Phases obtained from the Frozen Molten Systems Caesium–Tin–Halide and Caesium–Lead–Halide

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Phases and compositions obtained from the molten systems $CsPbCl_3$–$CsPbBr_3$ and $CsPbCl_nBr_{3-n}$–$CsSnCl_nBr_{3-n}$ have been identified and compared with those from the $CsSnCl_3$–$CsSnBr_3$ system. *X*-Ray powder data are consistent with all of the products being single-phase solid solutions based on the perovskite lattice and in which there is random distribution of Group IV metal and halide ions. ^{119}Sn Mössbauer data for the phases with cubic unit cells are characterised by high chemical shifts and narrow linewidths, indicative of the presence of tin(II) in octahedral sites. I.r. spectra of the cubic phases contain bands assignable to all of the possible stretching modes but only an average bending mode. There are no bands in the Raman spectra of the cubic phases. Colours obtained in the products are discussed in terms of the population of conductance bands by electrons from ns^2 orbitals of the Group IV metal ions.

CAESIUM tin and lead trihalides, $CsMX_3$ (X = Cl and Br), are known to have high-temperature phases which have the cubic perovskite structure; $CsSnBr_3$ is cubic at room temperature[1,2] while $CsSnCl_3$, $CsPbCl_3$, and $CsPbBr_3$ have the ideal perovskite lattice above 90,[1] 47,[3] and 137 °C[3] respectively. We have previously studied[1] the $CsSnCl_3$–$CsSnBr_3$ system in which cubic room-temperature phases are obtained if the $CsSnBr_3$ content is 34—100%. We now extend our studies of Groups IV halide perovskites and report on the phases obtained from the frozen molten systems $CsPbCl_3$–$CsPbBr_3$ and $CsPbCl_nBr_{3-n}$–$CsSnCl_nBr_{3-n}$ at room temperature, and on the high-temperature transformations of these phases.

RESULTS AND DISCUSSION

The $CsPbCl_3$–$CsPbBr_3$ *Systems*.—All the room-temperature products obtained from the molten systems had *X*-ray diffraction powder data which indexed (Table 1) as single tetragonal phases with unit-cell dimensions between those of the parent caesium lead trihalides. All the tetragonal compositions had high-temperature cubic unit cells (Table 1) with cell lengths between those for the perovskite phases of $CsPbCl_3$ and $CsPbBr_3$. The *X*-ray

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[1] J. Barrett, S. R. A. Bird, J. Donaldson, and J. Silver, *J. Chem. Soc.* (*A*), 1971, 3105.

[2] J. D. Donaldson and J. Silver, *J.C.S. Dalton*, 1973, 666.

[3] C. K. Moller, *Kgel Danske Videnskab Selskam Mat. Fys. Medd.*, 1954, **32**, 1.

data are thus consistent with the formation of single-phase solid solutions based on the perovskite lattice and in which there is random distribution of the Cl^- and Br^- ions. The colours of the cubic phases varied from pale yellow for $CsPbCl_3$ through to orange for $CsPbBr_3$ as the Cl content decreased.

TABLE 1

Unit-cell dimensions of the caesium tin and caesium lead halides

Molar composition	Cubic-cell length/Å for phase with $M_2 = Sn_2$	$M_2 = SnPb$	$M_2 = Pb_2$ [a]
$Cs_2M_2Cl_6$	5·56 [a]	5·57	5·61
$Cs_2M_2Cl_5Br$		5·63	5·65
$Cs_2M_2Cl_4Br_2$		5·64	5·68
$Cs_2M_2Cl_3Br_3$	5·66	5·70	5·73
$Cs_2M_2Cl_2Br_4$	5·73	5·74	5·77
$Cs_2M_2ClBr_5$	5·74	5·77 [a]	5·82
$Cs_2M_2Br_6$	5·80	5·85 [a]	5·87

Molar composition	Non-cubic unit-cell dimensions/Å of room-temperature compositions $a = b$	c
$Cs_2Pb_2Cl_6$	5·59	5·63 [b]
$Cs_2Pb_2Cl_5Br$	5·63	5·66 [b]
$Cs_2Pb_2Cl_4Br_2$	5·67	5·70 [b]
$Cs_2Pb_2Cl_3Br_3$	5·70	5·75 [b]
$Cs_2Pb_2Cl_2Br_4$	5·75	5·80 [b]
$Cs_2Pb_2ClBr_5$	5·79	5·85 [b]
$Cs_2Pb_2Br_6$	5·83	5·90 [c]
$Cs_2PbSnBrCl_5$	5·76	5·78 [b]
$Cs_2PbSnBr_6$	5·82	5·89 [b]

[a] High-temperature phases. [b] Tetragonal. [c] Monoclinic, 89·65°.

The $CsPbCl_nBr_{3-n}$–$CsSnCl_nBr_{3-n}$ *System.*—Room-temperature products obtained from the molten systems, in which the molar ratio of Pb : Sn was fixed at 1 : 1 but in which the proportions of Cl and Br were varied, were found to be cubic for $n > 1$ and tetragonal for $n < 1$. The *X*-ray data for the compositions studied are those for single phases with the cell dimensions given in Table 1. The *X*-ray data again suggest the formation of solid solutions, which would mean that there is random distribution of the halide and Group IV metal ions. It is surprising that the cubic room-temperature phases are found at the Cl-rich end of this system, although the Br-rich compositions do have high-temperature cubic forms (Table 1). The colours of the cubic phases varied from yellow for $Cs_2SnPbCl_6$ through orange and red to black for $Cs_2SnPbBr_6$ as the Cl content decreased.

TABLE 2

^{119}Sn Mössbauer parameters for the phases and compositions in tin-containing caesium Group IV metal halides

Phase or molar composition	$\delta \pm 0{\cdot}02$ [a] / mm s^{-1}	Δ / mm s^{-1}	$\Gamma \pm 0{\cdot}03$ / mm s^{-1}	T / K	Ref.
$CsSnCl_3$	1·70	0	1·42	80	*b*
$CsSnCl_2Br$	1·79	0	1·25	80	*b*
$Cs_2Sn_2Br_3Cl_3$	1·81	0	1·04	80	*b*
$CsSnBr_2Cl$	1·85	0	0·86	80	*b*
$Cs_2Sn_2Br_5Cl$	1·88	0	0·85	80	*b*
$CsSnBr_3$	1·93	0	0·84	80	*b*
$Cs_2SnPbCl_6$	1·90	0	1·10	80	*c*
$Cs_2SnPbCl_5Br$	1·92	0	0·92	80	*c*
$Cs_2SnPbCl_4Br_2$	1·94	0	0·90	80	*c*
$Cs_2SnPbCl_3Br_3$	1·96	0	0·90	80	*c*
$Cs_2SnPbCl_2Br_4$	1·96	0	0·83	80	*c*
$Cs_2SnPbClBr_5$	1·98	0	0·82	80	*c*
$Cs_2SnPbBr_6$	1·99	0	0·79	80	*c*
$CsSnBr_3$	2·09	0	1·07	4·2	*c*
$Cs_2SnPbBr_6$	2·20	0	0·97	4·2	*c*

[a] Relative to α-Sn. [b] Ref. 1. [c] This work.

^{119}Sn Mössbauer parameters (Table 2) for the compositions obtained from this system are similar to those of the cubic materials from the $CsSnCl_3$–$CsSnBr_3$ system. The spectra were characterised by high chemical shifts (δ) and narrow resonance linewidths (Γ), which we regard as indicative of the presence of tin(II) in octahedral sites.[1,2] Unit-cell lengths for the solid-solution compositions $Cs_2SnPbCl_nBr_{6-n}$ are greater than those for the corresponding $CsSnCl_nBr_{3-n}$ phases. This means that the tin-halide ion bonds should be longer in the Pb-containing phases. The higher chemical shifts for Pb-containing compositions compared to those for the Sn-only materials are consistent with the expected increase in the electrostatic character of the longer tin–halide ion bonds. Chemical shifts for both systems increased with increasing Br content, presumably because of greater electrostatic tin–halide ion distances in the perovskite-type lattices containing Br^-.

Mössbauer data for caesium tin lead mixed halides showed no evidence for the presence of more than one Sn site or of any resolvable quadrupole splitting of the resonance lines. The narrow linewidths suggest the presence of Sn^{II} in octahedral environments. The slight increase in linewidth as the Cl content of the phases increased is probably due to small disruptions of the *p*-electron density around Sn because of poorer packing of Cl^- in Cs-containing perovskite lattices. The Mössbauer data for the materials described in this work are therefore also consistent with the phases being solid solutions based on the perovskite lattice and with random distribution of the halide ions around the tin atom.

The linewidth of the Mössbauer spectrum of $Cs_2SnPbBr_6$ was greater at 4·2 than at 78 K, although the chemical shift was also greater. This means that, although there must be an increase in the asymmetry of the electronic environment of Sn^{II}, there must also be an increase in the *s*-electron density at the Sn nucleus. This could arise from a smaller population of the conducting bands[1] in this type of material by the Sn 5*s* electrons at lower temperatures.

Vibrational Spectra.—Vibrational spectra of the distinct phases and solid-solution compositions obtained from the systems $CsSnCl_3$–$CsSnBr_3$, $CsPbCl_3$–$CsPbBr_3$, and $CsSnCl_nBr_{3-n}$–$CsPbCl_nBr_{3-n}$ are listed in Table 3. The spectra of two types of material (distinct monoclinic phases and cubic phases and solid-solution compositions) from the $CsSnCl_3$–$CsSnBr_3$ system are reported. For the distinct monoclinic phases[1] $CsSnCl_3$ and $Cs_2Sn_2Cl_5Br$, every band in the i.r. spectra also appeared in the Raman spectra. This is consistent with the presence of the pyramidal trichlorostannate(II) ion with C_{3v} or lower symmetry[4] in monoclinic $CsSnCl_3$ and with

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[4] J. D. Donaldson, J. F. Knifton, J. D. O'Donoghue, and S. D. Ross, *Spectrochim. Acta*, 1966, **22**, 1173.

TABLE 3

I.r. and Raman spectra/cm^{-1} of caesium Group IV metal halides

(*a*) Sn Phases (for assignment see ref. 4)

Monoclinic phases

		ν_6	ν_4	[a]	ν_5	ν_3	ν_1
$CsSnCl_3$	I.r.	75	110	170	229	268	312
	R (red)	70	110	168	228	266	313
	R (yellow)	75	110	169	228	265	311
$Cs_2Sn_2Cl_5Br$	I.r.	76	110	170	227	266	312
	R (red)	76	110	165	226	266	312
	R (yellow)	75	110	170	226	263	312

Cubic phases (no Raman bands observed with red or yellow lasers; assignments following those in ref. 5)

		Lattice mode	Bending mode	Sn–Br Stretch	Sn–Cl Stretch
$Cs_2Sn_2Cl_4Br_2$	I.r.	68	135	220	309
$Cs_2Sn_2Cl_3Br_3$	I.r.	68	132	220	308
$Cs_2Sn_2Cl_2Br_4$	I.r.	68	128	220	306
$Cs_2Sn_2ClBr_5$	I.r.	68	120	219	305
$CsSnCl_3$ [b]	I.r.	70	172		310
$CsSnBr_3$	I.r.	68	118	218	

(*b*) Pb Phases

Cubic phases (assignments following ref. 5)

		Bending mode	Pb–Br Stretch	Pb–Cl Stretch
$CsPbCl_3$	I.r.	146		160
$Cs_2Pb_2Cl_5Br$	I.r.	144	[c]	162
$Cs_2Pb_2Cl_4Br_2$	I.r.	130	140	162
$Cs_2Pb_2Cl_3Br_3$	I.r.	118	135	162
$Cs_2Pb_2Cl_2Br_4$	I.r.	112	140	154
Tetragonal phases				
$Cs_2Pb_2ClBr_5$	I.r.	102	138	160
$CsPbBr_3$	I.r.	105	134	

(*c*) Sn–Pb Phases

Cubic phases (no Raman bands observed with red lasers; assignments following ref. 5)

		Lattice mode	Bending mode	Stretching modes			
				Pb–Br	Sn–Br	Pb–Cl	Sn–Cl
$Cs_2SnPbCl_6$	I.r.	60—70	154				310
$Cs_2SnPbCl_5Br$	I.r.	60—70	154				308
$Cs_2SnPbCl_4Br_2$	I.r.	60—70	138			160	308
$Cs_2SnPbCl_3Br_3$	I.r.	60—70	118	137	218	163	309
$Cs_2SnPbCl_2Br_4$	I.r.	60—70	118	138	218	160	309
	R					170	
Tetragonal phases							
$Cs_2SnPbClBr_5$	I.r.	60—70	114	140	218	160	309
	R					170	
$Cs_2SnPbBr_6$	I.r.	60—70	110	137	209		

[a] Not assigned. [b] Spectrum of cubic phase obtained at 100 °C. [c] Not observed.

the presence of a similar species based on three-coordinate Sn^{II} in $Cs_2Sn_2Cl_5Br$. I.r. spectra of $CsSnBr_3$ and of the cubic form of $CsSnCl_3$ contained three bands and, for a cubic perovskite of O_h symmetry, three i.r. t_{1u} modes are expected.[5] These three modes, which can be described as Sn–X stretching, XSnX bending, and a 'lattice' mode in which the alkali metal moves in antiphase with the remainder of the structure, are at 310, 172, and 70 cm^{-1} respectively in $CsSnCl_3$ and at 218, 118, and 68 cm^{-1} respectively in $CsSnBr_3$. The absence of any bands in the Raman spectra of these materials confirms their perovskite structure.[5] Mixed Cl and Br compositions from this system had i.r. spectra which showed both Sn–Cl and Sn–Br stretching frequencies very close to those in cubic $CsSnCl_3$ and $CsSnBr_3$ respectively and bending modes which had frequencies between those of the parent caesium tin trihalides. There were no bands in the Raman spectra of the mixed halide compositions and this is consistent with their structures being based on the cubic perovskite lattice.

I.r. spectra of the phases from the $CsPbCl_3$–$CsPbBr_3$ system were obtained at 100 °C to try to ensure that they were in their cubic forms. The parent compounds, $CsPbCl_3$ and $CsPbBr_3$, had only two bands in their i.r. spectra and these are attributed to Pb–X stretching and XPbX bending. The lattice modes were not observed. Although the spectrum of $CsPbBr_3$ was obtained below the transition temperature of its cubic form, the existence of only two bands in its spectrum is consistent with the view that its tetragonal form has a structure close to

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[5] S. D. Ross, 'Inorganic Infrared and Raman Spectra,' McGraw-Hill, London, 1972, p. 108.

that of cubic perovskite at 100 °C. The mixed halide compositions again showed bands attributable to both Pb–Cl and Pb–Br stretches at frequencies close to those in the parent compounds and one bending mode at a frequency between those of the caesium lead halides.

I.r. spectra of the caesium tin lead halides, Cs_2SnPbX_6 (X = Cl and Br), consisted of bands which are attributable to both Sn–X and Pb–X stretches, to a bending mode and the lattice mode. The frequencies of the bending modes lay between those found in $CsSnX_3$ and $CsPbX_3$, while the stretching modes had frequencies close to those in the parent compounds. Spectra of the tin–lead mixed halide compounds showed the lattice mode and one frequency attributable to XMX bending which had a value between those for $Cs_2SnPbCl_6$ and $Cs_2SnPbBr_6$. These mixed halide compositions also have bands attributable to all four possible M–X (M = Sn and Pb; X = Cl and Br) stretches at frequencies near to those of the parent compounds.

The vibrational spectroscopic data are contradictory in that they do not distinguish between a mixture of metal–halide domains and an average structure. The presence of only one bending mode and the absence of any Raman bands suggest a random structure, but the presence of every possible M–X stretch would favour[6] a structure containing domains of the possible metal halide environments.

The appearance of a Raman band at 170 cm^{-1} in $Cs_2SnPbClBr_5$ is consistent with the fact that this composition has a non-cubic unit cell at room temperature. To produce a Raman band, however, the distortion must destroy the centre of symmetry in the perovskite lattice and this most probably occurs by movement of the Group IV metal ion along the three-fold axis and towards a pyramidal environment. The appearance of a very weak Raman band at 170 cm^{-1} in $Cs_2SnPbCl_2Br_4$ suggests that a similar distortion must occur in this composition at room temperature although this is not indicated by the *X*-ray data.

Colours.—We have previously suggested[1] that the colours obtained in the caesium tin(II) halides, which have cubic-cell *X*-ray powder data, are due to the population of conductance bands by tin 5*s* electrons. The variation in colour of the mixed cubic caesium tin(II) chloride bromides with increasing Br^- content suggests that the conducting band is formed by the overlap of bromine orbitals. The lowest unoccupied Br orbitals are the 4*d*, and the t_{2g} set are suitably directed in the perovskite structure to produce a conductance band by mutual overlap. The Br–Br distance is *ca.* 4 Å and reasonable overlap should be achieved. Replacement of Br^- by Cl^- in $CsSnBr_3$ will reduce the halide–halide overlap but the low-lying conductance band will continue to exist in room-temperature phases so long as the cubic lattice, which favours the halide–halide overlap, persists. The distance from the Group IV metal ion to the central point of the halide–halide contact is *ca.* 2 Å and there should be sufficient overlap[7] to enable population of the band by the non-bonding atomic *s* electrons. The colours of the Pb-containing materials and their reduced conducting properties suggest that the population of the band by Pb 6*s* electrons is lower than that by Sn 5*s* electrons. This must be a function of the differences in energy between the 5*s* or 6*s* orbitals and the conductance band and of the greater availability of Sn 5*s* electrons because of the less effective nuclear charge. Materials containing both Sn and Pb have the colour of the Sn composition and this is in agreement with the above explanation.

Support for the suggestion that the conductance bands are populated by the outer *s* electrons of the Group IV metal ions comes from studies on the caesium cadmium bromides; $CsCdBr_3$ is white and non-conducting. Cadmium has no non-bonding outer *s* electrons to populate the conductance band and it is significant that replacement of one half of the Cd atoms in $CsCdBr_3$ by either Sn or Pb produces coloured phases and leads to semiconducting properties.

EXPERIMENTAL

All of the phases and compositions were obtained from molten systems and were identified by their *X*-ray diffraction powder data. The *X*-ray data were obtained with Phillips 11·64 cm cameras and with focussing Guinier cameras at the appropriate temperatures, using Cu-K_α radiation. Mössbauer spectra were obtained with a $BaSnO_3$ source and the absorber at 80 or 4·2 K. The chemical shift for the reference material from the source was 2·10 mm s^{-1} at 80 K. Parameters for $CsSnBr_3$ at 4·2 K have been recalculated from improved data. The Mössbauer apparatus has been described previously.[8] I.r. data were obtained on a Beckmann RIIC FS-720 spectrometer and the Raman data on a Cary 81 spectrometer using red and yellow lasers.

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