

## X-Ray Study of the $\text{PbCl}_{2-x}\text{I}_x$ and $\text{PbBr}_{2-x}\text{I}_x$ Systems

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Compounds from the systems  $\text{PbCl}_2/\text{PbI}_2$  and  $\text{PbBr}_2/\text{PbI}_2$  were examined by x-ray diffraction. The lattice parameters of these phases are presented and the refined crystal structures of the intermediate compounds  $\text{PbClI}$  and  $\text{PbBr}_{1.2}\text{I}_{0.8}$  are reported. Both structures have *Pbnm* symmetry, are isostructural with  $\text{PbCl}_2$ , and have the different halogens ordered in the two Cl sites. Phase studies showed that  $\text{PbCl}_2$  and  $\text{PbClI}$  have practically no mutual solubility, while  $\text{PbBr}_2$  and  $\text{PbBr}_{1.2}\text{I}_{0.8}$  have appreciable solubility ranges, particularly for  $\text{PbBr}_2$ -rich concentrations. At least 17% Br is present in the I site of  $\text{PbBr}_{1.2}\text{I}_{0.8}$ . Nevertheless, it is a distinct phase with miscibility gaps toward  $\text{PbBr}_2$  and  $\text{PbI}_2$ . This behavior is explained by the size disparity between the halogens. The intermediate phases do not form solid solutions with hexagonal  $\text{PbI}_2$ .

### Introduction

The optical properties of  $\text{PbCl}_2$  (1),  $\text{PbBr}_2$  (2), and  $\text{PbI}_2$  (3) have been described, but little structural information is available for mixed phases of the lead halides. Hirsch (4) investigated the  $\text{PbBr}_2/\text{PbI}_2$  system and described  $\text{Pb}_5\text{Br}_6\text{I}_4$  and  $\text{Pb}_5\text{Br}_3\text{I}_2$ . Heidrich *et al.* (5) also did optical and structural studies on the  $\text{PbI}_{2-x}\text{Br}_{2(1-x)}$  system. No study appears to exist for the  $\text{PbCl}_2/\text{PbI}_2$  system.

The structures of  $\text{PbCl}_2$  and  $\text{PbBr}_2$  (6) are known, and Mitchell (7) described the polytypism of  $\text{PbI}_2$ . The mixed halide  $\text{PbFCl}$  (8), which has a structure type *P4/nmm* exhibited by other compounds (9-11), has also been investigated.

This paper describes the investigation of the phase diagrams of the  $\text{PbCl}_{2-x}\text{I}_x$  and  $\text{PbBr}_{2-x}\text{I}_x$  systems and also presents structural evidence to support the conclusion that  $\text{PbClI}$  and  $\text{PbBr}_{1.2}\text{I}_{0.8}$  are two distinct

compounds isotypical with  $\text{PbCl}_2$ . The existence of  $\text{Pb}_5\text{Br}_3\text{I}_2$  could not be substantiated.

### Experimental

#### Synthesis

All compounds were prepared by the interaction of constituent components via melting in evacuated quartz ampoules. Single crystals needed for the structure study were easily obtained by slow cooling (2 to 5 deg/hr) the compositions from above the melting points. High-purity  $\text{PbCl}_2$  and  $\text{PbBr}_2$  (Fisher certified) were used.  $\text{PbI}_2$  was prepared by precipitation from a  $\text{Pb}(\text{NO}_3)_2$  (Mallinckrodt) solution with KI (Fisher certified).

#### Powder Diffraction

Powder patterns were obtained with a Guinier-Hägg focusing camera ( $r = 40$  mm). The radiation was monochromatic

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$\text{CuK}\alpha_1$  ( $\lambda = 1.5405 \text{ \AA}$ ) and Si ( $a = 5.4305 \text{ \AA}$ ) was an internal standard. Line positions on the films were determined with a David Mann film reader; the intensities were determined by oscilloscopic comparison of the film density with the strongest line of the pattern. The lattice parameters were refined by a least-squares procedure. The figures of merit ( $12a$ ,  $12b$ ) for  $\text{PbClI}$  were  $F_{30} = 59$  (0.010, 50) and  $M_{20} = 52$ . For  $\text{PbBr}_{1.2}\text{I}_{0.8}$ , the values were  $F_{40} = 17$  (0.036, 64) and  $M_{20} = 12$ . The higher  $|\Delta 2\theta|$  (0.036°) for the powder pattern of  $\text{PbBr}_{1.2}\text{I}_{0.8}$  can be attributed to a sample which contained material with a small range in composition due to the mixing of Br and I at one halogen site.

#### Single-Crystal Data and Structure Refinements

Precession patterns of single crystals were obtained with Mo radiation. Intensity data were collected with a Syntex P3 diffractometer (graphite monochromator,  $\text{MoK}\alpha$  radiation  $\lambda = 0.7107 \text{ \AA}$ ) by using an  $\omega$ -scan technique. In both cases, the nonextinction conditions, ( $h0l$ ):  $h + l = 2n$  and ( $0kl$ ):  $k = 2n$ , and second-harmonic generation tests (13) confirmed the centric space group  $Pbnm$  ( $cab$  form of  $Pnma$  (62)).

**PbClI.** A total of 729 reflections were recorded for  $2\theta \leq 65^\circ$  in one quadrant; there were 486 reflections with  $F_o^2 > 2\sigma(F_o^2)$ . The crystal had a rectangular shape ( $0.092 \times 0.033 \times 0.073 \text{ mm}$ ), and the variation of the normalized transmission factor ranged from 36 to 100%. Empirical corrections for absorption were obtained from  $\Psi$ -scan data for four reflections at various  $2\theta$  angles. After absorption and Lorentz-polarization corrections were applied, the data were refined with computer programs (locally modified) supplied by the Enraf-Nonius Corp. (14). The final  $R$ -factors were  $R = 0.063$  and  $R_w = 0.082$ . For  $R_w$ , the data were weighted according to  $1/\sigma^2(F_o)$  with an "ignorance factor" of 0.02 (15). At-

tempts to refine the multiplicity factors failed to detect any deviation from complete occupancy at all sites. Thus, Cl and I are completely ordered.

**PbBr<sub>1.2</sub>I<sub>0.8</sub>.** Intensity data were collected in two quadrants for  $2\theta \leq 55^\circ$ . The crystal had the shape of a thin plate,  $0.150 \times 0.075 \times 0.030 \text{ mm}$ , and the variation of the normalized transmission factors ranged from 26 to 100%. Empirical absorption corrections were applied by using  $\Psi$ -scan data for three reflections at various  $2\theta$  angles. After absorption and Lorentz-polarization corrections were made, the data were averaged to yield 659 independent reflections (501 reflections with  $F_o^2 > 2\sigma(F_o^2)$ ). The structure was refined to  $R = 0.035$  and  $R_w = 0.035$ , with 21 variables including the multiplicity factor for I. The value of the thermal parameter for the I atoms was found to be unusually high and the peak in the Fourier map was significantly lower than expected for I. The refined multiplicity factor for I indicated that the electron density at this site was equivalent to 94% of an I atom. This value indicated 17% of the sites were occupied by Br instead of I. The crystallographic composition of  $\text{PbBr}(\text{Br}_{0.17}\text{I}_{0.83})$  is in good agreement with the solid-state preparation of  $\text{PbBr}_{1.2}\text{I}_{0.8}$  and the assignment of  $\text{Pb}_5\text{Br}_6\text{I}_4$  by Hirsch (4).

#### Results and Discussion

**PbCl<sub>2</sub>/PbI<sub>2</sub> phase study.** Contrary to Mitchell (6) who found the  $P3m$  2H type of  $\text{PbI}_2$  to be the most common polytype, we found the  $P6_3mc$  4H type to be the most prevalent. This discrepancy is probably due to the fact that Mitchell (6) used a silica-gel method, whereas most of our samples were prepared from melts. Other samples prepared by precipitation or sublimation also crystallized in the 4H type. High-pressure treatment (59 kbar, 200°C, 1hr) of 4H-type material did not convert it into the 2H type. We, therefore, conclude that the 4H type is

TABLE I  
LATTICE PARAMETERS AND CELL VOLUMES FOR THE  $\text{PbCl}_{2-x}\text{I}_x$  COMPOUNDS

Composition	$x$	$a$ (Å)	$b$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	Space group	Comments
$\text{PbCl}_2$	0	7.605	9.027	4.520	310.3	$Pnam^a$	single phase
$\text{PbCl}_{1.98}\text{I}_{0.02}$	0.02	7.625	9.048	4.537	313.0	$Pnam$	single phase
$\text{PbCl}_{1.95}\text{I}_{0.05}$	0.05	7.625	9.050	4.538	313.2	—	two phase
$\text{PbCl}_{1.02}\text{I}_{0.98}$	0.98	8.179	9.599	4.577	359.3	—	two phase
$\text{PbClI}$	1.0	8.187	9.654	4.593	363.0	$Pnam$	single phase
$\text{PbCl}_{0.98}\text{I}_{1.02}$	1.02	8.203	9.667	4.590	363.9	—	two phase
$\text{PbCl}_{0.05}\text{I}_{1.95}$	1.95	4.530	—	13.909	247.2	—	two phase
$\text{PbCl}_{0.02}\text{I}_{1.98}$	1.98	4.523	—	13.903	246.3	$P6_3mc$	single phase
$\text{PbI}_2$	2.00	4.556	—	13.973	251.2	$P6_3mc$	single phase

<sup>a</sup> Space group  $Pnam$  is the  $acb$  form of  $Pnma(62)$ .

thermodynamically the most stable polytype. The structure types and lattice constants for various compositions are summarized in Table I. There is very little solid solubility near the end members  $\text{PbCl}_2$  and  $\text{PbI}_2$ . At the 1:1 mole ratio, a distinct  $\text{PbClI}$  composition can be observed. The phase behavior and the constancy of lattice parameters show that this phase has no appreciable solubility in either  $\text{PbCl}_2$  or  $\text{PbI}_2$ , even though it is isostructural with  $\text{PbCl}_2$ . This is due to the size disparity between the  $\text{Cl}^-$  and  $\text{I}^-$  ions.

*PbBr<sub>2</sub>/PbI<sub>2</sub> phase study.* The phase behavior of this system is similar to its chlo-

ride counterpart described above. Table II lists the structure types and the lattice constants for various compositions. The existence of a distinct phase near the 1:1 mole ratio is also quite apparent. The composition of this phase is approximately  $\text{PbBr}_{1.2}\text{I}_{0.8}$ , rather than  $\text{PbBrI}$ , and could be the  $\text{Pb}_3\text{Br}_6\text{I}_4$  phase reported by Hirsch (4). However, no evidence for the existence of  $\text{Pb}_5\text{Br}_8\text{I}_2$  was found. This is undoubtedly due to the fact that the present study used high-temperature preparative techniques, while Hirsch (4) prepared  $\text{Pb}_5\text{Br}_8\text{I}_2$  from aqueous solution and found it to be metastable.

TABLE II  
LATTICE PARAMETERS AND CELL VOLUMES FOR THE  $\text{PbBr}_{2-x}\text{I}_x$  COMPOUNDS

Composition	$x$	$a$ (Å)	$b$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	Space group	Comment
$\text{PbBr}_2$	0	8.038	9.518	4.717	360.9	$Pnam$	single phase
$\text{PbBr}_{1.9}\text{I}_{0.1}$	0.1	8.096	9.568	4.744	367.5	$Pnam$	single phase
$\text{PbBr}_{1.8}\text{I}_{0.2}$	0.2	8.128	9.605	4.755	371.0	$Pnam$	single phase
$\text{PbBr}_{1.7}\text{I}_{0.3}$	0.3	8.157	9.637	4.762	374.0	$Pnam$	single phase
$\text{PbBr}_{1.6}\text{I}_{0.4}$	0.4	8.160	9.636	4.768	374.9	—	two phase
$\text{PbBr}_{1.5}\text{I}_{0.7}$	0.7	8.622	10.429	4.416	397.0	—	two phase
$\text{PbBr}_{1.2}\text{I}_{0.8}$	0.8	8.627	10.446	4.420	398.3	$Pnam$	single phase
$\text{PbBr}_{1.0}\text{I}_{1.0}$	1.0	8.642	10.449	4.432	400.3	—	two phase
$\text{PbBr}_{0.2}\text{I}_{1.8}$	1.8	4.499	—	13.840	242.6	—	two phase
$\text{PbBr}_{0.1}\text{I}_{1.9}$	1.9	4.497	—	13.832	242.2	$P6_3mc$	single phase
$\text{PbI}_2$	2.0	4.556	—	13.973	251.2	$P6_3mc$	single phase

TABLE III  
POSITIONAL AND THERMAL PARAMETERS OF  $\text{PbX}_1\text{X}_2^a$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$\beta(1,1)$	$\beta(2,2)$	$\beta(3,3)$	$\beta(1,2)$	$\beta(1,3)$	$\beta(2,3)$
PbClI: $a = 9.669(10) \text{ \AA}$ , $b = 8.200(3) \text{ \AA}$ , $c = 4.605(2) \text{ \AA}$ , $V = 365.1(4) \text{ \AA}^3$ ; $R$ -factor = 0.063									
Pb	0.1240(2)	0.2082(2)	0.25	0.0093(3)	0.0114(2)	0.0355(8)	-0.0036(4)	0	0
Cl	0.0596(9)	0.859(1)	0.25	0.0044(7)	0.005(1)	0.031(4)	0.000(2)	0	0
I	0.8305(2)	0.4703(3)	0.25	0.0039(2)	0.0054(2)	0.0253(9)	0.0002(4)	0	0
PbBrI: $a = 10.452(1) \text{ \AA}$ , $b = 8.639(1) \text{ \AA}$ , $c = 4.427(1) \text{ \AA}$ , $V = 399.7(2) \text{ \AA}^3$ ; $R$ -factor = 0.035									
Pb	0.15804(8)	0.16220(9)	0.25	0.00699(7)	0.00893(8)	0.0321(3)	0.0012(2)	0	0
Br	0.0534(1)	0.8414(2)	0.25	0.0036(1)	0.0051(2)	0.0254(7)	-0.0001(3)	0	0
I <sup>b</sup>	0.8286(1)	0.5014(1)	0.25	0.0061(1)	0.0061(1)	0.0213(4)	-0.0013(2)	0	0
PbCl <sub>2</sub> : $a = 9.027 \text{ \AA}$ , $b = 7.605 \text{ \AA}$ , $c = 4.520 \text{ \AA}$ , $V = 310.3 \text{ \AA}^3$									
Pb	0.0956	0.2617	0.25						
Cl(1)	0.0742	0.8610	0.25						
Cl(2)	0.837	0.4768	0.25						

<sup>a</sup> All atoms on the mirror planes  $x$ ,  $y$ ,  $\frac{1}{2}$  of  $Pbnm$ .

<sup>b</sup> Multiplicity factor = 0.472(1), equivalent to 0.418 I + 0.082 Br.

The completely ordered phase PbBrI does not exist. The disordering of Br and I appears to occur only at the I site, as shown by structure data for the intermediate phase.

Table III lists the positional and thermal parameters for PbClI, PbBr( $\text{Br}_{0.17}\text{I}_{0.83}$ ), and PbCl<sub>2</sub> (16). The indexed powder patterns are reported in Tables IV and V. The struc-

tures of these compounds projected along the short  $c$  axes are shown in Figs. 1, 2, and 3. The interatomic distances are listed in Table VI.

#### Structures of PbClI and PbBr( $\text{Br}_{0.17}\text{I}_{0.83}$ )

Crystallographically, these two mixed dihalides as well as PbBr<sub>2</sub> have the PbCl<sub>2</sub>-type structure. PbCl<sub>2</sub> has the centric  $Pbnm$

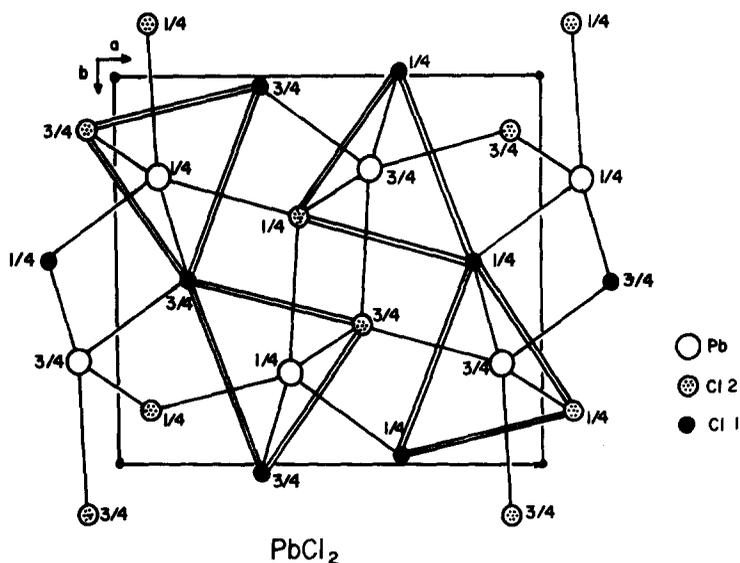


FIG. 1.  $c$ -Axis projection of the  $\text{PbCl}_2$  structure.

TABLE IV

X-RAY POWDER DIFFRACTION DATA FOR  $\text{PbBr}_{1.2}\text{I}_{0.8}$ 

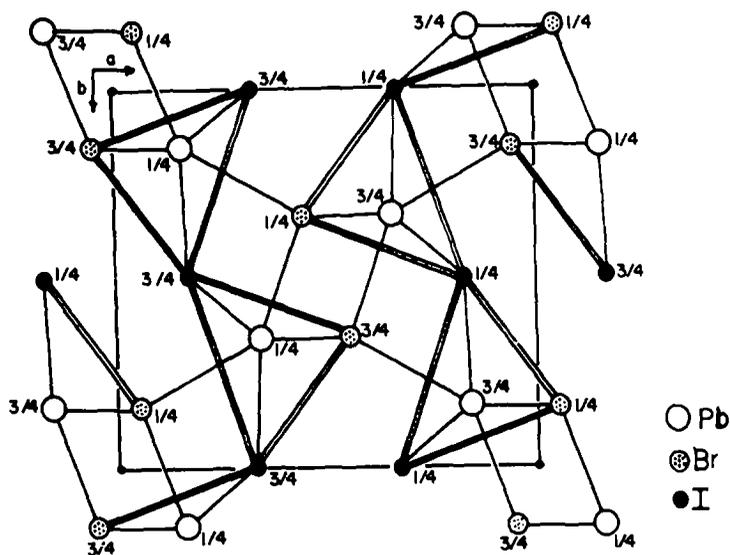
$2\theta$	$I/I_1$	$hkl$	$d_{\text{obs}}$	$d_{\text{calc}}$
13.473	30	110	6.5661	6.6517
17.107	40	020	5.1788	5.2228
19.980	70	120	4.4402	4.4678
21.915	55	011	4.0522	4.0702
22.381	60	210	3.9688	3.9869
24.215	10	111	3.6723	3.6811
26.841	10	220	3.3187	3.3258
27.665	5	130	3.2217	3.2288
28.948	40	201	3.0817	2.0869
30.204	100	211	2.9564	2.9603
32.296	90	310	2.7695	2.7725
32.746	40	031	2.7325	2.3750
33.724	65	221	2.6554	2.6574
34.385	100	131	2.6059	2.6072
		040		2.6114
35.925	60	140	2.4976	2.4994
40.690	95	330	2.2155	2.2172
40.780	100	002	2.2108	2.2098
41.216	60	321	2.1884	2.1885
41.474	60	141	2.1754	2.1756
42.778	10	410	2.1120	2.1122
44.483	10	022	2.0349	2.0351
		150		2.0304
45.454	35	241	1.9937	1.9937
		420		1.9935
45.745	25	331	1.9817	1.9818
		122		1.9807
		340	1.9332	1.9332
46.960	25	212		1.9327
		401		1.9383
47.664	50	411	1.9063	1.9057
48.367	35	250	1.8802	1.8802
49.404	5	151	1.8432	1.8450
		222		1.8405
50.125	10	421	1.8183	1.8172
		132		1.8236
51.554	2	341	1.7712	1.7712
52.510	25	060	1.7412	1.7409
52.891	60	251	1.7295	1.7302
		312		1.7280
		160	1.7074	1.7065
53.631	5	232		1.7124
		510		1.7023
		350	1.6914	1.6902
54.181	10	431		1.6935
54.307	15	042	1.6878	1.6864
55.443	30	142	1.6558	1.6555
		322		1.6612
58.943	40	332	1.5656	1.5652
59.310	10	441	1.5567	1.5564
60.167	10	521	1.5366	1.5362
60.617	5	412	1.5263	1.5269
61.046	20	261	1.5166	1.5164

TABLE V

X-RAY POWDER DIFFRACTION DATA FOR  $\text{PbClI}$ 

$2\theta$	$I/I_1$	$hkl$	$d_{\text{obs}}$	$d_{\text{calc}}$
18.340	5	020	4.8333	4.8268
21.355	80	120	4.1572	4.1580
		011		4.1476
21.694	10	200	4.0930	4.0935
23.584	40	210	3.7691	3.7687
24.031	90	111	3.7000	3.6999
28.933	100	121	3.0833	3.0825
29.791	20	130	2.9964	2.9948
30.653	95	211	2.9141	2.9135
33.992	60	031	2.6351	2.6355
34.095	50	310	2.6274	2.6261
35.765	60	131	2.5084	2.5087
37.221	30	040	2.4136	2.4134
37.836	40	320	2.3758	2.3756
39.174	70	002	2.2976	2.2966
39.474	15	311	2.2809	2.2798
40.679	25	231	2.2160	2.2159
42.808	5	321	2.1106	2.1100
43.466	25	330	2.0802	2.0813
		240		2.0790
43.742	10	141	2.0677	2.0672
44.211	5	400	2.0468	2.0468
45.055	35	122	2.0104	2.0103
46.247	10	212	1.9614	1.9611
48.011	5	241	1.8933	1.8940
		331		1.8958
48.666	20	401	1.8694	1.8695
49.225	5	222	1.8494	1.8500
49.998	10	132	1.8226	1.8224
52.486	10	421	1.7420	1.7433
		151		1.7392
52.926	20	312	1.7285	1.7288
54.494	10	430		1.7270
55.168	25	341	1.6824	1.6822
55.615	30	042	1.6634	1.6637
56.321	15	322	1.6511	1.6512
		251	1.6321	1.6322
58.398	5	142		1.6304
		160	1.5789	1.5787
		350		1.5761
59.942	20	332	1.5419	1.5422
		242		1.5413
60.576	5	402	1.5272	1.5280

(62) symmetry, and all the atoms lie on the mirror planes perpendicular to the short  $c$  axis at  $z = \pm \frac{1}{4}$ . Both  $\text{Cl}^-$  ions have four  $\text{Pb}^{+2}$  ions as their nearest neighbors, and the  $\text{Cl}(2)-\text{Cl}(2)$  separation across the center of symmetry is 5.41 Å, slightly larger than the 5.17 Å noted for  $\text{Cl}(1)-\text{Cl}(1)$ . The  $\text{Pb}^{+2}$

FIG. 2. *c*-Axis projection of the  $\text{PbCl}_2$  structure.

ion is surrounded by nine  $\text{Cl}^-$  ions in a rather distorted, tricapped trigonal prismatic coordination. Six of the nine Pb–Cl distances are relatively short and the rest are very much longer. All the long Pb–Cl bonds cluster on the same side showing the effect of the lone-pair electrons of  $\text{Pb}^{+2}$ .

From Table III, it is apparent that the halogen atom framework for the three halides is very similar and exhibits minimal shifts. This is also true for  $\text{PbBr}_2$  (16). Thus, in mixed halides, the larger  $\text{I}^-$  ions will preferentially enter the X(2) sites for which the X(2)–X(2) distances are larger.

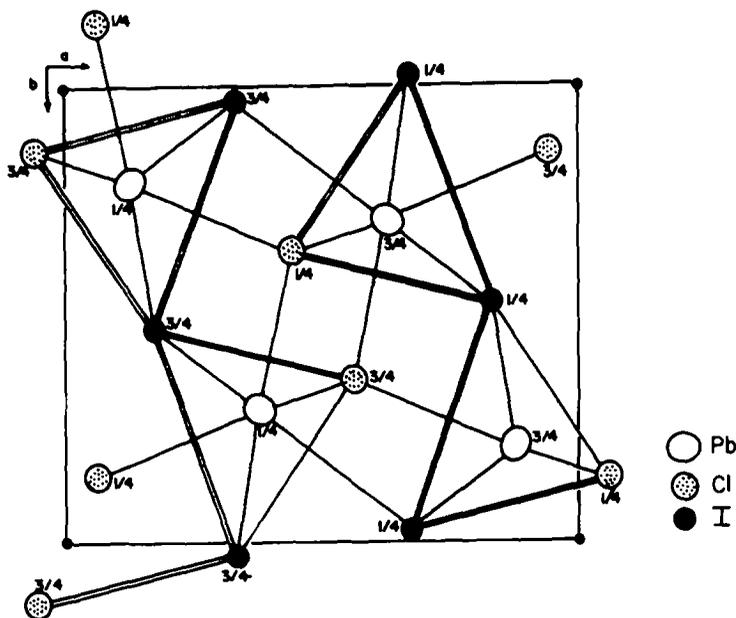
FIG. 3. *c*-Axis projection of the  $\text{PbBr}$  ( $\text{Br}_{0.17}\text{I}_{0.83}$ ) structure.

TABLE VI  
INTERATOMIC DISTANCE OF MIXED LEAD HALIDES  
IN Å

	PbCl <sub>2</sub>		PbBr <sub>1.17</sub> I <sub>0.83</sub>
Pb-Cl	2.931(3) × 1	Pb-Br	2.980(2) × 1
	2.960(2) × 2		3.128(1) × 2
	3.330(4) × 1		3.391(2) × 1
Pb-I	3.381(1) × 2	Pb-I	3.175(1) × 2
	3.356(1) × 1		3.656(1) × 2
	3.527(1) × 2		

The substitution of I for Cl(2) leads to an expansion of the lattice in the *a* and *b* directions and a significant shift of Pb<sup>2+</sup> away from the X(2)-X(2) pair to maintain proper Pb-Cl distances. The disparity of the two halide sites is much greater in PbCl<sub>2</sub> so that the smaller Cl<sup>-</sup> ion, with lower polarizability, is stable in the X(2) sites. Also, the X(1) site cannot accommodate the larger I<sup>-</sup> ion. Thus, there is complete ordering of Cl and I in the PbCl<sub>2</sub> structure with little solubility on either side of this composition.

Similar structural changes are also observed in PbBr(Br<sub>0.17</sub>I<sub>0.83</sub>). The shift of the Pb<sup>2+</sup> ion has no effective contact with the capping I<sup>-</sup> ion, which is 4.5 Å away. The Pb<sup>2+</sup> ion is, therefore, only 8-coordinated. The shift also leads to a pair of very short Pb-I bonds. This short Pb-I distance, resulting from the inclusion of 17% Br<sup>-</sup> ions in these sites, indicates the softness of the I<sup>-</sup> ion due to its high polarizability. Mixing of some Br<sup>-</sup> ions with I<sup>-</sup> ions at the X(2) sites is possible since the size difference for the halides is much smaller than in the case of PbCl<sub>2</sub>. However, I<sup>-</sup> ions do not occupy X(1) sites and the two halide sites remain strictly ordered. The similarity between the Br<sup>-</sup> and I<sup>-</sup> ions does allow some solubility of PbI<sub>2</sub> in PbBr<sub>2</sub>. From the powder data, it appears that the solubility limit is about 15-20%, and the variation of the lattice parameters indicates that I<sup>-</sup> can enter either Br(1) or Br(2) sites. A solubility range apparently exists around PbBr(Br<sub>0.17</sub>I<sub>0.83</sub>), as evi-

denced from the small variation of lattice parameters. However, the solubility range is very narrow, probably less than 5%.

One interesting aspect of these dihalide systems is the variation of the *c* dimension of the unit cells. While the *a* and *b* dimensions increase monotonically with the increase in the effective sizes of the halide ion, the *c* dimension increases in the region of PbX<sub>2</sub> and then decreases abruptly in the mixed halides. Since all atoms lie in the mirror planes perpendicular to the *c* axis, the shortening of the *c* axis brings the layers closer together. In this manner, the proper Pb-Cl and Pb-Br distances are maintained. Atoms which spread out within the layers cause the cell to expand. In PbBr(Br<sub>0.17</sub>I<sub>0.83</sub>), the *c* dimension is 4.427 Å, which is very close to the van der Waals diameter of 4.30 Å for iodine. Any further expansion of *a* and *b* by increasing the iodine content without a drastic structural change would bring the I<sup>-</sup> ions too close together. Such a situation develops before the 1:1 composition PbBrI is reached and, therefore, this composition does not exist.

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