# Mössbauer and Electronic-reflectance Spectroscopic Studies and Resistivity Measurements on the Systems $CsPb_{1-x}Sn_xBr_3$, $CsPb_{1-x}Sn_xBr_2Cl$, $M_xCs_{1-x}SnBr_3$, and $M_xCs_{1-x}SnBr_2Cl$ (M = Na, K, Rb, and $NH_4$)

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A series of coloured compounds of general formula $CsPb_{1-x}Sn_xX_3$ ($X_3$ = $Br_3$ or $Br_2Cl$) has been prepared. *X*-Ray and Mössbauer data show that the compounds have highly symmetrical tin–lead environments. Their electronic resistivity and optical-reflectance spectra are interpretable in terms of the partial filling of electronic bands produced by the interaction of orbitals of the bromine atoms. As *x* increases the band population increases, consistent with the lower ionisation energies of the tin 5*s* electrons compared to those of the lead 6*s* electrons. Replacement of $Cs^+$ by $Na^+$, $K^+$, $Rb^+$, or $[NH_4]^+$ shows that these singly charged ions have no effect on band formation. Replacement of $Br_3$ by $Br_2Cl$ raises the energy of the band due to the inclusion of the higher-energy chlorine orbitals.

COLOUR and electrical-conduction properties in solid tin(II) compounds are generally associated with high-symmetry tin environments. We have suggested [1] that these high-symmetry environments can occur in compounds which contain empty low-energy delocalised bands accessible to population by the tin non-bonding valence-shell electrons. The result of such band population would be to reduce the distortive effects of the non-bonding electrons as lone pairs. The low-energy delocalised bands accessible to the tin(II) non-bonding electrons in the perovskite $CsSnBr_3$ must arise from the overlap of empty orbitals on the bromine atoms which are in close-packed array. The effect on the structure and properties of $CsSnBr_3$ of the replacement of $Br^-$ with differing amounts of other halide ions has been studied.[2,3] We now report the effects of partial replacement of the metal-(I) and -(II) ions in halide perovskite lattices from studies on the replacement of $Cs^+$ by $Na^+$, $K^+$, $Rb^+$, and $[NH_4]^+$ and of $Sn^{2+}$ by $Pb^{2+}$ in both $CsSnBr_3$ and $CsSnBr_2Cl$.

## EXPERIMENTAL AND RESULTS

*Replacement of* $Sn^{2+}$ *by* $Pb^{2+}$ *in* $CsSnBr_3$ *and* $CsSnBr_2Cl$.—The compounds in Table 1 were prepared from molten systems containing the appropriate molar ratios of $CsSnX_3$ and $CsPbX_3$ ($X_3$ = $Br_3$ or $Br_2Cl$) or of the parent metal halides. Their powder *X*-ray diffraction data were obtained using Phillips 11.64-cm cameras with filtered Cu-$K_\alpha$ radiation. In each case these data were similar to those of either the cubic or the tetragonal parent materials.[2,4] The electronic-reflectance absorption edges were obtained using a Perkin-Elmer model 137 spectrophotometer.

*Replacement of* $Cs^+$ *in* $CsSnBr_3$ *and* $CsSnBr_2Cl$.—Samples of the products from 9 : 1 and 1 : 1 molten systems $CsSnX_3$–$MSnX_3$ (M = Na, K, Rb, or $[NH_4]^+$; $X_3$ = $Br_3$ or $Br_2Cl$) were characterised by their powder *X*-ray diffraction and $^{119}Sn$ Mössbauer data. The *X*-ray data for the 9 : 1 products are very similar to those of $CsSnBr_3$ and $CsSnBr_2Cl$, although some extra very weak lines do appear. The data for the 1 : 1 products, however, show breakdown to new non-cubic phases, particularly for the sodium and rubidium systems. The $Rb_{0.1}Cs_{0.9}SnBr_2Cl$ phase undergoes a low-temperature phase change. The powder *X*-ray diffraction data for the low-temperature phase are listed below to 2 Å and are similar to those for $Rb_{0.5}Cs_{0.5}SnBr_2Cl$. No new phases were found from the *X*-ray data of the potassium-substituted materials.

TABLE 1

Crystal class, absorption-edge data, and $^{119}Sn$ Mössbauer parameters for phases of composition $CsPb_{1-x}Sn_xBr_3$ and $CsPb_{1-x}Sn_xBr_2Cl$

| *x* | Crystal class | Absorption edge (±10 nm) | δ [a] (±0.03 mm s⁻¹) | Δ (±0.03 mm s⁻¹) | Γ (±0.05 mm s⁻¹) |
|---|---|---|---|---|---|
| (*i*) $CsPb_{1-x}Sn_xBr_3$ | | | | | |
| 0.0 | *b* | 533 | | | |
| 0.005 | *b* | 540 | | | |
| 0.01 | *b* | 565 | | | |
| 0.05 | *b* | 590 | | | |
| 0.10 | *b* | 600 | 2.00 | *ca.* 0 | 0.71 |
| 0.15 | *b* | 607 | | | |
| 0.20 | *b* | 625 | | | |
| 0.30 | *b* | 640 | | | |
| 0.40 | *b* | 650 | | | |
| 0.50 | *b* | 672 | 1.99 | *ca.* 0 | 0.79 |
| 0.75 | *c* | 690 | | | |
| 0.90 | *c* | 695 | 2.01 | *ca.* 0 | 0.80 |
| 1.00 | *c* | 700 | 1.93 | *ca.* 0 | 0.84 |
| (*ii*) $CsPb_{1-x}Sn_xBr_2Cl$ | | | | | |
| 0.0 | *c* | 500 | | | |
| 0.01 | *c* | 500 | | | |
| 0.05 | *c* | 539 | | | |
| 0.10 | *c* | 566 | 2.01 | *ca.* 0 | 0.80 |
| 0.20 | *c* | 592 | | | |
| 0.30 | *c* | 605 | 1.96 | *ca.* 0 | 0.85 |
| 0.40 | *c* | 602 | | | |
| 0.50 | *c* | 612 | 1.96 | *ca.* 0 | 0.85 |
| 0.60 | *c* | 624 | | | |
| 0.70 | *c* | 628 | | | |
| 0.80 | *c* | 627 | 1.91 | *ca.* 0 | 0.85 |
| 0.90 | *c* | 635 | 1.86 | *ca.* 0 | 0.85 |
| 1.00 | *c* | 650 | 1.86 | *ca.* 0 | 0.90 |

[a] Relative to α-Sn. [b] Tetragonal. [c] Cubic.

$Na_{0.5}Cs_{0.5}SnBr_3$: 7.60s, 5.99vw, 4.72vw, 4.11w, 3.71m, 3.45s, 3.22m, 3.00s, 2.98s, 2.90vvw, 2.79vvw, 2.68vvw, 2.38s, 2.19vvw, 2.11s, 2.05w, and 2.00w

$(NH_4)_{0.5}Cs_{0.5}SnBr_3$: 7.53m, 5.83w, 4.84vvw, 4.44vvw, 4.11s, 3.96vvw, 3.82vvw, 3.66vvw, 3.35s, 3.23vw, 3.12vw, 3.01m, 2.89vs, 2.72m, 2.67w, 2.59w, 2.50vvw, 3.27m, 2.33w, 2.28vvw, 2.23vvw, 2.20vvw, and 2.06m

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[1] J. D. Donaldson J. Silver, S. Hadjiminolis, and S. D. Ross, *J.C.S. Dalton*, 1975, 1500.

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

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

[4] J. D. Donaldson, D. Laughlin, S. D. Ross, and J. Silver, *J.C.S. Dalton*, 1973, 1985.

$Rb_{0.5}Cs_{0.5}SnBr_3$ (same as low-temperature $Rb_{0.1}Cs_{0.9}SnBr_3$): 9.17vvw, 8.23vvw, 7.50w, 6.19vw, 5.77w, 5.05vw, 47.5vw, 4.45vvw, 4.09vs, 3.98vw, 3.82vw, 3.73vw, 3.66vvw, 3.53vvw, 3.37s, 3.25s, 3.13s, 3.03s, 2.98w, 2.91s, 2.85s, 2.80w, 2.71m, 2.59vvw, 2.54vvw, 2.48vw, 2.36w, 2.24w, 2.19w, 2.13vvw, 2.09vvw, and 2.05s

$Na_{0.5}Cs_{0.5}SnBr_2Cl$: 7.63w, 5.91vvw, 4.71w, 4.05vw, 3.67vw, 3.21m, 3.02s, 2.95vw, 2.82vw, 2.65s, 2.37s, 2.18m, and 2.04vw

$(NH_4)_{0.5}Cs_{0.5}SnBr_2Cl$: 7.53s, 6.22vw, 5.77vw, 4.70w, 4.39w, 4.18w, 3.64w, 3.21w, 3.10vw, 3.00vs, 2.90s, 2.82s, 2.64s, 2.58vvw, 2.48vvw, 2.34s, 2.18vw, 2.08vw, and 2.04m

$Rb_{0.5}Cs_{0.5}SnBr_2Cl$: 7.53s, 6.22w, 5.72vvw, 5.20vvw, 4.76m, 4.41m, 4.18m, 4.06m, 3.92s, 3.77m, 3.62vvw, 3.22s, 3.10m, 2.97m, 2.88s, 2.81s, 2.75vvw, 2.70vvw, 2.64w, 2.54w, 2.49w, 2.40w, 2.31w, 2.23w, 2.12vw, 2.07vw, and 2.03vw

*Tin*-119 *Mössbauer Data.*—The $^{119}Sn$ Mössbauer parameters for the compounds studied are in Tables 1 and 2. The measurements were made at 80 K with the materials as absorbers in Perspex holders. The source motion for the Mössbauer effect was provided by a vertically mounted moving-coil drive which was built to a design by Cranshaw.[5] The solid-state waveform generator, 256-channel (N.M.710) store, A.D.C. (N.M.730), power supply (N.M.231), display unit (N.M.720), and print-out controller (N.M.195), supplied by J. and P. Engineering, Reading, give improved stability over the original design.[6] The gamma detector was a 1 × 0.1-cm NaI (Tl) scintillator and a palladium foil (0.3 mg $cm^{-2}$) was used to reduce the tin *X*-ray contribution to the counting rate. The source used was a 2.0-mCi $BaSnO_3$ source supplied by the U.K.A.E.A. Radiochemical Centre, Amersham. The spectrometer was calibrated by means of the natural iron spectrum using a cobalt–stainless-steel source.

TABLE 2

Mössbauer parameters for some of the compounds studied at 80 K

| Phases of composition | $\delta$ ($\pm$0.03 mm $s^{-1}$)[a] | $\Delta$ ($\pm$0.03 mm $s^{-1}$) | $\Gamma$ ($\pm$0.85 mm $s^{-1}$) |
|---|---|---|---|
| $CsSnBr_3$ | 1.93 | *ca.* 0 | 0.84 |
| $NaSnBr_3$ | 1.74 | *ca.* 0 | 1.09 |
| $KSnBr_3$ | 1.76 | *ca.* 0 | 1.96 |
| $RbSnBr_3$ | 1.72 | 0.76 | |
| $NH_4SnBr_3$ | 1.69 | 0.68 | |
| $Na_{0.1}Cs_{0.9}SnBr_3$ | 1.93 | *ca.* 0 | 0.94 |
| $K_{0.1}Cs_{0.9}SnBr_3$ | 1.93 | *ca.* 0 | 1.66 |
| $Rb_{0.1}Cs_{0.9}SnBr_3$ | 1.93 | *ca.* 0 | 0.88 |
| $(NH_4)_{0.1}Cs_{0.9}SnBr_3$ | 1.93 | *ca.* 0 | 0.91 |
| $Na_{0.5}Cs_{0.5}SnBr_3$ (1) | 1.92 | *ca.* 0 | 1.02 |
| (2) [b] | 1.86 | 0.85 | |
| $K_{0.5}Cs_{0.5}SnBr_3$ | 1.93 | *ca.* 0 | 1.26 |
| $Rb_{0.5}Cs_{0.5}SnBr_3$ (1) | 1.93 | *ca.* 0 | 1.29 |
| (2) [b] | 1.76 | 0.80 | |
| $(NH_4)_{0.5}Cs_{0.5}SnBr_3$ | 1.93 | *ca.* 0 | 2.04 |
| $Rb_{0.1}Cs_{0.9}SnBr_2Cl$ | 1.77 | *ca.* 0 | 1.93 |

[a] Relative to α-Sn. [b] Relaxed material.

*Electrical Measurements.*—Preliminary a.c. electrical measurements of resistivity were carried out using pressed disks of materials giving the results in Table 3. A two-probe method was used for resistivity studies. The circuit consisted of a known resistance in series with the sample and permits the measurement of the voltage drop across the resistance as a known voltage is applied across the sample. The results show that the resistivities of the compositions $M_{0.1}Cs_{0.9}SnBr_3$ (M = Na, K, or Rb) are similar to that of the parent perovskite, while values for the corresponding $M_{0.5}Cs_{0.5}SnBr_3$ are at least a factor of ten greater. These changes in resistivity correspond to a change in *X*-ray data and with the perovskite tolerance factors obtained for these materials.

TABLE 3

Resistivities of the compounds

| Compound | $\rho/\Omega$ cm |
|---|---|
| $CsSnBr_3$ | $10^3$ |
| $K_{0.1}Cs_{0.9}SnBr_3$ | $10^3$—$10^4$ |
| $Rb_{0.1}Cs_{0.9}SnBr_3$ | $10^3$—$10^4$ |
| $Na_{0.1}Cs_{0.9}SnBr_3$ | $10^3$—$10^4$ |
| $(NH_4)_{0.1}Cs_{0.9}SnBr_3$ | $10^4$—$10^5$ |
| $K_{0.5}Cs_{0.5}SnBr_3$ | $10^4$—$10^5$ |
| $Rb_{0.5}Cs_{0.5}SnBr_3$ | $10^6$—$10^7$ |
| $Na_{0.5}Cs_{0.5}SnBr_3$ | $10^5$—$10^6$ |
| $(NH_4)_{0.5}Cs_{0.5}SnBr_3$ | $10^4$—$10^5$ |
| $CsSnBr_2Cl$ | $10^5$—$10^6$ |
| $K_{0.1}Cs_{0.9}SnBr_2Cl$ | $10^5$—$10^6$ |
| $Rb_{0.1}Cs_{0.9}SnBr_2Cl$ | $10^5$—$10^6$ |
| $Na_{0.1}Cs_{0.9}SnBr_2Cl$ | $10^5$—$10^6$ |
| $(NH_4)_{0.1}Cs_{0.9}SnBr_2Cl$ | $10^4$—$10^5$ |
| $K_{0.5}Cs_{0.5}SnBr_2Cl$ | $10^6$—$10^7$ |
| $Na_{0.5}Cs_{0.5}SnBr_2Cl$ | $10^6$—$10^7$ |
| $(NH_4)_{0.5}Cs_{0.5}SnBr_2Cl$ | $10^6$—$10^7$ |
| $KSnBr_2Cl$ | $10^6$—$10^7$ |
| $RbSnBr_2Cl$ | $10^6$—$10^7$ |

The resistivity of $CsSnBr_2Cl$ is higher than that of $CsSnBr_3$. Again with this system the $M_{0.1}Cs_{0.9}SnBr_2Cl$ compounds have similar values to that of the cubic parent materials, while those for the corresponding $M_{0.5}Cs_{0.5}Br_2Cl$ series are at least a power of ten greater. In this series only $(NH_4)_{0.1}Cs_{0.9}Br_2Cl$ is anomalous and has a resistivity less than that of $CsSnBr_2Cl$.

## DISCUSSION

The tin atoms in the cubic perovskite $CsSnBr_3$ can be randomly replaced by lead. The *X*-ray data show that a cubic unit cell is maintained in the $CsPb_{1-x}Sn_xBr_3$ system when $x > 0.5$. For $x \leqslant 0.5$ the phases have tetragonal unit cells related to that of $CsPbBr_3$, which has a tetragonally-distorted perovskite lattice. Similar results were found for the replacement of tin by lead in the $CsPb_{1-x}Sn_xBr_2Cl$ system in which both the metal(II) and halide ions must be randomly distributed in a perovskite-like lattice. The $^{119}Sn$ Mössbauer data show the narrow linewidths and relatively high chemical shifts that are consistent with the presence of tin in a regular octahedral environment. All the compounds in these systems are coloured and the colours can be interpreted in terms of the direct population of empty potential valence bands by the tin(II) non-bonding valence-shell electron pair. The wavelength of the absorption edge (Table 1) increases with tin content. The gradual change in absorption-edge wavelength together with the similarities in the $^{119}Sn$ Mössbauer data for all the compositions studied suggests that there is a limit to the band-donation ability of an individual tin atom in a given lattice, particularly (as is the case for the Sn–Pb systems) if the cell size does not change appreciably.[4] The donor ability of the lead(II) ions is

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[5] T. E. Cranshaw, *Nuclear Instrument Methods*, 1964, **30**, 101.

[6] S. R. A. Bird, J. D. Donaldson, S. A. Keppie, and M. F. Lappert, *J. Chem. Soc.* (*A*), 1971, 1311.

obviously much less than that of the $Sn^{II}$, presumably because of the larger core charge in the former.[4] The ability of an $ns^2$ ion to donate electrons to an available band in the solid state must therefore reflect a property related to that of ionisation energy. It seems that the variations in the wavelengths of the absorption edges with the values of $x$ support the idea that the absorptions are due to transitions within a band of orbitals located on the cubically arranged halide ions.

From atomic-spectral data[7] the differences in energy between the 5*s* and 4*d* orbitals of an isolated bromine atom may be calculated as a function of its oxidation state. The general trend is for the 5*s* orbital to be lower in energy than the 4*d* orbital as the oxidation state of the bromine atom decreases. Although it is likely that crystal-field effects in the solid state could lower the $t_2$ set of 4*d* orbitals in $Br^-$ to an energy lower than that of the 5*s* orbital, it is convenient for the purpose of calculations to consider the formation of bands by the 5*s* orbitals. Using Slater-type orbitals[8] a calculation of the 5*s*–5*s* overlap integrals shows that, for the $CsPb_{1-x}Sn_xBr_3$ compounds, band formation is highly probable. This conclusion probably applies to the 4*d*(+2) orbitals which may be lower in energy than the 5*s* orbitals in the solid state, but detailed calculations have not been made because of uncertainties in the Slater-type orbitals.

If a 5*s* bromine band were formed, then it would at most be one-third populated by the tin or lead $ns^2$ electrons. The 6*s* electrons of lead are less easily removed than the 5*s* electrons of tin, as evidenced by the difference between the third ionisation energies of the elements: that of lead is 3 081 kJ $mol^{-1}$, while that of tin is 2 942 kJ $mol^{-1}$, a difference of 139 kJ $mol^{-1}$.[9] This means that the bromine band will be less populated as $x$ in $CsPb_{1-x}Sn_xBr_3$ decreases. In consequence, the lowest-energy electronic transition will move to higher wavelengths, as is observed. In the case of the $CsPb_{1-x}Sn_xBr_2Cl$ compounds, the band responsible for the absorption giving rise to the colour is less populated for any value of $x$, as compared to $CsPb_{1-x}Sn_xBr_3$. This is probably due to less efficient band formation with a consequent increase in energy of the band. The proposal of anion band formation is consistent with the change of colour with temperature and with the electrical data.

The $Cs^+$ ion in $CsSnBr_3$ can be partially replaced by other alkali-metal ions or by the ammonium ion. The Mössbauer data for the phases with 10 and 50% replacement of $Cs^+$ (Table 2) are similar to those for $CsSnBr_3$. The linewidths for the $M_{0.1}Cs_{0.9}SnBr_3$ compositions are narrow, indicative of tin in an octahedral site. The $K_{0.1}Cs_{0.9}SnBr_3$ and $Rb_{0.1}Cs_{0.9}SnBr_2Cl$ phases have much wider resonance lines, and this may indicate some distortion of the tin environments. The chemical shifts for the black, freshly prepared, samples of $M_{0.5}Cs_{0.5}SnBr_3$ are similar to those of the corresponding $M_{0.1}Cs_{0.9}SnBr_3$. Their greater linewidths suggest greater distortion of the tin(II) sites. The $M_{0.5}Cs_{0.5}SnBr_3$ compositions change over a long period to white non-cubic phases. The white products from the sodium and rubidium systems have lower Mössbauer chemical shifts and resolvable quadrupole splitting like those for the $MSnBr_3$ phases rather than $CsSnBr_3$.

When first cooled from molten systems the compositions obtained from both series have the same colour as the parent caesium compound. The series of compositions based on $CsSnBr_3$ are black except for $Na_{0.5}Cs_{0.5}SnBr_3$ which is dark grey but changes to black with a slight increase in temperature or pressure. The compositions from the $CsSnBr_2Cl$ series are dark red when first obtained from cooled melts. At liquid-nitrogen temperatures they are grey, but as the temperature is increased to room level they revert to red.

These observations, together with the *X*-ray and Mössbauer data, especially those for $Rb_{0.1}Cs_{0.9}SnBr_2Cl$, indicate that all the phases prepared are homogeneous and that when the $M_{0.5}Cs_{0.5}SnX_3$ compounds relax they form new non-cubic phases and do not revert to their parent materials. The change to non-cubic phases is associated with a change in colour and therefore with a trend towards distorted rather than octahedral environments. The resistivity data suggest that the $Cs^+$ ions do not contribute to the bands but merely support the cubic lattice which is necessary for the maximum overlap of the orbitals which form the anion bands.

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[7] C. E. Moore, ' Report on the International Commission on Atomic Energy Levels,' Nat. Bur. Stand., 1958, p. 3.

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[9] W. M. Latimer, ' Oxidation Potentials,' 2nd edn., Prentice-Hall, New Jersey, 1952.