Mechanical strength and electrical conductivity of reactively-sintered pseudobrookite-type
Al$_2$TiO$_5$–MgTi$_2$O$_5$ solid solutions

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Al$_2$TiO$_5$–MgTi$_2$O$_5$ solid solutions were synthesized by reactive sintering of α-Al$_2$O$_3$, TiO$_2$ anatase and MgCO$_3$ (basic) powders at 1400°C (and at 1300°C for some composition) for 2 h, with changing the MgTi$_2$O$_5$ ratio to form the composition of Al$_{2-x}$Ti$_x$Mg$_x$O$_5$ (x = 0.0–1.0) and evaluated their properties. With increasing MgTi$_2$O$_5$ molar ratio, the matrix Al$_2$TiO$_5$–MgTi$_2$O$_5$ grains became more anisotropic, and the coefficient of thermal expansion increased due to the decrease of microcracks. Al$_{2-x}$Ti$_x$Mg$_x$O$_5$ (x = 0.9) showed the maximum strength of 47.9 MPa. On the other hand, MgTi$_2$O$_5$ (x = 1.0) showed low bending strength of 13.2 MPa due to the grain growth during the sintering at 1400°C. Al$_{2-x}$Ti$_x$Mg$_x$O$_5$ (x = 0.7) sintered at 1300°C indicated the highest conductivity. The conductivity of pseudobrookite-type ceramics strongly depends on microcracks.

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1. Introduction

Al$_2$TiO$_5$ with pseudobrookite-type structure has been widely studied because of (a) its low coefficients of thermal expansion (CTE), (b) its high melting point and (c) its high thermal shock resistance. Since low thermal expansion materials are necessary under some specific high-temperature applications, such as a thermistor and a heat exchanger, pseudobrookite-type ceramics are widely used for these devices. The low CTE of Al$_2$TiO$_5$, however, is attributed to microcracks caused by anisotropic thermal expansion under cooling from the sintering temperature. Therefore, sintered Al$_2$TiO$_5$, usually not fully dense, generally shows low fracture strength. Bayer reported that the CTE of pseudobrookite-type Al$_2$TiO$_5$ for each crystalline axis (space grope: Cmcm) were $\beta_a = -3.0 \pm 0.3$, $\beta_b = 11.8 \pm 0.6$, $\beta_c = 21.8 \pm 1.1$ (×10°/°C) in a temperature range of 20–1020°C. The CTE of polycrystalline Al$_2$TiO$_5$ ceramics, however, was rather small as an oxide, typically reported as <2.0 × 10°/°C. Despite the fascinating low thermal expansion behavior, Al$_2$TiO$_5$ is not so thermally stable and decomposes into Al$_2$O$_3$ and TiO$_2$ below the equilibrium temperature of 1280°C, which limits the applications of Al$_2$TiO$_5$, particularly in reducing atmosphere.

Besides Al$_2$TiO$_5$, several ceramics with pseudobrookite-type structure, such as MgTi$_2$O$_5$ and Fe$_2$TiO$_5$ were investigated. Solid solutions of pseudobrookite-type structure (e.g. Al$_{2x-1}$Fe$_x$Ti$_x$O$_5$) and others have also been synthesized and their CTE, thermal stabilities and microstructures have been reported. MgTi$_2$O$_5$ with pseudobrookite-type structure has potentially good mechanical properties with high thermal shock resistance, because its thermal expansion anisotropy is smaller than Al$_2$TiO$_5$. MgTi$_2$O$_5$ has been investigated for a third-generation diesel particulate filter with low cost, high temperature stability and better mechanical properties than Al$_2$TiO$_5$. MgTi$_2$O$_5$ can be synthesized in an intermediate temperature range of 1000–1200°C because of relatively high temperature stability among pseudobrookite-type ceramics. MgTi$_2$O$_5$ stabilizes the crystal phase of Al$_2$TiO$_5$ by forming an all-proportional solid solution. Therefore MgTi$_2$O$_5$ has been used as a stabilizer of Al$_2$TiO$_5$ in order to restrain the decomposition of Al$_2$TiO$_5$ in a temperature range of 750–1300°C (decomposition temperature of MgTi$_2$O$_5$ is 130–230°C). For these reasons, Al$_2$TiO$_5$–MgTi$_2$O$_5$ solid solution with intermediate feature between Al$_2$TiO$_5$ and MgTi$_2$O$_5$ has been studied as low CTE material with relatively high fracture strength.

As for Al$_2$TiO$_5$–MgTi$_2$O$_5$ solid solutions, there have been several studies on CTE and microstructures. However, relatively few studies have been reported on the functional properties of pseudobrookite-type ceramics, such as dielectric properties, photocatalytic function and electrical properties.

In this study, we have synthesized Al$_2$TiO$_5$–MgTi$_2$O$_5$ solid solutions from α-Al$_2$O$_3$, TiO$_2$ anatase and MgCO$_3$ (basic) powders by reactive sintering method, with changing the MgTi$_2$O$_5$ ratio to form the composition of Al$_{2-x}$Ti$_x$Mg$_x$O$_5$ (x = 0.0–1.0) and evaluated their properties. First, CTE and fracture strength of Al$_2$TiO$_5$–MgTi$_2$O$_5$ solid solutions were systematically characterized. Second, electrical conductivity of these Al$_2$TiO$_5$–MgTi$_2$O$_5$ solid solutions were also systematically measured by AC impedance method. For the pseudobrookite-type Mg$_{2x}$Ti$_{3-x}$O$_5$(x = 0.2, 0.3, 0.5, 0.8 and 0.9), a systematic analysis of electrical conductivity at 800°C was carried out by Steiner et al. However, such a systematic analysis on the Al$_2$TiO$_5$–MgTi$_2$O$_5$ solid solutions has not yet been reported. Temperature dependence of electrical properties was discussed for a solid solution with the highest conductivity.

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2. Experimental

2.1 Sample preparation

Commercial α-Al2O3 (99.99% purity, Taimei Chemicals Co. Ltd., Saitama, Japan), TiO2 anatase (99% purity, Kojundo Chemical Laboratory Co. Ltd.) and MgCO3 (basic) (99.9% purity, Kojundo Chemical Laboratory Co. Ltd., with actual composition of Mg5(OH)2(CO3)4·2H2O) powders were used as starting materials. MgCO3 powder includes hydroxyl groups and hydrated water. Hence, prior to the powder mixing, each starting powder was characterized by thermogravimetry-differential thermal analysis (TG-DTA) to clarify the weight-loss during the heating up to 1000°C. Required powder weight was corrected using the TG-DTA results. α-Al2O3, TiO2 anatase and MgCO3 (basic) powders were weighed according to the final compositions of Al2TiO5–MgTi2O5 solid solutions, expressed as Al2x+1−yTi1+y−xMg0.5Ox, where x is the molar ratio of MgTi2O5. The powders were mixed by wet ball-milling with ZrO2 media for 2 h using ethanol. The slurries were dried in an evaporator, and then, dried at 80°C in air. The dried powders were dry ball-milled with ZrO2 balls for 2 h, and were sieved through a 150-mm mesh screen. Cylindrical pellets (diameter of 15 mm) and rectangular bars (4 × 6 × 50 mm) were prepared by the uniaxial press of mixed powders. The slurries were observed. Energy dispersive X-ray spectroscopy (EDS) was carried out for an elemental analysis of the sintered samples. For EDS analysis, un-coated coating. The increases of grain size and density difference between Al3+ ion and Ti4+ ion than the size-difference between Al1.8Ti1.1Mg0.1O5 = (x = 0.1) sample, despite low molar ratio of MgTi2O5, was composed of only pseudobrookite-type phase, because of the decrease in distortion of MO6 octahedra, due to the substitution of metal ions (2Al3+ ≡ Mg2+ + Ti4+). Figure 2 exhibits typical SEM images of the surfaces of Al2x+1−yTi1+y−xMg0.5Ox (x = 0.1, 0.3, 0.7 and 1.0) samples with Au coating. The increases of grain size and densifications with increasing MgTi2O5 molar ratio were confirmed. With increasing MgTi2O5 molar ratio, the matrix Al2TiO5–MgTi2O5 grains became more anisotropic. The grain size and anisotropy depended on the molar ratio of Al2TiO5: MgTi2O5. MgTi2O5 (x = 1.0) sample consisted of relatively dense matrix with larger grains (~10–50 μm in length). These results can be attributed to the linear decrease of formation temperature of pseudobrookite-type phase, as reported by Daimon. By the decrease of formation

2.4 Electrical properties

The surfaces of the sintered pellets were polished by waterproof abrasive paper to enhance electrode adhesion. Platinum paste electrodes and platinum wires were attached to the surfaces of sintered pellets and heated up to 1200°C for 1 h. The pellet was positioned in the center of a tubular furnace. Impedance spectra were measured at 750–1000°C in air over the frequency range of 5 Hz to 13 MHz. A K-type thermocouple was placed in the tubular furnace to monitor the temperature vicinity to the pellet. Prior to the impedance measurement, the temperature was kept at the target temperature for 20 min to stabilize the sample temperature.

3. Results and discussion

3.1 Phases and microstructure

Figure 1 shows XRD patterns of the samples with the composition of Al2x+1−yTi1+y−xMg0.5Ox (x = 0.1–1.0), where x is the molar ratio of MgTi2O5, obtained by reactive sintering at 1400°C for 2 h. By using the calibrated starting powder, XRD data of all samples sintered at 1400°C represented single Al2TiO5–MgTi2O5 solid solution [pseudobrookite-type phase, space group: Cmcm(63)]. The Al2x+1−yTi1+y−xMg0.5Ox (x = 1.0, i.e. MgTi2O5) sample was composed of only pseudobrookite-type phase. The easier formation of pseudobrookite-type MgTi2O5 (formable at 920°C) can be attributed to the smaller size-difference between Mg2+ ion and Ti4+ ion than the size-difference between Al3+ ion and Ti4+ ion. The Al2x+1−yTi1+y−xMg0.5Ox = (x = 0.1) sample, despite low molar ratio of MgTi2O5, was composed of only pseudobrookite-type phase, because of the decrease in distortion of MO6 octahedra, due to the substitution of metal ions (2Al3+ ≡ Mg2+ + Ti4+). By the decrease of formation

![Fig. 1. XRD patterns of Al2x+1−yTi1+y−xMg0.5Ox (x = 0.0–1.0) solid solutions sintered at 1400°C for 2 h. ICDD-JCPDS35-0792 (x = 1.0), ICDD-JCPDS 34-1062 (x = 0.6), ICDD-JCPDS 33-0854 (x = 0.3).](image-url)
exhibits relatively low thermal expansion values and Al$_2$(1-x)Mg$_x$O$_5$ (x = 0.0–1.0) solid solutions sintered at 1400°C for 2 h. In a specific composition (e.g., x = 0.3), some large and small grains were analyzed by EDS point analysis, however, there were almost no compositional difference.

### Table 1. Elemental Analysis of Surface of Al$_2$(1-x)Ti$_{1+x}$Mg$_x$O$_5$ (x = 0.1–1.0) Solid Solutions

<table>
<thead>
<tr>
<th>Al$<em>{2(1-x)}$Ti$</em>{1+x}$Mg$_x$O$_5$</th>
<th>Atomic (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Al</td>
</tr>
<tr>
<td>x = 0.1</td>
<td>20.7</td>
</tr>
<tr>
<td>x = 0.3</td>
<td>14.5</td>
</tr>
<tr>
<td>x = 0.7</td>
<td>5.9</td>
</tr>
<tr>
<td>x = 0.9</td>
<td>1.5</td>
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<tr>
<td>x = 1.0</td>
<td>1.1</td>
</tr>
</tbody>
</table>

temperature, pseudobrookite-type structure became more stable for solid-solutions, resulting more rapid and more anisotropic grain growth with increasing MgTi$_2$O$_5$ content.

EDS elemental analysis was carried out on the surface of uncoated samples. Table 1 summarizes atomic percent of Al$_{2(1-x)}$Ti$_{1+x}$Mg$_x$O$_5$ (x = 0.1–1.0) samples. Target composition and measured composition by EDS analysis were in good agreement with each other. In a specific composition (e.g., x = 0.3), some large and small grains were analyzed by EDS point analysis, however, there were almost no compositional difference.

### 3.2 Density and mechanical properties

**Figure 3** shows relative density as a function of composition [Al$_{2(1-x)}$Ti$_{1+x}$Mg$_x$O$_5$ (x = 0.0–1.0)] obtained by reactive sintering at 1400°C for 2 h. The relative densities of Al$_{2(1-x)}$Ti$_{1+x}$Mg$_x$O$_5$ (x = 0.1–1.0) were much higher than that of Al$_{2(1-x)}$Ti$_{1+x}$Mg$_x$O$_5$ (x = 0.0). Al$_{2}$Ti$_{1.9}$Mg$_{0.1}$O$_5$ (x = 0.9) sintered at 1400°C showed the highest relative density, 92.6%.

**Figure 4** represents CTE as a function of composition [Al$_{2(1-x)}$Ti$_{1+x}$Mg$_x$O$_5$ (x = 0.0–1.0)]. Al$_{2(1-x)}$Ti$_{1.9+x}$Mg$_{0.1}$O$_5$ (x = 0.1–0.3) exhibits relatively low thermal expansion values and Al$_{2(1-x)}$Ti$_{1+x}$Mg$_x$O$_5$ (x = 0.0–0.1) showed negative thermal expansion behavior up to 950°C. Thermal expansion increased with increasing MgTi$_2$O$_5$ ratio due to decrease of microcracks. Al$_{2(1-x)}$Ti$_{1+x}$Mg$_x$O$_5$ (x = 0.0), however, did not represent the lowest thermal expansion. In our previous work, we revealed that secondary phase dispersion is effective to reduce the Al$_2$Ti$_2$O$_5$ matrix grain size and to reduce the strong anisotropy of Al$_2$Ti$_2$O$_5$, which resulted in fewer microcracks. In the XRD result, Al$_{2(1-x)}$Ti$_{1+x}$Mg$_x$O$_5$ (x = 0.0) was mainly composed of pseudobrookite-type phase with some Al$_2$O$_3$ and TiO$_2$ phases. Therefore, coexisted Al$_2$O$_3$ and TiO$_2$ grains probably inhibited the anisotropic grain growth of Al$_2$Ti$_2$O$_5$.

**Figure 5** shows bending strength as a function of composition [Al$_{2(1-x)}$Ti$_{1+x}$Mg$_x$O$_5$ (x = 0.0–1.0)]. Al$_{2(1-x)}$Ti$_{1+x}$Mg$_x$O$_5$ (x = 0.0) indicated 8.1 MPa. Bending strength of Al$_{2(1-x)}$Ti$_{1+x}$Mg$_x$O$_5$ (x = 0.0–0.9) increased with increasing MgTi$_2$O$_5$ ratio due to the decrease of microcracks. Al$_{2}$Ti$_{1.9}$Mg$_{0.1}$O$_5$ (x = 0.9) showed the maximum strength of 47.9 MPa. On the other hand, MgTi$_2$O$_5$...
In this work, Al_{1.8}Ti_{1.1}Mg_{0.1}O_{5} (x = 1.0) showed very low bending strength of 13.2 MPa due to the grain growth during the sintering at 1400°C, despite its high relative density and high CTE. The low strength of MgTi_{2}O_{5} is attributable to the crack growth accompanied by the grain growth, as shown in Fig. 6, which shows mirror surfaces of Al_{2(1-x)}Ti_{1-x}Mg_{x}O_{5} (x = 0.9, 1.0) solid solutions sintered at 1400°C.

Fig. 6. Microstructure of Al_{2(1-x)}Ti_{1-x}Mg_{x}O_{5} (x = 0.9, 1.0) solid solutions sintered at 1400°C for 2 h: (a) x = 0.9 and (b) x = 1.0.

(x = 1.0) showed very low bending strength of 13.2 MPa due to the grain growth during the sintering at 1400°C, despite its high relative density and high CTE. The low strength of MgTi_{2}O_{5} is attributable to the crack growth accompanied by the grain growth, as shown in Fig. 6, which shows mirror surfaces of Al_{2(1-x)}Ti_{1-x}Mg_{x}O_{5} (x = 0.9, 1.0) solid solutions sintered at 1400°C.

3.3 Electrical properties

Figure 7 shows the electrical conductivity as a function of composition [Al_{(x=0.0-1.0)}Ti_{(x=0.0-1.0)}Mg_{0.0-1.0}O_{5}] at 1000°C in air. In this work, Al_{1.7}Ti_{1.7}Mg_{0.1}O_{5} (x = 0.1) indicated the lowest conductivity, and Al_{0.6}Ti_{1.7}Mg_{0.9}O_{5} (x = 0.7) indicated the highest conductivity. This complicated conductivity dependence is attributable to (1) grain size, (2) secondary phases (x = 0, i.e. Al_{2}O_{3} and TiO_{2} dispersion), (3) large microcracks for x = 0.9 and 1.0, and (4) density change (Fig. 3).

Since the composition of Al_{0.6}Ti_{1.7}Mg_{0.7}O_{5} (x = 0.7) showed the highest conductivity, we focused on this composition in the following part. In order to examine the effect of sintering temperature on the conductivity, the sample was also sintered at 1300°C as well as 1400°C. By lowering the sintering temperature (from 1400 to 1300°C), the sample had smaller grain size and hence smaller microcracks, as well as somewhat smaller density.

Fig. 7. Conductivity of Al_{(x=0.0-1.0)}Ti_{(x=0.0-1.0)}Mg_{0.0-1.0}O_{5} (x = 0.0–1.0) solid solutions sintered at 1400°C for 2 h: (a) x = 0.9 and (b) x = 1.0. 1300°C were 90.7 and 88.6%, respectively.

Figure 8 represents Cole–Cole plots of Al_{0.6}Ti_{1.7}Mg_{0.7}O_{5} (x = 0.7) sintered at (a) 1400°C and (b) 1300°C, measured over the frequency range 5 Hz to 13 MHz at temperature between 750–900°C in air. Two semicircular arcs, one with high frequency and another with low frequency, can be observed. The one with high frequency and the other one with low frequency corresponds to grain and grain boundary, respectively. The total resistivity of the sample sintered at 1400°C was higher than that of sintered at 1300°C at each measuring temperature, and each semicircular arc (grain and grain boundary) showed decrease in resistivity with increasing measuring temperature. The grain-boundary resistivity of the sample sintered at 1400°C was higher in spite of less grain boundaries than that of sample sintered at 1300°C.

The results in Fig. 9 suggest that conductivity of pseudobrookite-type ceramics strongly depends on microcracks. Several researchers reported that microcracks show crack healing at high temperature. The decrease of grain-boundary resistivity at high measuring temperatures is attributed to microcrack-healing behavior. For example, the grain boundary resistivity of the sample sintered at 1300°C had little effect on total resistivity at 900°C [see the insert of Fig. 9(b)]. The reason of small grain-boundary resistivity at 900°C can be explained as follows. According to the Bayer’s report, the average CTE (20–1020°C) of Al_{2}Ti_{2}O_{5} single crystal and MgTi_{2}O_{5} single crystal were calculated as 10.2 × 10^{-6} and 9.67 × 10^{-6}/K, respectively. While in this study, the measured CTE at 900–1000°C of the samples sintered at 1400 and 1300°C were 5.23 × 10^{-6} and 8.90 × 10^{-6}/K, respectively. The value of 5.23 × 10^{-6}/K for the sample sintered at 1400°C is clearly smaller than that of the calculated values of ~10 × 10^{-6}/K and that of the sample sintered at 1300°C.

Arrhenius plots of the conductivity and electrical properties of Al_{0.6}Ti_{1.7}Mg_{0.7}O_{5} (x = 0.7) sintered at (a) 1400°C and (b) 1300°C were 90.7 and 88.6%, respectively.
The activation energy (eV) in grain of samples sintered at 1400 and 1300°C were 3.9 and 3.6, respectively, while the activation energy in grain boundary of samples sintered at 1400 and 1300°C were 4.9 and 4.5, respectively. The sample sintered at 1400°C hence showed somewhat stronger temperature dependence than that at 1300°C. This result also suggested the increase of the amount of microcracks with increasing sintering temperature. In this study, the activation energy in grain boundary was higher than that in grain. Since the microcracks were mainly formed at grain boundaries, temperature dependence of the conductivity became more sensitive at grain boundary than in grain. These results are in good agreement with the microcrack-healing behavior explained for Fig. 9.

4. Conclusions

In this work, the properties of Al$_2$TiO$_5$–MgTi$_2$O$_5$ solid solutions can be summarized as follows:

(1) Except Al$_{2(1-x)}$Ti$_1$$_+$$x$Mg$_x$O$_5$ ($x = 0.0$, i.e. Al$_2$TiO$_5$), all samples sintered at 1300–1400°C were composed of single pseudobrookite-type phase. For Al$_2$TiO$_5$, a small amount of unreacted Al$_2$O$_3$ and TiO$_2$ were detected.

(2) The increases of grain size and densifications with increasing MgTi$_2$O$_5$ molar ratio were confirmed. Also thermal expansion increased with increasing MgTi$_2$O$_5$ ratio.

(3) Al$_{0.2}$Ti$_{1.9}$Mg$_{0.9}$O$_5$ ($x = 0.9$) showed 47.9 MPa as maximum strength. On the other hand, MgTi$_2$O$_5$ ($x = 1.0$) showed low bending strength (13.2 MPa) despite its high relative density and high CTE.

(4) Al$_{0.6}$Ti$_{1.7}$Mg$_{0.7}$O$_5$ ($x = 0.7$) sintered at 1300°C indicated the highest conductivity. The conductivity of pseudobrookite-type ceramics strongly depend on microcracks.
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