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, Al_2TiO_5 , MgTi_2O_5 and Fe_2TiO_5 , and in a solid solution of $0.5\text{Al}_2\text{TiO}_5$ – $0.5\text{MgTi}_2\text{O}_5$ were studied by the Rietveld method. The analysis revealed that the cation distributions of Al_2TiO_5 and Fe_2TiO_5 did not depend on the annealing temperature, whereas that of MgTi_2O_5 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 Al_2TiO_5 and Fe_2TiO_5 were almost the same as that of the maximum value of the random distribution of cations. Although the configuration entropy stabilized Al_2TiO_5 thermodynamically, the decomposition of Al_2TiO_5 should be attributed to the stable nature of corundum, and the rather “stretched” structure of Al_2TiO_5 would also cause its instability at low temperature.

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1. Introduction

Pseudobrookite-type titanates, such as Al_2TiO_5 , MgTi_2O_5 and Fe_2TiO_5 , show large thermal expansion anisotropy,¹⁾ 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),4)} 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, Al_2TiO_5 exhibits the largest thermal expansion anisotropy and a negative expansion coefficient along one crystallographic direction; therefore, the ceramics of Al_2TiO_5 have a lower thermal expansion than those of MgTi_2O_5 and Fe_2TiO_5 . Al_2TiO_5 ceramics are applied to the materials of a diesel particulate filter because of their high thermal shock resistance.^{5),6)} The mechanical strength can be improved by reducing the amount of grain boundary cracks by suppressing grain growth⁷⁾ because a sample with a large grain size tends to have a large amount of grain boundary cracks and low mechanical strength. However, this also brings about an increasing thermal expansion coefficient. We recently proposed the microstructure of Al_2TiO_5 ceramics with a small amount of rectangular large crystals distributed in the small-grained matrix.⁸⁾ The resultant ceramics have low thermal expansion and rather good mechanical properties.

Pseudobrookite-type oxides have interesting crystal chemistry.¹⁾ This structure has two types of cation octahedral sites, namely, 4c and 8f. In pseudobrookite-type titanates, two types of cations and three cations of nominal formula distribute into the two types of octahedral sites in the crystal. This distribution increases the configuration entropy, and the structure becomes stable at higher temperature. This stabilization is pronounced in the case of Al_2TiO_5 .¹⁾ This titanate is stable above 1280°C,⁹⁾

and the formation reaction of Al_2TiO_5 from the mixture of rutile and corundum is endothermic, i.e., Al_2TiO_5 is stabilized by the configuration entropy. This also means that Al_2TiO_5 decomposes at lower temperature, which is a problem for practical applications of Al_2TiO_5 ceramics.

The change in the distribution of the two types of cations in the two octahedral sites is very interesting. Wechsler and Navrotsky studied the dependence of the cation distribution in MgTi_2O_5 on temperature according to the change in the dimension of the *c*-axis¹⁰⁾ and found that occupancy by Ti^{4+} in the 4c site decreased with decreasing temperature. Brown and Navrotsky¹¹⁾ and Yang and Hazen¹²⁾ also studied the cation distribution in MgTi_2O_5 and obtained the same results. Norberg et al.¹³⁾ reported the cation distribution in Al_2TiO_5 , which was fabricated by the rapid cooling of a melt, as $^{[4c]}[\text{Al}_{0.626}\text{Ti}_{0.374}]^{[8f]}[\text{Al}_{0.687}\text{Ti}_{0.313}]\text{O}_5$. The cation was distributed almost randomly, and the Ti^{4+} ion slightly favored the 4c site. Skala et al.¹⁴⁾ studied the cation distribution of Al_2TiO_5 by high temperature neutron and X-ray diffractometry and reported an almost random distribution and little preference of Ti^{4+} ion 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 Al_2TiO_5 .

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, Al_2TiO_5 , MgTi_2O_5 , and Fe_2TiO_5 as well as a $0.5\text{Al}_2\text{TiO}_5$ – $0.5\text{MgTi}_2\text{O}_5$ solid solution.

The pseudobrookite-type titanate belongs to a orthorhombic crystal system, and there is some confusion about its space group. Here, we adopt *Bbmm* as the space group after Pauling,¹⁵⁾ 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), $\text{Mg}(\text{OH})_2$

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(99.9% pure, MH-30, Iwatani Chemical Industry, Japan), and hematite (99.99% pure, Kojundo Chemical Lab., Japan). These powders were weighed at appropriate ratios and mixed in an alumina mill and nylon coated metal balls. The weighted molar ratios of Al_2TiO_5 were shifted from the equimolar ratio to $\text{Al}_2\text{O}_3:\text{TiO}_2 = 1:1.02$ and $1.02:1$ to verify the solid solution range. As a result, there were only slight differences between the two ratios and no detectable range of solid solution, so the results with lower R_{wp} are described hereafter as the data of Al_2TiO_5 . After mixing, the samples were molded and CIPed into discs of $10\text{ mm}\phi \times 5\text{ mm}$ under 100 MPa. The discs of Al_2TiO_5 and MgTi_2O_5 were sintered at 1500°C for 2 h in an electric furnace and subsequently soaked at various lower temperatures for a long time and then water quenched. After sintering at 1500°C , Al_2TiO_5 samples were annealed at 1300, 1200, 1100 and 600°C for 1, 10 and 100 h. MgTi_2O_5 samples were annealed at 1400 to 400°C for 100 and 200 h after sintering at 1500°C . Additionally we investigated the cation distribution of the $0.5\text{Al}_2\text{TiO}_5\text{--}0.5\text{MgTi}_2\text{O}_5$ ($\text{AlTi}_{1.5}\text{Mg}_{0.5}\text{O}_5$) solid solution, of which samples were prepared using the above-mentioned procedure.

Samples of Fe_2TiO_5 with an equimolar composition of Fe_2O_3 and TiO_2 were crystallized into pseudobrookite-type titanate and hematite by heating at 1500°C in air. The crystallization of pseudobrookite-type titanate and hematite occurred because Fe^{3+} was partially reduced and formed a solid solution, $\text{Fe}_2\text{TiO}_5\text{--}\text{FeTi}_2\text{O}_5$.¹⁶⁾ Then, the samples were sintered in an oxygen atmosphere (50 mL/min) at 1200 and 1100°C and then annealed at lower temperatures of 1000°C for 8 h, 500 and 400°C for 100 h. These fired samples were furnace cooled in a flowing O_2 atmosphere.

The fired samples were crushed and the cation distribution was estimated by the Rietveld method (PDXL2 program, Rigaku, Japan). The X-ray diffraction (XRD) intensity was collected for 6 s every 0.02° intervals using a usual Bragg-Brentano type diffractometer (Ultima IV, Rigaku, Japan). In the estimation of the occupancy of the cations, the occupancy of Ti^{4+} ions in the 4c site was set as a variable x and the occupancies of the other ions in the sites were calculated. In the case of Al_2TiO_5 , as listed in **Table 1**, Ti^{4+} ions at the 8f site, Al^{3+} ions at the 4c site, and Al^{3+} ions in 8f site became $(1-x)/2$, $(1-x)$, and $(1+x)/2$, respectively. If cations are randomly distributed in the 4c and 8f sites of Al_2TiO_5 and Fe_2TiO_5 , x becomes 0.333 and $x = 0.667$ for MgTi_2O_5 . For the estimation of the cation distributions in the $0.5\text{Al}_2\text{TiO}_5\text{--}0.5\text{MgTi}_2\text{O}_5$ solid solution, however, a different vari-

able was used, which will be mentioned later. It is noteworthy that in Al_2TiO_5 and Fe_2TiO_5 , a perfect cation site preference was only achieved with $x = 1$, while $x = 0$ gave a random distribution of the same number of Al^{3+} and Ti^{4+} ions in the 8f cation site and the 4c site was occupied by Al^{3+} ion. In the case of MgTi_2O_5 , $x = 0$ gives perfect site preference. By changing the value x , the minimum values of R_{wp} indicated the most reliable structure and cation distribution. Using the estimated atomic positions, interionic distances were also calculated.

The Rietveld analysis was performed for Al_2TiO_5 samples heated at 1500°C for 2 h, and then annealed at 1300 and 500°C for 100 h, and at 1200 and 1100°C for 1 h; Fe_2TiO_5 samples heated at 1200 and 1100°C for 2 h, at 1000°C for 8 h, at 500 and 400°C for 100 h in an O_2 atmosphere; MgTi_2O_5 samples heated at 1500°C for 2 h and annealed at 1400 to 400°C for 100 and 200 h; and $\text{AlTi}_{1.5}\text{Mg}_{0.5}\text{O}_5$ solid solution samples heated at 1500°C for 2 h and annealed at 1200° , 1100 and 500°C for 100 h.

3. Results and discussion

3.1 Crystalline phases of the sintered and annealed samples

Al_2TiO_5 , MgTi_2O_5 and $\text{AlTi}_{1.5}\text{Mg}_{0.5}\text{O}_5$ samples were crystallized into pseudobrookite-type compounds by sintering at 1500°C . By annealing at 1100 and 1200°C for 1 h, Al_2TiO_5 was partially decomposed into rutile and corundum, as shown in **Fig. 1** (left). Their decomposition ratios were 14 and 4%, respectively, and these samples were analyzed by the Rietveld method. After the longer annealing time of 10 h at 1200°C , Al_2TiO_5 was completely decomposed, as also shown in **Fig. 1** (left). Annealing at a lower temperature of 600°C for 100 h, Al_2TiO_5 did not decompose. The solid solution of $\text{AlTi}_{1.5}\text{Mg}_{0.5}\text{O}_5$ was more stable than pure Al_2TiO_5 . This sample began to decompose after annealing at 1100°C for 100 h and was considerably, but not completely, decomposed at 1100°C for 200 h into rutile and spinel, as shown

Table 1. Variables of occupancy of cations in the two cation sites

Al ₂ TiO ₅ and Fe ₂ TiO ₅				MgTi ₂ O ₅		AlTi _{1.5} Mg _{0.5} O ₅			
4c	Ti ⁴⁺	<i>x</i>		Ti ⁴⁺	<i>x</i>	4c	Mg ²⁺	<i>y</i>	
	Al ³⁺	1 − <i>x</i>		Mg ²⁺	1 − <i>x</i>		Ti ⁴⁺	3(1 − <i>y</i>)/5	
8f	Ti ⁴⁺	(1 − <i>x</i>)/2		Ti ⁴⁺	(2 − <i>x</i>)/2		Al ³⁺	2(1 − <i>y</i>)/5	
	Al ³⁺	(1 + <i>x</i>)/2		Mg ²⁺	<i>x</i> /2		Mg ²⁺	(1 − 2 <i>y</i>)/4	
						8f	Ti ⁴⁺	3(3 + 2 <i>y</i>)/20	
							Al ³⁺	2(3 + 2 <i>y</i>)/20

Fig. 1. XRD profiles of Al_2TiO_5 with composition of $\text{Al}_2\text{O}_3:\text{TiO}_2 = 1.02:1$ (left) and $\text{AlTi}_{1.5}\text{Mg}_{0.5}\text{O}_5$ (right) samples fired at 1500°C for 2 h, and then annealed (a) at 1100°C for 1 h, (b) at 1200°C for 1 h, and (c) at 1200°C for 10 h for Al_2TiO_5 , and (d) 1100°C for 1 h, (e) 1100°C for 100 h, and (f) 1100°C for 200 h for $\text{AlTi}_{1.5}\text{Mg}_{0.5}\text{O}_5$. Diffraction peaks of Al_2TiO_5 and $\text{AlTi}_{1.5}\text{Mg}_{0.5}\text{O}_5$ (ATM) are not identified.

in Fig. 1 (right). The $\text{AlTi}_{1.5}\text{Mg}_{0.5}\text{O}_5$ sample did not decompose by annealing at 1200°C for 100 h. These results are the same as those reported by Buscaglia et al.¹⁷⁾ There was no change in the crystalline phases of MgTi_2O_5 and Fe_2TiO_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_2TiO_5 sample is shown in Fig. 2. The minimum R_{wp} occurred at $x = 0.4$ and was independent of the annealing temperature. In the case of Al_2TiO_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_2TiO_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 b -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 individual electrostatic bond strength between anions and cations was calculated as -2 divided by 3 or 4. The sum of the six bond

Fig. 2. XRD profile of Al_2TiO_5 with composition of $\text{Al}_2\text{O}_3:\text{TiO}_2 = 1:1.02$ fired at 1500°C for 2 h.

strengths between anions and 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 Navrotsky¹⁰⁾ are also plotted. The occupation of Al_2TiO_5 and Fe_2TiO_5 did not depend on the annealing temperature, while that of MgTi_2O_5 depended on the annealing temperature. The tendency and site occupation of the two cations of MgTi_2O_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_2TiO_5 and Fe_2TiO_5 and $x = 0.667$ in

Table 2. Typical results of Rietveld analysis, Al_2TiO_5 with composition of $\text{Al}_2\text{O}_3:\text{TiO}_2 = 1:1.02$ fired at 1500°C for 2 h

			a_0	b_0	c_0			
Lattice constant/Å			9.4359(8)	9.6425(7)	3.5930(3)	R_{wp}	R_p	S
						7.69%	5.53%	1.746
Site	Ion	x	y	z	Occupation	$B/\text{Å}^2$		
M1, 4c	Ti^{4+}	0.18610(11)	0.25	0	0.4	1.0461(11)		
	Al^{3+}				0.6			
M2, 8f	Ti^{4+}	0.13535(15)	0.56157(12)	0	0.3	0.69(3)		
	Al^{3+}				0.7			
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)

Fig. 3. Schematic of pseudobrookite-type Al_2TiO_5 structure.

Table 3. Neighboring ions and interionic distances (Å) around oxide ions, and electrostatic bond strength about the two octahedra of Al_2TiO_5 with composition of $\text{Al}_2\text{O}_3:\text{TiO}_2 = 1:1.02$ sample fired at 1500°C for 2 h

anion	O1, 4c		O2, 8f		O3, 8f	
nearest neighbor	M1 × 2	1.919	M2 × 1	1.807	M2 × 2	1.865
2nd nearest	M2 × 2	2.079	M1 × 1	1.835	M1 × 1	2.086
3rd nearest	O3 × 4	2.534	M2 × 1	1.903	M2 × 1	2.115
4th nearest	O2 × 4	2.968	O2 × 1	2.416	O1 × 2	2.534

anion	number of cation surrounding anion	electrostatic bond strength of anion	4c cation site		8f cation site	
			number of anion	charge	number of anion	charge
O1, 4c	4	-0.5	2	-1	1	-0.5
O2, 8f	3	-0.667	2	-1.333	2	-1.333
O3, 8f	4	-0.5	2	-1	3	-1.5
sum			6	-3.333	6	-3.333

Fig. 4. Occupations of Ti^{4+} ion in 4c site, broken lines mean random occupation. Data of Wechsler and Navrotsky¹⁰⁾ are plotted by X with error bar.

Table 4. Bond valence sum (BVS) and calculated cation charges using nominal charge and weighted by the occupancy (weighted nominal charge, WNC)

site	Al_2TiO_5 , 1500°C 2 h $x = 0.4$			Fe_2TiO_5 , 1100°C 2 h in O_2 $x = 0.23$			MgTi_2O_5 , 1500°C 2 h $x = 0.43$		
	4c	8f	total	4c	8f	total	4c	8f	total
BVS	3.18	3.11	9.40	3.19	3.30	9.80	2.99	3.44	9.87
WNC	3.40	3.30	10	3.23	3.39	10	2.86	3.57	10
(BVS-WNC)/WNC	-6.5%	-5.8%	-6.0%	-1.2%	-2.7%	-2.0%	4.5%	-3.6%	-1.3%

MgTi_2O_5 . The cation distribution in Al_2TiO_5 was slightly larger than the value and Ti^{4+} ion slightly favors the 4c site, a tendency that was previously reported.¹³⁾ 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 Al_2TiO_5 , 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 MgTi_2O_5 increased as the configuration entropy of this compound decreased at lower temperature. The decrease in the value of x means that Mg^{2+} ion favored the 4c site at lower temperature.

In the case of the $\text{AlTi}_{1.5}\text{Mg}_{0.5}\text{O}_5$ solid solution, there are three types of cations and a simplification is needed for the present Rietveld analysis. Because the Ti^{4+} and Al^{3+} ions in Al_2TiO_5 have little site preference, we assumed that these two ions have the same tendency of site occupancy, and the occupation of Mg^{2+} 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 R_{wp} 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^{2+} ion favored the 4c site, and this is the same tendency as MgTi_2O_5 . The same dependence of the site preference on the temperature was also observed in this experiment, so that the Mg^{2+} 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.^{18),19)} 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.

$$V_i = \sum_j \exp\left(\frac{l_0 - l_{ij}}{B}\right) \quad (1)$$

where V_i : effective valence of i cation; l_0 : constant for specific pair of oxide ion and cation,¹⁸⁾ which was calculated by weighing the occupancy of the cations in the sites; B : constant 0.37; l_{ij} : 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 occupancies, 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 Al_2TiO_5 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 Al_2TiO_5 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 MgTi_2O_5 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^{2+} is too large for the 4c site, although Mg^{2+} 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 ion is also shown. The ionic radii of the cations were those of coordination number 6, after Shannon.²⁰⁾ For the ionic radius 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_2TiO_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_2TiO_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 as²¹⁾

$$S_{\text{conf}} = -R \sum b_s N_s^i \cdot \ln N_s^i \quad (2)$$

where R is the ideal gas constant, b_s is the number of s sites per formula unit, and N_s^i is the fraction of i species in s site. The results are shown in **Fig. 8**. The S_{conf} of Al_2TiO_5 is approximately $15 \text{ Jmol}^{-1} \text{ K}^{-1}$. The contribution of configuration entropy to the free energy, $T\Delta S_{\text{conf}}$, is also plotted against temperature in

Fig. 5. Volumes of the two octahedra, 4c and 8f.

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.

Fig. 7. Distances between two centers, i.e., between cation position and average of six surrounding oxide ions.

Fig. 8. Configuration entropy S_{conf} and $T\Delta S_{\text{conf}}$. Al_2TiO_5 was partially decomposed at 1100 and 1200°C.

Table 5. Formation free energy of some oxides

oxide	ΔG^0 at 1000 K, kJ/mol
Fe ₂ O ₃ , 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 AlTi_{1.5}Mg_{0.5}O₅ solid solution.

Gani and McPherson²²⁾ reported the formation enthalpy ΔH_f of Al₂TiO₅ from rutile and corundum as 25.1 kJmol^{−1} at 1340°C. Considering this reaction occurred at an equilibrium temperature, the relation $\Delta H_f = \Delta S_f/T_f$ gives $\Delta S_f = 15.6$ Jmol^{−1} K^{−1}, and this value is almost the same as the configuration entropy shown in Fig. 8.

The configuration entropy of Al₂TiO₅ and Fe₂TiO₅ 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 Al₂TiO₅ and MgTi₂O₅, and AlTi_{1.5}Mg_{0.5}O₅ solid solution means stabilizing effect by the solid solution. Buscaglia et al.¹⁷⁾ estimated the stabilizing effect of Al₂TiO₅ by doping MgTi₂O₅ 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 Al₂TiO₅ is large. It is true that Al₂TiO₅ 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 Al₂TiO₅ because partially decomposed Al₂TiO₅ exhibits an almost random cation distribution, as shown in Fig. 8. The decomposition of Al₂TiO₅ occurs at lower temperature, due to the lower thermodynamic free energy of an equimolar mixture of corundum and rutile than that of Al₂TiO₅. If the thermodynamic free energy is compared with, for example, a gel state of mixture of Ti⁴⁺ and Al³⁺, Al₂TiO₅ would be more stable than the gel. In a certain sol–gel route, Al₂TiO₅ readily crystallizes at lower temperature of 600 or 700°C as a metastable phase.^{23),24)} It evidently shows that Al₂TiO₅ is more stable than the gel. Because the TiO₂ component is the same among the titanates of the present study, a stability of corundum would be attributed to the low temperature decomposition of Al₂TiO₅.

Table 5 shows the free energy of formation at 1000 K of some oxides concerning the three pseudobrookite oxides, which are calculated using thermodynamic constants from the textbook of Kubaschewski.²⁵⁾ Obviously, corundum is a very stable oxide and compounds containing the Al₂O₃ species must overcome the stability of corundum to exist stably. Additionally, the “stretched” structure of Al₂TiO₅, 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, Al₂TiO₅, MgTi₂O₅ and Fe₂TiO₅,

and a solid solution of Al₂TiO₅–MgTi₂O₅ were examined using X-ray diffraction and the Rietveld method. The cation distributions in two types of octahedra of Al₂TiO₅ and Fe₂TiO₅ 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 MgTi₂O₅ and found to exhibit temperature dependence; as the temperature was lowered, large Mg²⁺ 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 Al₂TiO₅ is not triggered by a change in the cation distribution, but thermodynamic stability of corundum may cause the decomposition of Al₂TiO₅.

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