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Mössbauer Study of Tin in γ-AgI

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Synopsis. Tin was deposited onto the surface of powdered γ-AgI and introduced into the matrix by solid-state diffusion at 300 °C. The ^{119}Sn Mössbauer spectra show that the deposit before heat treatment was epitaxially grown α-Sn and that the diffused tin was in the state of valency 4, occupying both the octahedral and tetrahedral interstices.

The state of tin in silver halides has been studied by means of Mössbauer spectroscopy. Meisel et al.[1)] doped the AgCl polycrystals with 0.05 mol% ^{119}Sn and reported that tin atom existed as Sn^{4+}, occupying an interstice surrounded by four cation vacancies. Efimov et al.[2)] also reported the presence of only Sn^{4+} in AgCl and AgI after study by means of emission Mössbauer spectroscopy. They introduced ^{119m}Sn into AgCl and AgI by fusing the corresponding salts with metallic ^{118}Sn and by then irradiating them with thermal neutrons. On the other hand, Lagunov and Polozenko[3)] prepared alloys of AgCl and tin enriched with ^{119}Sn and reported that the spectrum of the state of Sn^{4+} in AgCl was due to SnO_2 particles in AgCl. As we have found a sophisticated method by which a small amount of tin can be introduced into the crystalline powder,[4)] about 2.8 mol% of natural tin was introduced into the matrix of powdered AgI by the method; the Mössbauer spectra were then measured in order to elucidate the state of tin in AgI, which has not been clear hitherto.

Experimental

Freshly-prepared tin(II) chloride (8.4×10^{-5} mol) was dissolved in dry ethanol (20 cm^3), after which 3×10^{-3} mol of silver iodide (GR, Katayama Kagaku Kogyo Co., Ltd.), which has been sieved to 150—200 mesh, was added to the solution. The powder was suspended in the solution by means of supersonic waves and manual shaking. Sodium borohydride (5×10^{-4} mol) was then added to the solution at 3 °C. After the reduced tin has been deposited on the surface of the powder of AgI, the sediment was filtered out of the solution and washed thoroughly with oxygen-free water, dry ethanol, and finally dry ether under a nitrogen atmosphere in order to remove the reaction by-products. The sample powder was enveloped in an evacuated Pyrex glass ampoule, heated at 300 °C for 10 h, and then cooled to room temperature. The sample was identified as γ-AgI by the X-ray powder diffraction method before and after the heat treatment.

The Mössbauer spectra were recorded by the use of a constant-acceleration-type spectrometer with an accuracy of within 0.05 mm s^{-1}. The Mössbauer source of calcium stannate was used at room temperature, and the absorber was cooled at 93 K in a liquid nitrogen cryostat. The Mössbauer parameters were obtained from computer-fitted Lorentzian curves by the least-squares method.

Results and Discussion

The Mössbauer absorption spectra of the sample before and after heat treatment are shown in Fig. 1. The Mössbauer parameters obtained from the spectra are listed in Table 1. The isomer shift of tin deposited on the γ-AgI substrate was 2.12 mm s^{-1}, a value which agreed roughly with the value of α-Sn, 2.03 mm s^{-1}, but not with that of β-Sn, 2.56 mm s^{-1}. The α-form of tin was found for the first time, whereas the β-form of tin was found previously in our studies of colloidal tin suspension,[5)] tin deposit on the surface of α-Fe_2O_3 particles,[4)] and tin on NaCl and KCl particles.[6)] The α-form of tin may be formed by epitaxial growth. The γ-AgI substrate has a cubic structure of the zincblende type, while the deposited α-Sn, in contrast to β-Sn, has its corresponding cubic structure of the diamond type. Their structures are similar not only topologically but also metrically, so that the lattice constants are 6.489 Å and 6.473 Å respectively. Thus, one element of group 4B, Sn, fits into the 1B–7B compound, γ-AgI, neatly. It should also be noted that the isomer shifts of tin deposited on the surface of the particles of AgBr and AgCl were 2.33 and 2.40 mm s^{-1} respectively.[7)]

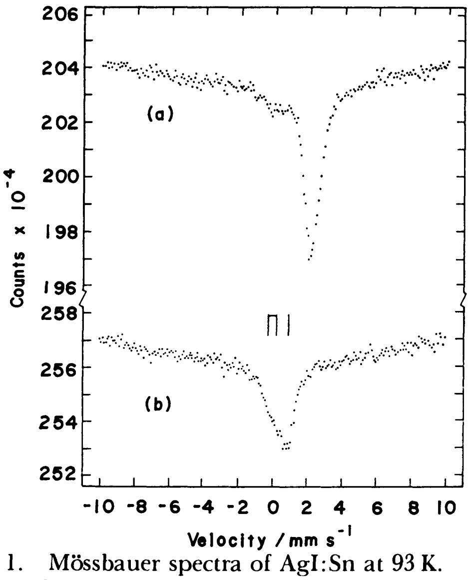

Fig. 1. Mössbauer spectra of AgI:Sn at 93 K.
(a) Before heating; (b) After heating at 300 °C for 10 h.

Table 1. ^{119}Sn Mössbauer Parameters for AgI : Sn at 93 K

	δ mm s^{-1}	Δ mm s^{-1}	Γ mm s^{-1}	Relative area
(a)	2.12	—	1.05	1.00
(b)	0.86	—	0.91	0.47
	0.07	0.30	1.05	0.53

(a) Before heating. (b) After heating.

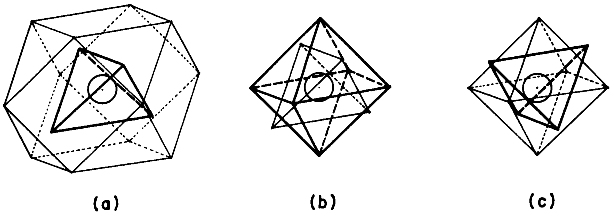

Fig. 2. Three models of the site for a tin atom in γ-AgI. (a) A site for the substitution; (b) and (c) Interstitial site. The circle shows the site for a tin atom. The polyhedra drawn in the thick line are the coordination polyhedra of iodine atoms and drawn in the thin line are the coordination polyhedra of silver atoms.

The absorption line of the tin in γ-AgI was near 0 mm s^{-1}, which corresponds to the Sn^{4+} oxidation state. The line shape was too complex to be attributed to a singlet peak, as in the results obtained by Efimov et al.[2] The parameters in Table 1(b) were derived on the assumption that the absorption line is a composite of a singlet component and a doublet component. The state of tin in γ-AgI will be inferred from the data thus obtained. Three models for the site of the foreign atom, Sn, are shown in Fig. 2. Figure 2(a) shows the silver atom site to be substituted, which is surrounded tetrahedrally by the first neighbors of four iodine atoms and cuboctahedrally by the second neighbors of twelve silver atoms. Two types of interstitial sites are examined; a wider one (Fig. 2(b)) and a narrower one which generates two subtypes in the vacancy distribution (Fig. 2(c)). The number of each site per unit cell is four. If it is assumed that the effective charge on a tin atom is four times as large as that on a silver atom, and that silver atoms nearest to the tin atom are removed to produce cation vacancies, only the tin atom at the interstitial site of Type b will give a singlet line due to the cubic symmetry, while any other sites, Type a or Type c, will give a doublet line. The data in Table 1(b) can be explained by the concurrent occupation of the sites of model b and c or a.

The plausibility of which models are occupied was examined by the use of the theories of the crystal potential and chemical bond.[8,9] Considering the electrostatic crystal potential of the doped crystal, the bond character of Ag–I, and the covalent or ionic radii of the three elements, we concluded that the occupation of the interstices is far more likely to occur than the substitution of a silver atom, and if the covalency (ca. 45%) acts predominantly, the Type c will be preferred to Type b.

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