Cation distribution of pseudobrookite-type titanates and their phase stability

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Pseudobrookite-type titanate has two types of oxide octahedra for different cation types. The cation distributions in the octahedra of three pseudobrookite type oxides, Al2TiO5, MgTi2O5 and Fe2TiO5, and in a solid solution of 0.5Al2TiO5–0.5MgTi2O5 were studied by the Rietveld method. The analysis revealed that the cation distributions of Al2TiO5 and Fe2TiO5 did not depend on the annealing temperature, whereas that of MgTi2O5 depended on the annealing temperature. The estimated cation distributions determined by the Rietveld method agreed with those determined by bond valence sum estimation. The configuration entropies of Al2TiO5s and Fe2TiO5s were almost the same as that of the maximum value of the random distribution of cations. Although the configuration entropy stabilized Al2TiO5 thermodynamically, the decomposition of Al2TiO5 should be attributed to the stable nature of corundum, and the rather “stretched” structure of Al2TiO5 would also cause its instability at low temperature.

Key-words : Pseudobrookite-type titanate, Cation distribution, Rietveld method, Configuration entropy

1. Introduction

Pseudobrookite-type titanates, such as Al2TiO5, MgTi2O5 and Fe2TiO5, show large thermal expansion anisotropy,1,2) and their sintering specimens contain grain boundary cracks.2) The grain boundary cracks are due to thermal stresses on grain boundaries caused by anisotropic contraction during cooling.3) These grain boundary cracks cause low mechanical strength and low thermal expansion in ceramics. The latter property is attributed to the fact that thermal expansion in the direction of a large thermal expansion coefficient only fills the gap of a grain boundary crack. Among the three titanates above, Al2TiO5 exhibits the largest thermal expansion anisotropy and a negative expansion coefficient along one crystallographic direction; therefore, the ceramics of Al2TiO5 with a small amount of rectangular crystal system, and there is some confusion about its space group. Brown and Navrotsky11) and Yang and Hazen12) also studied the cation distribution in MgTi2O5 and obtained the same results. Norberg et al.13) reported the cation distribution in Al2TiO5, which was fabricated by the rapid cooling of a melt, as [4c][Al0.626Ti0.374][8f][Al0.687Ti0.313]O5. The cation was distributed almost randomly, and the Ti4+ ion slightly favored the 4c site. Skala et al.14) studied the cation distribution of Al2TiO5 by high temperature neutron and X-ray diffraction and reported an almost random distribution and little preference of Ti4+ for the 4c site below 800°C, which was the same tendency found by Norberg. Their measurement at 1200°C is interesting, but the analyzed stoichiometry became an aluminum rich composition from the nominal formula of Al2TiO5.

Here, we report the results of our investigation on the cation distribution by the Rietveld method and bond valence sum. We also evaluated the change in the configuration entropy of the pseudobrookite type oxides, Al2TiO5, MgTi2O5, and Fe2TiO5 as well as a 0.5Al2TiO5–0.5MgTi2O5 solid solution.

The pseudobrookite-type titanate belongs to an orthorhombic crystal system, and there is some confusion about its space group. Here, we adopt Bbmm as the space group after Pauling,13) in which the length of the b-axis is longest and the c-axis is shortest.

2. Experimental procedure

The starting powders used in the experiments were corundum (99.99% pure, AKP-20, Sumitomo Chemical, Japan), rutile (99.98% pure, TP-3, Fuji Titanium Industry, Japan), Mg(OH)2

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DOI http://doi.org/10.2199/jcersj2.17086
Table 1. Variables of occupancy of cations in the two cation sites

| Cation Site | Al 2TiO 5 | Fe 2TiO 5 | MgTi 2O 5 | AlTi 1.5Mg 0.5O 5 |
|-------------|-----------|-----------|-----------|------------------|
| 4c Ti 4 +   | x         | ti 4      | x         | ti 4             |
| Al 1+       | 1 – x     | Mg 2+     | 1 – x     |                  |
| 8f Ti 4+    | (1 – x)/2 | ti 4      | (2 – y)/2 |                  |
| Al 1+       | (1 + x)/2 | Mg 2+     | x/2       |                  |

Fig. 1. XRD profiles of Al 2TiO 5 with composition of Al 2O 3:TiO 2 = 1.02:1 (left) and AlTi 1.5Mg 0.5O 5 (right) samples fired at 1500°C for 2h, and then annealed (a) at 1100°C for 1h, (b) at 1200°C for 1h, and (c) at 1200°C for 10h for Al 2TiO 5, and (d) 1100°C for 1h, (e) 1100°C for 100h, and (f) 1100°C for 200h for AlTi 1.5Mg 0.5O 5. Diffraction peaks of Al 2TiO 5 and AlTi 1.5Mg 0.5O 5 (ATM) are not identified.
in Fig. 1 (right). The AlTi$_3$Mg$_6$O$_{15}$ sample did not decompose by annealing at 1200°C for 100 h. These results are the same as those reported by Buscaglia et al.\textsuperscript{17} There was no change in the crystalline phases of MgTi$_2$O$_5$ and Fe$_2$TiO$_5$ by annealing.

### 3.2 Electrostatic preference of the octahedra to cation distribution according to Pauling’s second rule

Typical result of Rietveld analysis for Al$_2$TiO$_5$ sample is shown in Fig. 2. The minimum $R_p$ occurred at $x = 0.4$ and was independent of the annealing temperature. In the case of Al$_2$TiO$_5$, the structure with $x = 0.4$ was most reliable regardless of the annealing temperature. The other titanates were examined in the same way, and Table 2 shows typical results from these examinations. Using the data from Al$_2$TiO$_5$ fired at 1500°C, a schematic of four octahedra is shown in Fig. 3. In this figure, four oxide ions that are just above the cations are omitted. There are three types of oxide ions, one at the 4c site and two at 8f sites. The cations are situated inside each octahedron, but not at the center, because the octahedra are distorted. The three octahedra are connected by edge-sharing along the $a$-axis and the two octahedra of 8f cation are connected by apex-sharing with O1 ion. The apex connection causes the distortion of octahedra.

To examine the electrostatic stability, the number of cations around the anion was counted according to the calculated interionic distances listed in Table 3. Three types of oxide ions, one 4c and two 8f, were surrounded by 3 or 4 cations, and beyond these surrounding cations, oxide ions appeared again. Thus the number of anion charge number of anion charge number of cations resulted in a value of $-3.333$ for both the 4c and 8f cation sites. The total charge of the cations was 10, which was the same as that derived from the nominal formula of the pseudobrookite-type compounds. This means that the two cation sites are electrostatically equivalent and Pauling’s second rule suggests no site preference for the cation.

### 3.3 Cation distribution

The obtained cation distributions against the annealing temperature are shown in Fig. 4. In Fig. 4(b), data reported by Wechsler and Navrotsky\textsuperscript{10} are also plotted. The occupation of Al$_2$TiO$_5$ and Fe$_2$TiO$_5$ did not depend on the annealing temperature, while that of MgTi$_2$O$_5$ depended on the annealing temperature. The tendency and site occupation of the two cations of MgTi$_2$O$_5$ were almost the same as those reported by Wechsler and Navrotsky, and others. The large value of the sample annealed at 400 and 500°C is observed in Fig. 4(b). This was caused by very low diffusivity, they had not reached equilibrium.

As mentioned before, the random distribution of the cation results in $x = 0.333$ in Al$_2$TiO$_5$ and Fe$_2$TiO$_5$ and $x = 0.667$ in Al$_2$TiO$_5$ with composition of Al$_2$O$_3$:TiO$_2$ = 1:1.02 fired at 1500°C for 2 h.

Table 2. Typical results of Rietveld analysis, Al$_2$TiO$_5$ with composition of Al$_2$O$_3$:TiO$_2$ = 1:1.02 fired at 1500°C for 2 h

| Site | Ion     | $x$ | $y$ | $z$ | Occupation | $B$/Å$^2$ |
|------|---------|-----|-----|-----|------------|------------|
| M1, 4c | Ti$^{4+}$ | 0.1861(11) | 0.25 | 0 | 0.4 | 1.0461(11) |
| M2, 8f | Ti$^{4+}$ | 0.1353(15) | 0.56157(12) | 0 | 0.3 | 0.69(3) |
| O1, 4c | O$^{2-}$ | 0.7575(3) | 0.25 | 0 | 1 | 0.28(6) |
| O2, 8f | O$^{2-}$ | 0.0478(2) | 0.11620(15) | 0 | 1 | 0.52(4) |
| O3, 8f | O$^{2-}$ | 0.3126(2) | 0.07261(16) | 0 | 1 | 0.42(4) |

Table 3. Neighboring ions and interionic distances (Å) around oxide ions, and electrostatic bond strength about the two octahedra of Al$_2$TiO$_5$ with composition of Al$_2$O$_3$:TiO$_2$ = 1:1.02 sample fired at 1500°C for 2 h

| anion   | nearest neighbor | 2nd nearest | 3rd nearest | 4th nearest |
|---------|------------------|-------------|-------------|-------------|
| O1, 4c  | M1 × 2           | M2 × 2      | O3 × 4      | O2 × 4      |
| O2, 8f  | M2 × 2           | M1 × 1      | M2 × 1      | O2 × 1      |
| O3, 8f  | M1 × 1           | M1 × 1      | M2 × 1      | O1 × 2      |

| anion | electrostatic bond strength of anion | 4c cation site | 8f cation site |
|-------|--------------------------------------|---------------|---------------|
| O1, 4c | −0.5                                 | 2 −1          | 1 −0.5       |
| O2, 8f | −0.667                               | 2 −1.333      | 2 −1.333     |
| O3, 8f | −0.5                                 | 2 −1          | 3 −1.5       |

sum 6 −3.333 6 −3.333
MgTi₂O₅. The cation distribution in Al₂TiO₅ was slightly larger than the value and Ti⁴⁺ ion slightly favors the 4c site, a tendency that was previously reported. This value remains almost constant when varying the temperature, and therefore, the configuration entropy remained constant over the decomposition temperature range. It is notable that in the samples annealed at 1100 and 1200°C, decomposition began and three phases, rutile, corundum and Al₂TiO₅, coexisted. This means that the decomposition of aluminum titanate was not induced by a decrease in the entropy, i.e., by increasing the site preference of cations. On the other hand, site preference in MgTi₂O₅ increased as the configuration entropy of this compound decreased at lower temperature. The decrease in the value of x means that Mg⁺⁺⁺ ion favored the 4c site at lower temperature.

In the case of the AiTi₁₋ₓMgₓO₂ solid solution, there are three types of cations and a simplification is needed for the present Rietveld analysis. Because the Ti⁴⁺ and Al³⁺ ions in Al₂TiO₅ have little site preference, we assumed that these two ions have the same tendency of site occupancy, and the occupation of Mg⁺⁺⁺ ion in 4c site is assigned as y. In this case, individual variations of the ions at the sites are listed in Table 1. In this solid solution, the random distribution gives y = 0.167.

The resultant y values giving the lowest Rwp were 0.23, 0.20, 0.29, and 0.27 for samples heated at 1500, 1200, 1100 and 500°C, respectively. Since the measured y values were larger than the random distribution, the Mg⁺⁺⁺ ion favored the 4c site, and this is the same tendency as MgTi₂O₅. The same dependence of the site preference on the temperature was also observed in this experiment, so that the Mg⁺⁺⁺ ion preferred the 4c site at lower temperature.

### 3.4 Bond valence sum of the octahedra

For an estimation of the valence of the cation in the octahedron, a calculation of bond valence sum is often performed. Here, the bond valence sum was determined using the calculated distances from the central cation to the surrounding six oxide ions and was then compared with the result of the Rietveld analysis. The bond valence sum is derived by the equation below.

\[
V_i = \sum \exp \left( \frac{b - l_i}{B} \right)
\]

where \(V_i\): effective valence of i cation; \(l_i\): constant for specific pair of oxide ion and cation, which was calculated by weighing the occupancy of the cations in the sites; \(B\): constant 0.37; \(l_i\): measured distance between the i cation and j anion. The calculated bond valence sums and the estimated charge of the cation, which is calculated from the nominal charge weighted by the cation occupations, are listed in Table 4.

The charge of the cations by the bond valence sum and weighted nominal charge agreed to within approximately 5%. The estimated distributions of the cations in the octahedra by the Rietveld method are quite reasonable. The bond valence sums of Al₂TiO₅ were smaller than those of the weighted nominal values by 6.5 and 5.8% for the 4c and 8f sites, respectively. This means that the octahedra of Al₂TiO₅ are “stretched” according to a description in the Section 8.3 of Ref. 19, i.e., the bond lengths, as a whole of octahedron, between the cation and surrounding oxide ions are longer than that expected from usual relation of the cation and oxide ions. The cations in the octahedra are smaller than the space formed in the six coordinated oxide ions. The large bond valence sum of the 4c site in MgTi₂O₅ would mean that the octahedron is “compressed”, i.e., the bond lengths are shorter than that expected from cation and oxide ions. In this case the ion size of Mg⁺⁺⁺ is too large for the 4c site, although Mg⁺⁺⁺ ion tends to enter this site. The deviation of the calculated bond valence sum from the nominal valence of the ion is a simple measure to suggest how the cation fit in the octahedron of oxide ions. The relation between the size of cation and cavity of the octahedron is also shown in the next section.

### 3.5 Size and shape of the octahedra and site preference

As seen previously, the two cation sites are electrostatically equivalent, so the cation size and octahedron size should affect the site preference of cations. Using the obtained parameters, the volume of the two octahedra was calculated and is shown in...
Fig. 5. The 4c cation octahedron is smaller than the 8f cation octahedron, although the large Mg$^{2+}$ ion tended to enter the 4c site at a lower temperature. As shown in Fig. 3, the two octahedra are distorted and the volume itself is not a measure of the capability of accommodating the large cation. To show the distortion of the octahedra, the distances between the central cation and surrounding six oxide ions were calculated and are shown in Fig. 6. In this figure, the sum of the ionic radii of the cations and oxide ions is also shown. The ionic radii of the cations were those of coordination number 6, after Shannon. The ionic radii of the oxide ion, the radius for the coordination number 4, 1.38, and 3, 1.36 Å, was averaged with the weight of the number of oxide ions in the pseudobrookite-type structure, 3 and 2, respectively. The variations of the distance were large in the 8f cation site, which is marked by a triangle, while those of the 4c cation site, square mark, depended on the compounds.

Al$^{3+}$ has a small ionic radius, and its cation-anion distances exhibited the smallest values. The distance between Ti$^{4+}$ or Fe$^{3+}$ and the oxide ions is very similar to the average cation-anion distance of the octahedra. The “stretched” nature of Al$_2$TiO$_5$ derived from the bond valence sum is attributed to the small size of Al$^{3+}$.

Both octahedra were distorted, and the variation of the cation-anion distances of the 8f cation octahedron was large and almost the same among the titanates examined. On the other hand, the variation of the cation-anion distances of the 4c cation octahedron became small by increasing the cation size, i.e., going from Al$^{3+}$ to Fe$^{3+}$ and Mg$^{2+}$. This means that the octahedron of the larger cation becomes a nearly “regular” octahedron and the effective space to accommodate the cation becomes larger.

The distorted octahedra also result in a deviation of the cation position from the center of the six surrounding oxide ions. The difference in the position between the actual cation and the average of the positions of the six oxide ions was calculated as a distance between two centers and is shown in Fig. 7. The distance between the centers in the 8f cation site was almost the same among the titanates. The distance in the 4c site is smaller for titanates with larger cations and the 4c cation located near the center of the octahedron.

In other words, large cations can make the distorted 4c octahedron regular, and large cations tend to enter this 4c site. As shown in Fig. 3, an O1 ion in the 8f cation octahedron bridges the two octahedra, and this distortion renders the octahedron unsuitable for accommodating large cations. In the case of Fe$_2$TiO$_5$, the ionic radii of Fe$^{3+}$ and Ti$^{4+}$ are similar and no significant site preference occurs. This is a possible explanation for why Mg$^{2+}$ ions prefer the small 4c site at lower temperature.

3.6 Configuration entropy and contribution to the stability of the titanates

Configuration entropy stabilizes pseudobrookite-type titanates, especially at high temperature. Using the above-estimated cation distribution, the configuration entropy, $S_{conf}$ was calculated as:

$$S_{conf} = -R \sum b_i N_i \ln N_i$$

where $R$ is the ideal gas constant, $b_i$ is the number of s sites per formula unit, and $N_i$ is the fraction of i species in s site. The results are shown in Fig. 8. The $S_{conf}$ of Al$_2$TiO$_5$ is approximately 15 J mol$^{-1}$ K$^{-1}$. The contribution of configuration entropy to the free energy, $T \Delta S_{conf}$, is also plotted against temperature in

![Fig. 5. Volumes of the two octahedra, 4c and 8f.](image)

![Fig. 6. Distances between central cations and coordinated anions, square marks: 4c cation site, triangle marks: 8f cation site, solid marks: averaged distance, and open marks: individual distance. Summations of ionic radii of oxide ion and cations are also shown.](image)

![Fig. 7. Distances between two centers, i.e., between cation position and average of six surrounding oxide ions.](image)

![Fig. 8. Configuration entropy $S_{conf}$ and $T \Delta S_{conf}$ Al$_2$TiO$_5$ was partially decomposed at 1100 and 1200°C.](image)
Table 5. Formation free energy of some oxides

| oxide          | \( \Delta G^0 \) at 1000K, kJ/mol |
|---------------|----------------------------------|
| FeO, hematite | -987.4                           |
| Al\(_2\)O\(_3\), corundum | -1778.6                          |
| TiO\(_2\), rutile | -1027.9                          |
| MgO, periclase | -651.1                           |
| Al\(_2\)O\(_3\) + TiO\(_2\) | -2806.6                          |
| Fe\(_2\)O\(_3\) + TiO\(_2\) | -2015.3                          |
| MgO + 2TiO\(_2\) | -2707.0                          |

Fig. 8. The graph contains data from the Al\(_2\)Ti\(_3\)O\(_9\)-Mg\(_3\)Ti\(_2\)O\(_7\) solid solution.

Gani and McPherson\(^22\) reported the formation enthalpy \( \Delta H_f \) of Al\(_2\)TiO\(_3\) from rutile and corundum as 25.1 kJmol\(^{-1}\) at 1340°C. Considering this reaction occurred at an equilibrium temperature, the relation \( \Delta H_f / T_f \) gives \( \Delta S_f = 15.6 \text{Jmol}^{-1} \text{K}^{-1} \), and this value is almost the same as the configuration entropy shown in Fig. 8.

The configuration entropy of Al\(_2\)TiO\(_3\) and Fe\(_2\)TiO\(_3\) is almost the same as that of a random configuration, although there is some degree of site preference, as shown in Fig. 4. This also suggests that there is little motive force toward the perfect random distribution energetically. The difference between the configuration entropy values of Al\(_2\)TiO\(_3\) and Mg\(_2\)TiO\(_3\), and Al\(_2\)Ti\(_3\)Mg\(_2\)O\(_7\) solid solution means stabilizing effect by the solid solution. Buscaglia et al.\(^7\) estimated the stabilizing effect of Al\(_2\)TiO\(_3\) by doping Mg\(_2\)TiO\(_3\) under the assumption that the cation distribution was random. As shown in Fig. 8, their assumption is almost correct.

The stabilization effect of the configuration entropy on Al\(_2\)TiO\(_3\) is large. It is true that Al\(_2\)TiO\(_3\) is stabilized by an increase of configuration entropy, so the formation reaction from corundum and rutile is endothermic. However, it is not true that a decrease in the configuration entropy triggers the decomposition reaction of Al\(_2\)TiO\(_3\) because partially decomposed Al\(_2\)TiO\(_3\) exhibits an almost random cation distribution, as shown in Fig. 8. The decomposition of Al\(_2\)TiO\(_3\) occurs at lower temperature, due to the lower thermodynamic free energy of an equimolar mixture of corundum and rutile than that of Al\(_2\)TiO\(_3\). If the thermodynamic free energy is compared with, for example, a gel state of mixture of Ti\(^{4+}\) and Al\(^{3+}\), Al\(_2\)TiO\(_3\) would be more stable than the gel. In a certain sol-gel route, Al\(_2\)TiO\(_3\) readily crystallizes at lower temperature of 600 or 700°C as a metastable phase.\(^23\),\(^24\) It evidently shows that Al\(_2\)TiO\(_3\) is more stable than the gel. Because the TiO\(_2\) component is the same among the titanates of the present study, a stability of corundum would be attributed to the low temperature decomposition of Al\(_2\)TiO\(_3\).

Table 5 shows the free energy of formation at 1000K of some oxides concerning the three pseudobrookite oxides, which are calculated using thermodynamic constants from the textbook of Kubaschewski.\(^23\) Obviously, corundum is a very stable oxide and compounds containing the Al\(_2\)O\(_3\) species must overcome the stability of corundum to exist stably. Additionally, the “stretched” structure of Al\(_2\)TiO\(_3\), which is mentioned in the consideration of the bond valence sum, would mean that this ionic compound has a low electrostatic lattice enthalpy because the lattice enthalpy is inversely proportional to the interionic distances and a “stretched” structure means longer interionic distances.

4. Conclusion

The cation distribution and interionic distances of three pseudobrookite type oxides, Al\(_2\)TiO\(_3\), Mg\(_2\)TiO\(_3\) and Fe\(_2\)TiO\(_3\), and a solid solution of Al\(_2\)TiO\(_3\)-Mg\(_2\)TiO\(_3\) were examined using X-ray diffraction and the Rietveld method. The cation distributions in two types of octahedra of Al\(_2\)TiO\(_3\) and Fe\(_2\)TiO\(_3\) showed little preference and were independent of temperature. The configuration entropies of these oxides, however, were almost the same as that of a random distribution of cations. A cation distribution preference was observed in Mg\(_2\)TiO\(_3\) and found to exhibit temperature dependence; as the temperature was lowered, large Mg\(^{2+}\) ions tended to enter smaller 4c sites of the octahedron. The calculated bond valence sums of the titanates correspond to the cation distribution of the Rietveld analysis. Decomposition of Al\(_2\)TiO\(_3\) is not triggered by a change in the cation distribution, but thermodynamic stability of corundum may cause the decomposition of Al\(_2\)TiO\(_3\).

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