JOURNAL OF SOLID STATE CHEMISTRY **31**, 387–392 (1980)

Surface Studies of Electrically Conducting "$CsSn_2I_5$"

STEVEN L. SUIB* GALEN D. STUCKY,* RICHARD J. BLATTNER,† AND PAUL F. WELLER‡

** School of Chemical Sciences and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801; † Materials Research Laboratory, Urbana, Illinois 61801; and ‡ Western Illinois University, Macomb, Illinois 61455*

Received February 5, 1979

Single crystals of $CsSn_2I_5$ have been grown in sodium metasilicate gels and identified by X-ray powder and single-crystal diffraction methods. The $CsSn_2I_5$ crystals are good electrical conductors and show unusual photochemical behavior. The nature of these properties has been probed with Auger electron spectroscopy. This paper considers the synthesis, chemical characterization, and surface properties of $CsSn_2I_5$.

Introduction

Karantassis (*1*) was the first to report the synthesis of MSn_2I_5 compounds ($M =$ Cs,Rb) in 1926. The compounds were formed by adding the alkali halide to solutions of stannous iodide, and were not well characterized. Since the work of Karantassis, phase equilibria studies (*2*) and Mössbauer experiments (*3*) of the bromide and chloride derivatives of $CsSn_2I_5$ have been reported.

The gel method of crystal growth is a rather simple technique for the controlled crystallization of certain compounds (*4*). We have previously studied (*5*) the gel growth of single crystals of rubidium and cesium tin halides. We now extend our studies of the growth of these compounds and report on the surface properties of $CsSn_2I_5$ through the use of Auger electron spectroscopy.

Experimental

Crystal Growth

The $CsSn_2I_5$ crystals were prepared in sodium metasilicate gels. A mixture of 7.5 ml of 1.72 *M* stock solution of sodium metasilicate, 7.5 ml distilled water, and 6 ml of 1 *M* CsI was initially prepared. To this solution, 15 ml of 2 *M* glacial acetic acid was added. This mixture was then poured into a 5-cm test tube and allowed to set. After hardening of the gel, 6 ml of a saturated solution of SnI_2 dissolved in concentrated HI was added to the top of the set gel. This last step was carried out in a glove bag under nitrogen. The test tube was then capped with a rubber stopper and placed in a 35°C water bath. Crystallization started after about 1 hr. The crystals were separated from the gel using spatulas after crystal size reached a maximum. Procedures for obtaining large single crystals ($3 \times 3 \times 3$ mm) have been given elsewhere (*5*).

Chemical and Physical Measurements

Atomic absorption analyses, Volhard and Mohr titrations, and ion-selective electrode analyses were carried out in order to determine the stoichiometry of the crystals. A Perkin–Elmer Model No. 404 atomic absorption spectrometer was used to

0022-4596/80/030387-06$02.00/0

determine the Cs and Sn concentrations. The crystals were dissolved in 2 *M* KOH solution, and subsequently diluted prior to the atomic absorption analyses. Standard procedures (*6*) for the determination of I using Mohr and Volhard titrations were followed.

A Keithley 155 microvoltmeter, a Hewlett–Packard 6200B dc power supply, and a Leeds and Northrup 8690-2 millivolt potentiometer were used for the electrical conductivity measurements. The four current and voltage leads were made of chromel wire, and were attached by pressure. Conductivity measurements were also made on pressed powder pellets. All measurements were made in a flowing nitrogen atmosphere. Seebeck effect measurements were also taken on $CsSn_2I_5$ crystals. The samples were mounted between two copper bars, one of which was heated by a small furnace.

X-Ray powder patterns were obtained with a Phillips Instruments Model #12045 diffractometer. Single-crystal X-ray precession photographs were taken on a 12045/3 Phillips Electronics instrument with a Charles Supper Company No. 6007873 precession camera. Weissenberg photographs were obtained by using a 12045/3 Phillips Electronics instrument and a Nonius camera, Model No. 66082.

The thermal stability of $CsSn_2I_5$ was investigated by using a Perkin–Elmer differential scanning calorimeter, Model No. DSCl. The temperature was calibrated using indium metal. Samples were packed in aluminum containers, and the experiments were carried out under a high-purity nitrogen environment.

Auger electron spectrometric analyses were performed with a Physical Electronics Model 545 scanning Auger microprobe. The samples were mounted on the standard carousel at 30° grazing incidence to the primary electron beam. The sample chamber residual vacuum was $< 1 \times 10^{-9}$ Torr prior to all analyses. Primary electron energies of 5 keV were employed in the spectroscopy, depth profiling, and imaging modes. Depth profiles were obtained by repetitively monitoring the appropriate Auger transition with simultaneous 2-keV Ar^+ ion sputtering at an Ar pressure of about 5×10^{-5} Torr.

Results

Crystal Growth

$CsSn_2I_5$ is obtained by the following gel growth reaction:

$$2\,CsI + 3SnI_2(Sat) \xrightarrow[35°C,N_2]{Na_2SiO_3\cdot 9H_2O} CsSn_2I_5\text{ (orange)} + CsSnI_3\text{ (yellow)}. \quad (1)$$

The $CsSnI_3$ crystals are yellow with a needle-like habit and grow below the $CsSn_2I_5$ crystals. The $CsSn_2I_5$ crystals are octahedral in shape, but vary in color depending on whether the test tube has been exposed to, or kept absent from, ultraviolet or visible light or air. When grown in the absence of light, the crystals are orange and insulators. The same $CsSn_2I_5$ crystals, when grown in light, are black and are good semiconductors. Upon exposure to light, or to air in the dark, the exterior of the orange octahedral crystals turn black. (The black crystals grown in the presence of light also have an orange inner matrix.) This process can be followed during growth in the gel, with the crystals closest to the edge of the test tube, and to the light, turning black first.

Crystal and Physical Properties

Chemical analyses failed to detect any difference between the Cs/Sn/I ratios of the orange and black forms of the crystals. The calculated stoichiometry from these experiments is $CsSn_2I_5$. The crystals dissolve in aqua regia, except for a thin transparent film which remains in solution with the black form. (Note that SnO is black and soluble in aqua regia SnO_2 is white to transparent and insoluble in aqua regia.)

Thermal stability experiments indicated that both the orange and the black forms decompose above 500°K, and electrical conductivity measurements showed that the orange form is initially an insulator. On exposure to air the conductivity rises quickly to a value of 50 ohm^{-1} cm^{-1}, and black $CsSn_2I_5$ single crystals have a conductivity of 100 ohm^{-1} cm^{-1}. Seebeck effect measurements on the black form gave a value of -0.37 mV/°C for the Seebeck coefficient.

The orange $CsSn_2I_5$ form crystallizes in the tetragonal system in the not uniquely determinable space group $P4cc$ (#103) or $P4$—mcc (#124) with lattice constants a = 6.40 Å and c = 16.05 Å. A single-crystal X-ray structure determination of the orange form is presently underway, and will be reported elsewhere.

Auger Studies

An Auger electron spectroscopy study was undertaken to determine the surface composition of the $CsSn_2I_5$ system. Figure 1A shows the Auger spectrum of the black single-crystal form of $CsSn_2I_5$. The spectrum shows a doublet at 426 and 430 eV indicative of tin and a peak at 510 eV due to oxygen. It is noted that no Cs or I peaks are present. The black crystals, when crushed, have an orange interior and the Auger peaks for the crushed crystals are shown in Fig. 1B. The tin Auger peaks for the crushed crystal occur at 430 and 434 eV. An oxygen Auger peak again occurs at 510 eV and a doublet due to cesium is seen at 563 and 575 eV. The peak at 520 eV is due to iodine.

The ratios of the intensities of the Sn doublet peaks are characteristic of the chemical environment of the Sn atoms. In other words, the intensity ratio of the Sn doublet peaks is characteristic of chemical bonding. This has been shown to be the case for other group IV elements such as C (*7*), Si (*8*), and Ge (*9*). In the case of the crystal surface of the black form, the 430 eV/426 eV intensity ratio is greater than unity. A similar intensity ratio was observed on bulk stannic oxide powder, as is shown in Fig. 2B. In tin metal shown in Fig. 2A, this ratio is less than unity, as it is in the case of the crushed crystal in Fig. 1B. The Auger spectrum for SnI_2 is shown in Fig. 3A. The high energy to low energy tin intensity ratio in this instance

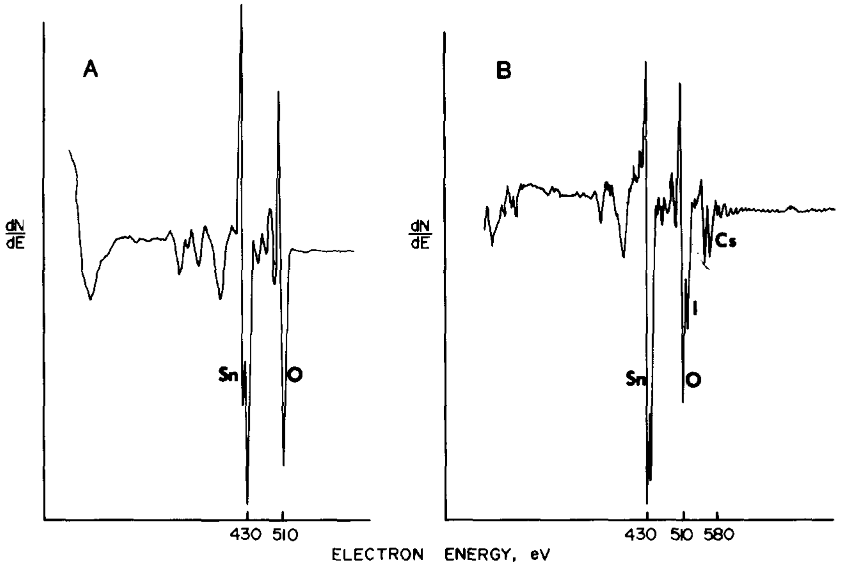

FIG. 1. Auger spectra of single-crystal $CsSn_2I_5$: (A) crystal surface, (B) crushed crystal.

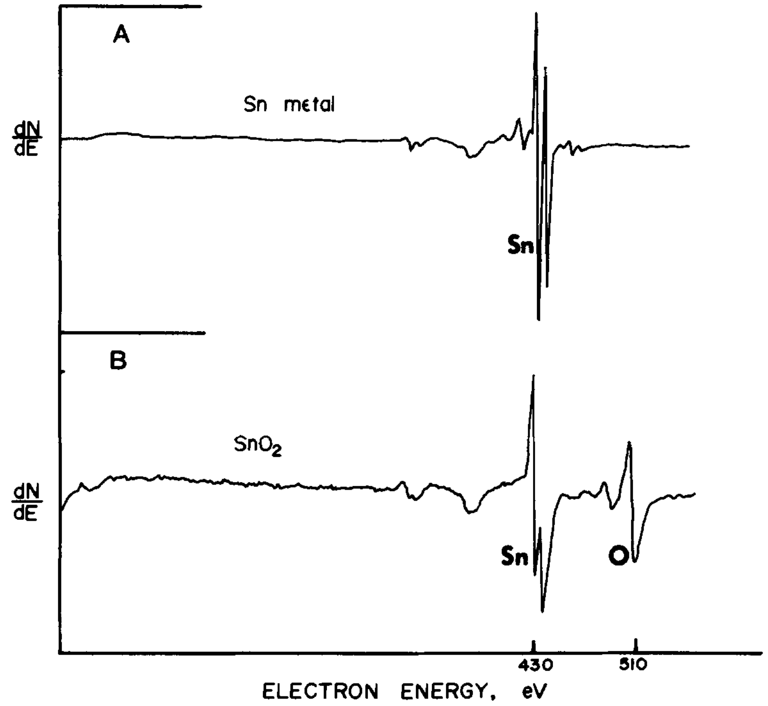

FIG. 2. Auger spectra of: (A) Sn metal, (B) SnO_2.

is very near unity.[1] The spectrum in Fig. 3B is that of SnO, which also gives an intensity ratio of less than unity similar to that in Figs. 1B and 4B.

Figure 4A shows the spectrum observed after profiling through a significant portion of the surface. At this lower depth Cs, Sn, and O are present. Iodine does not appear to be present at this point. The Auger spectrum for the crushed crystal is shown in Fig. 4B for comparison.

The Auger spectrum in Fig. 5 shows three peaks for tin at 427, 432, 437 eV for an orange $CsSn_2I_5$ crystal grown in the absence of light and air. The broad peak at 514 eV is due to oxygen and the cesium doublet occurs at 559 and 571 eV. Surface charging during

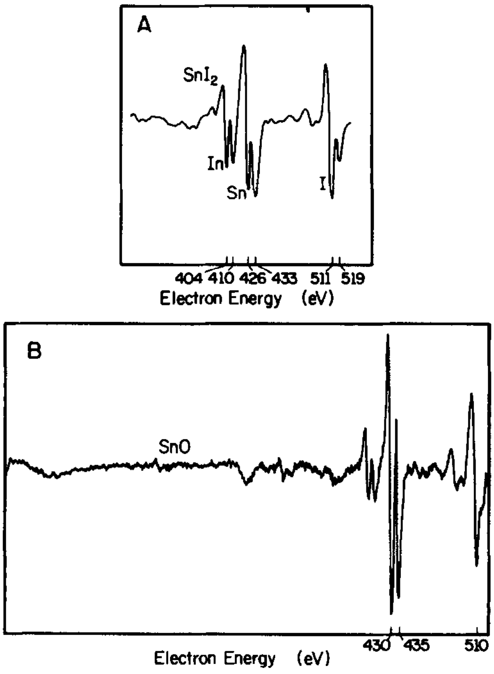

FIG. 3. Auger spectra of: (A) SnI_2, (B) SnO.

---

[1] For more extensive applications of lineshape and chemical shift behavior in the Auger experiment, see T. A. Carlson (Ed.), "Photoelectron and Auger Spectroscopy," Plenum, New York (1975).

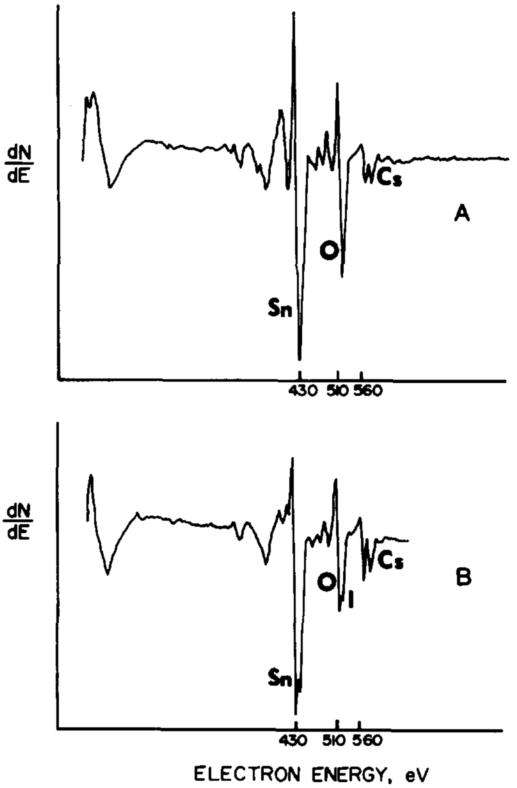

FIG. 4. Auger spectra of single-crystal $CsSn_2I_5$: (A) After depth profile, (B) crushed crystal.

the running of this spectrum may account for electron energy shifts. After only 15 sec of ion sputtering, surface charging was very apparent, and a good spectrum was not obtained for this underlying material. A deep orange color was observed in the Auger chamber in the area where the electron beam hit the crystal. No electron beam damage from ion sputtering in the Auger experiments was observed for any of the samples mentioned in this paper.

Discussion

These data suggest the proposed in-depth structure of $CsSn_2I_5$ as given in Fig. 6. The orange core is insulating and consists of $CsSn_2I_5$. There is then a transition region containing Sn_xO_y and some cesium in which the iodine level may be below the Auger detection limit (<1%). The Sn_xO_y may consist of black SnO and white SnO_2. On the surface there is a transparent layer of SnO_2 which is insoluble in aqua regia. In this surface layer cesium and iodine levels are below the Auger detection limit. This surface oxidation is photochemically enhanced by ultraviolet or visible light. The electrical conductivity is due to the SnO_2 surface layer rather than to conduction through the bulk crystal. The value of the Seebeck coefficient indicates that this compound is an N-type semiconductor, which is consistent with the known Seebeck coefficient of SnO_2.

Conclusions

The suggestions found in the previous section account for the color, electrical conductivity, and solubility of the $CsSn_2I_5$

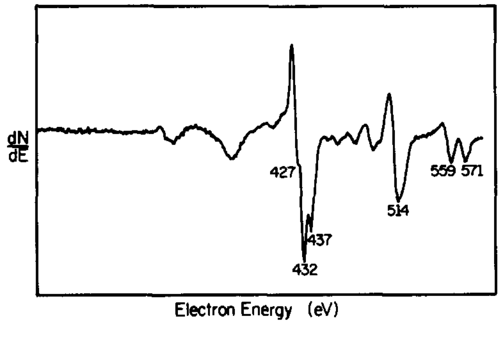

FIG. 5. Auger spectrum of orange single-crystal $CsSn_2I_5$.

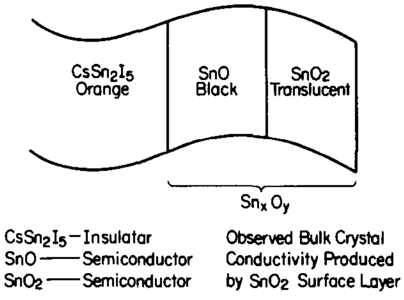

FIG. 6. Proposed in-depth structure of $CsSn_2I_5$.

crystals. The values of the conductivity and Seebeck coefficient and the color and solubility properties of the $CsSn_2I_5$ system are consistent with those of SnO_2 thin films as reported by Zellmer (*10*). The fate of the cesium and iodine lost from the tin oxide surface phases is presently unknown. The possibility also exists that some Sn metal may be present in the oxide surface phases. This study emphasizes the importance of surface chemistry and its potential effect on the electronic properties of solid-state materials.

Acknowledgment

The support of the National Science Foundation under grant DMR 77-23999 with the Materials Research Laboratory is gratefully acknowledged.

References

1. T. KARANTASSIS, *Bull. Soc. Chim.* **39**, 43 (1926).
2. J. D. DONALDSON, J. SILVER, S. HADJIMINOLIS, AND S. D. ROSS, *J. Chem. Soc. Dalton Trans.* 1500 (1975).
3. J. D. DONALDSON AND J. SILVER, *J. Chem. Soc. Dalton Trans.* 666 (1973).
4. H. K. HENISCH, "Crystal growth in Gels," Pennsylvania State Univ. Press, University Park (1973).
5. S. L. SUIB AND P. F. WELLER, submitted.
6. R. B. FISCHER AND D. G. PETERS, "Quantitative Chemical Analysis," Saunders, Philadelphia Pa. (1969).
7. E. N. SICKAFUS, *J. Vac. Sci. Technol.* **11**, 299 (1974).
8. C. C. CHANG, *in* "Characterization of Solid Surfaces," Chapt. 20, Plenum, New York (1976).
9. K. L. WANG AND A. JOSHI, *J. Vac. Sci. Technol.* **12**, 927 (1975).
10. D. L. ZELLMER, "Analysis and Electrochemistry of Semiconducting Tix Oxide," Ph.D. thesis, University of Illinois, Urbana, Ill. (1969).