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
Bell Telephone Laboratories, Inc.,
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Crystallographic Data for New Rare Earth Borate Compounds, $RX_3(BO_3)_4$

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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 CrKα 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.

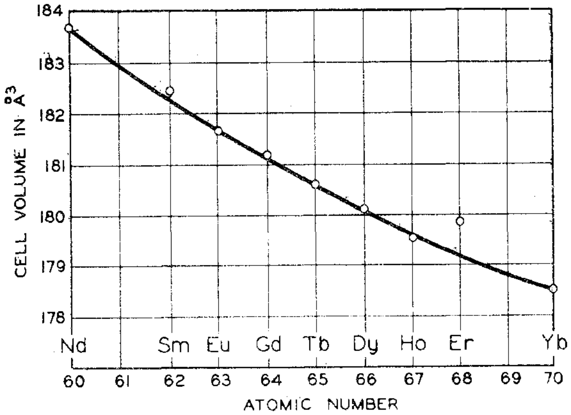

Fig. 1.—Variation of cell volume with atomic number of the rare earth ion.

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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).

TABLE I

CALCULATED AND OBSERVED *d* SPACINGS AND OBSERVED INTENSITIES FOR $YAl_3(BO_3)_4$

hk·l	Int. obsd.[a]	d_{obsd}	d_{calcd}	*hk·l*	Int. obsd.[a]	d_{obsd}	d_{calcd}
10·1	m	5.343	5.385	50·2	w	1.470	1.471
11·0	mw	4.628	4.646	01·5	vvw	1.4261	1.4261
02·1	m	3.504	3.518	41·3	mw	1.4201	1.4204
01·2	mw	3.293	3.303	51·1	w	1.4179	1.4175
21·1	mw	2.797	2.805	13·4	w	1.4059	1.4065
20·2	s	2.687	2.692	42·2	mw	1.4016	1.4023
30·0			2.683	20·5	vw	1.3633	1.3633
00·3	n.o.		2.415	40·4	w	1.3457	1.3461
12·2	ms	2.322	2.330	15·2	w	1.3402	1.3425
22·0			2.323	60·0			1.3413
11·3	m	2.140	2.143	12·5	w	1.3076	1.3082
13·1	m	2.128	2.133	33·3	vw	1.3038	1.3037
40·1	mw	1.937	1.939	43·1	w	1.3007	1.3012
31·2	mw	1.898	1.900	32·4	w	1.2926	1.2930
30·3	mw	1.792	1.795	52·0	mw	1.2880	1.2887
32·1	mw	1.786	1.789	34·2	w	1.2422	1.2428
10·4	w	1.765	1.767	31·5	w	1.2153	1.2154
04·2	n.o.		1.759	16·1	vw	1.2096	1.2101
41·0	mw	1.754	1.756	00·6	mw	1.2074	1.2075
22·3	m	1.673	1.674	05·4	mw	1.2031	1.2032
02·4	mw	1.651	1.652	04·5	w	1.1760	1.1758
23·2	mw	1.643	1.645	60·3	vw	1.1726	1.1726
05·1	vw	1.568	1.571	11·6	w	1.1690	1.1687
21·4	w	1.555	1.556	24·4	mw	1.1649	1.1648
33·0	vw	1.547	1.549	61·2	vw	1.1625	1.1624
24·1	w	1.487	1.488	44·0	vvvw	1.1618	1.1616

[a] n.o., not observed; s, strong; m, medium; w, weak; v, very.

TABLE II

CRYSTALLOGRAPHIC DATA FOR $RX_3(BO_3)_4$ COMPOUNDS

	Hexagonal indices				Rhombohedral indices			Calcd. density, g./cm.^{3}
	a_0 (Å.)	c_0 (Å.)	c_0/a_0	Vol. (Å.^{3})	a_0 (Å.)	α	Vol. (Å.^{3})	
$YAl_3(BO_3)_4$[a]	9.293	7.245	0.780	541.8	5.883	104°18.9′	180.6	4.372
$NdAl_3(BO_3)_4$[a]	9.334	7.308	.783	551.4	5.914	104°12.8′	183.8	4.161
$SmAl_3(BO_3)_4$[b]	9.31	7.29	.783	547.	5.90	104°13.3′	182.4	4.25
$EuAl_3(BO_3)_4$[a]	9.307	7.266	.781	545.0	5.894	104°17.0′	181.7	4.280
$GdAl_3(BO_3)_4$[a]	9.302	7.257	.780	543.8	5.890	104°18.0′	181.3	4.335
$TbAl_3(BO_3)_4$[a]	9.293	7.247	.780	542.0	5.884	104°18.7′	180.7	4.371
$DyAl_3(BO_3)_4$[b]	9.29	7.24	.779	540.	5.88	104°19.8′	180.2	4.41
$HoAl_3(BO_3)_4$[b]	9.28	7.22	.778	539.	5.88	104°21.3′	179.6	4.45
$ErAl_3(BO_3)_4$[c]	9.38	7.24	.780	540.	5.88	104°18.6′	180.0	4.46
$YbAl_3(BO_3)_4$[b]	9.26	7.21	.778	536.	5.87	104°22.5′	178.6	4.55
$GdCr_3(BO_3)_4$[b]	9.49	7.54	.794	589.	6.03	103°51.3′	196.2	4.64

[a] Lattice constants are within ±0.002 Å. [b] Lattice constants are within ±0.01 Å. [c] Lattice constants are within ±0.05 Å.

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