Crystal Preparation and Properties of Cesium Tin(II) Trihalides

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Synthesis methods for cesium tin(II) trihalides via aqueous solution and from the melts of anhydrous halides, which ensure freedom from oxidation and the effects of traces of water, are described. The halide compounds $CsSnCl_3$, $CsSnBr_2Cl$, $CsSnBr_3$, $CsSnBr_2I$, $CsSnBrI_2$, and $CsSnI_3$ all have the cubic perovskite structure at elevated temperatures, and all but the first two are good electrical conductors in this form. The growth of single crystals from the melt, and by vapor transport, is outlined.

The ^{35}Cl nuclear quadrupole resonance spectrum of monoclinic $CsSnCl_3$ consists of three lines, with frequencies 9.799, 11.005, and 11.695 MHz at 25°C, confirming the presence of pyramidal $SnCl_3^-$ ions in this structure. In $CsSnBr_3$, there is a single ^{81}Br nuclear quadrupole resonance line, with frequency 63.073 MHz at 25°C, which splits into two lines on cooling the sample below 19°C. The low-temperature form of $CsSnBr_3$ apparently has a tetragonally distorted perovskite structure, with $a = 11.59$ and $c = 11.61$ Å at 12°C. A single ^{127}I nuclear quadrupole resonance line was observed in the low temperature orthorhombic form of $CsSnI_3$, with frequency 79.707 MHz at 25°C, and the variation of the frequency of this line with temperature may indicate a minor phase change in $CsSnI_3$ at 35°C.

Introduction

The first reports of $CsSnX_3$ compounds were very brief accounts of their syntheses (*1, 2*). They were completely uncharacterized materials, however, until rather recent reports of structural and phase equilibria studies (*3–5*). Synthesis near room temperature yields white $CsSnCl_3$, black $CsSnBr_3$, and yellow $CsSnI_3$. The congruent melting points of these three compounds have been determined, or verified, to be near 383 (*4*), 450, and 452°C (*5*), respectively. The room temperature monoclinic crystal structure of the chloride with $a = 16.10$, $b = 7.425$, $c = 5.748$ Å, and $\beta = 93.2°$ (*6*), was verified, as was the recently determined cubic perovskite structure of $CsSnBr_3$ with $a = 5.804$ Å (*7*). This latter study indicated that the bromide is an electronic conductor at room temperature. This is a very unusual property for a material with an expected for-

bidden energy gap of several electron volts; it has been investigated and reported separately (*8*).

In the present work, we report on the structures, halogen nuclear quadrupole resonance properties, polymorphism, and single crystal growth of cesium tin(II) trihalides. An unusual characteristic of the halides was the apparent marked effect of trace amounts of water on their material properties. Careful attention to materials preparation procedures was found to be essential in their syntheses, and suitable methods of synthesis and single growth have been defined.

Materials Synthesis

Two methods have been used to synthesize the cesium tin(II) trihalides: precipitation from solution, and fusion of binary compound mixtures. Both preparation schemes yield the appropriate compounds, but the precipitation procedure has been more reliable. It does not require SnX_2 starting materials free from

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Sn(IV) (difficult syntheses in themselves), and permits preparation of the room temperature forms of $CsSnCl_3$ and $CsSnI_3$.

Precipitation from Solution

The three compounds $CsSnCl_3$, $CsSnBr_3$, and $CsSnI_3$, were prepared using the following general procedure. The anhydrous cesium halide (99.9% powder) and high purity tin metal (99.99% powder or granulated) were vacuum dried (10^{-5} Torr or less) at 100–200°C for several hours. The sample mixture was cooled to room temperature and transferred to a 250-ml round-bottom reaction flask under a flowing blanket of dry N_2, which had previously flushed the reaction flask and associated assembly for at least $\frac{1}{2}$ hr and was continued throughout the entire preparation sequence.

The required quantity of hydrogen halide was then slowly distilled into the raction flask, with constant stirring and gentle heating of the reactants. [HI was first decolorized with H_3PO_2 (9)]. The reactant mixture was finally refluxed 12–15 hr. Slow cooling over a 24-hr period yielded the $CsSnX_3$ product, which was collected via vacuum filtration under a nitrogen atmosphere. The products were washed with a few milliliters of distilled HX and cold, distilled water, and pressed "dry". Products could be dried further, and stored for extended periods (weeks) in vacuum or nitrogen-filled desiccators over 5 A Linde molecular sieves and KOH. For permanent storage, however, the dry compounds should be sealed in pyrex tubes, either under a dry, inert atmosphere or a 10^{-5}–10^{-6} Torr vacuum.

In general, the $CsSnCl_3$, $CsSnBr_3$, and $CsSnI_3$ compounds behaved similarly during preparation, with air sensitivity seeming to increase from chloride to bromide to iodide. Reactant ratios, CsX:Sn, were 1:1 with 0.010–0.10 mole CsX present and HX in excess by about a factor of 10. White flaky needles of $CsSnCl_3$ were obtained, although yellow crystals often formed initially; white Cs_2SnCl_6 is a probable contaminant if any oxidation occurs during preparation. Only black crystals of $CsSnBr_3$ were formed; yellow Cs_2SnBr_6 contamination is easily observable. Yellow needles of $CsSnI_3$ were obtained; greenish crystals probably indicate the presence of black Cs_2SnI_6. As discussed below, the trihalides change colors upon heating. After they have been melted, solid $CsSnCl_3$ is yellow, and $CsSnBr_3$ and $CsSnI_3$ are black solids.

Binary Compound Fusion

The trihalides were also synthesized by slowly heating carefully dried CsX and pure premelted SnX_2 (10, 11) (Sn(IV)-free) in pyrex tubes, continuously evacuated to 10^{-6} Torr, to temperatures about 50°C above the fusion temperatures, viz., to 425°C for $CsSnCl_3$ and 500°C for $CsSnBr_3$ and $CsSnI_3$. Reaction begins at relatively low temperatures, but fairly long reaction times (hours) or several melting–solidification cycles are required to ensure the removal of trace quantities of water and Sn(IV). Solid products, yellow for the chloride and black for the bromide and iodide, can then be sealed in pyrex tubes under vacuum or a dry inert atmosphere.

Mixed compounds such as $CsSnBr_2Cl$, $CsSnBr_2I$, and $CsSnBrI_2$ were also prepared using this fusion method, although the precipitation method is also applicable. Repeat fusions of the appropriate stoichiometries were necessary to obtain homogeneous products with consistent melting points.

Single Crystal Growth

Two methods of crystal growth have been used to prepare single crystals of the cesium tin(II) trihalides: the first is growth from the melt using the Bridgman–Stockbarger technique; the second employs sublimation and vapor transport. Using either method, it was critical to crystal growth that the starting material be premelted and free of all traces of water. Since only preliminary experiments have been conducted on $CsSnCl_3$, it is not included in the crystal growth descriptions.

Melt Growth. Single crystals of $CsSnBr_3$ and $CsSnI_3$ were prepared using the Bridgman–Stockbarger technique with vertical furnaces containing two 30-cm heating zones which could be independently adjusted to produce desired temperature profiles. Zone temperatures were adjusted and controlled (±5°C) using temperature controllers, such as West Instrument Model JAC, and chromel–alumel sensing and control thermocouples. For both materials, the hot zone, essentially flat for 12–15 cm, was controlled at 490°C and the bottom cool zone at about 300°C, resulting in a temperature gradient of 16–20°C/cm in the crystallization region between the two zones. The melting points of the compounds were 450 $\pm$ 5°C for $CsSnBr_3$ and 452 $\pm$ 5°C for $CsSnI_3$.

The premelted and water-free sample charges were sealed in Pyrex or quartz tubes (e.g., 0.8 cm i.d. and 12 cm long with bottoms pointed) under vacuum (10^{-5}–10^{-6} Torr) or under about 1/2 atm N_2 or Ar. After positioning in the hot zone region, the samples were heated at 490°C for 1–2 hr. They were then lowered through the temperature gradient at 1–5 cm/hr and finally annealed at about 280°C for 2–3 hr. The temperature was then reduced from 280°C to about 50°C in 4 or 5 steps over a period of 4–5 hr. The products of both compounds were shiny black and appeared to be composed of several large crystalline grains. Upon exposure to the atmosphere, $CsSnI_3$ developed a dark green surface layer immediately. Although the surface of the $CsSnBr_3$ crystals was apparently unaffected by the atmosphere, some form of surface reaction was indicated by the difficulty of soldering electrical contacts onto crystals exposed to the atmosphere for just a few minutes.

Vapor Growth. Relatively small single crystals of $CsSnBr_3$ and $CsSnI_3$ were prepared by sublimation of the premelted and water-free compounds. Samples of 0.25–0.75 g were preheated at 280°C in 10-mm i.d. Pyrex tubes, then sealed in vacuum to approximately 20 cm length, and placed in a dual zone furnace. A number of temperature profiles were investigated, and a sample or hot zone temperature of about 490°C and a cold zone temperature of about 275°C were found to give maximum crystal growth and size. Crystal formation occurred on the tube walls near the center of the tube, at a temperature of about 360°C. The size of the grown crystals did not appear to increase after about 200 hr.

The largest crystals obtained were about 1 mm long, exhibited a cubic habit, and were shiny black.

Properties

Powder X-ray diffraction patterns were obtained for all of the prepared materials at room temperature; several compounds were investigated at other temperatures. These data are summarized in Table I. White monoclinic $CsSnCl_3$ transforms to a cubic perovskite (yellow) at 117°C. (Agreement on the cubic form is with Ref. 7, not Ref. 6, as discussed in Ref. 7.) The $CsSnBr_3$ products indexed as cubic perovskite at 25°C with the data essentially duplicating that given in Ref. 7. At 12°C some weak extra lines appeared along with some splitting of the cubic lines. This pattern possibly indexes as a tetragonal cell with $a = 11.59$ and $c = 11.61$ Å. This distortion from cubic symmetry is small but is apparently real, since, nuclear quadrupole resonance (NQR) and DTA results verify a transition near 19°C (*8*). Room temperature single crystal data (*12*) for $CsSnI_3$ (yellow) show an orthorhombic cell with $a = 10.34$, $b = 4.77$, and $c = 17.79$ Å. At 152°C, this lattice transforms to the cubic perovskite form (black).

At least some of the nuclear quadrupole resonance frequencies of the halogen atoms have been obtained for each of the cesium tin trihalides. The methods and equipment used in this NQR work have been described previously (*13, 14*), but we have also used an oscillator

TABLE I

Some Properties of the Cesium Tin(II) Trihalides

Compound	Color at 25°C	Color after melting	Melting point (°C)	Crystal structure (25°C)	Transition to cubic (°C)	Cubic lattice constant (Å)[a]	Electrical conductor at 25°C
$CsSnCl_3$	white	yellow	380	monoclinic	117	5.59[22], 5.61[147]	no
$CsSnBr_3$	black	black	450	cubic	19	5.80[25]	yes
$CsSnI_3$	yellow	black	452	orthorhombic	152	6.18[185], 6.18[210]	black, yes
$CsSnBr_2Cl$	red	red	405	cubic	—	5.74[25]	poor
$CsSnBr_2I$	black	black	450	cubic	—	5.93[25]	yes
$CsSnBrI_2$	black	black	452	cubic	—	6.04[25]	yes

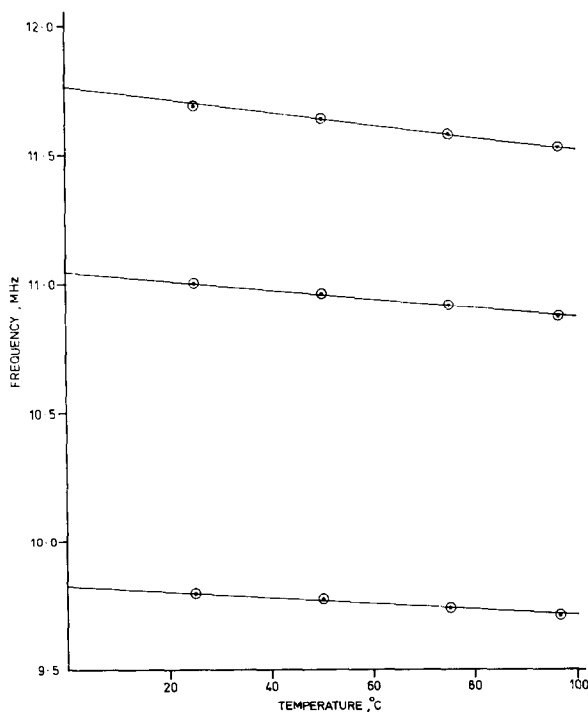[a] Right-hand superscript indicates temperature of measurement in °C.

FIG. 1. Variation of [35]Cl NQR frequencies with temperature for monoclinic CsSnCl₃.

described by O'Konski and Scheffer (15) for work at higher frequencies.

The white, monoclinic form of CsSnCl₃ showed three [35]Cl resonances of approximately equal intensities, with frequencies which varied with temperature as shown in Fig. 1. The frequencies at 25°C were 9.799, 11.005, and 11.695 MHz, with variations of frequency with temperature of −1.22, −1.66, and −2.49 kHz/°C, respectively. The signals disappeared above 115°C and also became very weak, because of the saturation of the resonance lines, below 0°C.

These three resonances in the monoclinic form of CsSnCl₃ correspond to the three inequivalent chlorine sites in the SnCl₃⁻ pyramidal ion present in this structure (6). We observed that traces of water caused the phase transition in CsSnCl₃ to reverse rapidly on cooling through 117°C, while the yellow perovskite form from which all water had been removed by prolonged evacuation at 100°C remained stable at room temperature for at least a year, and was also stable down to 77°K (see Ref. 6). The crystal structure (6) shows that water is not incorporated in the lattice of the monoclinic form of CsSnCl₃, so traces of

water apparently exert only a catalytic effect on the phase transition.

All attempts to observe resonances in the yellow cubic form of CsSnCl₃ at temperatures of 77°K, 25°C, and 130°C failed, even using samples carefully annealed for long times at 130°C. A variety of oscillators and oscillator conditions was used in this search.

The variation of NQR frequencies with temperature for the [81]Br isotope in CsSnBr₃ is shown in Fig. 2. A single resonance was observed in the range 19.6–100°C at 63.073 MHz; this resonance showed a variation with temperature of −3.21 kHz/°C. Below 19°C, this line split into two lines, which moved progressively further apart as the temperature was decreased. The intensity of the lower frequency resonance was about twice that of the other. These results clearly indicate a phase transition at about 10°C. This was observed to be relatively rapid in going from the low temperature form to the cubic form, but much slower in the reverse direction. It was not completely clear from our results on NQR if the phase transition is first order involving the complete disappearance of two lines at the
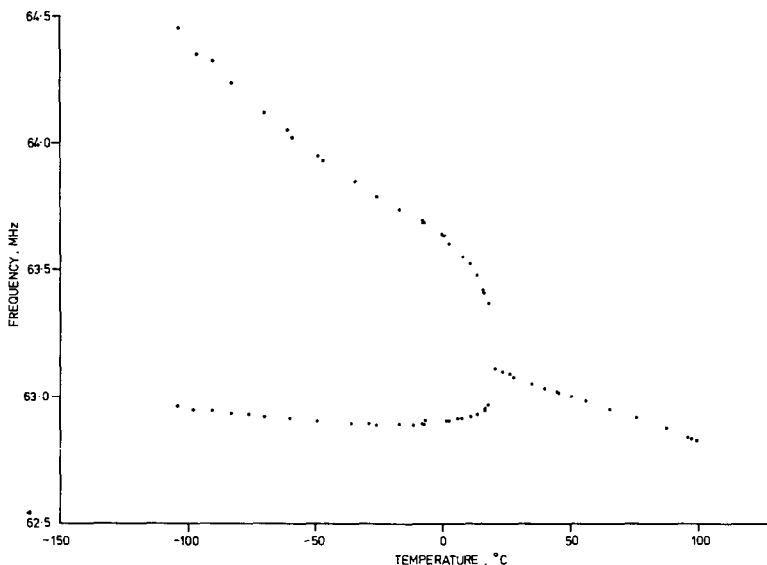
FIG. 2. Variation of [81]Br NQR frequencies with temperature for $CsSnBr_3$.

transition, with replacement by another line close to the intensity weighted mean frequency, or second order, with the two lines merging progressively into one line. The striking resemblance of this transition to the first-order transition at 47°C in $CsPbCl_3$ (16, 17) prompts us to suggest a similar displacive mechanism, and to suggest that the lower frequency line in the low-temperature phase of $CsSnBr_3$ can be assigned to bromine atoms on two-fold sites, while the higher frequency line can be assigned to bromine atoms on four-fold sites.

No NQR signals could be obtained from the high-temperature perovskite form of $CsSnI_3$ (black) from 77 to 450°K. There were great difficulties in operating oscillators with this compound possibly because of its high conductivity, and because very loosely packed samples with rather poor coil filling factors had to be used.

The low temperature form of $CsSnI_3$ (yellow), however, showed one resonance at 79.707 MHz at 25°C, which is tentatively assigned to the 1/2–3/2 transition of [127]I. The frequency of this line showed an approximately linear dependence on temperature from 35 to 105°C with a slope of −6.72 kHz/°C. There was a change of slope at 35 ± 5°C, the slope from −30 to 35°C being −9.08 kHz/°C. Below −30°C, the resonance became too weak to measure. The scatter of points near 150°C, as shown in Fig. 3, was greater than is usual in such measurements,

and there was some evidence for a hysteresis effect in the frequencies as the sample was cycled backwards and forwards across the transition point at 152°C. We were unable to observe any other resonance in the range 20–170 MHz; the 3/2–5/2 [127]I transition corresponding to the 79.7 MHz resonance was apparently too weak to observe. Also, no halogen resonances could be detected in $CsSnBr_2Cl$, $CsSnBr_2I$, or $CsSnBrI_2$.

The structure of the room temperature form of $CsSnI_3$ (yellow) has recently been determined (12). The unit cell is orthorhombic, containing 4 molecules, with dimensions $a = 10.34 \pm 0.01$, $b = 4.77 \pm 0.01$, and $c = 17.79 \pm 0.01$ Å. The space group is Pnma. This structure is very similar to that of NH_4CdCl_3 (18) and to the low temperature forms of $CsPbBr_3$ and $CsPbI_3$, which both have perovskite structures at elevated temperatures (19, 20). It contains double strings of edge-shared SnI_6 octahedra extending along the b-axis. The octahedra are more distorted than the corresponding $CdCl_6$ octahedra in NH_4CdCl_3, with two Sn–I distances of 3.19 Å, two of 3.23 Å, one of 3.46 Å, and one of 2.96 Å. Of the three inequivalent iodine sites in the crystal, one contains iodine bonded to two Sn atoms, with Sn–I distances of 3.19 Å, one contains iodine atoms bonded to three Sn atoms, with Sn–I distances of 3.23, 3.23, and 3.46 Å, while one is bonded to only one Sn atom with
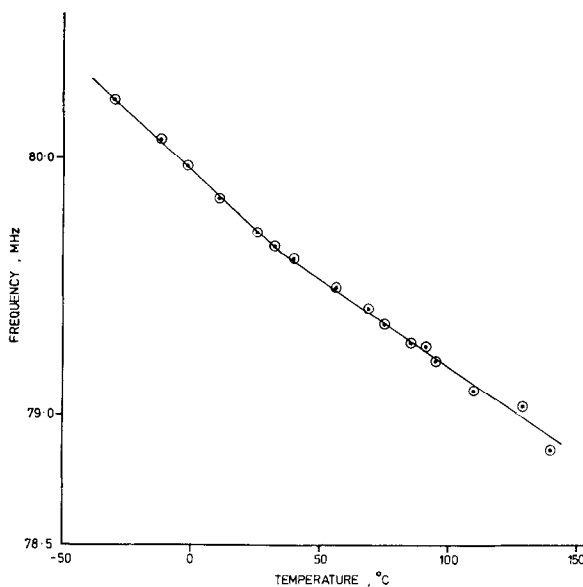
Fig. 3. Variation of ^{127}I NQR frequency with temperature for orthorhombic CsSnI$_3$.

a Sn–I distance of 2.96 Å. The observed NQR resonance is tentatively assigned to this latter iodine atom; resonances for the other iodine atoms are expected at considerably lower frequencies.

The slight inflection at 35°C in the graph of Fig. 3 presumably indicates a structural transition which must, however, be relatively minor as the X-ray patterns above and below this point are the same. The transition at 152°C, on the other hand, involves a major rearrangement of the lattice, including changes in the Sn–I distances from 2.96, 3.19, 3.23, and 3.46 Å to about 3.09 Å in the perovskite. This major rearrangement causes a complete change in the electrical properties of the compound.

There has been some discussion in the literature about the color and electrical conductivity changes of the cesium tin(II) trihalides, and particularly the tribromides, during heating (7). We have observed the following variations when the compounds were heated in vacuum or under an inert atmosphere of N$_2$ of Ar. White CsSnCl$_3$ changes to bright yellow near 117°C; the yellow solid gives a clear yellow melt. Both forms are electrical insulators. The yellow CsSnI$_3$ product begins to darken slightly above 100°C and turns black at 152°C. Between 350 and 400°C the sample turns slightly dark red. The melt is black and opaque and the vapor yellow. Upon solidification, CsSnI$_3$ is shiny black and remains

so when cooled to room temperature. Its resistivity at 25°C is 25 ohm-cm. Black CsSnBr$_3$ turns dark red between 350 and 400°C and melts to a clear deep dark-red liquid. Its vapor is yellow, with a rather high vapor pressure at 550°C. The color changes for CsSnBr$_3$ reverse upon cooling. The color changes previously reported for CsSnBr$_3$ (7) could be reproduced only by heating it in air. However, the reported electrical conductivity data that apparently correspond to these color changes (7) do not seem to apply to the pure compound. The 20 ohm-cm room temperature resistivity of the p-type CsSnBr$_3$ conductor appears to show metallic-type behavior between −100 and 350°C, with no major change in resistance observed (8).

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