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Structural Phase Transitions of the Polymorphs of $CsSnI_3$ by Means of Rietveld Analysis of the X-Ray Diffraction

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The successive phase transitions of the polymorphs of $CsSnI_3$ were studied by means of the powder X-ray diffraction and their crystal structures were analyzed at three different temperatures by the Rietveld method.

We have been interested in the structural variation in the series of compounds ABX_3 (A=alkaline metal and alkylammonium, B=Ge(II), Sn(II), and Pb(II), X=Cl, Br, and I) and their structures and bondings have been studied by means of halogen NQR, ^{119}Sn Mössbauer, and X-ray diffraction techniques. In several cases drastic structure changes associated with phase transitions have been found.1-5) Furthermore, metallic and ferroelectric compounds have been found in this category of samples.3,6,7) In our previous papers, we have classified the structure of the BX_3^- anion into four models referring to the structural data.1,2) This classification is based on the characteristic deformation of the octahedron having hypervalent central metals such as Ge(II), Sn(II), and Pb(II). In the octahedral coordinations around these hypervalent metals, two limiting structures have been found for the *trans* X-B-X bond, i.e., a symmetric *trans* X-B-X bond and an asymmetric *trans* X-B···X bond. The former symmetric bond, as is seen in the perovskite structure, is regarded as a typical 3c-4e (three-center four-electrons) bond and the latter asymmetric bond is regarded as a normal 2c-2e bond having a weak bond at the *trans* position. In the case of $CsSnI_3$, two modifications having different configurations around the Sn atom appear at room temperature. They are a greenish yellow phase and a metastable black phase. With increasing temperature the greenish yellow phase changes to the black phase having perovskite structure at 425 K (Fig. 1).1) Thereby the iodine bridge changes from a bent to a linear type and the environment around the Sn atom changes from a square pyramidal to a regular octahedral coordination. Furthermore, it is especially interesting that the electric conductivity increased by 10^4 times at the phase transition.3) Although this high-temperature modification remained black and metallic down to

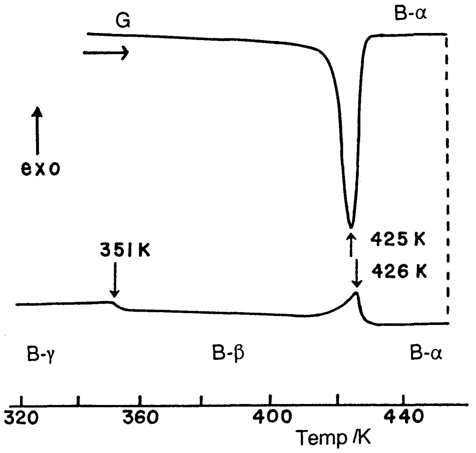

Fig. 1. DTA curves of $CsSnI_3$. The DTA sensitivity of the cooling run is 5 times larger than that of the heating run. 1)

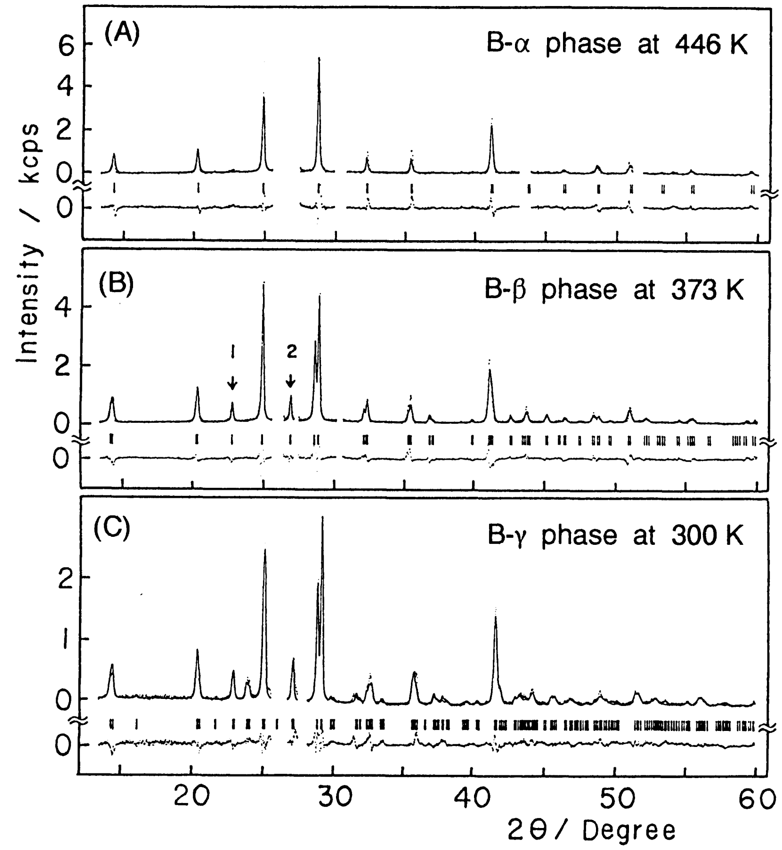

Fig. 2. Final results of the Rietveld refinements for (A):B-α phase, (B):B-β phase, and (C):B-γ phase. The best-fit profiles and the raw data are shown by solid-line and dots, respectively. The lower portion is a plot of the difference between them. The vertical marks below the profiles indicate the positions of all reflections included in the calculations.

77 K, two thermal anormalies on the DTA curve were observed at 426 K and 351 K (Fig. 1). In this paper, the successive phase transitions of the black phase (metastable phase) of CsSnI$_3$ were confirmed by the powder X-ray diffraction and their structures were analyzed by the Rietveld method. The high electric conductivity of the black phase was discussed on the basis of the structure by comparing with that of the greenish yellow phase.

CsSnI$_3$ grown from the melt has a lustrous black color (hereafter this modification is abbreviated as CsSnI$_3$(B)). It changed easily to greenish yellow crystals (abbreviated as CsSnI$_3$(G)) by grinding with an agate mortar. This polycrystalline sample of CsSnI$_3$(G) was confirmed to be identical to that obtained by Mauersberger and Huber by comparing the observed diffraction pattern with the simulated one.[8] The polycrystalline sample of CsSnI$_3$(B) used for the diffraction measurements was prepared in an X-ray cell heated above 440 K in an evacuated desiccator. The black sample exhibited successive phase transitions and these phases were abbreviated as B-α , B-β , and B- γ from the highest temperature form as shown in Fig. 1. The X-ray diffraction patterns were obtained by Rigaku Rad-B system using a newly devised high-temperature cell. The measurements were carried out under nitrogen atmosphere by a step count with the interval of 0.04° using Cu Kα radiation. The Fortran program developed by Izumi was used for the Rietveld analysis.[9] Figure 2 shows the final best-fit profiles obtained by the Rietveld method together with the raw data. The crystal data and the structural parameters are summarized in Tables 1 and 2. In order to avoid the thermal decomposition of the powdered sample, a rapid scanning speed (5°/m) was adopted at 446 K.

Table 1. Crystal data and experimental details for $CsSnI_3$(B)

	B-α phase	B-β phase	B-γ phase
Space group	Pm3m	P4/mbm	Pnam
Crystal system	Cubic	Tetragonal	Orthorhombic
Lattice constants / Å	a=6.219(2)	a=8.772(2) c=6.261(2)	a=8.688(1) b=8.643(1) c=12.378(1)
Z	1	2	4
Temperature / K	446	373	300
Number of parameters	18	20	28
2θ for refinement	10°-60°	10°-60°	10°-90°
R_F a)	0.118	0.075	0.043

a) $R_F = \sum | \sqrt{I(o)} - \sqrt{I(c)} | / \sum \sqrt{I(o)}$, where I(o) and I(c) are integrated intensity.

Table 2. Atomic coordinations of $CsSnI_3$ B-β (373K) and B-γ (300K) phases with standard deviations of the least significant figures in parenthese

Phase	Atom	Position a)	x	y	z	B/Å^2 b)
B-β	Cs	2d(mmm)	0	0.5	0	8.9(12)
	Sn	2b(4/m)	0	0	0.5	2.4(12)
	I(1)	2a(4/m)	0	0	0	3.3(12)
	I(2)	4h(mm)	0.210(2)	0.290(2)	0.5	5.1(12)
B-γ	Cs	4c(m)	0.006(2)	-0.040(2)	0.25	2.1(4)
	Sn	4b($\bar{1}$)	0.5	0	0	1.9(3)
	I(1)	4c(m)	0.476(3)	0.000(3)	0.25	2.5(5)
	I(2)	8d(1)	0.294(2)	0.705(2)	-0.019(1)	1.5(3)

a) Wyckoff notation and point symmetry in parenthesis. b) Isotropic thermal parameters.

As Fig. 2(A) shows, the diffraction pattern of the B-α phase was essentially same with that of $CH_3NH_3SnI_3$, suggesting that the crystal belongs to a cubic perovskite.1) In this cubic phase, all Sn-I bond lengths are equal to the one half of the cubic lattice constant (Sn-I:3.110 Å). With decreasing temperature below 426 K, new reflections such as shown by arrows 1 and 2 appeared between original reflections of the cubic phase. As shown in Table 1, the B-β phase belongs to a tetragonal system having lattice constants $a \approx \sqrt{2}a_{\mathrm{cubic}}$ and $c \approx a_{\mathrm{cubic}}$, in which a and b axes are along with [110] and $[1\bar{1}0]$ directions of the pseudo cubic cell. Using the coordinates shown in Table 2, the iodine bridging angles, Sn-I-Sn, were calculated as 161.9(8)° and 180° in the ab plane and parallel to the c axis, respectively. This corresponds to the mutual rotation of the adjacent SnI_6 octahedra by 9.1° in the opposite directions about the c axis. On further cooling below 351 K, another new reflections appeared associated with the phase transition from the B-β to B-γ phase. In the B-γ phase, the unit cell increases further two times along the c axis compared to the tetragonal phase. Figure 3(A) shows the structure of the B-γ phase and the chain structure of distorted SnI_6 units in $CsSnI_3$(G) is also presented in Fig. 3(B) for the sake of the comparison.8) The angles of the iodine bridges in the B-γ phase are 172.3(6)° (Sn-I(1)-Sn) parallel to c axis and 158.0(3)° (Sn-I(2)-Sn) in the ab plane. The Sn-I bond lengths are 3.102(2) Å (Sn-I(1)), 3.122(10) Å (Sn-I(2)), and 3.120(10) Å (Sn-I(2)') and are almost same with that in the cubic $CH_3NH_3SnI_3$ (Sn-I:3.116 Å).1) So that the SnI_6 octahedra remain almost regular during the successive phase transitions, although the iodine bridges are no longer perfect linear. This is consistent with

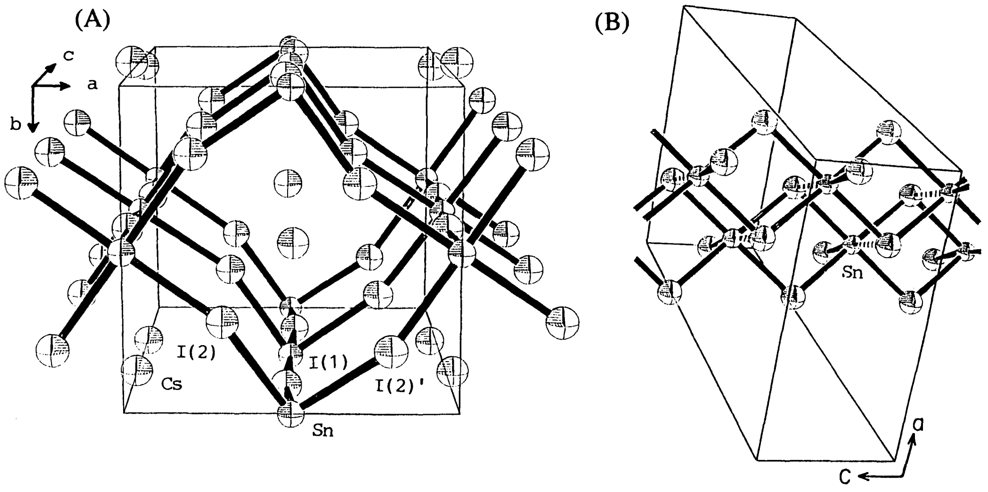

Fig. 3. ORTEP drawings of (A):$CsSnI_3$(B-γ) and (B): $CsSnI_3$(G).[8]

the ^{127}I NQR observation (two closely spaced ^{127}I NQR lines around 90 MHz) between 77 and 300 K and is also consistent with the ^{119}Sn Mössbauer spectrum having no quadrupole splitting.[1,3] As is apparent from Fig. 3, the crystal structure of $CsSnI_3$(B) is quite different from that of $CsSnI_3$(G). The differences between them can be summarized in the following two points. (1) In the $CsSnI_3$(G) , one short Sn-I bond (2.941 Å) located at the apical position has a weak bond at the *trans* position (Sn-I:3.469 Å). Whereas in the $CsSnI_3$(B), each octahedron is almost regular. (2) Iodine bridges in $CsSnI_3$(G) are formed at right angles, whereas in the $CsSnI_3$(B) the Sn-I-Sn bridges are almost linear as stated above. According to our previous paper, the conductivity of the $CsSnI_3$(B) increased gradually with decreasing temperature down to 77 K and no anomalies were observed at the phase transition temperatures. From the structural consideration of the two polymorphs, $CsSnI_3$(G) and (B), the metallic conductivity of the $CsSnI_3$(B) may be originated from the infinite linear chains having almost same Sn-I bond length. Thereby the band structure of the $CsSnI_3$(B) is not so much influenced by the slight bending of the chains.

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