121Sb Mössbauer Spectra of M or A-Doped Antimonic Acid (M = Ta and Nb, A = Bi and Y) Fine Nanoparticles Prepared by Soft Chemical Solution Process

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Abstract. 121Sb Mössbauer spectroscopic studies on the pyrochlore-type M or A-doped antimonic acids (M = Ta and Nb, A = Bi and Y) nanoparticles were carried out at 12 K in order to determine the oxidation state of Sb and also find more useful information for making clear the detail mechanisms of the photocatalytic property and the proton conductivity. The 121Sb Mössbauer results indicated that all of Sb were Sb 5+ in HSb1-xMxO3·nH2O (M = Ta and Nb) which Sb was partially substituted by M, however, small amount of Sb were Sb 3+ in H1-3xAxSbO3·nH2O (A = Bi and Y) which H was partially substituted by A. The amounts of Sb 3+ in the Bi-containing material were clearly larger than that in the Y-containing material. The photocatalytic properties and the proton conductivities of the pure and M or A-containing materials were discussed in relation to their 121Sb Mössbauer parameters, especially isomer shift (δ) and quadrupole coupling constant (e2qQ).

1. Introduction
We are interested in developing novel double oxide photocatalytic nano-materials with having not only strong adsorption capability but also high photocatalytic ability to water-splitting and decomposition of the organic pollutants [1-6]. In general, pyrochlore(P)-type compounds are presented by the formula A2M2O6O’ and correspond to the space group symmetry of Fd-3m [7]. As shown in Figure 1, the P-type structure is characterized by a three-dimensional (M4O12o) framework built up of vertex-linked MO6 octahedra. In this framework, there are interconnected tunnels with large cavities (8 per unit cell) [7]. Taking into account the compositional flexibility of the P-type structure, previously, we developed a novel series of P-type photocatalytic materials, Bi2MTaO7 (M = In, Ga and Fe), which were promisingly applied for water-splitting to produce the clean-energy of hydrogen [1,3,5]. Moreover, relationships between the photocatalytic activity under UV light irradiation and the P-type structural property were found. The photocatalytic activity became larger when the lattice distortion became larger and the closer the angle between the vertex-linked MO6 octahedra is to 180° [5].

Recently, we also reported the photocatalytic properties and 125Sb Mössbauer spectra of two kinds of P-type antimonic acids, HSbO3·nH2O (or Sb2O5·nH2O), fine nanoparticles prepared by using different starting materials [6]. For the P-type HSbO3·nH2O, A = H or H2O, M = Sb and O’ can be replaced by H2O. Its full structure has been determined by Slade et al. from the Rietveld refinement using neutron diffraction data [8]. The photocatalytic experiment indicated that the one prepared by using Sb(O-i-C3H7)3 showed very strong adsorption capability and high photocatalytic activity for methylene blue degradation under UV light irradiation. The 125Sb Mössbauer experiment confirmed that the one prepared by using Sb(O-i-C3H7)3 only contained Sb5+ with 4d10 electronic configuration, however, the another one prepared by using Sb metal...
powder contained a small amount of Sb\(^{3+}\) with \(4d^{10}5s^2\) electronic configuration. The high photocatalytic activity was pointed out due to the high dispersion, fine crystallinity and large relative surface area as well as only containing the octahedrally coordinated Sb\(^{5+}\) species with \(4d^{10}\) electronic configuration. Taking into account the previous reports by Inoue’s group [9], a small amount of Sb\(^{3+}\) species with \(4d^{10}5s^2\) electronic configuration are considered to be the main reason why the photocatalytic performances of the two kinds of antimonic acids were definitely different to each other.

In addition, Ozawa et al. successfully prepared three novel series of P-type M or A-doped antimonic acid (M = Nb, A = Bi and Y) fine nanoparticles by modifying the soft chemical solution process and found that the proton conductivities of the prepared materials were significantly enhanced after the M or A-doping [10-12]. The full structures of the M or A-doped materials were also been performed from the Rietveld refinement using powder X-ray diffraction data. In the Rietveld refinement, Sb and O1 atoms, consisting of the SbO\(_6\) octahedra, were placed on a 16\(c\) site (0, 0, 0) and a 48\(f\) site \((x, 1/8, 1/8)\), respectively; the O2 atoms of the H\(_2\)O or H\(_3\)O\(^+\) species were placed on a 32\(e\) site \((x, x, x)\). Varieties of the proton conductivities of the M or A-doped materials were qualitatively interpreted in terms of the strength of the hydrogen bonding between the oxygen atoms of the (Sb\(_2\)O\(_6\))\(^2-\) frameworks and H\(_2\)O or H\(_3\)O\(^+\) species, which changes according to the M or A-doping amount [10-12].

In this paper, \(^{121}\)Sb Mössbauer spectroscopic studies on the four kinds of M or A-doped antimonic acids (M = Ta and Nb, A = Bi and Y, M or A/Sb = 0.1) were conducted in order to determine the oxidation state of Sb and also try to find more useful information for making clear the mechanism of the photocatalytic property as well as the proton conductivity in detail.

![Figure 1. The [Sb\(_2\)O\(_6\)]\(^2-\) pyrochlore framework formed by vertex-shared SbO\(_6\) octahedra for pyrochlore-type HSbO\(_3\)·nH\(_2\)O.](image1)

![Figure 2. \(^{121}\)Sb Mössbauer spectra of M or A-doped antimonic acids (M = Ta and Nb, A = Bi and Y, the molar ratios of M or A/Sb = 0.1).](image2)

2. Experimental procedures

The samples used in the present study were supplied by Ozawa of National Institute for Materials Science in Japan. The molecular formulas of the Ta and Nb-containing materials were confirmed as HSb\(_{1-x}\)M\(_x\)O\(_3\)·nH\(_2\)O, which M locates on the position of Sb. The molecular formulas of the Bi and Y-containing materials were confirmed as H\(_{1-3x}\)A\(_x\)SbO\(_3\)·nH\(_2\)O, which A locates on the position of H. \(^{121}\)Sb Mössbauer spectra of the prepared materials were observed by a Wissel Mössbauer spectrometer system using a Ca\(^{121m}\)SnO\(_3\) source (16 MBq) and a Ge detector; in these experiments both the source and the samples containing Sb were kept at 12 K in a cryostat incorporating a closed-cycle refrigerator [13].

3. Results and discussions

Figure 2 shows \(^{121}\)Sb Mössbauer spectra of the pure and M or A-doped materials (M = Ta and Nb, A = Bi and Y, the molar ratios of M or A/Sb = 0.1) at 12 K obtained in the present study. The spectra of HSb\(_{1-x}\)M\(_x\)O\(_3\)·nH\(_2\)O (M = Ta and Nb) exhibited one absorption peak which is typical for Sb\(^{5+}\) species as that of the reported pure material, HSbO\(_3\)·nH\(_2\)O, prepared by using the Sb alkoxide complex as a starting material [6]. However, the spectra of H\(_{1-3x}\)A\(_x\)SbO\(_3\)·nH\(_2\)O (A = Bi and Y) were two distinct absorption peaks which are
typical for Sb\(^{5+}\) and Sb\(^{3+}\) species, respectively, as that of the reported pure material, HSbO\(_3\)-nH\(_2\)O, prepared by using the Sb metal powder as a starting material [6]. The amount of Sb\(^{5+}\) in the Bi-containing material was clearly larger than that in the Y-containing material. Therefore, the least square curve fitting was performed by assuming only one Sb\(^{5+}\) site in the Ta- and Nb-containing materials, one Sb\(^{5+}\) site and one Sb\(^{3+}\) site were assumed in the Bi- and Y-containing materials.

The spin numbers of \(^{121}\)Sb Mössbauer transition are 5/2 for the ground state and 7/2 for the excited state, respectively. The \(^{121}\)Sb Mössbauer spectra should be consist of 12 absorption lines in the case of the asymmetric parameter, \(\eta \neq 0\) and 8 absorption lines in the case of \(\eta = 0\). However, since the natural linewidth of \(^{121}\)Sb Mössbauer transition is broad to 2.1 mm s\(^{-1}\), the splitting cannot be completely observed [13].

In the present study, considering the symmetry of the cubic P-type structure, the \(^{121}\)Sb Mössbauer spectra were analyzed by assuming 8 quadrupole-split lines corresponding to the asymmetric parameter, \(\eta = 0\), from using a transmission integral method [14].

**Table 1.** \(^{121}\)Sb Mössbauer parameters of M or A-doped antimonic acids (M = Ta and Nb, A = Bi and Y, the molar ratios of M or A/Sb = 0.1) fine nanoparticles at 12 K (These parameters were obtained by assuming the asymmetric parameter, \(\eta = 0\)).

| Sample       | Site  | \(\delta\) (mm s\(^{-1}\)) | \(\delta^2 qQ\) (mm s\(^{-1}\)) | \(\Delta F_{\text{exp}}\) (mm s\(^{-1}\)) | \(A\) (%) |
|--------------|-------|-----------------------------|--------------------------------|------------------------------------------|---------|
| HSbO\(_3\)-H\(_2\)O | Sb\(^{5+}\) | 9.34                        | 4.7                           | 2.38                                     | 100     |
| HSb\(_{1-x}\)Ta\(_x\)O\(_3\)-H\(_2\)O | Sb\(^{5+}\) | 8.94                        | 3.2                           | 2.33                                     | 100     |
| HSb\(_{1-x}\)Nb\(_x\)O\(_3\)-H\(_2\)O | Sb\(^{5+}\) | 8.70                        | 3.5                           | 2.37                                     | 100     |
| H\(_{1-x}\)Bi\(_x\)SbO\(_3\)-H\(_2\)O | Sb\(^{5+}\) | 8.31                        | 2.8                           | 2.29                                     | 89      |
| H\(_{1-x}\)Y\(_x\)SbO\(_3\)-H\(_2\)O | Sb\(^{3+}\) | -7.61                       | 17.2                          | 11                                       |         |
| H\(_{1-x}\)Y\(_x\)SbO\(_3\)-H\(_2\)O | Sb\(^{3+}\) | 8.10                        | 1.9                           | 2.26                                     | 97      |
|               |       | -7.49                       | 16.8                          | 3                                        |         |

a. Isomer shift, relative to a standard absorber of InSb at 12 K (\(\delta = 7.91 \pm 0.05\) mm s\(^{-1}\) at 20 K [13]), the experimental error was estimated to be \(\pm 0.05\) mm s\(^{-1}\). b. Quadrupole coupling constant, the experimental error was estimated to be \(\pm 0.5\) mm s\(^{-1}\). c. Experimental line-width. d. Relative peak area. e. The water content was estimated to be 0.5.

The peak area ratio of Sb\(^{5+}\)/Sb\(^{3+}\) was 89:11 for the Bi-containing material. The result was clearly different to that measured by the KMnO\(_4\) titration method [11]. It showed that the existence of Sb\(^{5+}\) ion should be taken into account when a structural model for the Bi-containing material was proposed to apply for the Rietveld structural refinement [11]. The peak area ratio of Sb\(^{5+}\)/Sb\(^{3+}\) was 97:3 for the Y-containing material. The result was almost consistent to that measured by the KMnO\(_4\) titration method [10].

As listed in Table 1, all of the \(\delta\) values for the Sb\(^{3+}\) species were smaller than the pure material and were in order: \(\delta_{\text{pure}} > \delta_{\text{Ta}} > \delta_{\text{Nb}} > \delta_{\text{Si}} > \delta_{\text{Y}}\). The change trend of \(\delta\) was likely to be in opposition to the change trend of the maximal value of the proton conductivity that can be obtained on the M or A-doped materials in the same temperature. For example, the proton conductivities at room temperature were 8.3 x 10\(^{-5}\), 6.4 x 10\(^{-3}\), 4.8 x 10\(^{-3}\) and 3.8 x 10\(^{-3}\) S cm\(^{-1}\), respectively, for the pure (\(x = 0\)), Nb- (\(x = 0.09\)), Bi- (\(x = 0.081\)) and Y- (\(x = 0.12\)) containing materials. Here, the M or A/Sb mole ratios \(x\) were obtained by chemical analysis [10-12].

It is well-known that Mössbauer \(\delta\) mainly depends on the \(s\)-electron density at the Mössbauer nucleus and the variation of the \(^{121}\)Sb Mössbauer \(\delta\) for the Sb\(^{5+}\) and Sb\(^{3+}\) compounds are mainly because of the effects of the Sb 5s electrons [15]. So, here the \(\delta\) results for the Sb\(^{5+}\) species indicated that the 5s electron density at the Sb nucleus position decreased in order: \(\rho_{\text{pure}} < \rho_{\text{Ta}} < \rho_{\text{Nb}} < \rho_{\text{Si}} < \rho_{\text{Y}}\) after the M or A-doping since \(\Delta R/R < 0\) for \(^{121}\)Sb. Thus, we can reasonably suppose that the interactions between the Sb 5s and O 2p orbitals became bigger and then the Sb-O bond became stronger in the SbO\(_3\) octahedra after the M or A-doping. This should lead to that the strength of the hydrogen bonding between the oxygen atoms of the (SbO\(_3\))\(_2\) frameworks and H\(_2\)O or H\(_3\)O\(^{+}\) species became weaker after the M or A-doping since there is an equilibrium in the P-type antimonic acid: Sb-OH + H\(_2\)O ↔ Sb-O- + H\(_3\)O\(^{+}\) [8]. This should be considered to be the main reason for causing the increase of the proton conductivity since the proton conductivity of the P-type antimonic acid was known to be influenced by the strength of the hydrogen bonding between the...
oxygen atoms of the \((\text{SbO}_3)^2−\) frameworks and \(\text{H}_2\text{O}\) or \(\text{H}_3\text{O}^+\) species. This consequence is consistent to that obtained by the Rietveld structural analysis reported by Ozawa et al. [10-12].

By the way, the \(^{121}\text{Sb}\) Mössbauer parameters of the \(\text{Sb}^{3+}\) species were very different to the \(\text{Sb}^{5+}\) species. Comparing with the \(\text{Sb}^{5+}\) species, the \(\text{Sb}^{3+}\) species had very smaller \(\delta\) values and very larger \(\epsilon^2qQ\) values. This was caused by the different electron configurations of \(\text{Sb}^{5+}(4d^{10}5s^2)\) and \(\text{Sb}^{3+}(4d^{10})\).

All of the \(\epsilon^2qQ\) values of the M or A-doped materials were smaller than the pure material. The \(\epsilon^2qQ\) is a measure on the magnitude of the electric field gradient at the Mössbauer nucleus position. So, the \(\epsilon^2qQ\) results indicated that the electric field gradient, namely the distortion of the \(\text{SbO}_6\) octahedra existing in the P-type structure of \(\text{HSbO}_3 \cdot \text{nH}_2\text{O}\), became smaller due to the M or A-doping. The photocatalytic activities of the four M or A-doped materials \((M = \text{Ta and Nb}, A = \text{Bi and Y})\) [16] were investigated by using the same method and the same model micro-reaction as reported previously [6]. The results indicated that their photocatalytic activities were clearly lower than the pure material. That is to say, the photocatalytic ability of the P-type antimonic acid decreased when the distortion of the \(\text{SbO}_6\) octahedra became smaller due to the M or A-doping. This was consistent to the trend that we observed in the novel series of photocatalysts, \(\text{Bi}_2\text{TaMO}_7\) \((M = \text{In, Ga and Fe})\) [1, 3, 5]. As mentioned in the introduction section, we investigated the oxidation state and investigate the mechanism of the \(\text{Sb}\)-containing proton conductive and photocatalytic materials. All of the \(\text{Sb}\)-doped materials were smaller than the pure material. All of the \(\delta\) values of the M or A-doping materials were smaller than the pure material and were in order: \(\delta_\text{pure} > \delta_\text{Ta} > \delta_\text{Bi} > \delta_\text{Y}\). This implied that the \(\text{Sb}-\text{O}\) bond became stronger in the \(\text{SbO}_6\) octahedra after the M or A-doping and then the strength of the hydrogen bonding between the oxygen atoms of the \((\text{SbO}_3)^2−\) frameworks and \(\text{H}_2\text{O}\) or \(\text{H}_3\text{O}^+\) species became weaker after the M-doping. This should be related to the enhancement of the proton conductivity. All of the \(\epsilon^2qQ\) values of the M-doped materials were smaller than the pure material. This indicated that the distortion of the \(\text{SbO}_6\) octahedra existing in the P-type antimonic acid became smaller due to the M-doping. It should be related to the decrease of the photocatalytic ability that had been demonstrated experimentally by photocatalytic degradation of model organic pollutant.

4. Summary
The \(^{121}\text{Sb}\) Mössbauer spectroscopic studies on the four M or A-doped P-type antimonic acids were performed and the results indicated that the \(^{121}\text{Sb}\) Mössbauer spectroscopy was very effective to determine the \(\text{Sb}\) oxidation state and investigate the mechanism of the \(\text{Sb}\)-containing proton conductive and photocatalytic materials. All of \(\text{Sb}\) were confirmed in \(\text{Sb}^{5+}\) in \(\text{HSb}_{\text{3-x}}\text{M}_\text{x}\text{O}_3 \cdot \text{nH}_2\text{O}\) \((M = \text{Ta and Nb})\), however, small amount of \(\text{Sb}\) were confirmed in \(\text{Sb}^{3+}\) in \(\text{H}_{1.3-\text{A}}\text{SbO}_3 \cdot \text{nH}_2\text{O}\) \((A = \text{Bi and Y})\). The amount of \(\text{Sb}^{3+}\) in the \(\text{Bi}\)-containing material was clearly larger than that in the \(\text{Y}\)-containing material. All of the \(\delta\) values of the M or A-doped materials were smaller than the pure material and were in order: \(\delta_\text{pure} > \delta_\text{Ta} > \delta_\text{Bi} > \delta_\text{Y}\). This implied that the \(\text{Sb}-\text{O}\) bond became stronger in the \(\text{SbO}_6\) octahedra after the M or A-doping and then the strength of the hydrogen bonding between the oxygen atoms of the \((\text{SbO}_3)^2−\) frameworks and \(\text{H}_2\text{O}\) or \(\text{H}_3\text{O}^+\) species became weaker after the M-doping. This should be related to the enhancement of the proton conductivity. All of the \(\epsilon^2qQ\) values of the M-doped materials were smaller than the pure material. This indicated that the distortion of the \(\text{SbO}_6\) octahedra existing in the P-type antimonic acid became smaller due to the M-doping. It should be related to the decrease of the photocatalytic ability that had been demonstrated experimentally by photocatalytic degradation of model organic pollutant.

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