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E. I. DU PONT DE NEMOURS AND COMPANY, EXPERIMENTAL STATION, WILMINGTON, DELAWARE

Synthesis of Some New Perovskites Containing Indium and Thallium

BY R. D. SHANNON

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High-pressure synthesis of orthorhombic perovskite compounds of the type $A^{III}B^{III}O_3$ where one of the cations is In or Tl and the other is Fe, Cr, Y, Eu, Gd, Dy, Rh, or Mn is reported. The use of high pressure is shown to enlarge the perovskite stability field. Distortions of the ideal perovskite structure resulting from deviations in size of the A^{+3} or B^{+3} ions from ideal values are discussed. A plot of r_B^3 *vs.* unit cell volumes is used to derive effective (coordination number 6) ionic radii of Sc^{+3}, Ti^{+3}, V^{+3}, Cr^{+3}, Mn^{+3}, Co^{+3}, Ni^{+3}, and Rh^{+3}.

Introduction

The structure types exhibited by the $A^{III}B^{III}O_3$ compounds have been described in detail by Keith and Roy,[1] Roth,[2] and Schneider, *et al.*[3] Although the R_2O_3–In_2O_3 systems at normal pressures were studied by these authors, relatively few ABO_3 compounds of this type which contain either In^{+3} or Tl^{+3} were found. Syntheses involving large A^{+3} ions in $A^{III}In^{III}O_3$ compounds, *i.e.*, La^{+3}, Nd^{+3}, and Sm^{+3}, resulted in perovskite structures, whereas those with the smaller cations, Lu^{+3}, Yb^{+3}, Tm^{+3}, Er^{+3}, Y^{+3}, and Ho^{+3}, resulted in solid solutions of the C rare earth oxide structure type.[3] Compounds with pseudo-hexagonal cells of unknown structure were formed with intermediate size cations Gd^{+3}, Dy^{+3}, and Eu^{+3}.[4–6] Combinations of In_2O_3 or Tl_2O_3 with transition metal ions did not result in compound formation.

The recent high-pressure synthesis of several new indium-containing oxides with the corundum structure[7] or the $YAlO_3$ structure[8] indicated that the R_2O_3–In_3O_2 systems might yield new phases at high pressures. This paper concerns the high-pressure synthesis of a group of ABO_3 compounds with perovskite structures in which one of the cations is In or Tl and the other is Fe, Cr, Y, Eu, Gd, Dy, Rh, or Mn. The discovery of these compounds extends the stability field of the perovskite structure and provides some further examples of high-pressure transitions in which the cation undergoes an increase in coordination number. The unit-cell volume data for these new compounds and for previously known perovskites have been utilized to derive a set of effective B^{+3} radii in the same manner as used by Roth and Schneider.[9]

Experimental Section

The reactions were carried out in a tetrahedral anvil at a pressure of 65 kbars. The apparatus and pressure calibration techniques were identical with those described by Bither, *et al.*[10] In some cases the Pt container was used as the heating element, whereas in others the Pt cylinder was encased in a BN sleeve and heated by a surrounding graphite cylinder.

The reactants In_2O_3, Tl_2O_3, Cr_2O_3, and Fe_2O_3 were high-purity oxides purchased from Spex, Inc.; a spectrographic analysis of In_2O_3 showed (in ppm): Na, 100; Mg, 15; Si, 100; Fe, 100. Yttrium oxide and the rare earth oxides were obtained from American Potash and Chemical Co. with a stated purity of 99.9%. The individual oxides were mixed in alcohol, dried, and remixed dry. This process was repeated several times before pressurizing. The mixtures were then pelleted at 20,000 psi. The pellets were placed in the cylindrical Pt holders, pressurized at 65 kbars, and then heated slowly to temperature. Samples were held at temperature for 1 hr and then quenched by turning off the power. Since an estimated gradient of 100–300° from the center of the cylinder to the end normally occurs, samples were chosen from the center and end portions for X-ray analyses. Single crystals of $InCrO_3$ and $YInO_3$ were investigated to verify the space group. For the remaining samples powder data were obtained on a Guinier–de Wolff camera using monochromatized Cu $K\alpha$ radiation. Films were read with a Mann film reader; *d* values were calculated using λ (Cu $K\alpha$) = 1.54051. Cell constants were obtained by a least-squares refinement.

No chemical analyses were obtained since most samples appeared to be single phase and X-ray analysis showed no extraneous lines. In some cases the unreacted starting materials could be detected. Some samples were checked for possible nonstoichiometry by preparing samples with slight excesses of one or the other starting material.

Ambient-pressure stability of several products was determined by hot-stage microscopic observations. The product phase was then identified by X-ray powder diffraction. Resistivity data were taken on certain samples by the four-probe method as described by Bither, *et al.*[10] Single crystals were used when possible.

Results

Table I lists the new compounds, synthesis conditions, and physical property data. Table II lists calculated *d* values and observed *d* values and intensities.

In_2O_3–Cr_2O_3 and In_2O_3–Rh_2O_3.—Previous work on the In_2O_3–Cr_2O_3 system by Schneider, *et al.*,[3] showed a mixture of the C rare earth oxide phase and corundum phase solid solutions. No compound formation was reported. In the present work at 65 kbars, dark green, transparent crystals of the orthorhombic perovskite $InCrO_3$ were grown. X-Ray precession patterns confirmed the unit cell. Although it is not possible to distinguish between the space groups Pbnm and $Pbn2_1$,

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[1] M. L. Keith and R. Roy, *Am. Mineralogist*, **39**, 1 (1954).

[2] R. S. Roth, *J. Res. Natl. Bur. Std*, **58**, 75 (1957).

[3] S. J. Schneider, R. S. Roth, and J. L. Waring, *ibid.*, **65A**, 345 (1961).

[4] S. J. Schneider, *ibid.*, **65A**, 429 (1961).

[5] R. S. Roth, private communication.

[6] A. Waintal, J. J. Caponi, and E. F. Bertaut, *Solid State Commun.*, **4**, 125 (1966).

[7] R. D. Shannon, *ibid.*, **4**, 629 (1966).

[8] C. T. Prewitt and R. D. Shannon, Abstracts, American Crystallographic Association Meeting, Atlanta, Ga., Jan 25, 1967.

[9] R. S. Roth and S. J. Schneider, *J. Res. Natl. Bur. Std.*, **64A**, 309 (1960).

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TABLE I

PROPERTIES OF NEW In- AND Tl-CONTAINING PEROVSKITES

	Pressure, kbars	Temp, °C	a, A	b, A	c, A	Unit cell vol., A^3	Temp of stability, °C	Resistivity, $\rho_{25°}$, ohm-cm	E,^{b} ev
$InCrO_3$	65	1250 1500	5.170	5.355	7.543	208.83	≥1000	10^{11} (polyxtal)	0.3
$InRhO_3$	65	1350	5.301	5.435	7.586	218.56	≥1000		
$YInO_3$	65	1250 1500	5.500	5.787	8.053	256.31	≥1000	10^{10} (polyxtal)	1.0
$DyInO_3$	65	1450–1050^a	5.519	5.751	8.041	255.22			
$GdInO_3$	65	1450–1050^a	5.548	5.842	8.071	261.59			
$EuInO_3$	65	1450–1050^a	5.567	5.835	8.078	262.40		10^{11} (single xtal)	1.2
$TlCrO_3$	65	850	5.302	5.405	7.647	219.14	~500		
$TlFeO_3$		850	5.319	5.448	7.796	255.91	≥650	11 (polyxtal)	0.08

^{a} Cooled at 100°/hr to 1050° followed by quenching. ^{b} Derived from the slope of log ρ *vs.* $1/T$.

TABLE II

POWDER DIFFRACTION DATA FOR SOME INDIUM AND THALLIUM PEROVSKITES

Indices	$InCrO_3$			$InRhO_3$			$YInO_3$			$DyInO_3$			$GdInO_3$			$EuInO_3$			$TlCrO_3$			$TlFeO_3$		
	d_{obs}	d_{calc}	I	d_{obs}	d_{calc}	I	d_{obs}	d_{calc}	I	d_{obs}	d_{calc}	I	d_{obs}	d_{calc}	I	d_{obs}	d_{calc}	I	d_{obs}	d_{calc}	I	d_{obs}	d_{calc}	I
101	4.252	4.2643	1		4.3453		4.535	4.5420	2		4.5505			4.5721			4.5839		4.343	4.3569	4	4.389	4.3938	2
002	3.770	3.7717	15		3.7931		4.028	4.0267	4		4.0203			4.0354			4.0390		3.820	3.8234	56	3.899	3.8979	30
110	3.717	3.7194	13		3.7948		3.983	3.9867	26		3.9821			4.0229			4.0279		3.782	3.7849	100	3.807	3.8060	60
111	3.335	3.3359	24	3.393	3.3938	23	3.569	3.5729	36	3.565	3.5684	10	3.599	3.6004	20	3.603	3.6046	15	3.390	3.3921	56	3.421	3.4202	28
020	2.677	2.6777	26	2.718	2.7173	48	2.893	2.8934	96	2.875	2.8753	20	2.921	2.9208	30	2.918	2.9175	20	2.702	2.7026	1	2.724	2.7241	100
112	2.648	2.6483	100	2.683	2.6827	100	2.833	2.8331	100	2.828	2.8292	100	2.840	2.8491	100	2.852	2.8521	100	2.689	2.6899	100	2.724	2.7232	
200	2.584	2.5847	36	2.651	2.6505	48	2.749	2.7501	96	2.759	2.7597	30	2.773	2.7741	40	2.784	2.7835	30	2.650	2.6508	100	2.660	2.6595	56
021	2.524	2.5234	12	2.558	2.5582	10	2.722	2.7230	4	2.705	2.7074	5	2.746	2.7465	10	2.744	2.7440	10	2.546	2.5481	40	2.572	2.5717	20
210		2.3278			2.3823		2.486	2.4839	6		2.4881			2.5059			2.5123			2.3800			2.3900	
121		2.2677			2.3039		2.440	2.4403	1		2.4307			2.4614			2.4613			2.2966			2.3153	
103		2.2612			2.2823		2.412	2.4125	10		2.4110			2.4207		2.425	2.4240	5		2.2972			2.3349	
211		2.2243			2.2729		2.375	2.3736	10	2.375	2.3769	2	2.393	2.3932	5	2.399	2.3989	5	2.272	2.2725	20	2.285	2.2850	12
022	2.184	2.1834	10	2.202	2.2090	6	2.349	2.3497	2		2.3387			2.3661			2.3650		2.206	2.2069	88	2.233	2.2329	20
202	2.132	2.1321	16		2.1726		2.254	2.2710	10		2.2753			2.2860			2.2919		2.178	2.1785	100	2.197	2.1969	40
113	2.083	2.0831	16	2.104	2.1043	10		2.2267			2.2235		2.237	2.2363	2	2.239	2.2385	5	2.114	2.1142	30	2.146	2.1461	15
122	2.011	2.0114	2	2.038	2.0390	5	2.161	2.1608	10	2.166	2.1534	5		2.1764		2.177	2.1767	5	2.037	2.0375	6	2.059	2.0588	4
004	1.886	1.8859	24	1.897	1.8966	64	2.013	2.0134	56	2.010	2.0102	5	2.017	2.0177	30	2.019	2.0195	15	1.912	1.9117	90	1.949	1.9490	30
220	1.860	1.8597	36	1.897	1.8974		1.994	1.9934	98	1.991	1.9910	25	2.012	2.0115	20	2.014	2.0139	25	1.892	1.8924	100	1.903	1.9030	58
023	1.834	1.8330	10		1.8512		1.968	1.9680	15	1.960	1.9605	10	1.978	1.9788	10	1.978	1.9787	10	1.854	1.8543	28	1.880	1.8803	15
221	1.806	1.8056	20	1.841	1.8407	14	1.935	1.9350	26	1.933	1.9327	10	1.952	1.9518	15	1.954	1.9541	10	1.837	1.8370	52	1.849	1.8487	28
123		1.7276			1.7477			1.8529			1.8475			1.8638			1.8644			1.7503		1.773	1.7728	2
213	1.708	1.7082	2		1.7340			1.8232			1.8235			1.8337			1.8369		1.740	1.7396	4	1.759	1.7591	2
130		1.6874			1.7142			1.8203			1.8108		1.838	1.8374	2	1.835	1.8362	5		1.7059		1.718	1.7187	2
114	1.683	1.6820	2	1.691		5	1.798	1.7972	10	1.794	1.7945	2		1.8036			1.8053		1.707	1.7064	52	1.735	1.7348	20
301		1.6799			1.7209		1.787	1.7877	16		1.7935			1.8027			1.8086			1.7218		1.727	1.7289	2
222		1.6680		1.691	1.6969	5	1.787	1.7865		1.786	1.7842	2		1.8002			1.8023		1.696	1.6961	30	1.710	1.7101	14
131	1.647	1.6467	46	1.672	1.6721	20	1.776	1.7755	30	1.766	1.7665	5	1.791	1.7915	20	1.791	1.7905	20	1.665	1.6650	80	1.678	1.6784	38
310	1.640	1.6403	2		1.6804		1.748	1.7478	2		1.7523			1.7632			1.7684		1.680	1.6797	30	1.686	1.6860	8
311	1.603	1.6029	2	1.641	1.6406	4	1.708	1.7080	6		1.7121			1.7225		1.727	1.7275	5	1.641	1.6406	14	1.648	1.6479	6
024	1.542	1.5419	24	1.555	1.5552	14	1.653	1.6526	40	1.647	1.6475	15	1.660	1.6601	20	1.661	1.6605	20	1.562	1.5607	0	1.585	1.5851	25
132		1.5403		1.562	1.5621	26	1.658	1.6587	40	1.651	1.6510	15	1.672	1.6722	20	1.672	1.6715	10	1.559	1.5579	60	1.572	1.5726	54
204	1.524	1.5235	22	1.542	1.5424	10	1.624	1.6245	46	1.625	1.6248	10	1.632	1.6318	30	1.635	1.6346	25	1.551	1.5506	60		1.5720	
312	1.504	1.5042	48	1.537	1.5364	35	1.603	1.6033	80	1.607	1.6064	30	1.616	1.6157	50	1.620	1.6199	35	1.538	1.5378	100	1.547	1.5474	54
223	1.495	1.4952	4	1.517	1.5177	7		1.6004			1.5983		1.611	1.6110	2	1.613	1.6127	5	1.520	1.5195	20	1.535	1.5353	10
133	1.401	1.4011	18	1.419	1.4189	7	1.507	1.5066	17	1.501	1.5004	10	1.517	1.5173	10	1.517	1.5170	5	1.418	1.4177	30	1.433	1.4335	16
115		1.3981			1.4088			1.4934			1.4911			1.4981			1.4995		1.418	1.4180			1.4428	
322		1.3527			1.3799			1.4455			1.4460		1.459	1.4571	2		1.4599			1.3794			1.3885	
040		1.3389			1.3587		1.446	1.4467	8	1.437	1.4376	2	1.459	1.4604			1.4588			1.3513			1.3621	
224		1.3242			1.3414		1.417	1.4165	28	1.415	1.4146	20	1.425	1.4245	25	1.426	1.4260	20		1.3449			1.3616	
041		1.3182			1.3374		1.425	1.4239	6	1.415	1.4152		1.437	1.4371	2	1.435	1.4355	5		1.3307			1.3417	

Pbnm is assumed to be the most probable space group on the basis of the similarity between $InCrO_3$ and the prototype of the orthorhombic perovskites—$GdFeO_3$.[11,12] Indium, rather than Cr, is assumed to be in the A site because of its larger size. Compositions of $6In_2O_3$–$4Cr_2O_3$ and $4In_2O_3$–$6Cr_2O_3$ resulted in a perovskite and excess In_2O_3 or Cr_2O_3, respectively, indicating that no extensive solid solution occurred on either side of the stoichiometric composition.

No reference to work on the In_2O_3–Rh_2O_3 system at ambient pressures could be found. Samples of the 1:1 stoichiometric mixture pressed at 1350° were dark gray, sintered pellets which gave a perovskite powder pattern. Once more In^{+3} was assumed to be in the A site.

Y_2O_3–In_2O_3.—Schneider, *et al.*,[3] reported complete solid solution of Y_2O_3 and In_2O_3 with the C rare earth oxide structure at ambient pressures. At the higher pressures used in this work, however, reactions of stoichiometric mixtures of Y_2O_3–In_2O_3 led to the formation of a perovskite phase and traces of an unidentified phase. A mixture of $6In_2O_3$–$4Y_2O_3$ at 1500° showed the perovskite and a trace of In_2O_3 II at the cold end; at the center was found the perovskite and an unidentified phase. An excess of Y_2O_3 in the ratio of 6:4, however, showed no trace of either the B or C modification of Y_2O_3 at the cold end, indicating the possibility of some solid solution. The center of the specimen was identical with the sample with excess In_2O_3.

R_2O_3–In_2O_3 where R = Gd, Dy, or Eu.—Schneider[4] reports that all three of these systems contain a 1:1 compound with pseudo-hexagonal symmetry. He also states that a metastable perovskite occurred in Eu_2O_3–In_2O_3 mixtures. Roth[5] has recently pointed out that these three 1:1 compounds are probably isostructural with $HoMnO_3$ ($P6_3cm$, a = 6.14, c = 11.4).[6] Furthermore Waintal, *et al.*,[6] have shown that hexagonal $GdMnO_3$ and $DyMnO_3$ transform to orthorhombic perovskites under high pressure (P = 45 kbars, T = 950°). At 65 kbars and 1450° all three R_2O_3–In_2O_3 mixtures form perovskites. The samples were dense, sintered pellets and no indication of melting was observed. The $EuInO_3$ perovskite had formed only at the cold end. The central portion contained a mixture of In_2O_3 II and $Eu(OH)_3$ indicating the presence of water in the starting materials. The d values, how-

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ever, are not those of Schneider's 1:1 solid solution phase.

Tl_2O_3–Fe_2O_3 and Tl_2O_3–Cr_2O_3.—No references were found on thallium–iron or thallium-chromium oxide systems. Reactions at 850° and 65 kbars produced gray, metallic-looking powders whose X-ray powder patterns indicated perovskite structures. Reaction at 850° and 3 kbars did not result in perovskite formation.

Discussion

In Figure 1 is shown the perovskite stability field with new perovskites, apparently only stable at high pressures, indicated by the solid circles. The remaining points in the plot were taken from several sources.[1,3,12–21] With the exception of effective radii derived in this paper as indicated below, the radii used are those of Ahrens.[22] Since no reliable compilation of trivalent ionic radii for 12-fold coordination exists, uncorrected 6-fold radii have been used for construction of the diagram. In general, perovskite formation at normal pressures can be predicted by consideration of the tolerance factor $t = (R_A + R_O)/\sqrt{2}(R_B + R_O)$, where R is the appropriate ionic radius. Empirically, perovskites are found to be stable in the range $1.0 \geqslant t \geqslant 0.78$.[23]

Strictly speaking, pressure should be considered as a third variable and a three-dimensional diagram should be constructed. However, for simplicity the presence of the new compounds is merely shown as an enlargement of the field. In another paper the effect of high pressure on the extension of the stability field for the corundum structure was demonstrated.[7] In the case of the corundum structure, the stability field is enlarged to include In_2O_3 and Tl_2O_3. At normal pressures, the sizes of In^{+3} and Tl^{+3} apparently do not permit a sufficiently close approach of the oxygen layers to permit close packing. At high pressures, the packing density of the oxygen layers is increased and the corundum structure forms. The primary cation coordination is not changed.

A second effect of pressure on the stability field can occur because of the high relative compressibility of the anion compared to the cation. This effectively increases the coordination of the cations. Since it is well known that structure type is determined to a large extent by the cation/anion radius ratio, it is only natural that stability fields are determined by the additional factor of the radius ratios of the cations.

Using the Ahrens radius for Tl^{+3}, $TlCrO_3$ and $TlFeO_3$ fit well into the middle of the field. This would imply that they could be synthesized at normal pressures. The inability to form $TlCrO_3$ and $TlFeO_3$ perovskite phases at 3 kbars suggests that the effective radius of Tl^{+3} is considerably smaller than the Ahrens value of 0.95 A and should probably be less than 0.85 A. The appearance of the $RGaO_3$ perovskites in the middle of the field can be ascribed to the preference of fourfold Ga^{+3} coordination;[12] pressure is required to stabilize the sixfold coordination.

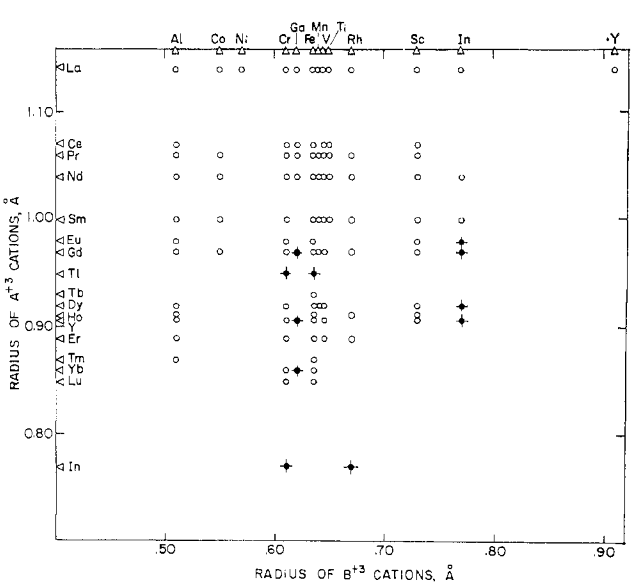

Figure 1.—Stability field of $A^{III}B^{III}O_3$ perovskites.

The three rare earth indium perovskites and $YInO_3$ all fall outside the boundary experimentally determined to be $t = 0.78$. Their stability at 65 kbars might be ascribed to the difference in compressibility between the rare earth or Y^{+3} and In^{+3} ions; pressure presumably would increase the ratio of r_A/r_B. $InCrO_3$ and $InRhO_3$ are believed to be the first compounds containing In^{+3} as the A^{+3} cation and provide two further examples of high-pressure transitions involving an increase of cation coordination. These perovskites also fall outside the phase boundary of the perovskite field. Since perovskites can be thought of as arising from close-packed AO_3 layers, this probably reflects the closer approach of the radii of In^{+3} and O^{2-} at high pressures.

The degree of distortion from the ideal perovskite structure increases as the tolerance factor, t, decreases from the ideal value of 1.0, *i.e.*, as the size of the A^{+3} ion decreases or the size of the B^{+3} ion increases. Thus, the new In perovskites should show greater distortion than other orthorhombic perovskites. Geller[16] used the difference $a' - b'$ and the deviation of the angle β from 90° for the monoclinic pseudo-cell to measure this distortion. Table III shows these values tabulated for the indates, the orthochromites, $InRhO_3$, and $TlFeO_3$. As expected, all of the indates show a large degree of distortion, generally increasing as the size of the A^{+3} ion decreases. The orthochromites show the same trend as the indates with the greatest degree of distor-

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TABLE III

COMPARISON OF DISTORTIONS IN RARE EARTH CHROMITES AND INDATES

	a, A	b, A	c, A	Unit cell vol., A^3	a′, A	b′, A	β, deg	a′ − b′, A
$YInO_3$	5.500	5.787	8.053	256.31	4.026	3.992	92.9	0.035
$DyInO_3$	5.519	5.751	8.041	255.22	4.020	3.985	92.4	0.035
$GdInO_3$	5.548	5.842	8.071	261.59	4.035	4.028	93.0	0.007
$EuInO_3$	5.567	5.835	8.078	262.40	4.039	4.032	92.7	0.007
$SmInO_3$[a]	5.589	5.886	8.082	265.9	4.041	4.068	93.0	−0.027
$NdInO_3$[a]	5.627	5.891	8.121	269.2	4.060	4.073	92.6	−0.013
$LaInO_3$[a]	5.723	5.914	8.207	277.72	4.103	4.115	91.9	−0.011
$InCrO_3$	5.170	5.355	7.543	208.83	3.722	3.772	92.0	−0.050
$YCrO_3$[b]	5.247	5.518	7.540	218.30	3.807	3.770	92.9	0.037
$TlCrO_3$	5.302	5.405	7.647	219.14	3.823	3.786	91.1	0.038
$GdCrO_3$[b]	5.312	5.514	7.611	222.9	3.828	3.806	92.1	0.022
$SmCrO_3$[b]	5.372	5.502	7.650	226.1	3.845	3.825	91.4	0.020
$NdCrO_3$[b]	5.412	5.494	7.695	228.8	3.856	3.848	90.9	0.008
$PrCrO_3$[b]	5.444	5.484	7.710	230.2	3.864	3.855	90.4	0.009
$LaCrO_3$[b]	5.477	5.514	7.755	234.2	3.886	3.878	90.4	0.008
$InRhO_3$	5.301	5.435	7.586	218.56	3.793	3.796	91.4	−0.003
$TlFeO_3$	5.319	5.448	7.796	225.91	3.898	3.807	91.3	0.091

[a] R. S. Roth, *J. Res. Natl. Bur. Std.*, **58A,** 75 (1957). [b] S. Geller, *Acta Cryst.*, **10,** 243 (1957).

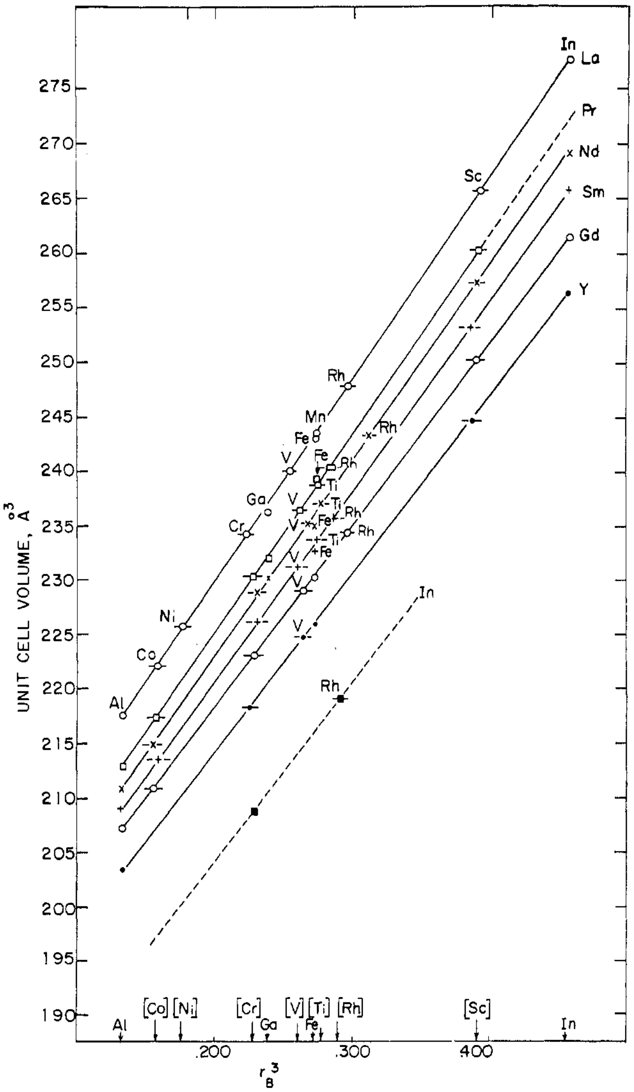

Figure 2.—Unit-cell volume *vs.* r_B^3 for $A^{III}B^{III}O_3$ perovskites.

tion in $InCrO_3$. There are several anomalies however. (1) The values of $a' - b'$ for $GdInO_3$ and $EuInO_3$ are very low; this may, however, be part of a trend since these values for the Sm, Nd, and La indates are all negative. (2) Geller[16] noted that $a' - b'$ was positive in all cases except that of $YScO_3$. We find that negative values appear in $InCrO_3$ and $InRhO_3$ and in the indates studied by Schneider, *et al.*[3] This may be characteristic of perovskites containing both small A^{+3} and B^{+3} ions, although $EuInO_3$ and $DyInO_3$ do not fall into this category. (3) Although the unit-cell volumes correspond to the series arranged according to Ahrens radii, the *b* axes are smaller and the *c* axes are larger than would be expected.

A linear relationship sometimes exists between unit-cell dimensions of a particular structure and ionic radii. Roth and Schneider[9] used this relationship to determine effective cation radii in compounds with the C rare earth oxide structure. Radii significantly different from those of Ahrens[22] were found for Mn^{+3}, Sc^{+3}, and In^{+3}. A similar plot for the perovskite structure of unit-cell volume *vs.* r_B^3 has been carried out (Figure 2). Since the B site in $YFeO_3$ and $GdFeO_3$ has been shown by Coppens and Eibschütz[11] to be only slightly distorted, the sixfold radii of Ahrens should be reliable in the absence of major covalency effects. It was assumed that the radii of Al^{+3}, Fe^{+3}, Ga^{+3}, and In^{+3} were relatively free of deviations from their ionic

TABLE IV

EFFECTIVE COORDINATION NUMBER 6 RADII OF B^{+3} IONS

	Ahrens[22]	From $LnBO_3$ perovskites	From R_2O_3 corundum	Other sources
Sc	0.81	0.73	. . .	0.73,[b,c] 0.68[d]
Ti	0.76	0.65	0.66	0.66[a]
V	0.74	0.64	0.62	0.63[a]
Cr	0.63	0.61	0.61	0.61[a,c]
Mn	0.66	0.64	. . .	0.56[d]
Fe	0.64	0.64	0.64	0.64[a]
Co	0.63	0.54	. . .	p.55[e]
Ni	. . .	0.56		0.57[e]
Rh	0.68	0.66	0.65	

[a] R. E. Newnham and Y. M. de Haan, *Z. Krist.*, **117,** 235 (1962). [b] H. Muller-Buschbaum and H. Schnering, *Z. Anorg. Allgem. Chem.*, **336,** 295 (1965). [c] D. W. J. Cruickshank, H. Lynton, and G. A. Barclay, *Acta Cryst.*, **15,** 491 (1962). [d] R. S. Roth and S. J. Schneider, *J. Res. Natl. Bur. Std.*, **64A,** 309 (1960). [e] G. Blasse, *J. Inorg. Nucl. Chem.*, **27,** 748 (1965).

values arising from covalency of d character. Indeed, a linear relationship was found for these ions. The remaining B^{+3} ions have unfilled d orbitals and might be expected to have smaller radii. The radii derived for Co^{+3}, Ni^{+3}, Cr^{+3}, V^{+3}, Mn^{+3}, Rh^{+3}, and Sc^{+3} are listed in Table IV along with those of Ahrens. Since a significant amount of covalency in the B–O bonds exists, these radii should be called effective rather than ionic radii. As expected, all of the effective radii are smaller than those listed by Ahrens. The radii of Co^{+3} (low spin) and Ni^{+3} agree well with those recently quoted by Blasse.[24] The sixfold radius of Sc^{+3} is in excellent agreement with the value determined by Müller-Buschbaum and Schnering[25] in $CaSc_2O_4$ and by Cruickshank[26] in $Sc_2Si_2O_7$ (0.73).

A similar plot for the A^{+3} ions resulted in a rapid increase in slope as r_A decreases, thus preventing the determination of the 12-fold radii. Dalziel[27] and Schneider, *et al.*,[3] found the same effect. This increase may be caused by the deviation from 12-fold coordination. Coppens and Eibschütz[11] showed a very irregular coordination of the Gd^{+3} and Y^{+3} ions in $GdFeO_3$ and $YFeO_3$.

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[24] G. Blasse, *J. Inorg. Nucl. Chem.*, **27**, 748 (1965).

[25] H. Müller-Buschbaum and H. Schnering, *Z. Anorg. Allgem. Chem.*, **336**, 295 (1965).

[26] D. W. J. Cruickshank, H. Lynton, and G. A. Barclay, *Acta Cryst.*, **15**, 491 (1962).

[27] J. A. W. Dalziel, *J. Chem. Soc.*, 1993 (1959).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
INDIANA UNIVERSITY, BLOOMINGTON, INDIANA

Solubility of Copper(I) Bromide in Sodium Bromide Media

BY DENNIS G. PETERS AND RANDALL L. CALDWELL

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Pure, solid copper(I) bromide, CuBr, has been prepared by means of controlled-potential coulometry, and a study was performed of its solubility in aqueous sodium bromide media ranging in concentration from approximately 0.05 to 1.5 *F*. Within this range of bromide concentrations, the predominant species of copper(I) are $CuBr_2^-$ and $CuBr_3^{2-}$. At an ionic strength of 2.0 and a temperature of 25°, the concentration equilibrium constants for the reactions $CuBr(s) + Br^- = CuBr_2^-$ and $CuBr_2^- + Br^- = CuBr_3^{2-}$ are $K_1K_2K_{s0} = (3.8 \pm 0.4) \times 10^{-3}$ and $K_3 = 10.2 \pm 0.9$, respectively. Potentiometric measurements have demonstrated that dimeric or higher polymeric forms of copper(I) are not present to any significant extent in the solutions investigated. In a solution consisting of 1 *F* sodium bromide and 1 *F* sodium nitrate, the formal potential ($E°'$) for the copper(I)–copper(0) couple is close to −0.111 v *vs.* sce or +0.130 v *vs.* nhe.

During a recent chronopotentiometric investigation of the reduction of copper(I) to copper metal in potassium bromide medium,[1] it was discovered that the only study of the solubility of copper(I) bromide (CuBr) in bromide solutions was published by Bodländer and Storbeck[2] over 60 years ago. However, the solubility data reported by these workers were obtained at inconstant ionic strength under somewhat unfavorable conditions for which, owing to atmospheric oxidation as well as disproportionation of copper(I), a mixture of elemental copper, copper(I), and copper(II) existed. Furthermore, aside from a single measurement of the solubility of CuBr in 0.5 *F* potassium bromide solution, the bromide ion concentrations employed by Bodländer and Storbeck were comparatively low and confined to a relatively narrow range of values. Only a partial description of the solubility behavior of CuBr in bromide solutions is obtainable from this previous work, and heretofore no quantitative information has been available concerning the identities and stabilities of the soluble copper(I) species which exist at high bromide concentrations.

The goals of the present investigation were the accurate measurement of the solubility of CuBr in relatively concentrated sodium bromide media, the identification of the species of copper(I) present in such solutions, and the evaluation of the equilibrium constants for the pertinent chemical reactions. In the work discussed below, controlled-potential coulometry has been employed as a technique both for the *in situ* preparation of pure solid CuBr and for the determination and study of the solubility of CuBr in sodium bromide solutions equilibrated with this solid.

Experimental Section

Reagents.—Stock solutions containing known initial concentrations of copper(II) bromide and sodium bromide, from which copper(I) was electrochemically generated, were prepared by weight from reagent grade chemicals. Sufficient sodium nitrate was included in each stock solution to provide an ionic strength of 2.0.

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[1] D. G. Peters and L. A. Franklin, *J. Electroanal. Chem.*, **9**, 385 (1965).

[2] G. Bodländer and O. Storbeck, *Z. Anorg. Allgem. Chem.*, **31**, 458 (1902).