The Mössbauer Effect in Tin(II) Compounds. Part XIII.[1] Data for the Products from Molten Caesium–Tin(II)–Halide Systems

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The ^{119}Sn Mössbauer parameters and the *X*-ray diffraction powder data for the products obtained from the molten mixed halide systems $CsSnX_3$–$CsSnX'_3$ (X and X' = F^-, Cl^-, Br^-, and I^-) are reported. The nature of the solidus–liquidus curves for these systems and the colours of the mixtures at the melting points, suggest that every phase has a cubic high-temperature modification. Two types of product are obtained from the cooled melts (i) complexes containing tris(ligand)stannate(II) species and (ii) compositions which have cubic or near cubic unit cells based on the perovskite lattice. The Mössbauer data for the latter materials are characterised by relatively high chemical shifts and narrow line widths which suggest that the tin(II) is in a regular octahedral environment. Even the presence of F^- in the $CsSnBr_3$ and $CsSnI_3$ lattices does not lead to the disruption of the tin(II) bonding electrons normally associated with the presence of Sn–F bonds.

TIN in most of its tin(II) derivatives[2] has a trigonal pyramidal environment which can be described in terms of distortion of an octahedral co-ordination. This distortion could arise from a tendency towards covalency and sp^3 hybridisation of the tin(II) orbitals, or from crystal-field effects.[2] We have, however, recently described[3] a series of caesium trihalogeno-stannates(II), $CsSnBr_{3-x}Cl_x$, which have cubic unit cells. Their structures are of the perovskite-type and the tin(II) is apparently in a regular octahedral site. Because of its size, tin(II) should be in an octahedral environment in ionic halides. Any distortion of this co-ordination will depend upon whether the stabilisation energy gained from *s*–*p* mixing is large enough to overcome the forces producing the regular octahedron. The small energy separation[2] between the ground and first excited states of the tin(II) ion generally leads to distortion. The stabilisation energy will, however, decrease rapidly with increasing tin–halide bond distance and this means that crystal field distortion should be greatest in the tin(II) fluorides. We now report on a study of the products obtained from the molten mixed halide systems $CsSnX_3$–$CsSnX'_3$. The ^{119}Sn Mössbauer and *X*-ray diffraction data for the products are discussed in terms of the probable tin(II) environments.

The solid products $CsSnF_{3-x}X_x$ (X = Cl, Br, or I), $CsSnCl_{3-x}X_x$ (X = Br or I) and $CsSnBr_{3-x}I$ were obtained by cooling melts containing the required proportions of caesium and tin(II) halides. The four possible mixed halide phases CsSnX'X''X''' were also obtained from melts containing the necessary proportions of caesium and tin(II) halides.

The solidus–liquidus lines show that continuous variation in composition is achieved at the melting temperature for all the systems studied. $CsSnBr_3$ is known[3] to be cubic ($a = 5{\cdot}795 \pm 0{\cdot}002$ Å) at room temperature while $CsSnCl_3$ has a high temperature cubic form.[3,4] We have shown by *X*-ray powder diffraction studies that the transition to the high-temperature form of $CsSnCl_3$ occurs at 90 °C and that the cubic form has a cell edge of $5{\cdot}560 \pm 0{\cdot}005$ Å. $CsSnI_3$ has a yellow low-temperature form which has an orthorhombic cell, and a high temperature black form. $CsPbI_3$ is also known to exist in two modifications, a yellow form and a black form said to be tetragonal.[5] Yellow $CsPbI_3$ is orthorhombic ($a = 4{\cdot}797 \pm 0{\cdot}005$; $b = 10{\cdot}46 \pm 0{\cdot}01$; $c = 17{\cdot}78 \pm 0{\cdot}02$ Å) and is a distorted perovskite, since $CsSnI_3$ has a similar unit cell ($a = 4{\cdot}790 \pm 0{\cdot}003$; $b = 10{\cdot}43 \pm 0{\cdot}01$; $c = 17{\cdot}63 \pm 0{\cdot}02$ Å) it is reasonable to suppose it also has a similar structure.

When $CsSnF_3$ is heated to a temperature near its melting point and cooled new lines appear on its *X*-ray powder photograph. These lines are consistent with the existence of a cubic form of $CsSnF_3$ with $a = 4{\cdot}47$ Å. It therefore appears that all of the caesium trihalogenostannates(II), with the possible exception of $CsSnI_3$, have cubic forms which are stable just below their melting points, and that this explains the nature of the solidus–liquidus lines for these systems. All of the cubic trihalogenostannates(II) are more highly coloured than the non-cubic forms, and we have previously suggested[3] that this is due to the presence of low energy conductance bands in their perovskite-type structures. The colours obtained in these systems at high temperatures are:

$CsSnF_3$ grey	$CsSnF_2Cl$ light grey	$Cs_2Sn_2F_3Cl_3$ cream	$CsSnFCl_2$ cream-yellow	$CsSnCl_3$ yellow
$CsSnF_3$ grey	$CsSnF_2Br$ dark grey	$Cs_2Sn_2F_3Br_3$ steel grey	$CsSnFBr_2$ black	$SsCnBr_3$ black
$CsSnF_3$ grey	$CsSnF_2I$ brown	$Cs_2Sn_2F_3I_3$ brown-black	$CsSnFI_2$ black	$CsSnI_3$ black
$CsSnCl_3$ yellow	$CsSnCl_2Br$ orange	$CsSn_2Cl_3Br_3$ bright red	$CsSnClBr_3$ dark red	$CsSnBr_3$ black
$CsSnCl_3$ yellow	$CsSnCl_2I$ yellow-brown	$Cs_2Sn_2Cl_3I_3$ black	$CsSnClI_3$ black	$CsSnI_3$ black
$CsSnBr_3$ black	$CsSnBr_2I$ black	$Cs_2Sn_2Br_3I_3$ black	$CsSnI_2Br$ black	$CsSnI_3$ black

All low temperature systems where $CsSnI_3$ is in excess are yellow.

The materials obtained at room temperature from mixed halide systems containing Br have cubic unit cells over a range of composition. The ranges over which cubic phases in the various systems are found are: 40—

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[1] Part XII, S. R. A. Bird, J. D. Donaldson, and J. Silver, *J.C.S. Dalton*, 1972, 1950.

[2] J. D. Donaldson, *Progr. Inorg. Chem.*, 1967, **8**, 287.

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

[4] F. R. Poulson and S. E. Rasmussen, *Acta Chem. Scand.*, 1970, **24**, 150.

[5] K. N. Møller, *Mat. Fys. Medd. Dan. Vid. Selsk*, 1959, 32.

100% $CsSnBr_3$ in the $CsSnCl_3$–$CsSnBr_3$ system, 60—100% $CsSnBr_3$ in the $CsSnF_3$–$CsSnBr_3$ system and in the $CsSnBr_3$–$CsSnI_3$ system from 92—100% $CsSnBr_3$. The formation of continuous ranges of solid solutions with cubic cell dimensions in the Br-containing systems is consistent with simple replacement of one halide ion by another in the perovskite-type lattices.

Ranges of solid solution in the $CsSnI_3$ rich systems also appear to exist. These are based on the orthorhombic $CsSnI_3$ structure but the data obtained are complicated by the ease of oxidation of the material to Cs_2SnI_6.[6]

The powder data for the room temperature products from $CsSnF_3$–$CsSnX_3$ systems show distinct phases at $CsSnF_2X$. The data for materials with composition between $CsSnF_3$ and $CsSnF_2X$ show the presence of both of these materials. The $CsSnF_3$–$CsSnCl_3$ system also has a distinct phase at $CsSnCl_2F$ but the $CsSnF_3$–$CsSnX_3$ ($X = Br$ or I) systems have cubic and orthorhombic room temperature products at the 1 : 2 compositions. The powder data for the distinct phases are more like those of the materials which are known to contain distinct SnX_3^- ions than those of cubic $CsSnBr_3$.

The *X*-ray powder data for CsSnClBrF are complicated and suggest that the material is not based on a perovskite lattice. The data for CsSnClBrI, CsSnClIF, and CsSnIBrF are those of distorted perovskite structures.

The ^{119}Sn Mössbauer data for the caesium tin(II) halides obtained from molten systems are in Tables 1 and 2. Compounds 1—7 are distinct *X*-ray phases and their Mössbauer data are similar to those for materials known to contain the trifluorostannate(II) [7-9] ions. The *X*-ray and Mössbauer [10,11] data are thus consistent with the presence of $SnX_2X'^-$ ions in compounds 2, 3, 5, and 6 and $SnXX'X''^-$ in compound 7. The chemical shifts (δ) for the series of compounds $CsSnF_{3-n}Cl_n$ ($n = 0$—3) increase with *n*. The chemical shifts for the bromide and iodide-containing materials (compounds 5—7) are also higher than that for $CsSnF_3$. In view of the known tendency [2,7-9] of F to form strong bonds to Sn^{II} these are the expected trends for the replacement of F by other halogens. The trends in quadrupole splittings (Δ) for these complexes are interesting in that all species SnF_2X^- have higher, and $SnFX_2^-$ lower, values of Δ than $CsSnF_3$. The imbalance in *p*-electron density around the tin atoms must therefore be at a maximum for complexes containing two Sn–F bonds. The complexes with only one Sn–F bond have splittings closer to that for $CsSnCl_3$ than $CsSnF_3$ and are much lower than those normally observed for fluoride containing tin(II) materials. Compounds 8 and 9 are also distinct *X*-ray phases having cubic unit cells based on the perovskite lattice. The tin in these compounds is presumably in a regular octahedral environment and this is reflected in relatively high chemical shifts and narrow line widths (Γ) in their Mössbauer data. We have previously discussed [3] the phases obtained from the $CsSnBr_3$–$CsSnCl_3$ system. Although $CsSnI_3$ (compound 10) has an orthorhombic cell its Mössbauer data suggests that the tin atoms are in an octahedral environment.

TABLE 1

The ^{119}Sn Mössbauer data for caesium tin(II) halides

(*a*) Complexes with distinct powder patterns not based on the perovskite lattice

		δ * ± 0·03 mm s^{-1}	Δ ± 0·03 mm s^{-1}	Γ ± 0·03 mm s^{-1}
1	$CsSnF_3$	0·93	1·86	
2	$CsSnF_2Cl$	1·02	1·90	
3	$CsSnCl_2F$	1·47	1·00	
4	$CsSnCl_3$ (monoclinic)	1·59	0·90	
5	$CsSnF_2Br$	1·02	1·96	
6	$CsSnF_2I$	0·96	1·82	
7	CsSnClBrF	1·58	1·08	

(*b*) Distinct phases based on perovskite lattice

		δ * ± 0·03 mm s^{-1}	Δ ± 0·03 mm s^{-1}	Γ ± 0·03 mm s^{-1}
8	Cubic $CsSnCl_3$	1·70	*ca.* 0	1·42
9	Cubic $CsSnBr_3$	1·93	*ca.* 0	0·79
10	Orthorhombic $CsSnI_3$	1·92	*ca.* 0	0·83

* δ Relative to α-Sn at 80 K.

TABLE 2

Molar compositions representing solid solutions based on the perovskite lattice

	Composition	δ * ± 0·03 mm s^{-1}	Δ ± 0·03 mm s^{-1}	Γ ± 0·03 mm s^{-1}
11	$CsSnBr_2F$	1·92	*ca.* 0	0·84
12	$Cs_2Sn_2Br_5F$	1·93	*ca.* 0	0·83
13	$CsSnFI_2$	1·87	*ca.* 0	0·91
14	$Cs_2Sn_2FI_5$	1·91	*ca.* 0	0·83
15	$Cs_2Sn_2Cl_5I$	1·74	*ca.* 0	1·42
16	$CsSnCl_2I$	1·76	*ca.* 0	1·29
17	$Cs_2Sn_2Cl_3I_3$	1·77	*ca.* 0	1·24
18	$CsSnClI_2$	1·84	*ca.* 0	1·10
19	$Cs_2Sn_2ClI_5$	1·92	*ca.* 0	1·08
20	$Cs_2Sn_2Br_5I$	1·93	*ca.* 0	0·83
21	$CsSnBr_2I$	1·92	*ca.* 0	0·84
22	$Cs_2Sn_2Br_3I_3$	1·80	*ca.* 0	0·96
23	$CsSnBrI_2$	1·86	*ca.* 0	0·93
24	$Cs_2Sn_2BrI_5$	1·91	*ca.* 0	0·91
25	CsSnClIF	1·86	*ca.* 0	0·91
26	CsSnClBrI	1·86	*ca.* 0	0·95
27	CsSnClFI	1·87	*ca.* 0	0·95

* δ Relative to α-Sn at 80 K.

Table 2 contains the Mössbauer data for cooled melts of various compositions which are not distinct *X*-ray phases but are based on ranges of solid solution around perovskite-type lattices. The data are characterised by the relatively high chemical shifts and narrow lines which are indicative of the presence of octahedral coordinated tin(II). The Sn–Cl bond length in cubic $CsSnCl_3$ (2·78 Å) [3,4] is known to be longer than those found in the monoclinic modification (2·55, 2·52, and 2·50 Å). This is consistent with an increase in the

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[9] J. D. Donaldson and B. J. Senior, *J. Chem. Soc.* (*A*), 1967, 1821.

[10] R. J. M. Clark, L. Marescu, and P. J. Smith, *J. Chem. Soc.* (*A*), 1970, 2687.

[11] M. Goldstein and G. C. Tok, *J. Chem. Soc.* (*A*), 1971, 2303.

electrostatic character of the Sn–X bonds in the materials containing octahedral co-ordinated tin(II) environments. Compositions $CsSnBr_2F$ and $Cs_2Sn_2Br_5F$ have the same powder data as $CsSnBr_3$ and their Mössbauer parameters are also very similar. Here the Sn^{II} ion must be in an octahedral environment which is not distorted by the presence of F^-. This means the Sn–F bonds must be long and that F^- ions are randomly distributed on sites that should be occupied by the Br^-. The Cs^+ and Br^- ions must hold the lattice together and dictate the lattice cell size and prevent the close approach of F^- which would disrupt the tin(II) bonding orbitals.

The other F^--containing compositions (13, 14, 25, 27) in Table 2 have similar Mössbauer data and must have similar tin(II) environments. The only other fluorine-containing tin(II) material which has Mössbauer data indicative of an undistorted octahedral environment is $Sn(SbF_6)_2$ [12] (δ = 2·34, Δ = 0, Γ = 1·21).

The line width of 1·42 for cubic $CsSnCl_3$ suggest a slight distortion of the electronic environment of Sn^{II} in its material. It is interesting that the Γ becomes narrower in the $CsSnCl_3$–$CsSnI_3$ systems (compounds 15—18) as the iodine content increases and moves towards the octahedral tin environment of $CsSnI_3$.

Two types of caesium tin(II) halides have been identified in the systems studied: (i) materials which have X-ray and Mössbauer data which suggest that they contain pyramidal tris(ligand)stannate(II) species and (ii) compositions which have cubic or near cubic unit cells based on the perovskite lattice and which show a range of solid solution around $CsSnX_3$. The nature of the solidus–liquidus lines and the colours obtained at high-temperatures suggest that all of the phases have high-temperature cubic lattices although some of these transform to non-cubic tris(ligand)stannates(II) on cooling. All of the caesium tin(II) halides which contain predominantly Br^- or I^- have perovskite or distorted perovskite lattices in which the packing forces involved must give lattice energies high enough to prevent the distortive forces of s–p mixing in tin(II) materials. Even the presence of F^- in $CsSnBr_3$ or $CsSnI_3$ lattices, does not lead to distortion of the tin(II) bonding orbitals as it does in most other compounds containing Sn–F bonds.

EXPERIMENTAL

All of the phases reported were prepared from molten systems containing the required proportions of caesium and tin(II) halides. The melts were kept under an atmosphere of oxygen-free nitrogen and the X-ray diffraction powder patterns of the products were obtained with Cu-K_α radiation using Phillips 11·64 cameras.

The $CsSnF_3$–$CsSnCl_3$ *System.*—The solidus–liquidus line for this molten system is a smooth descending curve from $CsSnF_3$ to $Cs_2Sn_2F_3Cl_3$ and then it rises sharply to $CsSnCl_3$. The only distinct phases identified in the cooled melts were $CsSnF_3$, $CsSnF_2Cl$, $CsSnCl_2F$, and $CsSnCl_3$. All other products were mixtures of these phases and none of them had cubic cells although the cooled melt of $CsSnF_3$ contained lines in addition to its known pattern which could be indexed as a cubic cell with a = 4·47 Å. The powder data for $CsSnCl_3$ were based on its known monoclinic cell and those for the other distinct phases are:

$CsSnF_2Cl$: 4·16vw, 4·06vw, 3·79vw, 3·76vs, 3·62w, 3·50w, 3·41vs, 3·11s, 3·02w, 2·98w, 2·89vw, 2·85vw, 2·77vw, 2·70s, 2·43s, 2·38s, 2·13w, 2·11w, 2·06m, 2·03w, 1·984s, 1·929m, 1·875mw, 1·844w, 1·803w.

$CsSnCl_2F$: 7·03vw, 6·33w, 5·56m, 4·56w, 4·27w, 4·16m, 3·82s, 3·69w, 3·59m, 3·50m, 3·45m, 3·42w, 3·35w, 3·27m, 3·22vvw, 3·13mw, 3·08mw, 3·00m, 2·97m, 2·92w, 2·83w, 2·76m, 2·69m, 2·39m, 2·35m, 2·27s, 2·25w, 2·16w, 2·13w, 2·12w, 2·07w, 2·02w, 1·986w, 1·943w.

The $CsSnF_3$–$CsSnBr_3$ *System.*—The solidus–liquidus line is a smooth curve with a minimum at 60% $CsSnF_3$. The products identified in the cooled melts containing >60% $CsSnBr_3$ had cubic unit cells identical to that of $CsSnBr_3$ (a = 5·795 ± 0·002 Å) and the only other distinct phases were $CsSnF_3$ and $CsSnF_2Br$.

$CsSnF_2Br$: 4·47vw, 4·13m, 3·96vw, 3·77s, 3·43s, 3·40vw, 3·25w, 3·13s, 3·04w, 2·92m, 2·89m, 2·79m, 2·58w, 2·48w, 2·38ms, 2·37ms, 2·11vw, 2·06ms, 2·01ms, 1·945w, 1·903w, 1·888s, 1·834m, 1·785w.

The $CsSnF_3$–$CsSnI_3$ *System.*—The solidus–liquidus line falls steeply from $CsSnF_3$ to 90% $CsSnF_3$, and rises to $CsSnI_3$ with incongruities at 58, 54, and 4% $CsSnF_3$. The iodide rich products from the melts ($CsSnI_3$ > 80%) had orthorhombic unit cells based on that of $CsSnI_3$ (Table 3) and the product of composition $CsSnFI_2$ had a powder pattern based on this cell but with a few additional lines. The high temperature phases in this system on the $CsSnI_3$

TABLE 3

$CsSnI_3$

Yellow orthorhombic

a = 4·790 ± 0·003; b = 10·43 ± 0·01; c = 17·63 ± 0·02 Å

I	d/Å obs.	hkl	d/Å(calc.)
m	8·98	011	9·00
w	6·75	012	6·73
m	4·23	111	4·23
vvw	4·06	014	4·06
m	3·88	023	3·90
s	3·51	113	3·50
s	3·45	121	3·46
vs	3·35	015	3·35
vs	3·27	122	3·27
s	2·84	105	2·84
w	2·78	131	2·78
w	2·73	034	2·73
m	2·68	$\bar{1}32$	2·68
s	2·38	043	2·38

$CsSnCl_3$

Yellow cubic

a = 5·56 at 90 °C

vvw	5·57	100	5·56
vs	3·92	110	3·916
w	3·209	111	3·205
vs	2·780	200	2·780
w	2·481	210	2·483
vs	2·267	211	2·266
vs	1·964	220	1·962
vw	1·858	300 221	1·859
m	1·758	310	1·756
w	1·605	222	1·603
m	1·484	321	1·483

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[12] T. Birchall, B. Della Valle, E. Martineau, and J. B. Milne, *J. Chem. Soc.* (*A*), 1971, 1855.

rich side were black but on grinding the yellow orthorhombic phase was also formed. The distinct phases identified in the fluoride rich regions were $CsSnF_3$ and $CsSnF_2I$.

$CsSnF_2I$: 5·16m, 4·16w, 3·82m, 3·52m, 3·36vs, 3·28w, 3·11m, 2·74m, 2·70w, 2·58w, 2·48w, 2·40m, 2·34vs, 2·12m, 1·976m, 1·928vs, 1·906s, 1·863m, 1·793ms, 1·755m.

The $CsSnCl_3$–$CsSnBr_3$ *System*.—The solidus–liquidus line is a smooth one with a minimum at 28% $CsSnBr_3$. The products obtained from this system have been described in detail in earlier work.[3]

The $CsSnCl_3$–$CsSnI_3$ *System*.—The solidus–liquidus line is a smooth curve with a minimum at 50% $CsSnCl_3$. Non-cubic distinct phases found in the cooled melts were $CsSnCl_3$, $CsSnCl_2I$, and $CsSnClI_2$. The iodide rich systems had orthorhombic unit cells based on that of $CsSnI_3$. The materials with compositions from 50% $CsSnI_3$ to 100% $CsSnI_3$ were found to exist in both yellow and black forms.

$CsSnCl_2I$: 6·97w, 6·06w, 5·62w, 5·29vw, 4·55w, 4·31m, 4·17vw, 4·04w, 3·97w, 3·88s, 3·71m, 3·65vw, 3·36s, 3·30vw, 3·20s, 3·15vw, 3·00s, 2·86s, 2·78w, 2·74s, 2·54vw, 2·21s, 2·13w, 2·09m, 1·973w, 1·805w.

$CsSnClI_2$: 6·11vw, 5·35vw, 4·75vw, 4·21vw, 3·97vs, 3·51w, 3·43m, 3·36m, 3·28m, 3·24s, 3·13s, 3·05m, 2·85vw, 2·80s, 2·50m, 2·38m, 2·15s, 1·982m, 1·959m, 1·710w.

Tke $CsSnBr_3$–$CsSnI_3$ *System*.—The solidus–liquidus line is a shallow smooth curve with a minimum at 50% $CsSnBr_3$. The $CsSnBr_3$ rich side is cubic and the $CsSnI_3$ is orthorhombic at room temperature, high temperature powder data on $CsSnBr_3$ shows that it does not undergo a phase change before melting. The $CsSnI_3$ goes to a black form at high temperature but the material did not give any new powder lines which could be compared with $CsPbI_3$ because of the rapid oxidation of $CsSnI_3$. All products in the melt are black at high temperatures but the $CsSnI_3$ rich products rapidly relax to yellow materials based on orthorhombic $CsSnI_3$. Melts of CsSnClBrF, CsSnClBrI, CsSnFIBr, and CsSnClIF were also prepared and their *X*-ray powder data are given.

CsSnClFBr (pink-orange material): 6·68w, 5·46s, 4·65m, 4·23m, 4·04s, 3·87vs, 3·64m, 3·51vs, 3·31m, 3·19w, 3·13w, 3·07vs, 2·87m, 2·81w, 2·73ms, 2·66w, 2·34w, 2·33m, 2·30s, 2·20m, 2·012m, 1·971w, 1·912s, 1·853m, 1·639m, 1·555s, 1·510w, 1·486m, 1·436mw.

CsSnClFI (yellow-green powder, black melt): 5·31w, 4·74m, 3·94vs, 3·63w, 3·34w, 3·14vs, 3·03s, 2·87vs, 2·46m, 2·09vs, 1·974m, 1·770w, 1·66w, 1·543w, 1·526vw, 1·460vw, 1·449mw, 1·291vw.

CsSnFBrI (black powder): 6·00m, 4·23s, 3·46s, 3·37s, 3·00s, 2·69w, 2·45w, 2·31w, 2·13s, 1·738vw.

CsSnClBrF (black powder): 6·82vw, 6·21w, 5·73w, 4·83vw, 4·70w, 4·34vvw, 4·19vw, 4·04m, 3·93m, 3·73w, 3·41s, 3·35m, 3·22vs, 3·14vw, 3·08w, 2·93vvs, 2·86vvw, 2·83w, 2·71w, 2·67w, 2·56w, 2·53w, 2·33w, 2·19vw, 2·15w, 2·12mw, 2·03w, 1·967w, 1·934w, 1·768m, 1·736m, 1·543w, 1·493w, 1·287w,

The Mössbauer spectra of the solids were obtained with the absorber and a $BaSnO_3$ source at 80 K. The errors quoted are total experimental errors not simply those arising from computer fitting. The chemical shift for the reference material, α-Sn from the source was 2·10 mm s^{-1} at 80 K. The percentage resonance dips for all materials were 14—25% when $>100{,}000$ counts per channel had been accumulated. The Mössbauer apparatus has been described.[13]

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