1. Introduction

In the past decade, several metastable and cation-ordered fluorite-related ABO₄ phases have been synthesized by the oxidation of the pyrochlore-type A₂B₂O₇, which is one of the oxygen-deficient and cation-ordered fluorite-related phases.¹⁻⁷ When the pyrochlore-type A₂B₂O₇ phase containing cations susceptible to oxygen is oxidized at moderate temperatures (≤873 K), the extra oxygen atoms are inserted into the original oxygen-vacant-site of the pyrochlore phase without cation-diffusion. As a result, the structural framework of the precursor remains the same.

The transformation started in the precursor pyrochlore phase is termed oxygen-intercalation.²⁻⁷ This process was explained in analogy of transformations of MX₂ compounds among rutile, fluorite-related and rutile-related phases. The transformation mechanism from fluorite-related phase to rutile-related phase was explained by the process of the collective oxygen migration, i.e., shearing of oxygen stacking, the ordered arrangement of the constituent cations in the oxidized phase of rutile and fluorite, which is different from the transformation from the precursor. Therefore, it was inferred that a greater driving force, i.e., the high oxygen chemical potential in our case, was needed for the formation of rutile-related phase.

Previously, we reported the oxygen-intercalation into the Sn–Nb–O pyrochlore phase containing SnIV phases.⁵⁻⁹ In that case, we observed surprise transformation from pyrochlore phase to cation-ordered α-PbO₂ and rutile related phases in addition to the transformation from pyrochlore phase to cation-ordered fluorite phase. Specifically, when the pyrochlore-type Sn₄₋₁.₆₂(Nb₃₋₂SnIV₀.₄₁)O₂.₅₅ was oxidized below 723 K in a 1%O₂/Ar atmosphere, the cation-ordered fluorite-related and the rutile-related SnIV₀.₈₁(Nb₀.₇₃SnIV₀.₂₇)O₂.₅₁ were formed. When the oxidation was demonstrated below 723 K in an O₂ atmosphere, the α-PbO₂ related SnIV₀.₂₈₁(Nb₀.₇₃SnIV₀.₇₆)O₂.₅₃ appeared. The formation of α-PbO₂ and rutile related SnIV₀.₈₁(Nb₀.₇₃SnIV₀.₂₇)O₂.₅₁ from the pyrochlore-type Sn₄₋₁.₆₂(Nb₃₋₂SnIV₀.₄₁)O₂.₅₁ could be understood assuming that the fluorite-related SnIV₀.₈₁(Nb₀.₇₃SnIV₀.₂₇)O₂.₅₁ phase was formed as a transient state between the rutile-related and fluorite-related phases. Because the constituent cations in the oxidized phase of SnIV and NbV are very small for the fluorite-related structure, the transiently formed fluorite-related phase immediately transformed into α-PbO₂ and rutile-related phases. The mechanism of the transformation from fluorite-related phase to rutile-related phase was explained by the analogue of the transformations of MX₂ compounds among rutile, α-PbO₂ and fluorite structures during pressurization and depressurization of several GPa₁₀⁻¹⁵. Based on the transformation mechanism reported by Hyde et al.,¹⁶ collective oxygen migration, i.e., shearing of oxygen stacking, is needed for the transformation from the fluorite-related phase into the α-PbO₂ and rutile-related phases, whereas only the diffusion of oxygen atoms intercalated is needed for the formation of the fluorite-related phase from the precursor. Therefore, it was inferred that a greater driving force, i.e., the high oxygen chemical potential, is needed for the formation of α-PbO₂ or rutile-related phase than that for the formation of the fluorite-related phase. Because no long-range cation diffusion occurred during the shearing of the oxygen stacking, the ordered arrangement of the respective cations of SnIV and [Nb, SnIV] in the precursor pyrochlore phase was left in the resulting α-PbO₂ and rutile-related phases.

Previously, we also demonstrated the oxygen-intercalation into the pyrochlore phase for Sn–Ta–O system.¹⁶ α-PbO₂ related...
SnIV0.82(Ta0.94SnIV0.06)O4.11 did not appear by the oxidation of the precursor SnIV1.64(Ta1.88SnIV0.12)O6.58 pyrochlore both under 1\%O2/Ar and O2 atmospheres, although the oxidized phases appeared dependent on the oxidation atmosphere for Sn–Nb–O system, i.e., fluorite-related phase and small amount of α-PbO2 and rutile related phases for 1\%O2/Ar atmosphere and α-PbO2 related phases for O2 atmosphere. The complex Ta-oxides isostructural with the complex Nb-oxides are frequently found due to the similarity in the ionic size of Ta and Nb. The α-PbO2-related SnIV0.82(Ta0.94SnIV0.06)O4.11 phase must be present in the SnIV–Ta–O system.

We expected in the previous study that direct transformation from the pyrochlore phase into α-PbO2-related SnIV–Ta–O phase, however we did not succeed in synthesizing it. In the present study, we attempted to synthesize the α-PbO2-related SnIV–Ta–O phase by transformation from the fluorite-related SnIV–Ta–O phase. For that purpose, the cation-ordered fluorite-related SnIV0.82(Ta0.94SnIV0.06)O4.11 phase was subjected to higher-temperature annealing, because thermally assisted shearing of oxygen stacking in the fluorite-related phase was expected based on the previous result, in which small amount of rutile related phase was found for the oxidation of SnIV1.64(Ta1.88SnIV0.12)O6.58 pyrochlore above 773 K in 1\%O2/Ar. Successfully, α-PbO2-related SnIV0.82(Ta0.94SnIV0.06)O4.11 was obtained by the annealing of fluorite-related SnIV0.82(Ta0.94SnIV0.06)O4.11 phase at 973 K in an O2 atmosphere. The structural feature of the α-PbO2-related SnIV0.82(Ta0.94SnIV0.06)O4.11 was discussed on the basis of its X-ray diffraction (XRD) and 119Sn-Mössbauer spectra. Differences in the oxidation behavior of the pyrochlore precursor and transformation condition from the fluorite-related to the α-PbO2-related forms between the Sn–Ta–O and Sn–Nb–O systems were discussed.

2. Experimental

The starting cation-ordered fluorite-related SnIV0.82(Ta0.94SnIV0.06)O4.11 was prepared by the oxidation of the precursor Sn–Ta–O pyrochlore phase. Details of the precursor preparation were described in a previous paper. The chemical composition and the cation distribution for the pyrochlore phase in the present study were expressed by the chemical formula of SnIV1.64(Ta1.88SnIV0.12)O6.58. The starting cation-ordered fluorite-related SnIV0.82(Ta0.94SnIV0.06)O4.11 was prepared as follows. Approximately 0.3 g of the powdered SnIV1.64(Ta1.88SnIV0.12)O6.58 pyrochlore, which was placed in an alumina crucible, was set in a closed-end-type silica glass tube (19-mm i.d.). The tube was then placed in a furnace and connected to an evacuation system consisting of a rotary vacuum pump and a gas flow system. In order to avoid oxidation of the precursor during the heating process, the silica glass tube was kept evacuated during the heating. After the pre-selected oxidizing temperature of 673 K was attained, the evacuation was stopped and the oxidizing gas of O2 was introduced at a flow rate of 100 ml min−1. After the oxidation for 5 h, the silica glass tube was removed from the furnace and cooled to a room temperature; the oxidizing gas was kept flowing during the cooling process. The obtained sample was then unloaded. It was confirmed that the obtained sample was the cation-ordered fluorite-related phase and the composition and the cation distribution were expressed by the chemical formula of SnIV0.82(Ta0.94SnIV0.06)O4.11 based on the X-ray diffraction (XRD), inductively-coupled plasma atomic emission spectroscopy (ICP-AES) and thermogravimetric (TG) analyses.

Annealing of the fluorite-related phase and characterization of the obtained samples were conducted as follows. The starting cation-ordered fluorite-related phase was annealed in flowing O2 gas at 873–1573 K for 5 h. The O2 gas remained flowing during the heating and cooling processes. The obtained crystalline phases were identified by XRD. The lattice parameters of the obtained phase were calculated using the least square procedure. High purity silicon powder (5N) was mixed with the sample as an internal standard. The 119Sn-Mössbauer spectra of the starting cation-ordered fluorite-related phase and its annealed phase were recorded in the constant acceleration mode by transmission using a conventional spectrometer at room temperature. The source used was 56Co (Rh) as the source. The origin of the isomer shift was determined from the center of the BaSnO3 spectrum.

3. Results

Figure 1 shows the powder XRD profiles of the samples obtained by the annealing of the cation-ordered fluorite-related SnIV0.82(Ta0.94SnIV0.06)O4.11 at 873–1573 K for 5 h under flowing O2 gas. When the fluorite-related phase was annealed at 873 K, the diffraction peaks of the fluorite-related phase slightly broadened, and a small and broadened peak, which might be attributable to the α-PbO2 related phase, appeared around 2θ = 24°. For the annealing at 973 K, the diffraction peaks due to the fluorite-related phase completely vanished, and the diffraction peaks indicated by the open triangles in the figure appeared. The XRD profile of the sample annealed at 973 K was very close to that of the α-PbO2-related SnIV0.82(Ta0.94SnIV0.06)O4.11 phase; therefore, the phase annealed at 973 K was identified as the α-PbO2-related form of SnIV0.82(Ta0.94SnIV0.06)O4.11. For the annealing at 1073 K, the diffraction peaks due to the α-PbO2-related phase were not observed.
The note-nm, of broad diffractions due to the low crystallinity. Therefore, the space group of model A from the XRD because the phase obtained by annealing of the cation-ordered phase was slightly sharpened. Above 1273 K, the diffractions due to SnO2 and Ta2O5 appeared; the cation-ordered SnIV0.82(Ta0.94SnIV0.06)O4.11 phases were decomposed into SnO2 and Ta2O5. Above 1273 K, the diffractions appeared around 2ª = 90°, and no diffraction around 2ª = 15° appeared; the cation-disordered phase was slightly sharpened.

Figure 2(a) shows the XRD profile for the sample obtained by the annealing at 1073 K, i.e., the same as Fig. 1(d). Figures 2(b) and 2(c) show the calculated XRD profiles for the following two model structures A and B: The model A is the cation-ordered α- PbO2-related SnIV0.82(Ta0.94SnIV0.06)O4.11; atomic positions of model A were determined based on the diffusionless transformation from the fluorite form to α-PbO2 form. Details in the transformation will be described in the section 4.1. The model B is the simple α-PbO2-type (SnIV0.44Ta0.47)O2.055, in which the Sn4+ and Ta3+ ions are not in an ordered arrangement. The structural parameters for the two models A and B are summarized in Tables 1 and 2, respectively. When the diffusionless transformation as described in sec. 4.1 ideally develops, the crystal system of the sample after the transformation should be a monoclinic system with a = 0.769 nm, b = 0.947 nm, c = 0.769 nm, α = 90°, β = 96.34°, and γ = 90°. However, we could not determine the space group of model A from the XRD because of broad diffractions due to the low crystallinity. Therefore, the space group Pfl, the lattice parameters and the atomic positions of model A given in Table 1 are only hypothetical. The noteworthy difference that was found in the calculated XRD between the cation-ordered and cation-disordered phases was that distinct diffraction around 2ª = 15° appeared for the cation-ordered phase, and no diffraction around 2ª = 15° appeared for the cation-disordered phase. In the observed XRD as shown in Fig. 2(a), no diffraction could be found around 2ª = 15°; the XRD profile was quite identical to the calculated one for the cation-disordered α-PbO2-type (SnIV0.44Ta0.47)O2.055. Therefore, the phase obtained by annealing of the fluorite-related α-PbO2-related SnIV0.44Ta0.47O2.055 was attributed to a cation-disordered α-PbO2-type (SnIV0.44Ta0.47)O2.055 from the view point of the XRD results. However, as described later, the cations of SnIV and [0.94Ta0.06SnIV+] did not completely mix, and they were still in an ordered arrangement in microscopic region.

Figure 3 shows the 119Sn-Mössbauer spectra for the α-PbO2-related and the fluorite-related form of SnIV0.44Ta0.47O2.055. The Mössbauer parameters of the isomer shift, IS, quadrupole splitting, QS, and full-width at half maximum, Γ, are summarized in Table 3. The QS value for the α-PbO2-related form was approximately half that for the cation-disordered fluorite-related form. This value was comparable to that for the rutile-type SnO2.20 The QS value showed that the local symmetry around Sn

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### Table 1. The structure parameters using for XRD simulation for the cation-ordered α-PbO2-related SnIV0.44Ta0.47O2.055

| Atom        | Site | x    | y    | z    | Occupancy |
|-------------|------|------|------|------|-----------|
| SnIV(1)     | 1a   | 0.036| 0    | 0.214| 0.82      |
| SnIV(2)     | 1a   | 0.214| 0.25 | 0.536| 0.82      |
| SnIV(3)     | 1a   | 0.536| 0.5   | 0.714| 0.82      |
| SnIV(4)     | 1a   | 0.714| 0.75  | 0.036| 0.82      |
| Ta2O5(1)    | 1a   | 0.536| 0    | 0.714| 0.82      |
| Ta2O5(2)    | 1a   | 0.714| 0.25 | 0.036| 1         |
| Ta2O5(3)    | 1a   | 0.536| 0    | 0.214| 1         |
| Ta2O5(4)    | 1a   | 0.714| 0.75  | 0.536| 1         |

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### Table 2. The structure parameters used for XRD simulation for the cation-disordered α-PbO2-type (SnIV0.44Ta0.47)O2.055

| Atom        | Site | x    | y    | z    | Occupancy |
|-------------|------|------|------|------|-----------|
| SnIV(1)     | 4c   | 0    | 0.178| 0.25 | 0.44      |
| Ta2O5(1)    | 4c   | 0    | 0.178| 0.25 | 0.47      |
| O           | 8d   | 0.276| 0.41 | 0.425| 1         |

| Occupancy   | Site | x    | y    | z    | Occupancy |
|-------------|------|------|------|------|-----------|
| Orthorhombic| Pbcn | 0.472| 0.573| 0.513| nm       |
| Triclinic   | P1   | 0.769| 0.947| 0.769| nm       |

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**Fig. 2.** Comparison of XRD profiles of (a) observed for the sample obtained by the annealing of the fluorite-related phase at 1073 K, (b) calculated for the cation-ordered α-PbO2-related SnIV0.82(Ta0.94SnIV0.06)O4.00 assuming that the phase is the pseudo-monoclinic system of space group Pfl with lattice parameters of a = 0.769 nm, b = 0.947 nm, c = 0.769 nm, α = 90°, β = 96.34° and γ = 90°, and (c) calculated for the simple α-PbO2-type (SnIV0.44Ta0.47)O2.05 assuming that the phase is orthorhombic of space group Pbcn (No. 60) with lattice parameters a = 0.472 nm, b = 0.573 nm and c = 0.513 nm. The diffraction peak appeared around 2ª = 15° [indicated by the bold arrow in (b)] comes from its 4 times larger lattice volume than that of the simple α-PbO2 structure due to the ordering of Sn IV and [0.94Ta0.06SnIV+]. In a previous paper about the Sn-Nb-O system, the crystal system of the cation-ordered α-PbO2 form was assumed to be orthorhombic, whose unit cell volume is 8-times larger than that of the simple α-PbO2 structure. The crystal system is corrected to the triclinic mentioned above, whose unit cell volume is 4-times larger than that of the simple α-PbO2 structure.
for the pyrochlore-type oxides such as Gd$_2$Zr$_2$O$_7$\(^{21,22}\) and
presence of the anti-phase domain boundaries (APBs) as reported
at 2°~15° for the cation-ordered phase can be explained by the
superlattice diffraction around 2°~15° due to the cation-ordering.

### 4. Discussion

#### 4.1 Ordering of cations in the α-PbO$_2$-related Sn$^{IV}$$_{0.82}$(Ta$_{0.94}$Sn$^{IV}$)$_{0.06}$O$_{4.11}$

In the XRD profiles for the α-PbO$_2$-related form [Figs. 1(c) and 1(d) and Fig. 2(a)], there was no superlattice diffraction at 2°~15°, which was caused by the order arrangement of the respective cations of Sn$^{IV}$ and [0.94Ta + 0.06Sn$^{IV}$]. The XRD results suggested that the phase obtained by annealing of the cation-ordered fluorite-related Sn$^{IV}$$_{0.82}$(Ta$_{0.94}$Sn$^{IV}$)$_{0.06}$O$_{4.11}$ was the cation-disordered α-PbO$_2$-type [Sn$^{IV}$$_{0.44}$Ta$_{0.44}$]O$_{2.05}$. However, we propose that the cations in the obtained phase are respectively ordered because of the following two reasons. (i) The transformation mechanism from the fluorite-related form to the α-PbO$_2$-related form can be interpreted by the shear of the oxygen stacking without a long-range ionic diffusion.\(^{23}\) This transformation mechanism is similar as the diffusionless transformation mechanism from fluorite form to α-PbO$_2$ form in the MX$_2$\(^{10,15}\) system.\(^{9},9,16\) The fluorite-related Sn$^{IV}$$_{0.82}$(Ta$_{0.94}$Sn$^{IV}$)$_{0.06}$O$_{4.11}$ cannot be mixed without ionic diffusion. (ii) When the fluorite-related form transformed into the other phase at high temperature where ionic diffusion occurs, the stable phases, such as SnO$_2$ and Ta$_2$O$_5$, must appear as observed in Figs. 1(e) and 1(f); the metastable α-PbO$_2$-related form should not appear. The absence of the superlattice diffraction at 2°~15° for the cation-ordered phase can be explained by the presence of the anti-phase domain boundaries (APBs) as reported for the pyrochlore-type oxides such as Gd$_2$Zr$_2$O$_7$\(^{21,22}\) and Ce$_2$Zr$_2$O$_7$.\(^{11}\) Figure 4 shows a schematic drawing of the transformation mechanism from the cation-ordered fluorite-related form to the α-PbO$_2$-related form with and without APBs. It is plausible that the shearing of the oxygen stacking occurs with an irregular distance upon the transformation from the fluorite-related form to the α-PbO$_2$-related form. The irregular shearing distance of the oxygen stacking in the cation-ordered fluorite-related form introduces the APBs parallel to the [010] plane during the transformation. The sample with low APB-density is required in order to refine the crystal structure, but we could not obtain such a sample at present. Therefore, we could not determine detailed structural information for the cation-ordered α-PbO$_2$-related form.

#### 4.2 Comparison of transformation conditions between Sn-Ta-O and Sn-Nb-O systems

Three cation-ordered phases, i.e., fluorite-, α-PbO$_2$-, and rutile-related phases have been successfully synthesized in the Sn-Ta-O system similar to the Sn-Nb-O system.\(^{9,10,14}\) The transformation conditions of the respective phases were slightly different.

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**Table 3. Mössbauer parameters for the cation-ordered fluorite- and α-PbO$_2$-related forms of Sn$^{IV}$$_{0.82}$(Ta$_{0.94}$Sn$^{IV}$)$_{0.06}$O$_{4.11}$**

| Sample                        | Isomer shift, \(IS\) / mm s$^{-1}$ | Quadrupole splitting, \(QS\) / mm s$^{-1}$ | FWHM, \(\Gamma\) / mm s$^{-1}$ |
|-------------------------------|-----------------------------------|------------------------------------------|--------------------------------|
| Cation-ordered α-PbO$_2$-related form | 0.05                              | 0.53                                     | 1.12                           |
| Cation-ordered fluorite-related form | 0.25                              | 0.97                                     | 1.29                           |

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**Fig. 3.** $^{119}$Sn Mössbauer spectra of Sn$^{IV}$$_{0.82}$(Ta$_{0.94}$Sn$^{IV}$)$_{0.06}$O$_{4.11}$ phases for (a) the α-PbO$_2$-related form, and (b) the starting fluorite-related form.

**Fig. 4.** Schematic drawing of the transformation mechanism from the cation-ordered fluorite-related Sn$^{IV}$$_{0.82}$(Ta$_{0.94}$Sn$^{IV}$)$_{0.06}$O$_{4.11}$ to the α-PbO$_2$-related Sn$^{IV}$$_{0.82}$(Ta$_{0.94}$Sn$^{IV}$)$_{0.06}$O$_{4.11}$, (a) for the APB-free cation-ordered α-PbO$_2$-related form, and (b) for the cation-ordered α-PbO$_2$-related form containing APBs. The APBs parallel to the [010] plane are introduced by the irregular sliding of the oxygen stacking.
between the Sn–Ta–O and Sn–Nb–O systems. For instance, the time to complete the oxidation of the precursor pyrochlore for the Sn–Ta–O system (5 h) was much shorter than that for the Sn–Nb–O system (120 h; reported in a previous paper), and the appearing temperature of the α-PbO2-related phase for the Sn–Ta–O system (≥973 K) was much higher than that for the Sn–Nb–O system (723 K). In this subsection, we qualitatively discuss the origin of those differences.

According to a previous study, CeVIITaO3 could not be oxidized to CeVIIIOTaO3, however, the oxidation of CeVIIINbO3 stopped at the composition of CeIII,0.5CeVII,0.56NbO4.53 and the completely oxidized CeVIIINbO3.5 could not be obtained.23,24) In other words, the Ce ion was more highly oxidized for the tannatate than for the niobate. The observation in our study that the higher oxidation rate of the pyrochlore phase of SnIV,0.62(Ta1.86SnIV0.14)O6.55 than SnIV,0.62(Nb1.86SnIV0.14)O6.55 was consistent with the oxidation behavior of CeVIIITaO3 and CeVIIINbO4. Therefore, the highly oxidized state of the cation is usually stabilized in the complex oxide containing a highly basic counter cation. For example, in alkaline-earth iron oxides with a perovskite-related structure, the highly oxidized FeIV was rather stabilized in BaFeO3.4 than in SrFeO3.4,27) the fact that BaO is more basic than SrO is well-known chemistry.27) In the present case, the observed higher oxidation rate of SnIII in the Sn–Ta–O system than that in the Sn–Nb–O system corresponds to a higher stabilization of SnIV in the Sn–Ta–O system than in the Sn–Nb–O system. Based on the above example of FeIV-stabilization in BaFeO3.4 and SrFeO3.4, higher basicity of Ta2O5 than Nb2O5 is suggested. There are few reports discussing the difference in basicity between Ta2O5 and Nb2O5. Because the basicity of the M2O5 oxide is generally high-pressure form for Nb2O5 and Ta2O5 under ambient pressure,30) According to their study, the transformation temperature from Ta2O5 to Nb2O5 was higher than that for Nb2O5. For the complex oxides of γ-Ba4Ta3O9 which has two tetrahedral sites and one octahedral site, the occupancy of Ta ion in the octahedral site tends to be higher than that of Nb ion.31) These showed that the high coordination number was more stable for Ta ion than Nb ion.

In the present case, the Ta and Nb in the fluoride-related forms are 7- or 8-fold coordinated as described in a previous paper,16) while those are 6-fold coordination in the α-PbO2-related form. Therefore, the higher transformation temperature from the fluoride-related form to α-PbO2-related form for the Sn–Ta–O system than that for the Sn–Nb–O system was consistent with the previous reports. Although the ionic sizes of Nb and Ta are approximately the same due to the lanthanide contraction, Ta probably prefers a high coordination number compared to Nb.

5. Conclusion

In the present study, we have successfully synthesized the α-PbO2-related SnIV,0.62(Ta0.94SnIV0.06)O4.11. The structural feature of the phase and its formation condition were discussed. The obtained conclusions are summarized as follows:

1) SnIV,0.62(Ta0.94SnIV0.06)O4.11 with an α-PbO2-related structure was obtained by annealing of the cation-ordered fluoride-related SnIV,0.62(Ta0.94SnIV0.06)O4.11 at 973 ≤ T ≤ 1073 K in an O2 atmosphere.

2) In the XRD profile of the α-PbO2-related phase, the superlattice diffraction due to the cation ordering could not be observed while the superlattice diffraction appeared for the α-PbO2-related SnIV,0.61(Nb0.93SnIV0.07)O4.085. This observation was attributed to the large amount of APBs parallel to the [101] plane in the α-PbO2-related phase. In the APB-free domain, the respective cations of Sn and [0.94Ta + 0.06Nb] should be ordered similar to the manner observed in the precursor SnIV,0.62(Ta0.98SnIV0.02)O4.58 pyrochlore.

3) The transformation temperature from the fluoride-related form to the α-PbO2-related form for SnIV,0.62(Ta0.94SnIV0.06)O4.11 was approximately 250 K higher than that for SnIV,0.81(Nb0.93SnIV0.07)O4.085. Taking into account the fact that Ta and Nb have 7- and 8-fold coordinations in the fluoride-related form and 6-fold coordination in the α-PbO2-related form, it was inferred that Ta preferred the high coordination number compared to Nb, although the ionic sizes of Nb and Ta are approximately the same.

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