Formation and Optical Absorption Spectra of Mixed Valence State of Tl in $Tl_2Nb_2O_{6+x}$ with Pyrochlore Structure

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The new thallium mixed valence compound $Tl_2Nb_2O_{6+x}$ ($0.1 < x < 1.1$) with a defect pyrochlore structure was synthesized by inserting excess oxygen under an oxygen atmosphere up to 2 MPa. A distinct red shift with ca. 0.25 eV of absorption edge was observed on going from $x = 0.1$ to $x = 1.1$, and a new and weak absorption band was observed for the samples with large x, at 0.6 eV for $x = 1.1$ and at 0.8 eV for $x = 0.9$. The induced band was tentatively ascribed to be due to intervalence charge transfer between Tl^+ and Tl^{3+}. As x increased, full width at half maximum of $Tl4f_{7/2}$ increased from 2.4 to 3.0 eV in X-ray photoemission spectra. ^{205}Tl NMR spectra showed the unusual behavior that the absorption due to Tl^+ vanished as x increased to ca. 1. Electrical conducting properties of these compounds were semiconductive, independent of x. The optical and electrical properties demonstrated the presence of the mixed valence states of Tl in these oxides.

Mixed valence states of cations in solids have attracted much interest because of their unique electrical and optical properties.[1,2] Robin and Day classified materials into three categories according to the characteristic of electron transfer between the ions with different valence states: In the materials belonging to class I, electron transfer from the lower valence cation to the higher one is very difficult, thus it is an electrical insulator. The compounds which require small energy for the electron transfer are classified as class II, and show semiconductive electrical properties and optical absorptions due to intervalence charge transfer transitions, peaking at a longer wavelength which differs from that of each ion with different valence. The compounds classified into class III show metallic or degenerated semiconductive electrical properties because of easy electron transfer.

In the family of post transition metal oxides, some valence states mixed between ns^0 and ns^2 electronic configurations are expected. In these mixed valence oxides, no compounds which belong to class II except for $BaBiO_3$ ($Ba(Bi^{3+}_{0.5}, Bi^{5+}_{0.5})O_3$) has been known. (Besides, $BaBiO_3$ changes drastically from class II to III by the substitutions of Bi with Pb or Ba with K.[3,4])

The purpose of the present study is to find a new mixed valence oxide of post transition metallic cations which belong to class II. $Tl_2Nb_2O_6$[5—8] is selected as a candidate of host materials. Tl ions in this compound exist as monovalent Tl^+ with $6s^2$ electronic configuration. The crystal structure of the compound is of defect pyrochlore type, which is derived from normal pyrochlore type, $A_2B_2X_6Z$ by introducing vacancies in the anionic sites of Z (8b site).[9] In the crystal, Tl^+ ion occupies only the 16d site (A site) and the occupation factor of oxygen at the 8b site is zero.

The approach employed in the present study for converting the single valence compound to the mixed valence one is based on the expectation that the monovalent Tl^+ ions will be oxidized by introducing excess oxygens into the empty Z sites (8b). Since a Z site is surrounded by four A sites, the nearest neighboring $6s^2$ ions in the vicinity of excess O^{2-} are oxidized to Tl^{m+} ($m \geqq 1.5$), if the excess plus charges are uniformly distributed over the four Tl^+ cations. It is reasonable to expect that a small structural relaxation will allow one particular Tl^+ to be oxidized to Tl^{3+} with $6s^0$. The actual valence state of the Tl atoms may be in between $Tl^{1.5+}$ and Tl^{3+}. In the former case, excess -2 charges on the introduced oxygen are uniformly neutralized by the first four neighboring Tl^+ ions. In the latter case, the -2 charges are compensated by one particular Tl^+ ion within the four. Therefore, we may anticipate that the newly formed Tl^{m+} ions and the precursor Tl^+ ions are almost in similar local environments (although Tl^{3+} seem to attract an excess anion to some extent), if introduction of oxygens into the pre-existing vacant 8b sites are done at a relatively lower temperature.

In the present paper, the preparation of $Tl_2Nb_2O_{6+x}$ with x in the region $0.1 < x < 1.1$ is reported along with changes in optical absorption spectra with changing x. Formation of mixed valence state of thallium is confirmed from the increase of full width at half maximum (FWHM) of Tl4f core level in X-ray photoemission spectra as x increase.

^{205}Tl NMR spectra suggested the unusual chemical states of Tl ions. The results will be discussed in comparison with the absorption spectrum of $BaBiO_3$, emphasizing the effect of the valence state of Tl and the local structure of thallium ions.

Experimental

$Tl_2Nb_2O_{6+x}$ samples in the shape of polycrystalline discs were prepared in the following procedure. Starting powders of Tl_2CO_3 (99.9%) and Nb_2O_5 (99.9%) were mixed with an agate mortar and pestle by adding methanol, and the dried mixture was calcined at 573 K for 3 h and then at 773 K for 10 h in air. The resulting powders of $Tl_2Nb_2O_{6+x}$ were ground and pelletized. In order to control oxygen content x, the pellets were sintered at various temperatures (773—973 K) under different atmospheres (oxygen and nitrogen) for 10 h. The sample with smallest value of x, 0.1 was obtained at 973 K under nitrogen. The specimen with largest value of x, 1.1 was obtained at 773 K under oxygen atmosphere of 2 MPa.

Oxygen contents were determined by iodometric titration. The samples in the form of powder were dissolved into hydrochloric acid in an Teflon® autoclave heated at 443 K. Diffuse reflectance spectra were measured using a Hitachi U-4000 spectrometer. The reflectance was transformed into absorbance by using Kubelka–Munk function. For the purpose of examining valence states of thallium ions, X-ray photoemission spectra were obtained at 300 K with Shimadzu ESCA-850, using $\mathrm{Mg}\,K\alpha$ radiation. For the same purpose, ESR measurements were carried out at 300 or 77 K with Varian E-12 EPR spectrometer. NMR measurements on ^{205}Tl ($I=1/2$; NA = 70.5%) were done at 300 K with a Bruker Model CXP-100 pulsed broad line spectrometer at 51.937 MHz as described in another report.10) Electrical conductivities were measured by DC two-probe method at the temperature range of 240—350 K under 0.1 Pa.

Results

Crystalline Phase Identified and Excess Oxygen Content. Table 1 shows content of excess oxygen x in the sample ($Tl_2Nb_2O_{6+x}$) prepared under different atmospheres. Under these preparation conditions, x ranged from 0.1 to 1.1. Even in nitrogen atmosphere, no sample with $x=0$ was obtained. For $x=1.1$ the average positive charge on each Tl is 2.1, assuming valence state of niobium ions to be +5. If we assume Tl^{3+} and Tl^{+} mixed valence state, Tl^{3+}/Tl^{+} ratio is close to 1.

Figure 1 shows X-ray powder diffraction patterns of the samples. The diffraction patterns agreed with the data of $Tl_2Nb_2O_6$ (cubic, *Fd*3*m*, $a \approx 1.067$ nm5)) All the diffraction peaks can be indexed as those of the pyrochlore structure. There was no indication of formation of any other crystalline phase. Figure 2 shows dependence of the cubic lattice constant on excess oxygen content, x. The lattice constant was found to contract with increasing content of excess oxygen, and the contraction of the lattice upon oxygen-uptake appears to be saturated at $x \approx 1$. This seems to correspond to a structural change. Powder neutron diffraction measurements are now in progress to determine the crystal structure in detail.

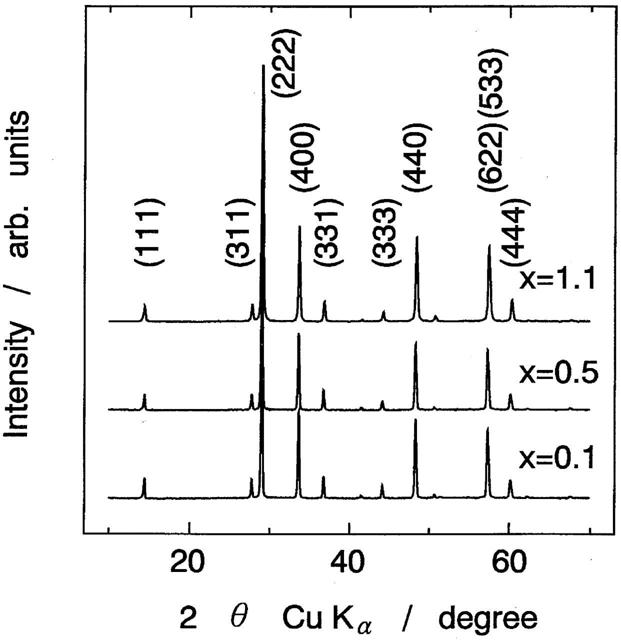

Fig. 1. X-Ray powder diffraction patterns of $Tl_2Nb_2O_{6+x}$ with $x=0.1$, 0.5, and 1.1. Diffraction peaks were indexed by assuming a pyrochlore structure.

Physical Properties. Colors of the sintered discs changed from brown to black on increasing x, as shown in Table 1. Figure 3 shows absorbance spectra of $Tl_2Nb_2O_{6+x}$. In accordance with the color change upon x, there appeared a large red shift in the absorption edges. It was noted that a decrease of ca. 0.25 eV in the energy of an absorption edge was observed in the range of x from 0.1 to 0.7. Also noted is the appearance of an weak absorption band (dashed arrows) which was considered to be an intervalence charge transfer band at ca. 0.8 eV for $x=0.9$ or ca. 0.6 eV for $x=1.1$. The absorption band seemed to appear only in the case of Tl^{3+}/Tl^{+} ratio ca. 1, a result different from data from mixed valence halides. The intervalence band shifts to a lower photon energy side with increasing x at the range from 0.9 to 1.1.

Table 1. Excess Oxygen Content of the Samples Determined by Iodometric Titration

Sample No.	Sintering temperature K	Atmosphere	x	Color
1	973	N_2 1×10^5 Pa	0.1	Light brown
2	973	Air	0.5	Dark brown
3	903	Air	0.7	Dark brown
4	873	Air	0.9	Brown black
5	873	O_2 2×10^4 Pa	1.1	Black

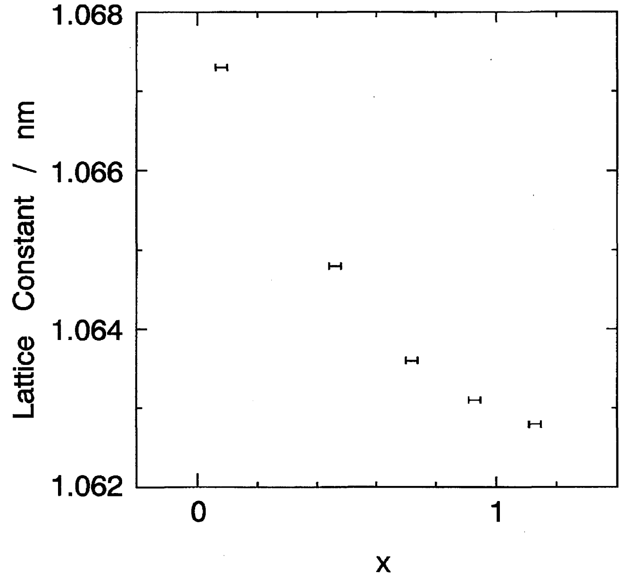

Fig. 2. Cubic lattice constants for the $Tl_2Nb_2O_{6+x}$ as a function of x.

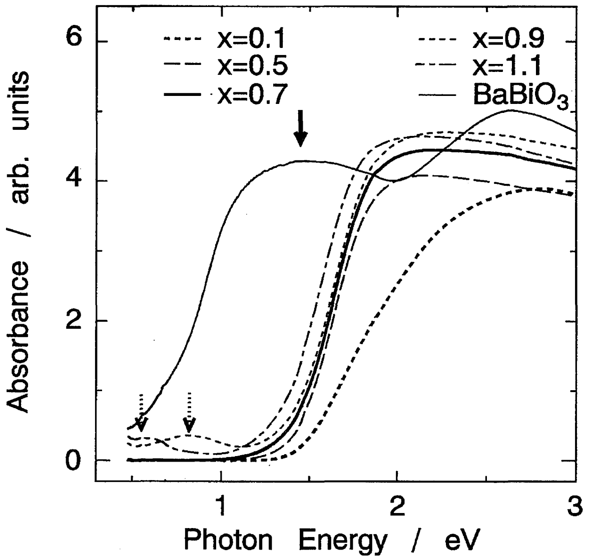

Fig. 3. Optical absorption spectra of $Tl_2Nb_2O_{6+x}$ and $BaBiO_3$ transformed from diffuse reflectivity spectra, using Kubelka–Munk function.

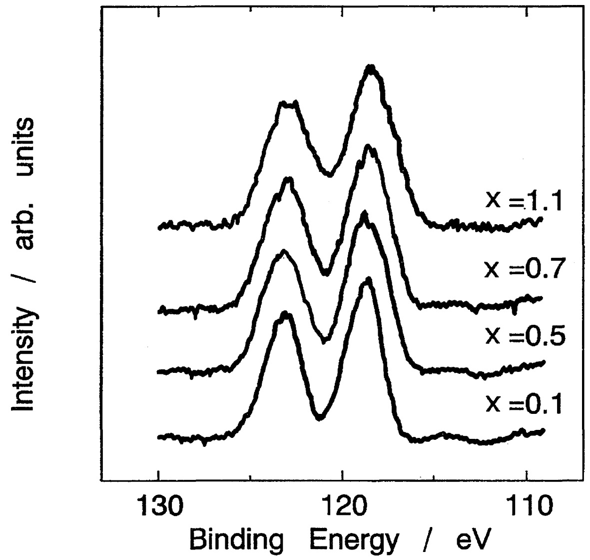

Fig. 4. The X-ray photoemission spectra of $Tl_{7/2}$ for the $Tl_2Nb_2O_{6+x}$ excited with unmonochromatized Mg $K\alpha$ radiation.

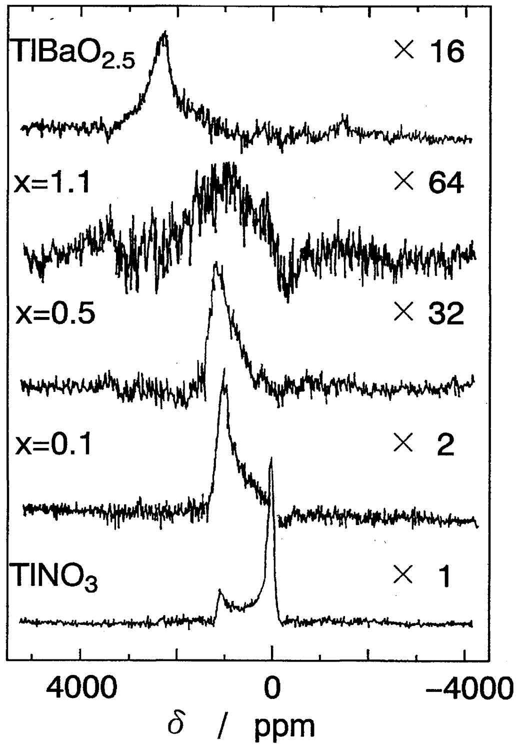

Fig. 5. ^{205}Tl NMR spectra of $Tl_2Nb_2O_{6+x}$ measured at 300 K. The numbers in the upper right are the amplification in the measurements. $TlNO_3$ and $TlBaO_{2.5}$ are the reference materials including Tl^+ and Tl^{3+}, respectively.

Figure 4 shows Tl4f X-ray photoemission spectra of the samples. As x increased, FWHM of the spectrum increased from 2.4 to 3.0 eV in the region from $x = 0.1$ to $x = 1.1$. Figure 5 shows ^{205}Tl NMR spectra for $Tl_2Nb_2O_{6+\delta}$ sample. The chemical shifts are quoted relative to an external standard of $TlNO_3$ aqueous solution. The intense signal observed in the spectrum of $x = 0.1$ sample was identified as Tl^+ from the comparison with that of $TlNO_3$. The intensity of the absorption peak due to Tl^+ vanished with increase in x from 0.1 to 1.1. No clear absorption peak ascribed to Tl^{3+} was detected in $Tl_2Nb_2O_{6+\delta}$. No ESR signal was detected at 300 or 77 K.

Figure 6 shows conductivity-temperature plots of the samples with x=0.1, 0.5, and 1.1 in the form of sintered pellets. In the temperature range of the measurements, thermogravimetric measurements showed no significant change in x. Desorption of excess oxygen started at ca. 773 K. Semiconductive and thermal activation type behavior with an apparent activation energy of ca. 0.6 eV was found. The relation between conductivities and x was not observed clearly, because the samples used were sintered polycrystalline discs, and the

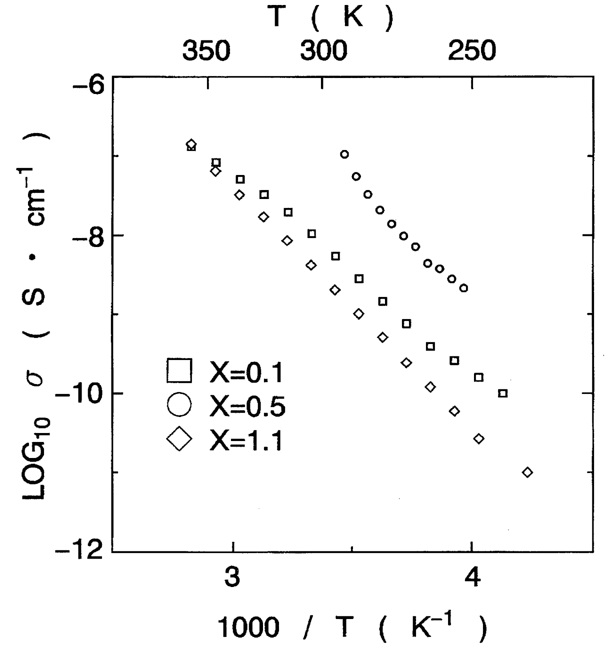

Fig. 6. Temperature-dependent conductivity of polycrystalline pellets of $Tl_2Nb_2O_{6+x}$. The measurement was carried out by means of DC two-probe method in the atmosphere of 0.1 Pa.

conductivities obtained were not viewed as intrinsic properties.

Discussion

Firstly, the phenomena induced by excess oxygen are discussed. The introduction of excess oxygen may cause the following phenomena generally: (1) formation of mobile positive holes (positive hole doping), (2) formation of mixed valence states in cations (trapped holes), or (3) mixed valence states in oxygens, for example, $O_2{}^{2-}$ ($O+O^{2-}\rightarrow O_2{}^{2-}$). The observed low conductivities shown in Fig. 6 are the experimental evidence that rejects the first possibility. ESR could monitor chemical species bearing a half spin such as $O_2{}^{-}$, and Raman measurements suggested the absence of the molecular anion $O_2{}^{2-}$. However, the results of iodometric titration are strong experimental evidence of the existence of excess oxygens in the solids. Therefore, the possibility of compensation is discounted. The absorption spectra in Fig. 3 suggest the formation of mixed valence state in Tl in the view of intervalence charge transfer band. This seems to be only possible explanation of the uptake of oxygens. The band was very weak relative to that of $BaBiO_3$ shown by arrow at ca. 1.4 eV in Fig. 3. This indicates that the interaction between $6s^0$ and $6s^2$ on thallium ions in $Tl_2Nb_2O_{6+x}$ is weak, and this compound belongs to class II. The intense band at ca. 1.4 eV (arrow) in $BaBiO_3$ might be expected to be caused effectively by the breathing mode$^{11)}$ in perovskite structure. Although no clear resolution of the peaks due to Tl^+ and Tl^{3+} was observed in Fig. 4, the peak width increased significantly with increasing x, suggesting that the fraction of Tl^{3+} relative to Tl^+ is enhanced with x. Also, the NMR spectra do not deny this possibility. The unusual behavior in the spectra was discussed in another report.$^{10)}$

Finally, we address a possible explanation of the fact that there are a few post transition metal mixed valence oxides in class II. There are a number of mixed valence compounds in class II (for example, Cs_2SbCl_6) in the family of post transition metal halide complexes. The origin of the difference between the halides and oxides is explained as follows. Since -2 charge on an oxygen ion is larger than that (-1) on halides, the coulombic repulsive force between oxygen anions and ns^2 electron pair on a cation becomes large. This may result in the fact that ns^2 cations in oxides cannot take local environment similar to that in halides. In the case, ns^2 electrons form directional bonding state with anion orbitals and have been called "cationic inert pair".

Summary

(1) Thallium mixed valence compound $Tl_2Nb_2O_{6+x}$ $(0.1 < x < 1.1)$ was synthesized by introducing oxygen into a defect pyrochlore type polycrystalline $Tl_2Nb_2O_6$ by means of heating under various atmospheres. The sample with $x = 1.1$ was prepared by heating under O_2 of 2 MPa at 773 K. Oxygen content was measured by iodometric titration.

(2) The X-ray diffraction patterns of $Tl_2Nb_2O_{6+x}$ $(0.1 < x < 1.1)$ showed cubic pyrochlore structure. The lattice constant decreased linearly in the range from $x = 0.1$ to $x = 0.5$ with increasing x and it saturated at $x \approx 1.0$.

(3) FWHM of Tl4f$_{7/2}$ increased as x increased. No ESR signal of $Tl_2Nb_2O_{6+x}$ $(0.1 < x < 1.1)$ rejected the possibility of the existence of Tl^{2+}. These results suggested a mixed valence state between Tl^+ and Tl^{3+}.

(4) A distinct red shift of absorption edge to ca. 0.25 eV was observed on going from $x = 0.1$ to $x = 1.1$. In addition, a new band observed at 0.6 eV for $x = 1.1$ or at 0.8 eV for $x = 0.9$ was tentatively ascribed to be due to intervalence charge transfer between Tl^+ and Tl^{3+}.

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