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Studies on the Effects of Doping Cesium Metal(III) Halides of the Type $Cs_3M_2^{III}X_9$ (M^{III} = Sb or Bi, X = Cl or Br)

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A series of compounds, $Cs_3M_2^{III}X_9$ (M^{III} = Sb and Bi, X = Cl or Br) are doped with impurity ions (Ba^{2+}, Ca^{2+}, Sn^{2+}, Pb^{2+}, Mg^{2+}, Fe^{2+}, Tl^{3+}, In^{3+}, Se^{4+}). Lattices doped with Sn(II), Pb(II) and Se(IV) are colored. Sn-119*m* Mössbauer data are consistent with the donation of Sn-5*s* electron density from tin(II) to a conduction band to give a pseudo-tin(IV) electronic environment.

Introduction

Compounds of the type $Cs_3M_2^{(III)}X_9$ (M^{III} = Sb and Bi, X = Cl and Br) crystallize in forms isostructural with, or closely related to, that of $Cs_3As_2Cl_9$ (*1–3*). This structure type has two-thirds of the possible octahedral voids occupied and has the metal(III) in a distorted octahedral environment of halide ions, with three short and three longer M–X bond distances. The known crystal structures of the two antimony chloride derivatives all have distorted Sn environments. α-$Cs_3Sb_2Cl_9$ (*1*) contains Sb in a site with three Sb–Cl bonds of 2.42 Å and three of 2.82 Å. In β-$Cs_3Sb_2Cl_9$ (*2*), the short bond lengths are 2.42–2.52 Å and the longer distances 2.8–2.9 Å. The Bi environment in $Cs_3Bi_2Cl_9$ is even more distorted with Bi–Cl distances of 2.47–2.56 and 2.60–3.08 Å. The Cs and Cl atoms in this structure are approximately close packed, but the M^{III} environment is typical of the low-symmetry sites found for ions distorted by the presence of a nonbonding lone pair of electrons. These materials are white and do not have the high-symmetry environments usually associated (*4*) with the appearance of color and semiconducting properties in compounds containing ns^2 ions. In this work we show that the $Cs_3M_2X_9$ matrices have colored forms whose properties can be explained by the direct population of solid-state bands by the metal(III) nonbonding electrons. We have previously shown that similar effects occur in other compounds of Sn (*5*) and compounds containing other ns^2 ions such as Sn(II) (*6*). In this study ns^2 ions other than Sn(III) and Bi(III) are used as dopants to study the possible acceptor properties of the band structure arising from the approximately close-packed Cs–halogen sublattice in $Cs_3M_2X_9$.

Experimental

The host matrix $Cs_3M_2X_9$ materials are precipitated when an acidic solution of CsX (X = Cl, Br) is added to an acidic solution

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of MX_3 (M = Sb, Bi) and can be obtained as crystalline solids by recrystallization from the hot mother liquor. The chlorides show color changes from white to yellow at 98°C ($Cs_3Sb_2Cl_9$) and 115°C ($Cs_3Bi_2Cl_9$) and commence thermal decomposition at 169 and 235°C, respectively. The bromides, $Cs_3Sb_2Br_9$ and $Cs_3Bi_2Br_9$, are yellow and orange, respectively, and begin to decompose at 182 and 457°C.

To introduce a dopant into the $Cs_3M_2X_9$ lattice, varying amounts of doping ions (Ba^{2+}, Ca^{2+}, Sn^{2+}, Pb^{2+}, Mg^{2+}, Fe^{2+}, Tl^{3+}, In^{3+}, and Se^{4+}) are dissolved in the MX_3 solutions; in the case of Sn^{2+}, the principal dopant investigated, the Sn : Sb ratio is varied from 2 : 1 to 1 : 8. The CsX content is kept below that required for precipitating all the Sb or Bi to prevent the formation of $CsSnX_3$. No such contamination of the doped product has been found. These precipitates are recrystallized from their hot mother liquor and dried *in vacuo*. The final doped crystals are analyzed for Sn by the Donaldson and Moser method (*7*) after removal of Sb by precipitation of Sb_2S_3 with H_2S from a 5% HF solution (*8*). The H_2S reduces Sn(IV) to Sn(II) and therefore only total Sn could be determined for Sn-containing materials although both Sn(II) and Sn(IV) can be analyzed in the Bi compounds. The other dopants are only investigated qualitatively and no analyses have been carried out. In all cases the X-ray powder data are indistinguishable from those of the parent $Cs_3M_2X_9$ compounds, except that when a large excess of SnX_2 is used, it is found to be coprecipitated.

Results

The color changes in $Cs_3M_2X_9$ compounds are similar to that observed in $CsSnCl_3$; this undergoes a phase transition at 96°C, from a white monoclinic form with a distorted Sn(II) environment, to a yellow cubic form with the octahedral site of an ideal perovskite structure. These effects in $CsSnCl_3$, and in the related high-symmetry materials $CsSnBr_3$, have been explained in terms of the direct population of empty solid-state bands formed by the overlap of halogen d orbitals by the nonbonding ns^2 lone pair. It seems likely that the appearance of color in $Cs_3Sb_2Sl_9$ and $Cs_3Bi_2Cl_9$ is associated with a reduced distortion of the M^{III}–Cl environment which allows such an overlap. DTA data obtained for the pure $Cs_3M_2X_9$ materials are highly complex, with several thermal effects below the decomposition temperature which undoubtedly arise from changes in the rotational modes of the complex bridged structure.

Color is also introduced into the $Cs_3M_2X_9$ lattice when the material is doped with other ns^2 species such as Sn(II), Pb(II), and Se(IV) but not when it is doped with ions which do not have an ns^2 outer electronic configuration. No color changes are observed when the lattices are doped, for example, with Sn(IV), Mg(II), Ca(II), Ba(II), Fe(II), Tl(III), and In(III). Lattices doped with Sn(II), Pb(II), and Se(IV), however, develop the following colors:

Dopant/ lattice	$Cs_3Sb_2Cl_9$	$Cs_3Bi_2Cl_9$	$Cs_3Sb_2Br_9$	$Cs_3Bi_2Br_9$
Sn(II)	Yellow	Yellow	Brown	Brown
Pb(II)	Yellow	Yellow	Brown	Brown
Se(IV)	Yellow	Yellow	Black	Black

The recrystallized Sn-doped precipitates of $Cs_3Sb_2X_9$, for example, are yellow and deepen in color as the Sn concentration increases. The analytical data (Table I) show that only a small amount of Sn is present in the lattice and that the Mössbauer chemical shifts are very small, lie in the Sn(IV) region, and decrease with increasing Sn concentration. However, analysis of the Bi compounds shows the Sn to be present as Sn(II) with only slight traces of Sn(IV) impurities.

TABLE I

^{119}Sn Mössbauer and Analytical Data for Sn(II)-Doped Phases

Host compound	Percentage Sn	δ^a (mm · sec^{-1})	Γ (mm · sec^{-1})
$Cs_3Sb_2Cl_9$[b]	0.8	0.70	0.85
	1.3	0.56	0.85
	4.0	0.49	0.90
$Cs_3Bi_2Cl_9$	0.4	0.72	0.95
	1.2	0.60	0.95
	3.0	0.50	0.95
$Cs_3Sb_2Br_9$[b]	0.3	0.87	0.90
	0.4	0.82	0.85
	4.9	0.46	0.85
$Cs_3Bi_2Br_9$	0.3	0.87	0.95
	0.6	0.72	0.95
	3.8	0.55	0.95

[a] At 80°K, relative to $BaSnO_3$.

[b] Analyzed as total Sn content.

Discussion

The materials containing low Sn(II) levels are less strongly colored than those with a higher Sn(II) content within the same host lattice and the bromides are much darker than the chlorides. While the Sn Mössbauer chemical shifts are very low for all these phases, being typical of Sn(IV) rather than Sn(II), the analytical results for the Bi phases show an absence of Sn(IV). The very low chemical shifts are therefore not due to the oxidation of Sn(II) to Sn(IV). Further, the decrease in chemical shift with increasing Sn content suggests that a Sn(IV) site is not produced. This is proved by the absence of color on doping with Sn(IV). Therefore these data are due to Sn(II) ions with very low 5*s* electron densities. The narrow linewidths indicate that the Sn atoms are in high-symmetry environments. These observations can be explained if it is assumed that a small amount of Sn(II) replaces *M*(III) in the lattice and it is sited in an octahedral halogen environment. Charge balance would be maintained by the replacement of one *M*(III) by Sn with a second Sn occupying a previously vacant octahedral site, or by vacancies in the halide lattice.

The radius of the octahedral hole in α-$Cs_3Sb_2Cl_9$ (0.78 Å) is smaller than the Sn(II) radius (0.95 Å). However, this discrepancy would be reduced by the loss of considerable *s*-electron density from the tin. Such a loss of *s*-electron density has already been demonstrated in $CsSnBr_3$ (*9*), where the 5*s* electron density is lost to the conduction bond at high temperatures. Such donation of the *s* electrons into a band would explain the highly colored nature of these materials and the low pseudo-tin(IV) Mössbauer chemical shift, and provide a mechanism for the *s*-electron loss. The similar properties of the Pb(II) doped materials may be explained in the same way.

An alternative explanation is that the substitution of a trivalent ion by a divalent ion produces vacancies in the halide sublattice with the formation of color centers. If this is true the doping of the $Cs_3M_2X_9$ lattice by other divalent ions should produce colors similar to Sn and Pb. The doping experiments were therefore repeated using Mg(II), Ca(II), Ba(II), and Fe(II) ions larger, smaller, and of similar size to Sn(II). In all systems for each cation, the precipitated materials were the same color as that of the parent $Cs_3M_2X_9$ compounds, which implies that the colors do not result from lattice defects. A black precipitate formed on the addition of CsBr solution to a solution of $SbBr_3$ containing Se(IV) has not been investigated further but it is consistent with the donation of the Se(IV) *s* electrons to a solid-state band. Since the precipitate is not formed until the CsBr solution is added the reduction of Se(IV) by Sb(III) can be ruled out. Doping by In(III) and Tl(III), which do not contain *s* electrons, gives the colors expected of the parent compounds.

The electron-donation mechanism is further supported by the mixed Sb–Bi materials (*10*). Compared with $Cs_3Sb_2X_9$, the ^{129}Sb, Sb(III) Mössbauer chemical shift in Cs_3SbBiX_9 is less negative (a decrease in *s*-electron density), yet Cs_3SbBiX_9 is more colored than either the pure Sb or Bi compounds. This may be due to the Bi fitting into a smaller hole in the lattice (than in the pure Bi compound), with a resulting decrease in 6*s*-electron density by donation and with less room to distort away from the center of the X_6 octahedron, a possible increase in site symmetry.

The results of the doping experiments suggest that the reason for the lack of color in the chlorides is related to the Sb and Bi atoms being in distorted octahedral sites, rather than high-symmetry environments. If the symmetry of the site of the Group V metal is increased an increase in color would be expected. This leads to the prediction that on heating, $Cs_3M_2X_9$ would become more colored. We have shown that this occurs at 98°C for $Cs_3Sb_2Cl_9$ and 115°C for $Cs_3Bi_2Cl_9$, and it seems likely that the symmetry of the Group V metal site has increased and led to color production. The observation that the Sb compound becomes colored at a lower temperature than that of the isostructural Bi compound is also consistent with the more highly colored nature of the element higher in the group, as is also found in Group IV chemistry e.g., $CsSnBr_3$ (black) and $CsPbCr_3$ (orange).

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