Solid-state Properties of Materials of the Type Cs_4MX_6 (where M = Sn or Pb and X = Cl or Br) ‡

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Two new compounds Cs_4SnBr_6 and Cs_4SnCl_6 have been prepared and the $CsBr$–$SnBr_2$ phase diagram is described. Phases of the type $Cs_4Sn_{1-n}Pb_nBr_{6-x}Cl_x$ (where n = 0—1, x = 0—6) have been examined by X-ray diffraction, electrical conductivity, Mössbauer spectral, and optical reflectance techniques. The electrical conductivity and optical properties of the phases are explained in terms of the population of solid-state bands by the non-bonding electron pairs of the Group 4 atoms. The structures of all the phases are related to that of Cs_4PbCl_6 which has been redetermined.

We have previously reported the existence of the compounds $CsSnBr_3$ and $CsSn_2Br_5$ and described the band structures in $CsSnBr_3$ and related materials.[1] We have also investigated the structural, electronic, and optical properties of phases from the systems $CsSn_xPb_{1-x}Br_{3-y}Cl_y$ [2] and $CsSn_2Br_{5-y}Cl_y$.[3] A close relationship was found between the properties of the tin-containing phases and the analogous lead compounds. A differential thermal analysis (d.t.a.) study [4] of the system $CsBr$–$PbBr_2$ has confirmed the existence of the phases $CsPbBr_3$ and Cs_4PbBr_6 that were first described by Møller.[5,6] We now report on a detailed investigation of the $CsBr$–$SnBr_2$ system. We show the existence of a new, distinct compound Cs_4SnBr_6 and describe the solid-state properties of this compound and of related materials. The only previous study of the $CsBr$–$SnBr_2$ system covered only the 0—70% CsBr range of compositions and could not have detected the existence of Cs_4SnBr_6.[7]

Results and Discussion

The $CsBr$–$SnBr_2$ *Phase System*.—The phase diagram (Figure 1) was obtained from cooling-curve data and the phases present in the cooled melts were identified by *X*-ray powder diffraction photography. The diagram is eutectic in type and shows that three phases of intermediate composition, one dystectic and two meritectic, are formed giving rise to two eutectic and two meritectic points.

The congruent melting compound, $CsSnBr_3$, melts at 448 °C while the two incongruently melting phases correspond to $CsSn_2Br_5$ and Cs_4SnBr_6. No evidence is found for the phase detected by Belyaev and Shurginov [7] at a composition of $2CsBr\cdot 3SnBr_2$, but the existence of distinct compounds at $CsBr\cdot 2SnBr_2$ and $4CsBr\cdot SnBr_2$ which they failed to detect is shown. The phases $CsSn_2Br_5$, $CsSnBr_3$, and Cs_4SnBr_6 can also be prepared from solution.

When first prepared from the melt or from solution Cs_4SnBr_6 is black with a metallic lustre but it rapidly turns first yellow, then white in the presence of moist air. This process can be reversed by standing the compound over a suitable desiccant or by gentle heating. Chemical analysis shows that the black compound is Cs_4SnBr_6 and that the yellow form contains variable amounts of water. Freshly prepared samples of Cs_4SnBr_6 gradually lose their colour after exposure to the atmosphere for a period of about 1 week, but samples stored over a desiccant retain their black colour longer and deteriorate only after a period of about 6 months. These observations suggest that the presence of water plays a major role in the process causing the loss of the intense black colour of freshly prepared Cs_4SnBr_6. The *X*-ray powder patterns of both the white and the black phases are found to be identical showing that the two forms have identical bulk structures. In an *X*-ray powder study, the white form was heated over the range 20—300 °C and the only changes in the observed pattern were those due to thermal expansion of the lattice, even though the sample changed colour from white to black during heating. The water molecules in the white phase must therefore be absorbed into voids in the lattice that do not affect its bulk structure, although in these positions they must affect the electronic structure of the anhydrous material.

The $Cs_4SnBr_{6-x}Cl_x$ *System*.—In addition to the bromide an analogous light green chloride of formula Cs_4SnCl_6 was prepared from aqueous or ethane-1,2-diol solutions. The *X*-ray powder pattern shows that the chloride is isostructural with the bromide.

A series of solid solutions of general formula $Cs_4SnBr_{6-x}Cl_x$ (x = 0—6) was prepared from the melts. The powder patterns of these intermediate phases confirmed that they were isostructural with the parent compounds, and that there was a gradual decrease in cell size with increasing chloride content. The decrease in cell size was accompanied by a colour change from black in Cs_4SnBr_6, through dark red in $Cs_4SnBr_4Cl_2$, to the light green Cs_4SnCl_6. These colour changes are paralleled by the shift in the optical absorption edges of these phases (Table 1) from 1.79 to 2.70 eV in Cs_4SnBr_6 and Cs_4SnCl_6 and indicate a large change in the optical band gap. A similar change in absorption edge is observed in the $CsSnBr_{3-x}Cl_x$ system [1] and a similar range of colours has been observed in the $CsSn_2Br_{5-x}Cl_x$ system.

The $Cs_4Sn_{1-n}Pb_nBr_{6-x}Cl_x$ *System*.—*X*-Ray powder photographs of samples of Cs_4PbBr_6 and Cs_4PbCl_6 prepared from melts show that these two compounds are isostructural with the corresponding tin(II) compounds. In order to study the effects, therefore, of replacement of tin(II) by lead(II) and bromide by chloride the two systems of solid solutions, $Cs_4Sn_{0.5}Pb_{0.5}Br_{6-x}Cl_x$ (x = 0—6) and $Cs_4Sn_{1-n}Pb_nBr_6$ (n = 0—1) were prepared. Both series of phases are highly coloured, the

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‡ *Supplementary data available* (No. SUP 23503, 5 pp.): thermal parameters, complete bond lengths and angles, structure factors for Cs_4PbCl_6. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Non-S.I. unit employed: eV ≈ 1.60×10^{-19} J.

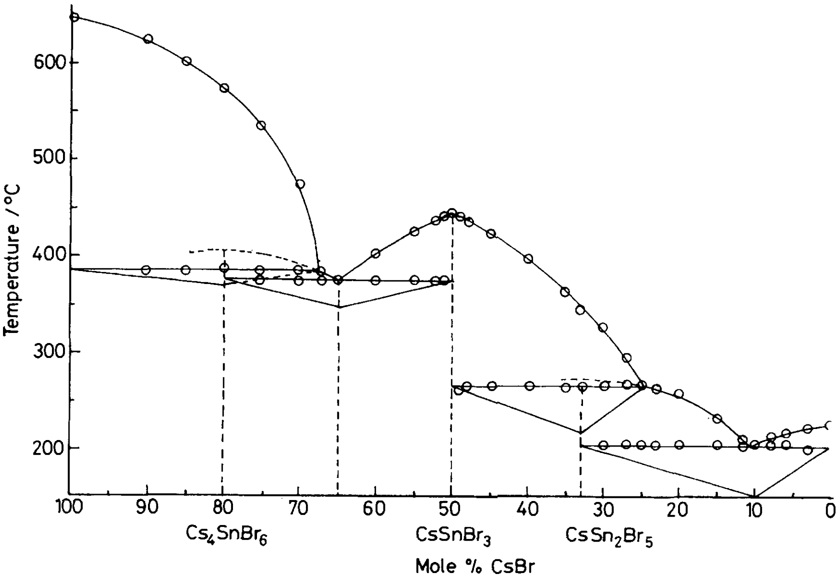

Figure 1. Equilibrium diagram of the CsBr–SnBr$_2$ system

Table 1. Reflectance electrical and Mössbauer data for Cs$_4$MBr$_{6-x}$Cl$_x$ phases

Compound	Absorption edge (eV)	Electrical conductivity ($10^6\ \Omega^{-1}\ cm^{-1}$)	Mössbauer parameters (mm s^{-1}) at 80 K [a]		
			δ (±0.01)	Δ (±0.01)	Γ (±0.01)
Cs$_4$SnBr$_6$ (black)	1.79	0.04	4.09	0	0.9
(white)	3.40	—	3.95	0	1.05
Cs$_4$SnBr$_4$Cl$_2$	1.87	0.05	4.01	0	1.35
Cs$_4$SnCl$_6$	2.70	0.02	3.85	0.89	1.60
CsSnBr$_3$ [b]	1.80	9.00	3.98	0	0.84
Cs$_4$Sn$_{0.75}$Pb$_{0.25}$Br$_6$	1.82	0.1	4.03	0	1.24
Cs$_4$Sn$_{0.5}$Pb$_{0.5}$Br$_6$	1.84	0.09	4.08	0	1.32
Cs$_4$Sn$_{0.5}$Pb$_{0.5}$Br$_4$Cl$_2$	2.19	—	4.05	0	1.32
Cs$_4$Sn$_{0.5}$Pb$_{0.5}$Br$_3$Cl$_3$	—	0.02	3.95	0.68	1.46
Cs$_4$Sn$_{0.5}$Pb$_{0.5}$Br$_2$Cl$_4$	2.57	—	3.89	0.77	1.55
Cs$_4$Sn$_{0.5}$Pb$_{0.5}$Cl$_6$	2.71	0.001	3.82	0.87	2.80

[a] Relative to BaSnO$_3$. [b] J. D. Donaldson, R. M. A. Grimsey, and S. J. Clark, *J. Phys.* (*Paris*), 1979, **40**, C2—289.

Cs$_4$Sn$_{0.5}$Pb$_{0.5}$Br$_{6-x}$Cl$_x$ systems varying in colour from the black hexabromo-phase through reds to the light yellow hexachloride.

As Sn^{II} is replaced by Pb^{II} in Cs$_4$SnBr$_6$, fresh compositions within the range $n = 0$—0.8 are black with an absorption edge of *ca.* 1.8 eV whereas phases of higher lead content range from dark red to the yellow Cs$_4$PbBr$_6$ and have correspondingly large absorption edges (Figure 2). As in the case of pure Cs$_4$SnBr$_6$, the mixed phases lost their colour over a period of time due to the absorption of moisture, again with no change in structure. The rate of change is greatest in the tin-rich phases and decreases with increasing lead content, the orange-yellow Cs$_4$PbBr$_6$ being stable even in moist air.

Structure Redetermination of Cs$_4$PbCl$_6$.—Møller[5] previously determined the crystal structures of Cs$_4$PbCl$_6$ and Cs$_4$PbBr$_6$, and showed them to be related to that of K$_4$CdCl$_6$.[8] However, the *X*-ray powder data obtained in the present study were found to differ from those reported by Møller and suggested the possibility of a different structure. In view of this and the poor refinement of Møller's structures the crystal structure of Cs$_4$PbCl$_6$ has been redetermined from diffractometer data.

This structure determination shows that the Pb atoms are surrounded by a regular octahedron of six Cl atoms at a distance of 2.88 Å. As this is considerably less than the sum of the Pb^{2+} and Cl$^-$ ionic radii for six-co-ordination (3.02 Å) this suggests that there is a strong interaction between the Pb and Cl. Figure 3 shows the arrangement of the six PbCl$_6$ octahedra within the unit cell projected down the *c* axis.

Along the *c* axis, between the PbCl$_6$ octahedra are situated the six Cs(1) atoms in special positions 6a of the space group. These lie at the centre of a trigonal prism of Cl atoms with a Cs–Cl distance of 3.41 Å. The remaining 18 Cs(2) atoms occupy special positions 18c in the space group. These sites have somewhat lower symmetry, and are surrounded by eight Cl atoms at distances of 3.56—3.69 Å.

The major difference between the structure reported here and that of Møller lies in the refinement of the atomic positions of the Cl atoms. The values $x = 0.040$, $y = 0.164$, $z = 0.095$ obtained by Møller are equivalent to 0.164, 0.040, 0.405 which differ from our positions $x = 0.190$, $y = 0.027$, and $z = 0.101$ by a shift along *c* and small adjustments in *x* and *y* and this accounts for the lower residual obtained by us.

In order to examine the role of the two Cs sites the replace-

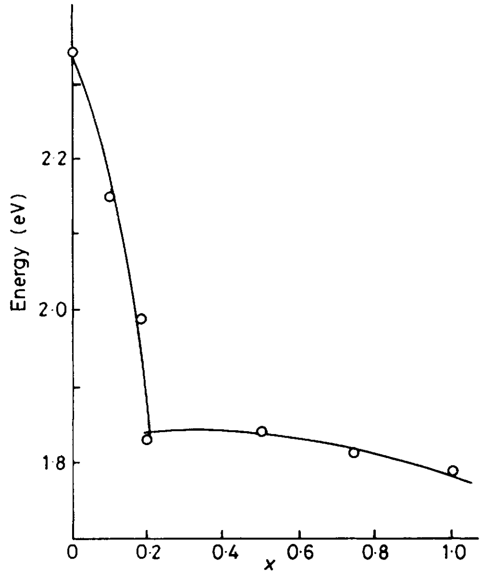

Figure 2. Absorption edges of phases in the system $Cs_4Sn_{1-x}Pb_xBr_6$

ment of Cs by *p*b in the isostructural Cs_4SnBr_6 was studied. Up to 75% of the Cs, corresponding to 18 Cs(2) atoms, can be replaced without changing the structure or properties of the solid. Replacement of all the Cs, however, results in the loss of the Cs_4PbBr_6 structure. This is consistent with easy replacement of the Cs atoms on the 18e sites and the importance of the remaining Cs atoms in stabilizing the structure. If the hexagonal cell is regarded as a distortion of a cubic lattice the reason for the presence of two Cs sites is evident. In a cell with cubic symmetry the Cs atoms would be indistinguishable but the distortion of the cube along a three-fold axis to form the hexagonal cell results in the compression of the environment of the six Cs atoms lying along the unique axis to give the observed structure.

Mössbauer and Electronic Properties.—The ^{119}Sn Mössbauer data given in Table 1 show behaviour very similar to that of the system $CsSnBr_{3-x}Cl_x$–$CsPbBr_{3-x}Cl_x$ previously reported.[2] The Cs_4SnBr_6 phase has the high chemical shift and narrow linewidth consistent with an O_h symmetry environment around the Sn^{II} and a stereochemically inactive lone pair. As Sn^{II} is replaced by Pb^{II} there is no substantial change in the chemical shift, while the replacement of Br by Cl leads to a smaller shift. In both cases the site symmetry, as reflected in the linewidth and quadrupole splitting, is reduced. This would arise from the electric field gradient produced by an increasing imbalance in the *p*-electron density around the Sn^{II}. Similar changes are also observed in the white form of Cs_4SnBr_6.

As the changes in the Mossbauer parameters are observed the optical band gap (absorption edge) and the electrical band gap (as related to the electrical conductivity of the samples) both increase significantly. This is particularly noticeable in the absorption edges of Cs_4PbCl_6 (2.37 eV), Cs_4PbBr_6 (2.34 eV), and Cs_4SnBr_6 (1.79 eV). These compounds are isostructural but replacement of Pb by Sn in Cs_4PbBr_6 produces a rapid decrease in absorption edge (Figure 2) before levelling off at *ca.* 20% Sn^{II}. More striking is the change in the absorption edge between the black and white forms of Cs_4SnBr_6. The presence of only small amounts of water has very little effect on the tin(II) electronic environment, as shown from the Mossbauer data, and none on the crystal structure, but produces large changes in the electronic band structure, almost doubling the optical band gap.

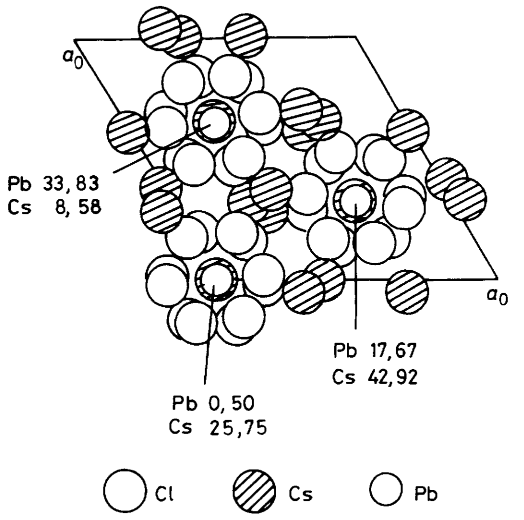

Figure 3. The structure of Cs_4PbCl_6 projected down its c_0 axis. The values indicate the fractional atomic co-ordinates, $(z/c) \times 10^2$

We have previously suggested[1] that the optical and electrical properties of $CsSnBr_3$ and related phases are due to the delocalization of the Sn 5*s*-electron density into solid-state bands formed by the overlap of empty Br 4*d* orbitals. In both Cs_4SnBr_6 and $CsSnBr_3$ the Sn^{II} atoms occupy sites of O_h symmetry with similar Sn–Br distances (3.08 and 2.90 Å respectively), in which case it is not unreasonable to suppose that the semiconductor properties of the compounds and phases discussed in this paper arise from the same mechanism. The poorer semiconducting properties of the lead(II)-rich phases result from the reduced overlap between the Sn 5*s* orbitals and the Br *d* orbitals arising from the presence of the larger Pb^{2+} ions while, in addition, the Pb 6*s* electrons are more tightly bound to the Pb^{2+} ion than is the case with Sn. Similarly, the smaller Cl 3*d* orbitals will overlap with each other, and with the *s* orbitals, less than do the larger Br 4*d* orbitals. Also the presence of water molecules in Cs_4SnBr_6 serves to disrupt the electronic structure by reducing halogen–halogen overlaps.

Experimental

Preparations.—The samples were prepared by slow cooling, in an atmosphere of nitrogen, of melts containing the appropriate molar ratios of CsX and MX_2. The pure tin compounds were also prepared by dissolving sufficient SnX_2 to give a molar ratio of 4 : 1, in a boiling, almost saturated solution of CsX in water or ethane-1,2-diol. To reduce the probability of oxidation the solution contained a small piece of tin metal and a trace of the parent acid and the synthesis was carried out under an atmosphere of oxygen-free nitrogen. After slow cooling the crystalline product was filtered off, washed with a minimum of cold water or ethane-1,2-diol followed by diethyl ether, and finally dried over a suitable desiccant.

Where appropriate the products were analysed: Sn^{II} was determined by Donaldson and Moser's method,[9] halide potentiometrically with $AgNO_3$, and water by thermogravimetry. The apparatus used to measure electrical conductivity[1] and Mossbauer spectra has been described previously.[10] The absorption edges were recorded on a Perkin-Elmer model 137 spectrophotometer by specular reflectance.

Table 2. Final atomic co-ordinates for Cs_4PbCl_6 with estimated standard deviations in parentheses

Atom	x	y	z
Pb	0	0	0
Cs(1)	0	0	0.25
Cs(2)	0.371 8(3)	0	0.25
Cl	0.190 0(9)	0.027 4(9)	0.100 9(6)

Table 3. Selected interatomic distances (Å) and angles (°) with standard deviations in parentheses

Pb–Cl	6 × 2.885(12)
Cs(1)–Cl	6 × 3.414(11)
Cs(2)–Cl	2 × 3.563(12)
	3 × 3.507(11)
Cl–Pb–Cl	90.0(5)

Crystal-structure Determination of Cs_4PbCl_6.—Cell dimensions obtained from precession and Weissenberg photographs were refined from powder data.

Crystal data. Cs_4PbCl_6, $M = 951.5$, Trigonal, $a = b = 13.187(5)$, $c = 16.641(5)$ Å, $U = 2\,506.1$ Å^3, $F(000) = 2\,424$, $D_m = 3.69$ g cm^{-3} (displacement of chlorobenzene), $Z = 6$, $D_c = 3.78$ g cm^{-3}, space group $R\bar{3}c$ or $R3c$ (no. 167 or 161) from systematic absences $hkil$ when $-h + k + l \neq 3n$ and $h\bar{h}0l$ when $l \neq 2n$, Mo-K_α radiation ($\lambda = 0.7107$ Å, $\mu = 195.65$ cm^{-1}).

Intensity data were collected with a Stoe two-circle diffractometer; 284 independent reflections were corrected for Lorentz and polarization factors but not for absorption.

Refinement was begun with the co-ordinates for Pb and Cs atoms used by Møller and the Cl atom was located in a subsequent difference-Fourier map to give R 0.10. Refinement was continued after applying corrections for anomalous dispersions on all atoms and introducing anisotropic thermal parameters. Use of the weighting scheme $w = [\sigma^2(F) + 0.0023F^2]$ gave a final residual of R 0.075. This final refinement confirmed $R\bar{3}c$ as the space group. The final atomic positions are listed in Table 2, selected bond lengths and angles in Table 3.

The X-ray powder data for the isostructural compounds Cs_4PbBr_6 and Cs_4SnBr_6 were indexed on the basis of these data and the cell dimensions were then refined using the indexed powder data to obtain the unit cells of these compounds. Assuming that the atomic co-ordinates of the Pb, Sn, and Br atoms were the same as those of Pb and Cl in Cs_4PbCl_6, the interatomic distances in Cs_4PbBr_6 and Cs_4SnBr_6 were then calculated (Table 4). The programs used have been described elsewhere.[11]

Table 4. Calculated interatomic distances (Å) in Cs_4MBr_6

	M = Sn	M = Pb
M–Br	3.08	3.13
Cs(1)–Br	3.60	3.66
Br(1)–Br(1)	4.36	4.41
Br(1)–Br(2)	4.11—5.12	4.18—5.19

For M = Sn: $a = b = 13.58 \pm 0.03$; $c = 16.95 \pm 0.01$ Å. For M = Pb: $a = b = 13.71 \pm 0.02$; $c = 17.23 \pm 0.07$ Å.

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