powder photographs indicate a different diffraction pattern. The color of the Eu_2TeO_6 phase is gray. At temperatures above 800°, their weight decreases, and at about 950° it corresponds to that of the sesquioxide.

Domange, Flahaut, and Chirazi[9] have reported that the air oxidation of Ce_2O_2Te produced $Ce(TeO_4)_2$, and that at 550°, this tellurate dissociated into the dioxide with vaporization of TeO_2. However, since cerium commonly exhibits an oxidation state of four, this difference in behavior is not surprising.

When the phases Ln_2TeO_5 are heated at about 950° in a hydrogen atmosphere, they are reduced to the monotelluroöxides, providing a confirmation of the analytical data. This behavior is identical with that reported for the corresponding selenium and sulfur compounds.[2]

X-Ray powder diffraction data, obtained with CuKα radiation ($\lambda_{\alpha u}$ = 1.5418 Å.), are listed for Nd_2O_2Te in Table I. The observed density obtained from a pellet compacted at 20,000 p.s.i. is 5.33 ± 0.03 g./cc., compared to a calculated density of 5.40 g./cc. based on a simple tetragonal cell with one molecule per unit cell. However, because of a large number of extinctions, a suitable tetragonal space group has not been found. Unit cell dimensions and calculated densities of the isostructural compounds are listed in Table II. The *d* spacings obtained for Ce_2O_2Te agree with those reported by Domange, Flahaut, and Chirazi,[9] who report no attempt to index them.

TABLE I

INTERPLANAR *d* SPACINGS AND RELATIVE INTENSITIES OF Nd_2O_2Te

hkl	*d* calcd. (Å.)	*d* obsd. (Å.)	Relative intensities[a]
102	2.925	2.928	100.00
110	2.844	2.852	47.61
004	2.131	2.132	9.04
200	2.012	2.012	18.33
114	1.705	1.705	18.33
212	1.658	1.659	32.38
204	1.462	1.461	7.85
220	1.422	1.424	3.57
106	1.339	1.339	3.57
302	1.279	1.278	7.04
310	1.272	1.272	5.23
224	1.183	1.183	2.38

[a] Relative intensities were determined with a Siemens diffractometer.

The X-ray powder photographs of the isostructural phase Ln_2TeO_5 are somewhat similar to that of the Ln_2O_2Te phase in that groups of lines are present in the former where the principal lines existed in the latter, but that of the isostructural Ln_2TeO_6 series is very different. Neither of these phases, both of which possess lower than cubic symmetry, has been indexed.

TABLE II

UNIT CELL DIMENSIONS AND CALCULATED DENSITIES FOR LANTHANUM(III) MONOTELLUROÖXIDES

Compound	a_0 (Å.)	c_0 (Å.)	Calcd. density (g./cc.)
La_2O_2Te	4.108 ± 5	8.687 ± 5	4.96
Ce_2O_2Te	4.073	8.576	5.13
Pr_2O_2Te	4.050	8.533	5.24
Nd_2O_2Te	4.023	8.519	5.40
Sm_2O_2Te	3.987	8.424	5.71
Eu_2O_2Te	3.965	8.362	5.85
Gd_2O_2Te	3.951	8.342	6.04
Dy_2O_2Te	3.916	8.260	6.36

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
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Electric Discharge Reactions of Phosphorus Trichloride and Germanium Tetrachloride

BY WILLIAM L. JOLLY, CHARLES B. LINDAHL, AND RICHARD W. KOPP

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If a microwave discharge is established[1] in a stream of PCl_3 vapor at 1–5 mm. pressure, the emerging vapor contains metastable species of remarkably long half-life. If this vapor is allowed to pass through a series of four traps cooled to *ca.* −20, −45, −63, and −196°, successively, PCl_5 condenses in the *ca.* −20° trap, a red material is formed in the −45° trap, a yellow-tan material is formed in the −45 and −63° traps, and PCl_3 condenses in the −63 and −196° traps. The red and yellow-tan materials are non-volatile at room

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(9) H. Domange, J. Flahaut, and A. N. Chirazi, *Bull. soc chim. France*, 150 (1959).

(1) As described by W. L. Jolly, "Synthetic Inorganic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1960, p. 113.

temperature, amorphous to X-rays, and contain variable amounts of phosphorus and chlorine with P:Cl ratios of 5.5–50:1 and 2.5–5.0:1, respectively. A run at 1 mm. pressure with a flow rate of 0.08 g. of PCl_3/min. caused 71.5% of the PCl_3 to be decomposed, whereas a run at 5 mm. pressure with a flow rate of 1 g. of PCl_3/min. caused only 3.5% decomposition.

If a mixture of PCl_5 and the red and yellow materials is exposed at room temperature to a stream of vapor emerging from the discharge, the red and yellow materials disappear, but the PCl_5 remains. On long standing, the red and yellow materials react with PCl_5 to form PCl_3.

If the vapor emerging from the discharge is allowed to fill an evacuated bulb to a pressure of several mm., red and yellow materials and PCl_5 can be condensed by cooling part of the bulb with liquid nitrogen 3 hr. after closing off the bulb. After 15 hr., only PCl_3 can be condensed. We estimate a half-life of approximately 30 min. for the back-reaction of the metastable species to re-form PCl_3. The mass spectrum of the vapor from the discharge (as determined with a Consolidated 21-103a spectrometer) was found to be the same as that for pure PCl_3.

If H_2 is mixed with the PCl_3 entering the discharge in ratios of $P_{H_2}/P_{PCl_3} > 1$, red phosphorus is deposited throughout the line beyond the discharge; the thickness of the deposit decreases with increasing distance from the discharge. Hydrogen chloride forms, but no PCl_5 forms.

A plug of bronze wool placed past the PCl_3 discharge reacts to form CuCl. No PCl_5 or red or yellow solids are formed in subsequent cold traps, but small amounts of P_2Cl_4 are condensed in a −45° trap. In a 73-min. run we found that 0.5% of the PCl_3 reacted to give 48 mg. of P_2Cl_4 in 77% yield. We identified P_2Cl_4 by its mass spectrum and melting point of −29 to −28° (lit.[2-4] m.p. −28°). The gain in weight of the copper wool could be accounted for by the CuCl formed within ±20%.

The data are consistent with the assumption that the vapor leaving the PCl_3 discharge contains PCl_5 and one or more of the following reduced species: P, P_2, or PCl. Upon condensation, the reduced species immediately disproportionates or reacts with PCl_3 to form a red phosphorus-like subchloride of phosphorus (*e.g.*, P_5Cl). The radical PCl_2 cannot be present in a significant amount in view of the fact that 71.5% of the PCl_3 can be decomposed in the over-all reaction. From the following equations it is clear that if the initial discharge products were PCl_2 and PCl_5, it would be impossible to decompose more than 58% of the PCl_3.

$$\begin{array}{c} PCl_3 \longrightarrow \underbrace{[0.67PCl_2]} + 0.33PCl_5 \\ \downarrow \\ 0.05P_5Cl + 0.42PCl_3 \end{array}$$

However, if the initial discharge products were PCl and PCl_5, it would be possible to decompose as much as 86% of the PCl_3.

$$\begin{array}{c} PCl_3 \longrightarrow \underbrace{[0.5PCl]} + 0.5PCl_5 \\ \downarrow \\ 0.07P_5Cl + 0.14PCl_3 \end{array}$$

And if the initial discharge products were PCl_5 and either P or P_2, it is conceivable that 100% of the PCl_3 might be decomposed.

$$\begin{array}{c} PCl_3 \longrightarrow \underbrace{[0.4P]} + 0.6PCl_5 \\ + \downarrow 0.029PCl_3 \\ 0.086P_5Cl \end{array}$$

The bronze wool is an efficient catalyst for the back-reaction to form PCl_3 (up to 71.5% PCl_3 decomposition without bronze and only 0.5% with bronze). In addition, the bronze reduces PCl_5 to PCl_3 and somehow catalyzes the reaction of the reduced species with PCl_3 to form P_2Cl_4.

Numerous variations of the apparatus described by Wartik[5] (in which B_2Cl_4 is prepared by passing BCl_3 through a 60-cycle discharge between bronze wool plugs) were tried in an attempt to find an efficient process for the reaction

$$2PCl_3 + 2Cu \xrightarrow{\text{discharge}} P_2Cl_4 + 2CuCl$$

Our best results were achieved with a static system in which a discharge was established between two bronze wool plugs over a pool of PCl_3 at 0°. Yields of as high as 75 mg. of P_2Cl_4 in 15 min. were obtained; however prolongation of the runs did not proportionately increase the yields. Apparently the CuCl coating which forms on the bronze wool reduces the reactivity of the bronze. Thus

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[2] A. Besson and L. Fournier, *Compt. rend.*, **150**, 102 (1910).

[3] A. Stock, A. Brandt, and H. Fischer, *Chem. Ber.*, **58**, 643 (1925).

[4] A. Finch [*Can. J. Chem.*, **37**, 1793 (1959)] observed a melting point of −34°.

[5] T. Wartik, paper no. 55 presented before the Division of Inorganic Chemistry at the 138th National Meeting of the American Chemical Society, New York, N. Y., September, 1960.

the method does not compete with that of Sandoval and Moser,[6] who used a discharge over a solution or suspension of phosphorus in PCl_3 and obtained yields of 4–5 g. of P_2Cl_4 in 7 hr.

The yield of Ge_2Cl_6 from a microwave discharge[7] in $GeCl_4$ is improved by placing bronze wool immediately after the discharge zone. Similarly, by passing $GeCl_4$ through a series of 60-cycle discharges between bronze wool plugs, as much as 0.5 g. of Ge_2Cl_6 per hr. may be prepared. As in the analogous P_2Cl_4 synthesis, the yields are not much improved by longer running times.

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[6] A. A. Sandoval and H. C. Moser, paper no. 55 presented before the Division of Inorganic Chemistry at the 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962.

[7] D. Shriver and W. L. Jolly, *J. Am. Chem. Soc.*, **80**, 6692 (1958).

CONTRIBUTION FROM THE
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Crystallographic Data for New Rare Earth Borate Compounds, $RX_3(BO_3)_4$

BY A. D. MILLS

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A new series of rare earth borates, of the general formula $RX_3(BO_3)_4$, where R is yttrium or a rare earth and X is aluminum or chromium, has been prepared by Ballman.[1] These samples are of interest in the fundamental study of rare earth compounds, and also are of interest because they are piezoelectric and fluorescent. For these reasons, lattice constant, density, and unit cell volume determinations were made on all the compounds and these data are reported in this paper.

Experimental and Discussion

Initially the compounds were prepared from a molten salt solvent of potassium sulfate and molybdic anhydride. All of the reported compounds, except those of ytterbium, holmium, and terbium, were made in this way. Later a lead borate flux was used and the ytterbium, holmium, and terbium compounds reported were grown from this medium. Yttrium aluminum borate also was grown in the lead borate flux and a slight shift in the lattice constant was observed with flux change. It should be noted that for the purpose of luminescence studies a few of the compounds had other rare earths added in amounts less than 0.1%. On one occasion 1% or less of the lead from the flux was occluded in the crystals. It was felt that this would not markedly affect the lattice constants.

The X-ray powder photographs were taken with Straumanis-type Norelco cameras (114.6-mm. diameter) using $CrK\alpha$ radiation. Knox[2] found these compounds to belong to space group $D_3{}^7$-R32 and to be isostructural with huntite, $CaMg_3(CO_3)_4$.[3] These results were based on (1) a single crystal X-ray diffraction study, (2) the morphology, and (3) the symmetry of the piezoelectricity.

All the patterns of the $RAl_3(BO_3)_4$ and $RCr_3(BO_3)_4$ indicate that the crystals are isostructural. The observed and calculated interplanar spacings and the observed intensities of $YAl_3(BO_3)_4$ are given in Table I as representative of the whole family of compounds.

The crystallographic data for the $RX_3(BO_3)_4$ compounds are given in Table II. The lattice constants and cell volumes were calculated using hexagonal indices and then were converted to the rhombohedral indices.

The cell volumes decrease slightly with increasing atomic number of the rare earth ion, following the lanthanide contraction, Fig. 1. It will be noted that the cell volume for the erbium compound is larger than the curve indicates, but within the attainable accuracy for this sample.

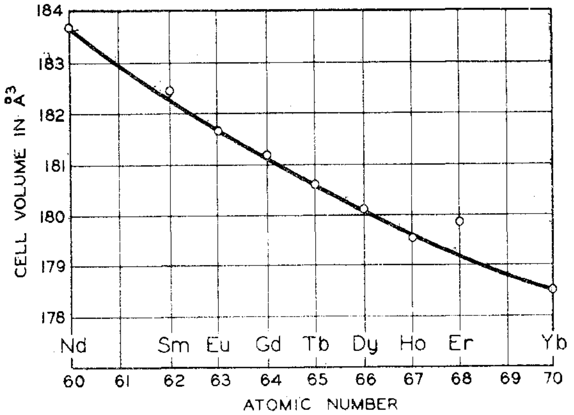

Fig. 1.—Variation of cell volume with atomic number of the rare earth ion.

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[1] A. A. Ballman, *Am. Mineralogist*, in press.

[2] K. Knox, Abstracts of Boulder ACA Meeting, 1961, to be published.

[3] D. L. Graf and W. F. Bradley, *Acta Cryst.*, **15**, 238 (1962).