively and recognized three distinct structural types: (a) La_2WO_6 which is unique by itself; (b) the group Ce_2WO_6 through Ho_2WO_6 [although Borchardt (*2*) did not prepare Ce_2WO_6 and included the Ho compound with the remaining rare earth tungstates]; and (c) the small rare earths from Er_2WO_6 through Lu_2WO_6 [Y_2WO_6 also belongs to this structural category]. While giving some representative d values for Pr_2WO_6, Borchardt (*2*) did not report any structures or cell dimensions. Blasse (*3*) postulated a structure for the large rare earth tungstates based on a distortion of La_2MoO_6, whose structure was solved by Sillen (*4*). As we stated earlier (*5*), we were unable to use Blasse's (*3*) data for satisfactory refinements. More recently, Pokrovskii et al. (*6*) reported *C2/c* symmetry for the large rare earth tungstates, which is in agreement with the cell we derived from single crystal work with $Gd_{1.70}Bi_{0.30}MoO_6$ (*5*). The space group for the small rare earths was given by Pokrovskii (*6*) as *P2/m*, *P2*, *Pm*, P2$_1$/*m* or *P*2$_1$, based on Y_2WO_6 single crystals. McCarthy et al. (*7*) could not obtain satisfactory indexing and refinement with the cell given by Pokrovskii (*6*) and tried an even larger one by trial and error. We find that Pokrovskii's (*6*) symmetry provides the basis for excellent refinements of the small rare earth tungstates. Furthermore, we can state that the suggested space groups can be narrowed down to centrosymmetric ones since a second harmonic generation test with these compounds proved negative.

It is the purpose of this paper to report refined cell dimensions for all the rare earth tungstates including Y but excepting the La compound. Ce_2WO_6 and high-pressure modifications of Dy_2WO_6 and Ho_2WO_6 are reported for the first time.

Experimental

All the tungstates described in this paper were prepared by standard solid state techniques, using high-purity (99.99% from Kerr–McGee Co.) rare earth oxides and WO_3 (Fisher analytical grade). Since all compounds appear to melt above 1700°C and are quite stable in air, firings were carried out in air at temperatures up to 1600°C. Only Ce_2WO_6 was prepared via a symproportionation according to:

$$6CeO_2 + W + 2WO_3 \rightarrow 3Ce_2WO_6$$

in sealed platinum capsules. Attempts were made to grow single crystals of La_2WO_6 by the Czochralski technique. This compound has the lowest melting point of the series, 1610°C by optical pyrometry. However, the growth on an Ir wire was invariable polycrystalline and

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TABLE I

REFINED CELL DIMENSIONS OF THE LARGE Ln_2WO_6 COMPOUNDS FOR BOTH BODY-CENTERED[a] AND C-CENTERED CELLS

	a, Å	b, Å	c, Å	β, °	V, Å^3	a', Å	β', °
Ln							
Ce	5.570	11.524	15.947	91.83	1023.0	16.723	107.61
Pr	5.546	11.436	15.923	91.85	1009.4	16.691	107.54
Nd	5.522	11.384	15.857	91.80	996.31	16.626	107.58
Sm	5.464	11.259	15.724	91.72	966.81	16.490	107.62
Eu	5.442	11.211	15.681	91.73	956.4	16.443	107.59
Gd	5.425	11.173	15.624	91.59	946.7	16.396	107.72
Tb	5.398	11.118	15.562	91.57	933.7	16.332	107.73
Dy	5.369	11.067	15.504	91.45	921.1	16.278	107.80
Ho	5.336	11.037	15.449	91.38	909.6	16.222	107.81

[a] The unprimed values refer to the body-centered cell, and the primed values to the C-centered cell with $c' = a$, $b' = b$.

X-ray studies indicated that it was 2-phase suggesting that La_2WO_6 does not melt congruently. Attempts were also made to grow Er_2WO_6 from a $BaCl_2$ flux. While some small needle-like single crystals could be obtained this way, the cell dimensions of these single crystals did not satisfactorily index the Guinier pattern of the bulk product suggesting that there may be a deviation from true Er_2WO_6 stoichiometry. All powder patterns were obtained with a Hägg–Guinier camera using Cu$K\alpha_1$ radiation and an internal standard of KCl ($a_0 = 6.2931$ Å at 25°C).

Results and Discussion

Although we were unable to obtain pure single crystals of La_2WO_6 and also could not index its complex powder pattern, this composition is worthy of comment. La^{3+} is the largest readily available trivalent ion (except for the actinides); as the end member of the Ln_2WO_6 series it is not surprising that La_2WO_6 transforms into a new structure, although in three other tungstate and molybdate cases, the $Ln_2(WO_4)_3$, $Ln_2(MoO_4)_3$, and Ln_2MoO_6 series, it remains isostructural with the other large rare earths. Regarding Ce_2WO_6, Borchardt (*2*) stated that it does not form in air since the apparently thermodynamically more stable $Ce_2(WO_4)_3$ is formed. We therefore selected the process described in the experimental section to prepare Ce_2WO_6. Under those conditions the compound readily forms and it is much lighter in color (tan to pale brown) than Ce_2MoO_6 (*5*). The cell dimensions of Ce_2WO_6 are those expected for a Ce^{+3}–W^{+6} valence distribution, and the electrically insulating behavior of Ce_2WO_6 further supports this normal valence distribution. Lattice parameters for this compound and for the other large rare earth tungstates are summarized in Table I. Body-centered cells are also given because of their direct relationship to the subcell (*5*). This structure prevails up to Dy_2WO_6 according to Borchardt (*2*), Blasse (*3*), and Pokrovskii (*6*). However, we find that Ho_2WO_6

TABLE II

CELL DIMENSIONS AND X-RAY DENSITIES FOR THE HIGH-PRESSURE β MODIFICATIONS OF Dy_2WO_6 AND Ho_2WO_6

					X-Ray density g/ml^{-1}	
	a, Å	b, Å	c, Å	β, °	α form	β form
Ln						
Dy	11.4091	5.3603	7.6200	104.309	8.903	9.066
Ho	11.3644	5.3394	7.6000	104.412	8.723	8.896

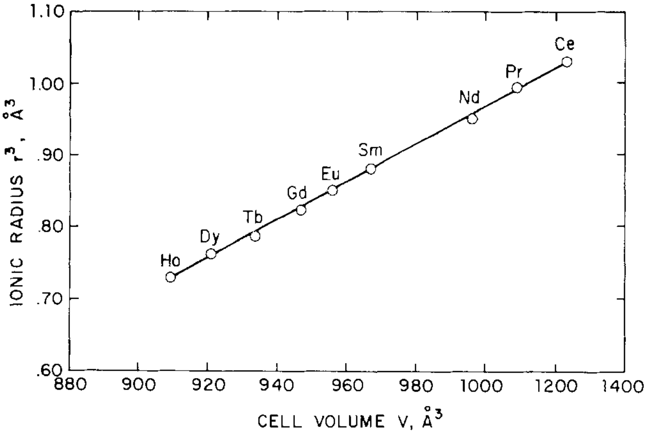

FIG. 1. Cell volume vs r^3 for the large Ln_2WO_6 compounds.

prepared as described in the experimental section also crystallizes in the $C2/c$ space group. In comparing the cell volume of 909.60 Å^3 (453.30) with that of the other Ho_2WO_6 modification reported by Pokrovskii (*6*) of 443.35 Å^3 it is indicated that the latter form crystallizes in a denser structure. We therefore attempted to convert low-pressure α-Ho_2WO_6 of $C2/c$ symmetry into a high-pressure modification by the application of 65 kbar at 1100°C for one hour. This treatment did result in a complete conversion of our low-pressure Ho_2WO_6 into the $P2/m$ form.[2] Although the previous authors (*2*, *3*) did not indicate the use of pressure to prepare Ho_2WO_6, we can now explain the existence of both modifications. A similar treatment with α-Dy_2WO_6 also completely converted it to the high-pressure β form. Tb_2WO_6 did not convert. The cell dimensions for these modifications together with a comparison of the X-ray densities are summarized in Table II. It is particularly noteworthy that Ho^{3+} with an octahedral ionic radius of 0.901 Å crystallizes in one structure and Y^{3+} with a radius of 0.900 Å in the other. The substitution of 0.03 mole of Bi for Y in $Y_{1.97}Bi_{0.03}WO_6$ also resulted in the $P2/m$ structure with cell dimensions, $a = 11.241$ Å, $b = 5.336$ Å, $c = 7.714$ Å, $\beta = 104.47°$ and a cell volume of 448.05 Å^3. This is exactly intermediate to the α (446.65) and β (453.30) form of Ho_2WO_6. The cell volumes as a function of the reported ionic radii for the large rare earth tungstates are shown in Fig. 1.

X-ray patterns of the small rare earth tungstates from Er_2WO_6 to Lu_2WO_6 (and also Y_2WO_6) could easily be indexed based on the cell suggested by Pokrovskii (*6*). The cell dimensions are summarized in Table III. Interestingly, the β angle is essentially unchanged in both structural

TABLE III

REFINED CELL DIMENSIONS OF THE SMALL Ln_2WO_6 COMPOUNDS

Ln	a, Å	b, Å	c, Å	β, deg	V, Å^3
Er	11.319	5.318	7.578	104.46	441.7
Tm	11.287	5.302	7.554	104.51	437.6
Yb	11.259	5.282	7.529	104.60	433.3
Lu	11.225	5.268	7.523	104.65	430.4
Y	11.362	5.336	7.591	104.39	445.8

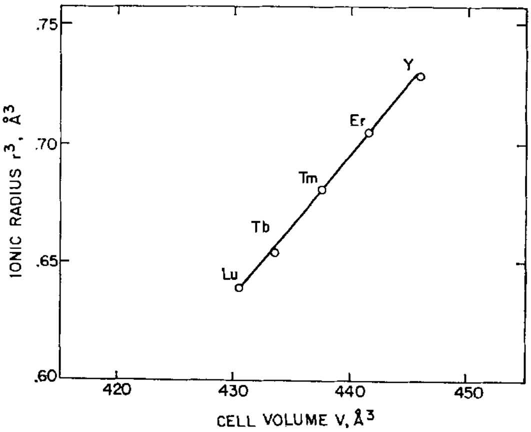

FIG. 2. Cell volume vs r^3 for the small Ln_2WO_6 compounds.

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[2] Later experiments indicated that as little as 3 kbar was sufficient for this conversion.

types, while *a*, *b*, and *c* change systematically. Based on a negative second harmonic generation test on Y_2WO_6 and Tm_2WO_6, we suggest centric P2/*m* or *P*2$_1$/*m* as the most likely correct space groups for the small rare earth tungstates. The cell volume vs ionic radii curve for these small Ln_2WO_6 compounds is given in Fig. 2.

In attempting to prepare single crystals of the small tungstates, we introduced some Bi into Er_2WO_6, since this procedure had proved successful with Gd_2MoO_6 (*5*). Much to our surprise we found that as little as 0.01 mole of Bi in $Er_{1.99}Bi_{0.01}WO_6$ changed the structure, and apparently, at least at this concentration, no solid solutions were formed. The powder pattern of $Er_{1.99}Bi_{0.01}WO_6$ could be accounted for on the basis of a rhombohedral cell with $a = 6.4466 \pm 3$ Å and $\alpha = 98.49 \pm 3°$. The corresponding hexagonal cell is $a = 9.7669 \pm 5$ Å and $c = 9.3727 \pm 6$ Å. This structure thus might be related to rhombohedral ULu_6O_{12} (*8*) where the hexagonal cell is $a = 9.797$ Å and $c = 9.204$ Å. It might also be related to the rare earth tellurates, For example, the powder pattern of Er_2TeO_6 has been indexed on the basis of a hexagonal cell where $a = 10.42$ Å and $c = 9.90$ Å (*9*).

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