JOURNAL OF MATERIALS SCIENCE 10 (1975) 1449–1451

Crystal growth of caesium tin(II) trichloro-bromides

R. H. ANDREWS, J. D. DONALDSON, J. SILVER
Department of Chemistry, Chelsea College, London, UK

E. A. D. WHITE
Department of Electrical Engineering, Imperial College, London, UK

Crystals of compounds occurring in the solid solution range $CsSnBr_3$–$CsSnCl_3$ have been prepared by pulling from the melt and by Bridgman growth. The materials show a consistent change in colour and electrical resistivity from the black metallic conductor $CsSnBr_3$ to the bright yellow $CsSnCl_3$. The as-grown compounds undergo various structure changes from the cubic, high temperature form to lower symmetry forms on standing. These changes have been followed by DTA; they are also apparent as colour changes. X-ray examination indicates that the compounds react with atmospheric moisture to form monohydrates. The products showed some differences in their structural stability from powders of the same composition precipitated from solution. These differences are attributed to particle size effects analogous to those encountered in ferroelectric perovskites.

1. Introduction

Materials of the type $CsSn^{II}X_3$ are of current interest because of the temperature sensitive structure transitions that occur in members of the series, and the unusual octahedral co-ordination of the tin(II) and its consequences on the electrical conductivity of the materials.

Some structural information and Mossbauer studies have been reported for these materials [1] and an interpretation of the electrical conductivity in terms of the contribution of the lone-pair $5s^2$ electrons of the tin(II) to bands provided by the orbital interaction of the halide atoms has been proposed [2]. To investigate the materials in more detail it is necessary to study single crystals. The growth of a series of solid-solution crystals from the system $CsSnBr_3$–$CsSnCl_3$ is described in this paper. This series was chosen because of the progressive colour changes with composition observed in powder specimens prepared by wet chemical methods.

2. Crystal growth

The relative stability and the low melting points of the compounds enabled both the Czochralski and Bridgman techniques to be used for growth. For the former, a standard type of crystal puller was used with RF heating and a platinum crucible as susceptor. In all cases the materials could be melted in a dry nitrogen atmosphere with only slight evaporation losses. These were most pronounced for the bromide compound; the evaporating species was identified as $SnBr_2$. No evidence of any structural differences between the two ends of a crystal boule were found, even for $CsSnBr_3$. The effect of $SnBr_2$ loss from the melts did, however, tend to increase crystal interface instability, presumably due to constitutional supercooling. Effectively growth took place from an increasingly dilute $CsBr$–$CsSnBr_3$ solution as the loss of $SnBr_2$ progressed.

The crystals were pulled at rates of approximately 5 mm h^{-1}. Nucleation on an alumina rod was generally successful, and necking-in gave crystals containing few grain boundaries. Successive growth on single crystal pieces as seeds gave crystals free from voids or cracks although some low-angle boundaries remained. Growth became progressively easier with increasing chlorine content.

For Bridgman growth, the materials were placed in Pyrex ampoules and vacuum outgassed at room temperature before sealing. The ampoules were lowered through a two-zone vertical furnace at a rate of 5 mm h^{-1}; the temperature gradient between the zones was approximately 20° C cm^{-1}.

The products from the Bridgeman growth contained large single crystal grains of several mm^2 cross-section. No evaporation loss was apparent in the ampoule, and the resulting boules were readily removed from the glass capsules.

The materials studied formed a consistent series with respect to the melting points, colour and high temperature structure. The melting points were measured by DTA and hot-stage microscopy to an estimated accuracy of ± 2° C. The values obtained are given in Table I.

TABLE I

Composition	Melting point (° C)
$CsSnBr_3$	448
$CsSnBr_2Cl$	425
$CsSnBr_{1.5}Cl_{1.5}$	423
$CsSnBrCl_2$	410
$CsSnCl_3$	368

The as-grown materials, with the exception of $CsSnBr_3$, changed colour on standing for several hours; this change has been shown to be associated with the reversion of the structure to the low temperature forms. In the case of $CsSnBrCl_2$ and $CsSnCl_3$ the low temperature form is monoclinic [3], but the exact symmetry has yet to be established for $CsSnBr_2Cl$ and $CsSnBr_{1.5}Cl_{1.5}$. The determination of the nature of the structural modification is complicated by the fact that on crushing the materials they rapidly pick up moisture to form compounds analogous to the hydrated form of $CsSnCl_3 . H_2O$, the preparation and characterization of which has been described by Donaldson and Silver [4]. The colour changes for the various structural modifications formed from the as-grown materials are summarized in Table II.

TABLE II Colour changes in $CsSnX_3$ materials

Composition	As-grown colour (cubic form)	Colour on standing
$CsSnBr_3$	black	black (cubic)
$CsSnBr_2Cl$	dark red	dark-wine (nd)
$CsSnBr_{1.5}Cl_{1.5}$	bright red	dull red (nd)
$CsSnBrCl_2$	orange	orange-brown (mc)
$CsSnCl_3$	yellow [1, 4]	cream (mc) [3]

nd = structure not determined; mc = monoclinic.

3. Characterization of the crystal products

The crystals were examined by X-ray powder photography and single crystal methods. The results of the preliminary investigations of the structures of the as-grown crystals and of the subsequent changes interpreted with respect to the DTA results, are summarized below.

It is not possible to comment with certainty on the stoichiometry of the crystal products at this stage. However, the similarity in X-ray diffraction patterns with those for the precipitated materials described by Barrett *et al.* [1] suggest that any departures from stoichiometry must be slight.

TABLE III Transition temperatures (° C)

Composition	Lower transition	Higher transition
$CsSnBr_3$	—	160–180
$CsSnBr_2Cl$	55	210–230
$CsSnBr_{1.5}Cl_{1.5}$	60	220–240
$CsSnBrCl_2$	72	190–205
$CsSnCl_3$	86, 90, 125	—

3.1. $CsSnBr_3$

Identified by X-ray powder [1] and single crystal diffraction to be a cubic perovskite structure. High temperature X-ray examination above the observed DTA peak at 160 to 180° C showed no discernible structure change, but preliminary electrical measurements showed that at about 160° C the material becomes highly conducting and that the process is ionic. Thus it appears reasonable that that DTA peak corresponds to the onset of ionic mobility (of the tin(II) ions) in the perovskite structure. A similar interpretation may be placed on the DTA peaks recorded at temperatures about 200° C in the other compositions.

3.2. $CsSnBr_2Cl$ and $CsSnBr_{1.5}$ $Cl_{1.5}$

The colour change in both of these materials is related to structural relaxation from the cubic perovskite to the low-temperature and finally to the hydrated forms. In earlier work [1, 5], it was found that the precipitated, powder forms of these materials still showed the cubic structure after standing for some weeks at room temperature. This suggests that the high surface/volume ratio of the powder allows the cubic structure to be retained. A similar situation is found in $BaTiO_3$ which can retain the cubic perovskite form well below the Curie temperature when the particle size is very small [6]. In the present materials the X-ray diffraction lines of the powder photographs indicate very small crystallite sizes for the precipitated materials.

Specimens in the cubic form showed no DTA peaks at 60 or 72°C respectively. These peaks are consequently identified with the temperature sensitive structure transitions. The high temperature peaks are again attributed to the conductivity changes occurring in the materials.

3.3. CsSnBrCl

This composition showed similar behaviour to the other mixed bromochlorides. The low temperature DTA peak fits in a progressively increasing series. However, the higher temperature peak has fallen compared with the composition $CsSnBr_{1.5}Cl_{1.5}$. The reasons for this change have yet to be established.

3.4. $CsSnCl_3$

Examination of the crystals after crushing and standing in air (thus converting them to $CsSnCl_3.H_2O$), in a Nonius X-ray continuously recording high temperature camera showed that the hydrated form was stable to 86°C. At this temperature it changed to the anhydrous monoclinic form. At 90°C the characteristic pattern of the cubic form appeared, but the monoclinic form persisted up to 125°C. This information enabled the three well-defined peaks obtained by DTA at 86, 90 and 125°C to be identified with the transitions:

$$CsSnCl_3.H_2O \rightarrow CsSnCl_3 \text{ (monoclinic) } 86°C;$$

$$CsSnCl_3.H_2O \rightarrow CsSnCl_3 \text{ (cubic) } 90°C;$$

$$CsSnCl_3 \text{ (monoclinic) } \rightarrow CsSnCl_3 \text{ (cubic) } 125°C.$$

No high temperature DTA peaks were found for this material up to the melting point. Significantly no abnormalities in the electrical conductivity/temperature curves have been found (Table III).

4. Conclusion

The work reported here is an initial appraisal of the structural characteristics of an unusual and interesting family of compounds. Further detailed studies on the single crystals grown will be needed to determine the exact nature of the high temperature DTA peaks, and of the structure transitions that occur both with respect to temperature and the readily reversible reaction with water.

Acknowledgement

The authors wish to thank Dr J. A. Barrie and Mr R. N. Sheppard of the Polymer Characterisation Laboratory of Imperial College for the DTA investigations.

References

1. J. BARRETT, S. R. A. BIRD, J. D. DONALDSON and J. SILVER, *J. Chem. Soc.* (*A*) (1971) 3105.
2. J. D. DONALDSON and J. SILVER, *J. Inorg. Nuclear Chem. Letters* **10** (1974) 537.
3. F. R. POULSON and S. E. RASMUSSEN, *Acta Chem. Scand.* **24** (1970) 150.
4. J. D. DONALDSON and J. SILVER, *J. Chem. Soc. Dalton* (1973) 666.
5. J. D. DONALDSON, D. LAUGHLIN, S. D. ROSS and J. SILVER, *ibid* (1973) 1985.
6. M. SCHOIJET, *Brit. J. Appl. Phys.* **15** (1964) 719.

Received 10 June 1974 and accepted 17 February 1975.